Resumos de Trabalhos Científicos

17ª RAU

REUNIÃO ANUAL DE
USUÁRIOS DO LNLS

12 E 13 FEV 2007

Ministério da
Ciência e Tecnologia

BRASIL
UM PAÍS DE TODOS
GOVERNO FEDERAL

Sumário

Parte I Plenárias

Parte II Biologia Estrutural

Parte III Biologia Molecular e Química de Proteínas

Parte IV Ciência Atômica e Molecular

Parte V Geociência, Meio-ambiente e Aplicações em Materiais Biológicos

---

Parte VI Matéria Mole e Fluídos Complexos

Parte VII Materiais Estruturais e Aplicações na Indústria

Parte VIII Métodos e Instrumentação

Parte IX Microfabricação

Parte X Propriedades Estruturais, Eletrônicas e Magnéticas de Sólidos

---

Parte XI Superfícies, Interfaces e Nanossistemas

Parte I

Plenárias

The European X-ray Free-Electron Laser Project in Hamburg

Altarelli, M.

European X-ray Free-Electron Laser Project Team, DESY, Notkestraße 85 22607 Hamburg Germany

In the quest for more brilliant x-ray sources, a number of projects worldwide are pursuing the realization of a source of extremely brilliant (peak brilliance $\sim 10^{33}$ photons/s/mm^2/mrad^2 /0.1%BW), ultra-short ($\sim$ 100 fs) pulses of spatially coherent x-rays with wavelengths down to 0.1 nm, and to exploit them for revolutionary scientific experiments in a variety of disciplines spanning physics, chemistry, materials science and biology. In the US and in Japan, Free-Electron Lasers (FEL) are being developed based on room-temperature linear accelerators (Linacs). In Europe, the superconducting linear accelerator technology developed at DESY within the TESLA collaboration, and successfully applied to produce laser-like radiation in the 100 to 13 nm range at the FLASH facility at DESY, is adopted. The most important advantage of the superconducting technology is the possibility to produce up to 30 000 pulses per second, instead of 60 or 120 foreseen in the Japanese and American projects, respectively. In the European facility, it is foreseen that electron bunches, accelerated to 17.5 GeV in a $\sim$ 1.7 km long Linac, pass through long (up to 200 m) undulators, where they generate bursts of coherent x-rays via the process known as SASE (Self-Amplified Spontaneous Emission). Commissioning with first beam of the facility is expected to take place in 2013. An initial contingent of 5 photon beamlines with 10 experimental stations is foreseen, where experiments exploiting the high intensity, the coherence and the time structure of the new source are going to be performed. A brief illustration of some of the potential experiments is presented. The study of molecular configuration rearrangements during chemical reactions down to the sub-ps scale; the dynamics of fluctuations on unprecedented time and length scales; the experimental access to regions of the phase diagram of materials so far only found in astrophysical environments or under conditions unfavorable for accurate experiments are some of the examples discussed. One of the most fascinating perspectives is the possibility to investigate the structure of macromolecules with atomic resolution without the need for crystallization, which has been thoroughly discussed in recent years by J. Hajdu and others. The feasibility of such an experiment with a single ultra-short and ultra-intense pulse depends on the compatibility between the time required to obtain a diffraction pattern from which an electron density map with the requested resolution can be reconstructed, and the time in which the molecular structure is destroyed by multiple photoelectric ionization, culminating in the Coulomb explosion of the molecule. Preliminary results at the FLASH facility, with 32 nm radiation pulses, have demonstrated the feasibility of image reconstruction for test nano-objects with a 25 fs pulse, achieving a resolution of $\sim$ 60 nm [1].

[1] H. Chapman et al., Nature Physics **2**, 839 (2006)

SOLEIL: a new photon source from Infra-Red to hard X-rays for a pluridisciplinary research

Sauvage-Simkin, M.

Synchrotron SOLEIL, Saint-Aubin, France

SOLEIL, the French synchrotron radiation facility, will receive its first users in 2007. In a first step, eleven beamlines offering a broad panel of experimental set-ups, will be opened to French and European scientists coming from all disciplines. After an introduction of the outstanding properties of synchrotron radiation produced in electron storage rings, and its further tailoring by specially designed magnetic insertion devices in the so-called third generation sources, an overview of the SOLEIL scientific programme will be given. The presentation will then be focused on selected fields of applications exploiting the brilliance, stability and time structure of the beams:

- Materials Science with both electronic and atomic structure investigations within multiscale approaches from the millimeter to the nanometer range and ultimate energy resolution.
  Magnetic properties assessment (statics and dynamics), making use of the polarization and time structure of the photon beams.
- In situ studies of chemical reactivity (catalysis, synthesis, electrochemistry)
- Photoexcitation in dilute matter with consequences for environmental science and astrophysics.

A brief comparison between similar facilities in operation or construction will be presented. To conclude, elements of planning and beamtime allocation for the coming years will be given.

New x-ray detector developments at Brookhaven National Laboratory

Siddons, D. P.

Brookhaven National Laboratory

The talk will describe ongoing developments at BNL with an emphasis on the two fields of x-ray spectroscopy and x-ray imaging detectors. The new spectroscopy system is primarily aimed at the synchrotron x-ray microprobe community, and is an integrated system consisting of multi-element silicon detector, scanning system and real-time data deconvolution and processing. The imaging detectors under development are designed specifically to satisfy the needs of the LCLS project at Stanford. These same devices will, however, be powerful detectors for synchrotron users, and we will discuss their design and current state of development.

Parte II

Biologia Estrutural

1

Crystallization of prephenate dehydratase from *Mycobacterium tuberculosis* H37Rv

Vivan, A.L.[1], Dias, M. V. B.[2], Azevedo Jr., W. F.[3], Basso, L. A.[3], and Santos, D. S.[3]

[1] Universidade Federal do Rio Grande do Sul - Porto Alegre RS Brazil
[2] Universidade Estadual Paulista - São José do Rio Preto - São José do Rio Preto SP Brazil
[3] PUC - Rio Grande do Sul - Porto Alegre RS Brazil

According to the World Health Organization, one-third of the world population is asymptomatically infected with Mycobacterium tuberculosis and approximately eight million people will develop active tuberculosis (TB) and three million people will die every year (WHO, 2005). The reemergence of TB, the proliferation of multidrug resistant strains (MDR-TB) and lack of adequate public resources creates a need to developing new drugs against TB and shorten the duration of treatment. The shikimate pathway is present in algae, fungi, bacteria and parasites from the phylum Apycomplexa and absent from mammals (PITTARD et al, 1996; ROBERTS et al., 1998). In mycobacteria, chorismate is the precursor of aromatic amino acids and the aromatic amino-acid biosynthesis pathway is an alternative target for the development of atimycobacterial agents (RATLEDGE, et al.,1982). The prephenate dehydratase catalyses the decarboxylation and dehydratation of prephenate to form phenylpyruvate. The structure of prephenate dehydratase may provide a structural model to be used in structural based drug design of a new generation of antiTB drugs. Crystallization trials were iniatially performed by the hanging-drop vapour diffusion method at 19C. The well solution contained 0.1 M HEPES buffer pH 7.5, 28% PEG 400, 0.2 M calcium chloride. Small crystals of prephenate dehydratase appeared seven days after the drops were done. The data set for prephenate dehydratase was collected at a wavelenght 1,438 Å using the Synchrotron Radiation Source (Station MX1, LNLS, Campinas) and a CCD detector (MAR CCD). The crystal diffracted 3.2 Å of resolution and belongs to the orthorhombic space group I222 or $I2_12_12_1$. Molecular replacement was used to solve the structure with program AmoRe (NAVAZA, 1994). As a model research was used phenyalanine hydroxylase (2PHM), but did not yield any meaningful results. This could be due the low identity between the search model and the structure under study. Heavy-atom screening is in progress to try to solve the structure by multiple isomorphous replacement.

Acknowledgements

This work was supported by CAPES, LNLS, FAPESP and Millennium Initiative Program MCT-National Research Council of Brazil (CNPq).

2

Structural Studies of Selenocysteine Synthase (SELA) from *Escherichia coli*

Cassago, A.[1], Oliveira, C. L. P[2], Torriani, I.[2], and Thiemann, O. H.[1]

[1] Universidade de São Paulo - São Carlos - São Carlos SP Brazil
[2] Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil

The biosynthesis of the 21th amino acid, selenocysteine (Sec or U) requires a complex enzymatic machinery composed of Selenocysteine Synthase (SELA) exclusive of prokariotes, Selenocysteine Elongation Factor (SELB or EFSec), Selenophosphate Synthetase (SELD) and a specific tRNA^{sec} named Selenocysteine Insertion tRNA (SELC). Our aim is to elucidate the protein-tRNA recognition mechanism by the structural investigation of Escherichia coli SELA in solution by Small Angle X-ray Scattering (SAXS) with and without tRNA. SAXS measurements of the SELA protein in the absence of the tRNA^{Sec}, were performed using the SAXS1 beamline at the Laboratório Nacional de Luz Síncrotron (LNLS). Data analysis allowed the determination of the global SELA structure as a homodecamer composed of five SELA dimers with a maximum diameter of 185, a molecular mass of 527 +/- 27kDa and a radius of gyration of 67.3. Higher resolution data were subsequently collected for SELA in the presence and absence of tRNA^{sec} using 2D detection at the SAXS2 beamline of the LNLS. Clear differences were noted between the scattering curves and pair distance distribution functions calculated for the two cases indicating the formation of complexes between the protein SELA and tRNA^{sec}. Since these preliminary results are consistent with obtained previously by Transmission Electron Microscopy (TEM), real space information was used as a guide to perform shape analysis from the SAXS data, to obtain the solution structure of SELA and obtain evidence of its binding with tRNA^{sec} .

Acknowledgements
This work was supported by IFSC and LNLS

3

Biophysical studies on the quaternary structure of a C-type lectin from *Bothrops jararacussu* venom - BJ-32 (BjcuL) in solution

Silva-Jr, F. P.[1], Correa-Neto, Carlos[2], Alexandre, GMC[1], Oliveira, C. L. P.[3], Torriani, I.[3], Ramos, C.H.I.[4], and De Simone, S. G.[1]

[1] Fundação Instituto Osvaldo Cruz - Rio de Janeiro RJ Brazil
[2] Instituto Vital Brazil - Niterói RJ Brazil
[3] Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil
[4] Centro de Biologia Molecular e Estrutural - Campinas SP Brazil

BJ-32 (also known as BJcuL) is a galactose binding C-type lectin from the venom of *Bothrops jararacussu* with a remarkble ability to agglutinate several species of trypanosomatids. Many lectins are thought to be oligomers containing more than one 16 kDa carbohydrate recognition domain (CRD). Recently, the crystal structure of RSL, a very close homologue (89% id) of BJ-32, revealed a decameric protein composed of two 5-fold symmetric pentamers arranged in a staggered, back-to-back orientation. Although the quaternary structure disclosed by X-ray crystallography is compatilble with the multivalent interactions required for the biological function, crystal packing artifacts cannot be ruled out. The objective of the present work was to use small angle X-ray light scattering (SAXS), intrinsic fluorescence (IF) spectroscopy and analytical ultracentrifugation (AUC) to determine the oligomerization state of native BJ-32 in solution. The Kratky plot indicated that the analyzed BJ-32 sample (at 4 mg/mL) behaved as a compact, natively-folded, protein during SAXS experiments. BJ-32 presented 36.72 +/- 0.04Å for radius of gyration and 100Å as maximum dimension. The BJ-32 MW was calculated as 147.5 +/- 2.0kDa. These results are in bare agreement with a decameric structure composed of 14.5 kDa monomers, as is observed by SDS-PAGE analysis of the native protein in reducing conditions. Indeed, the *ab initio* BJ-32 model presented a good superposition with the decameric structure of its close homologue RSL. Moreover, AUC experiments confirmed that BJ-32 is a decamer in solution. We observed an concentration dependent increase in BJ-32 IF until 1.2 mg/ml, indicating that different oligomeric states could be present since the assembly of subunits could interfere on the quantum yield of these states. The center of mass (CM) was only slightly shifted to red in high concentrations indicating that association does not accompany a drastic conformational change.

Acknowledgements
This work has been supported by the Brazilian Council for Cientific Reasearch (CNPq) and the Brazilian Synchrotron Light Laboratory (LNLS) under proposal D11A - SAXS1 3325.

4

Crystallization and X-ray diffraction data collection of a Lys49-PLA$_2$, the PrTX complexed with *p*-bromophenacyl bromide from *Bothrops pirajai* venom.

Marchi-Salvador, D. P.[1], Fernandes, C. A. H.[1], Soares, A. M.[2], and Fontes, M. R. M.[1]

[1] Universidade Estadual Paulista - Botucatu - Botucatu SP Brazil
[2] Universidade de São Paulo - Ribeirão Preto - Ribeirão Preto SP Brazil

Phospholipases A$_2$ are among the main components of *Bothrops* venoms and consists of a broad range of enzymes defined by their ability to catalyze specifically the hydrolysis of the center (*sn*-2) ester bond of substrate phospholipids. PrTX-I is a basic myotoxic Lys49-PLA$_2$, purified from *Bothrops pirajai* venom, which is catalytically inactive on artificial substrates, but promotes blockade of neuromuscular transmission. Alkylation of His48 residue of active site with *p*-bromophenacyl bromide (BPB), reduced 47% and 15% of its myotoxic and edema inducing activity, respectively. The neuromuscular blockage was completely absent in BPB-treated PrTX-I and the lethality (LD$_{50}$) was strongly reduced. These toxic activities reduction is not totally understand and the structure of this complex may contribute to this study. Here, we report the crystallization experiments and preliminary X-ray diffraction results of PrTX-I complexed with BPB (PrTX-I-BPB). Crystals of this complex were obtained by hanging-drop vapour-diffusion method in which the protein solution was equilibrated against a reservoir solution containing 0.1M sodium acetate pH 5.4-5.6, 20% 2-propanol and 18-25% (w/v) polyethylene glycol 4000, at 291K after approximately four weeks. X-ray diffraction data of a single PrTX-I-BPB crystal were collected at a wavelength of 1.427 (at 100K) using a Synchrotron Radiation Source (Laboratório Nacional de Luz Síncrotron, LNLS, station MX1, Campinas, Brazil). Data were processed using the denzo/scalepack program at 2.3 resolution. The crystals belong to P2$_1$ space group with cell constants **a**=38.62, **b**=70.02, **c**=43.82 and β=102.62^o. The data are 97.9% complete with R_{merge}=10.7% and I/σ (I)=1.76. The volume of the unit cell is compatible with a dimer (V_m=2.141^3/Da, 42.6% solvent content). The crystal structure was determined using molecular replacement techniques implemented by AMoRe program since the crystal is not isomorphous with the native.

Acknowledgements
This work has received financial support from FAPESP, FUNDUNESP, CNPq and LNLS.

5

The 1.55 X-ray structure of the Bowman-Birk inhibitor from *Vigna unguiculata* (BTCI) in complex with β-trypsin and its structural properties in association with proteinases

Barbosa, J.A.R.G.[1], Silva, L. P.[2], Teles, R. C. L.[3], Esteves, G. F.[3], Azevedo, R. B.[3], Ventura, M. M.[3], and Freitas, S. M.[3]

[1] Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil
[2] Empresa Brasileira de Pesquisas Agropecuárias - DF - Brasília DF Brazil
[3] Universidade de Brasília - Brasília DF Brazil

The structure of the BTCI in complex with β-trypsin was solved and refined at 1.55 to a crystallographic R_{factor} of 0.154 and R_{free} of 0.169, and represents the highest resolution of a Bowman-Birk inhibitor structure to date. The atomic coordinates have been deposited in the Protein Data Bank (code 2G81). The structure of BTCI folds into two similar compact subdomains with seven disulfide bonds and three β-strands forming an antiparallel β-sheet. BTCI binds to one molecule of trypsin driven mainly by electrostatic forces with the participation of Lys26, the P1 residue. This protein-protein interface is also stabilized by two water molecules, many other residues involving in the hydrogen bond network, and a patchy surface with hydrophobic side chains and polyethylene glycol molecule near the reactive site. The conformational rigidity of the reactive loop is characteristic of the specificity against trypsin, while hydrophobicity and conformational mobility of the anti-chymotryptic subdomain confer the self-association tendency, indicated by atomic force microscopy (AFM), of BTCI in complex and free form. This structural peculiarity, the absence of hydrophobic core and the high content of disulfide bonds result in a constrained conformation that is responsible for the remarkable stability exhibited by this inhibitor. The enzymatic assays indicated that when BTCI is in binary complexes, no significant differences in inhibition constants for producing a ternary complex with trypsin and chymotrypsin were detected. These results indicate that binary complexes present no conformational change in their reactive site for both enzymes confirming that these sites are structurally independent. The free chymotrypsin observed in the AFM assays, when the ternary complex is obtained from trypsin-BTCI binary complex and chymotrypsin, could be related more to the self-association tendency between chymotrypsin molecules and the flexibility of the reactive site for this enzyme than to binding-related conformational changes.

Acknowledgements
This work was supported by LNLS (ReNaBiME) and CNPq.

6

Estrutura cristalográfica da forma selvagem e de dois mutantes da enzima InhA redutase de Mycobacterium tuberculosis complexada com NADH e com isoniazida

Dias, M. V. B.[1], Prado, A. M. X.[1], Vasconcelos, IB[2], Fadel, V.[1], Basso, L. A.[2], Santos, D. S.[2], and Azevedo Jr., W. F.[2]

[1] Universidade Estadual Paulista - São José do Rio Preto - São José do Rio Preto SP Brazil
[2] PUC - Rio Grande do Sul - Porto Alegre RS Brazil

Tuberculose é um dos principais problemas de saúde pública mundial, matando aproximadamente cerca de 2 milhões de pessoas em todo o mundo. Dois fatores contribuem fortemente para o aumento de número de casos de tuberculose: a co-infecção de M. tuberculosis e HIV e o aumento de cepas resistentes aos principais medicamentos de primeira linha. Desta forma, o desenvolvimento de novos medicamentos contra tuberculose é bastante necessário, assim como o entendimento do mecanismo de resistência de bacilos aos medicamentos já existentes. Desta forma, este trabalho tem como objevo determinar as bases estruturais do mecanismo de resistência de dois mutantes encontrados em isolados clínicos resistentes ao principal medicamento em uso contra tuberculose, a isoniazida (INH). O principal alvo da isoniazida é a InhA, uma enzima relacionada com a biossíntese de ácidos micólicos em M. tuberculosis. Para isso, a InhA na sua forma selvagem e dois mutantes resistentes a isoniazida (I21V e S94A) foram cristalizados em complexo com NADH e isoniazida. Um cristal para cada mutante foi submetido a fonte de Raios X no LNLS. Os dados de difração de raios X para os três conjuntos foram processados e integrados utilizando respectivamente os programas mosflm e scala. A estrutra das proteínas foram determinadas por substituição molecular utilizando o programa AMoRe e refinadas utilizando o programa Refmac5. Os cristais difaram todos a 2.2 anstrom de resolução. As estruturas obtidas a partir destes dados apresentam valores de Rfactor e Rfree em torno de 18,5 e 22,0 por cento, respectivamente. Todas estruturas apresentam bom qualidade estereoquímica com mais de 96 por cento dos residuos em regiões permitidas. A análise das estruturas revelam que o mecanismo de resistência pode ocorrer principalmente devido a alteraçãoes em interações de Van der Walls e em moléculas de água presente no sítio ativo da enzima, fazendo com que ocorra uma menor afinadade pela molécula de NAD-INH. Com entendimento do mecanismo de resistência de M. tuberculosis a principal droga em uso, talvez seja possível o desenvolvimento de outras novas drogas que apresentem uma maior eficácia contra esta bactéria.

Acknowledgements
fapesp, processo: 03/12472-2

7

Análise, Identificação e Caracterização das Diferentes Lesões Formadas em DNA pelo Tratamento Fotoquimioterápico de Psoralenos Mais Luz Ultravioleta A Através de Espectrometria de Massas (QTOF)

Paula-Pereira Jr., M. V.[1], Alves, A. M.[1], Felicio, D. L.[1], SOARES, M.R.[2], Leitão, A.C.[1], and C. Lage[1]

[1] Universidade Federal do Rio de Janeiro - Rio de Janeiro RJ Brazil
[2] Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil

Estudamos a formação de lesões e a importância dos mecanismos de reparo destas lesões produzidas pela fotoquimioterapia de Psoralenos mais Luz Ultravioleta A (PUVA), protocolo utilizado na Dermatologia e importante no tratamento de doenças como psoríase, vitiligo e micose fungóide. Sua aplicação baseia-se em sua ação genotóxica, com indução da formação de adutos específicos que envolvem a intercalação da molécula de psoraleno entre as fitas de DNA (bases pirimídicas). Dois adutos podem ser formados: Monoadutos, ligações entre psoraleno e apenas uma das fitas de DNA, e crosslinks, ligações entre psoraleno e as duas fitas de DNA. Objetiva-se comparar a genotoxicidade, identificando lesões formadas in vitro, com a utilização de Espectrometria de Massas (QTOF), representando poderosa técnica de identificação qualitativa destes adutos. Uma vez monoadutos tendo ação citotóxica, relevante na terapêutica, e crosslinks demandando reparos mais mutagênicos, faz-se necessário investigar a diferença entre formação de monoadutos e crosslinks pelo PUVA. Foram feitas injeções no espectrômetro de massas de amostras de DNA controle e tratados com PUVA, submetidas à hidrólise. Psoralenos utilizados em diferentes concentrações: Psoraleno (PSO), 8-Metoxipsoraleno (8MOP) e Angelicina (ANG). O tratamento gerou diferentes lesões (Monoadutos e crosslinks), envolvendo bases pirimídicas e os três psoralenos supracitados. Estes resultados confirmam o potencial genotóxico do tratamento PUVA e apresentam grande relevância em termos de que a construção de psoralenos mais eficazes e menos danosos para as células normais se faz necessária para que ocorra o avanço e o melhoramento dos tratamentos utilizados na Dermatologia.

Acknowledgements

Desenvolvimento do Trabalho: Universidade Federal do Rio de Janeiro - Instituto de Biofísica Carlos Chagas Filho - Programa de Biologia Molecular e Estrutural - Laboratório de Radiobiologia Molecular

Laboratório Nacional de Luz Síncrotron - Centro de Biologia Molecular e Estrutural - Laboratório de Espectrometria de Massas

Apoio Financeiro: FAPERJ, CNPq

8

Binding of thyroid hormone receptor to different hormone response elements

Figueira, A. C. M.[1], Mario de Oliveira Neto[1], Bernardes, A.[1], Lima, L. M. T. R.[2], and Polikarpov, I.[1]

[1] Universidade de São Paulo - São Carlos - São Carlos SP Brazil
[2] Universidade Federal do Rio de Janeiro - Rio de Janeiro RJ Brazil

Thyroid receptor is included in nuclear receptor superfamily, one of the most abundant classes of transcriptional regulators in metazoans in which they regulate physiological functions as diverse as reproduction, differentiation, development, metabolism, metamorphosis or homeostasis. Thyroid hormone nuclear receptors (TRs) bind to DNA and activate transcription as heterodimers with the retinoid X receptor (RXR), homodimers, or as monomers. TRs are constitutively associated with chromatin and modulate gene expression by binding specific DNA sequences called thyroid response elements (TREs) that are found in the promoters of T3-regulated genes. They can bind, mostly as homodimers, to a palindromic elements (as TREpal and F2), or to a direct repeats spaced by four nucleotides (DR4), preferentially as heterodimers with the partner retinoid X receptors (RXRs). In this study we show the fluorescence anisotropy of the binding of two different constructions of TR (one with DBD domain - TR DBD; and one with DBD and LBD domains- TR DL) to four different DNAs sequences (F2, TREpal, DR-1 e DR-4). By these experiments, we were able to estimate the dissociation constants for each TRE used at the experiments. Also we show the interferences of salt and MgCl2 in this binding. We also built the low resolution models of TR LBD-DBD with the TREs: F2, TRE Pal and DR-4, by SAXS experiments. These study was done to verify if the DNA binding causes very strong modifications in the tertiary structure of the proteins, and to have an idea of how TR binding DNAs. Our results show that TR DL can bind DNA as dimers and that their envelopes are not so different when the protein is not bound to DNA. The TR DL can bind DNA better than TR DBD for palindromic sequences, and that the salt presence induces to complex Protein-DNA dissociation. Further, our study reveals that the binding of protein with direct response elements have lower affinity when compared with the palindromic elements, in DBD-LBD construction. The presence of MgCL2 improves the affinity to natural elements (palindromic) and decrease the affinity for the DRs and interferes into binding of DBD domain for the direct repeats binding. Maybe would be necessary the presence of LBD domain to stabilize the complex.

Acknowledgements
This work was supported by FAPESP.

9

Structural Analysis of the SBDS Protein Family

Oliveira, J. F.[1], Zanchin, N. I. T[1], and Guimarães, B.G.[1]

Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil

Shwachman-Diamond Syndrome (SDS; OMIM 260400) is an autosomal recessive disorder characterized by clinical features that include hematological dysfunction, pancreatic exocrine insufficiency and skeletal abnormalities. SDS patients are significantly predisposed to the development of hematological abnormalities, including cytopenias, myelodysplasia and acute leukemia. SDS therefore represents an important model for understanding the genetic determinants underlying the multistep progressions to leukemia. Disease-associated mutations were described in a gene designated SBDS that encodes a predicted protein of 250 amino acids with no homology to other proteins of known function. The SBDS protein is a member of a highly conserved protein family with orthologs in organisms ranging from plants, Archaea, and yeast to vertebrate animals, suggesting that it may have a fundamental, conserved biochemical role. Several lines of circumstantial evidence suggest that SBDS has a role in RNA metabolism. Aiming at contributing to the understanding of the molecular function of SBDS protein we are performing structural studies on SBDS homologues from *Pyrococcus abyssi*, *Saccharomyces cerevisiae*, *Trypanosoma cruzi* and *Homo sapiens*. We have produced, purified and submitted the proteins to crystallization. Crystals of *Pyrococcus abyssi* SBDS (PaUPF0023) were obtained in different crystallization conditions with ammonium phosphate as precipitant. Crystals diffracted up to 3.5 Å resolution and extensive refinement of crystallization conditions did not improve, until present, the diffraction quality. Crystallization trials of homologues from *S. cerevisae*, *T. cruzi* and *H. sapiens* are in progress. Interestingly, trypanosomatid SBDS differs from its orthologs on presenting an extended C-terminal. Characterization of *T. cruzi* SBDS C-terminal domain by circular dichroism, limited proteolysis and NMR analysis revealed that the domain is unfolded. Complementary studies are being performed in order to characterize the role of the C-terminal domain in trypanosomatid SBDS.

Acknowledgements
Financial Support: FAPESP, LNLS

10

Expression, Purification and Crystallization of LIC10793, a Putative Leptospiral Surface Antigen

Giuseppe, P. O.[1] and Guimarães, B.G.[1]

Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil

Recently, the genome sequences of three *Leptospira interrogans* serovars were reported. It has allowed the *in silico* identification of new vaccine candidates against leptospirosis, an infectious disease presumed to be the most widespread zoonosis in the world. One of the potential leptospiral antigens revealed by the genome sequence of serovar copenhageni is LIC10793. LIC10793 is predicted to be a lipoprotein located at the bacterial outer membrane surface. Nevertheless, BLAST analysis showed that LIC10793 does not have any close sequence similarity to proteins of known function. In the absence of experimental data and when sequence-based methods fail, functional clues can be provided from the proteinŠs three-dimensional structure. We thus started a work aiming at the structural characterization of LIC10793 by X-ray crystallography. The protein was produced in *Escherichia coli*, purified and submitted to crystallization. Thin clustered plates were obtained in 40 out of the 240 tested crystallization conditions. Some of the conditions were refined and the use of micro-seeding technique was crucial to obtain better quality crystals. X-ray diffraction data were collected at the LNLS protein crystallography beamline D03B-MX1. LIC10793 crystals diffract up to 2.2 resolution and belong to the space group $P2_12_12_1$, with unit-cell parameters a=77.67 b=84.75 c=130.06 . Crystallization trials using the seleno-methionine labeled protein are in progress, aiming at the structure determination using the MAD method.

Acknowledgements
Financial support: FAPESP, LNLS

11

Identificação de Novas Lesões Formadas em DNA Através de Ensaios in vitro e in vivo de Tratamento Fotoquimioterápico PUVA (Psoralenos + Luz Ultravioleta-A) Via Espectrometria de Massas (QTOF).

Paula-Pereira Jr., M. V.[1], Alves, A. M.[1], Felicio, D. L.[1], SOARES, M.R.[2], Leitão, A.C.[1], and C. Lage[1]

[1] Universidade Federal do Rio de Janeiro - Rio de Janeiro RJ Brazil
[2] Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil

A fotoquimioterapia PUVA (Psoralenos mais luz ultravioleta-A), utilizada na Dermatologia no tratamento de diferentes patologias, como psoríase e vitiligo, consiste na indução da formação de adutos entre psoraleno e nucleotídeos do DNA; os monoadutos (em apenas uma das fitas) e crosslinks (duplamente formados entre psoraleno e fitas opostas do DNA), resultando efeitos genotóxicos e mutagênicos que inviabilizam manutenção e replicação celular. Células de E. coli tratadas com agentes físicos e químicos, lançam mão do reparo de lesões formadas no DNA pelo Reparo por Excisão de Nucleotídeos (NER) do Complexo Protéico UvrABC. Amostras de DNA com diferentes concentrações de psoralenos utilizados nos experimentos foram submetidos a dose de radiação UV-A (320-400nm). As amostras foram hidrolisadas e analisadas via Espectrometria de Massas (QTOF). Além de lesões já esperadas no DNA em bases pirimidínicas (Citosina e Timina), foram identificadas lesões até então não descritas como substratos-alvo da ligação com psoralenos: ligação com bases purínicas (Adenina e Guanina), fator maior de mutagenicidade do tratamento PUVA e possível desencadeador de neoplasias. O presente estudo também identificou formação de sítios abásicos no DNA, também não descritos como lesões formadas pelo tratamento PUVA, abrindo linha de perspectiva da utilização de segunda via enzimática de reparo das lesões, o Reparo por Excisão de Bases (BER). Os dados reforçam a necessidade de remodelar protocolos PUVA, em vias de futuras utilizações de psoralenos mais eficazes no tratamento e confirmando a sua potencialidade junto à Dermatologia.

Acknowledgements
Desenvolvimento do Trabalho:

Universidade Federal do Rio de Janeiro - Centro de Ciências da Saúde- Instituto de Biofísica Carlos Chagas Filho -Programa de Biologia Molecular e Estrutural - Laboratório de Radiobiologia Molecular

Associação Brasileira de Tecnologia de Luz Síncrotron - Laboratório Nacional de Luz Síncrotron - Centro de Biologia Molecular e Estrutural - Laboratório de Espectrometria de Massas

Apoio Financeiro: FAPERJ e CNPq

12

STRUCTURES OF BOVINE BETA-TRYPSIN IN COMPLEX WITH BENZAMIDINE DERIVATIVES

Perilo, C.S.[1], Nagem, R. A. P.[1], Martins, V. T.[1], Pereira, M. T.[2], and Santoro, M. M.[1]

[1] Universidade Federal de Minas Gerais - Belo Horizonte MG Brazil
[2] UNIVERSIDADE FEDERAL DE MINAS GERAIS - MG Brazil

Serine proteinases play a central role in several physiologic processes, spanning from digestion to key regulatory mechanisms. Since proteolytic reactions control many biological processes, discovery of new and stronger inhibitors of proteolysis is an important field of modern chemistry. Trypsin is a well-studied serine proteinase specific for carboxyl terminus of lysine and arginine. A large number of synthetic trypsin inhibitors is derived from benzamidine, which is a model system for the basic alpha-amino acids arginine and lysine. The reactive site of trypsin, as well as its complex with benzamidine has been completely characterized by X-ray crystallography. Thermodynamic studies have shown that p-substituted benzamidine, berenil and pentamidine are even stronger inhibitors of trypsin than benzamidine itself, although the crystallographic structures of these complexes have not been solved yet. In this context, the objective of the present study is to solve the structure of the complexes between beta-trypsin and benzamidine inhibitor derivatives (p-aminobenzamidine, berenil and pentamidine) using X-ray crystallography. Bovine beta-trypsin was purified by chromatography. Crystals of beta-trypsin in complex with p-aminobenzamidine, berenil and pentamidine were grown at 18 Celsius degrees by the hanging drop vapor diffusion method, using ammonium sulfate and/or PEG 3350/4000 as precipitants. Diffraction data were collected at the Brazilian Synchrotron Light Laboratory. Preliminary analyses of electron density maps for the complexes revealed the presence of the ligands in the catalytic cleft of the enzyme. Refinement and structural comparison of the complexes are being conducted at the Instituto de Ciências Biológicas at the Universidade Federal de Minas Gerais (ICB/UFMG).

Acknowledgements

This work was supported by CNPq and FAPEMIG Special acknowledgements to LNLS for facility used.

13

O Domínio MPN da proteína Mov34 é Independente de Metal

Sanches, M[1], Alves, B.S.C.[1], Zanchin, N. I. T[1], and Guimarães, B.G.[1]

Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil

Proteossomos são grandes complexos multi-protéicos envolvidos no processo de degradação de proteínas indesejadas e mal-enoveladas. Em células eucarióticas as proteínas intracelulares são ubiquitinadas antes de serem degradadas pelo complexo proteossomo 26S, que é formado pela associação ATP-dependente do proteossomo 20S (núcleo proteinase multicatalítico) com dois complexos 19S. A proteína PSMD7 (Proteasome 26S non-ATPase subunit 7), também conhecida como Mov34, é um dos componentes ATP-independetes da subunidade regulatória 19S, que possui um motivo KEKE característico no seu C-terminal.

A proteína humana Mov34 foi descrita como contendo um domínio N-terminal com o motivo estrutural MPN (Mpr1p, Pad1p N-terminal), normalmente encontrados em subunidades de complexos multi-proteínas. Neste trabalho foram resolvidas as estruturas cristalográficas de duas construções desse domínio N-terminal da hMov34: uma contendo os aminoácidos de 1 até 186 (MPN1-186) e outra contendo os aminoácidos 1 até 177 (MPN1-177). Todos os conjuntos de dados foram coletados na linha MX1 do LNLS. As comparações estruturais entre essas estruturas com outra estrutura de *A. fulgidus* confirmam a existência do motivo MPN na proteína hMov34. Análises estruturais e biofísicas mostraram que a proteína hMov34 não liga metal, em oposição à estrutura dependente de zinco de *A. fulgidus*. Comparações de seqüência de aminoácidos da hMov34 com outras proteína contendo o domínio MPN mostraram que essas proteínas relacionadas à hMov34 também são independentes de metal. Esses dados levam à conclusão de que existem dois tipos de domínios MPN: um dependente de metal, relacionado à proteína RPN11 e que pode apresentar atividade isopeptidase, e outro domínio estrutural livre de metal, relacionado às proteínas RPN8 e hMov34, provavelmente envolvido em processos de interação proteína-proteína e na estabilidade de complexos.

14

Structural Studies The Hgxprt From *Pyrococcus Horikoshii*

Dantas, D.S.[1], Pereira, G. A. G.[1], and Medrano, F. J.[2]

[1] Universidade Estadual de Campinas - Campinas SP Brazil
[2] Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil

Purine phosphoribosyltransferases are involved in the salvage of purine bases. They catalyse the reversible transfer, dependent of magnesium, of a phosphoribosyl group from 5-phospho-α-D-ribosyl 1-pyrophosphate to a purine base releasing pyrophosphate, resulting in the correnponding nucleotide monophosphate. HPRT from P. horikoshii shows significant differences in key residues in three of the four catalytic loops. Here, with the study of this protein from a hyperthermophylic microorganism we would like to get some insights into the sequence rearrangements that a protein should go through to gain the necessary stability to perform its activity at high temperature. We have cloned the gene coding for the HPRT from P. horikoshii in the pET15b expression vector, and expressed in E. coli. The protein was purified in two steps: heating at 75 °C (1 hour) followed by centrifugation to eliminate all the precipitated material and a second step of affinity chromatography. We have carried out steady-state kinetic assays to discover the specificity of this protein. The reaction is more efficient with hypoxanthine, followed by guanine and xanthine, with a great dependence of the catalytic constant with temperature, being more efficient at higher temperatures. We show that this protein is able to salvage hypoxanthine, guanine and xanthine. Further studies will give us insights on the effect of sequence rearrangements on the final structure of the protein.

Acknowledgements
This work was supported by FAPESP

15

Avaliação da influência de flavonóides na estrutura e função da fosfolipase A_2 de *Crotalus durissus cascavella*

Santos, M.L.[1], Iglesias, C.V.[1], Toyama MH[1], and Aparicio, R.[1]

Universidade Estadual de Campinas - Campinas SP Brazil

Fosfolipase A_2 (PLA_2; EC 3.1.1.4) é uma enzima envolvida na formação de ácidos graxos e lisofosfolipídeos. Em adição a sua função enzimática, PLA_2s de veneno de cobras exibem diversos efeitos farmacológicos, incluindo neurotoxicidade, indução de eventos inflamatórios e edemas. Estudos recentes revelaram que o tratamento da fosfolipase A_2 isolada de veneno de *C. d. cascavella* (uma PLA_2 do grupo II) com o flavonóide morina, apresentou uma considerável diminuição da atividade enzimática e bactericida, mas sua capacidade inflamatória e neurotóxica não foram afetadas. Esses efeitos foram relacionados com mudanças na estrutura secundária da PLA_2 (Iglesias, C.V. et al., 2005, *Toxicon* 46: 751-758). Neste trabalho estudamos a influência de alguns flavonóides na estrutura da PLA_2 de *C. d. cascavella* através do Espalhamento de raios X a Baixos Ângulos (SAXS). Os resultados mostraram que não houve desenovelamento da PLA_2 depois do tratamento com os flavonóides. Obtivemos também modelos de baixa resolução para a fosfolipase A_2 nativa e tratada com os flavonóides.

Acknowledgements

Agradecemos o apoio técnico na linha de SAXS (D11A-SAXS1) do LNLS e ajuda durante a aquisição dos dados. Este trabalho foi financiado pela FAPESP e FAEPEX/PRP/Unicamp.

16

Structural studies of two bZIP (SCF12 and SCF5) transcription factors from sugarcane

Kiyota, E.[1], Santos, M.L.[1], Schlögl, P. S.[2], Aparicio, R.[1], and Menossi[1]

[1] Universidade Estadual de Campinas - Campinas SP Brazil
[2] Universidade Federal de Santa Catarina - Florianópolis SC Brazil

Transcription factors recognize specific sequences of DNA and regulate transcription interacting with promoter regions of genes and with basal components of the transcriptional machinery. These factors are involved in the control of many intracellular processes. Basic leucine zipper (bZIP) proteins form a large family of transcription regulators in plants and other eukaryotes. These proteins are characterized by a conserved region rich in basic amino acid residues that binds to the target DNA and the leucine zipper region. The leucine zipper region is alpha-helical and is formed by several heptad repeats of hydrophobic residues, responsible for bZIP interactions. Dimerization process can regulate interaction between bZIP and the transcription pre-initiation complex and also modulates interaction with target DNA, becoming a mechanism of gene expression control. Here, are present the cloning, expression and purification of a novel sugarcane bZIP (SCF12). Structural studies in solution by circular dichroism spectroscopy for SCF12 and Small Angle X-ray Scattering (SAXS) for SCF5 bounded to DNA, including low resolution models are also shown. SCF5 expression and functional characterization was previously reported (Schlögl, P. S. *et al.*, 2004, *Plant Sci.* **167**:583-595).

Acknowledgements
We are grateful to LNLS for technical assistence. This work was supported by FAPESP.

17

Estruturas de baixa resolução do hTRB (DBD) na ausência e presença do elemento responsivo do DNA (F2).

Mario de Oliveira Neto[1], Figueira, A. C. M.[1], Santos, MA[1], A.F. Craievich[2], and Polikarpov, I.[1]

[1] Universidade de São Paulo - São Carlos - São Carlos SP Brazil
[2] Universidade de São Paulo - São Paulo - São Paulo SP Brazil

Os receptores nucleares são proteínas responsáveis pela regulação da transcrição de genes-alvo, mediando os efeitos pleiotrópicos dos hormônios lipofílicos nas células. Estes receptores agem como fatores de transcrição agindo diretamente através da associação física com uma grande variedade de reguladores hormonais ou de outro tipo, assim como sinais metabólicos, estando intimamente relacionados a diversas doenças, principalmente a vários tipos de câncer, sendo, por isso, considerados “ alvos ” para novas terapias. Os grupos de agonistas (glucocorticóides, estrogênios, antiestrogênios, vitamina D, retinóides, androgênios, antiandrogênios e tiroxina) e antagonistas que atuam nestes receptores, constituem hoje a classe de fármacos mais procurada para a prática médica, sendo, portanto, um dos mais importantes alvos para o desenvolvimento de medicamentos. Estes receptores são proteínas modulares, possuindo dois domínios principais, o domínio de ligação ao ligante (LBD - Ligand Binding Domain) e o domínio de ligação ao DNA (DBD - DNA Binding Domain), o qual possui alta identidade seqüencial entre os diversos receptores, sendo responsável tanto pela ligação específica do receptor a seqüência de DNA alvo, assim como possui fraca capacidade de dimerização. Até o momento o complexo cristalográfico do Receptor Tireoideano ligado ao elemento responsivo do DNA F2 (hTRB F2), assim como nenhum outro DBD de receptor nuclear disposto neste sitio de ligação é avaliado, estudos de SAXS permitem a visualização do hTRB na presença e na ausência do elemento responsivo do DNA F2 com uma resolução de aproximadamente 20 Angstrons, possibilitando a construção tridimensional do complexo.

Acknowledgements
Este trabalho é suportado por CBME - FAPESP

18

Estructura de la fosfofructoquinasa-2 de *Escherichia coli*. Presencia del motivo conservado NXXE en el sitio activo

Caniuguir, A.[1], Cabrera, R.[1], Ambrosio, A.L.B.[2], Garrat, R. C.[2], Guixé, V.[1], and Babul, J.[1]

[1] Universidad de Chile - Santiago Chile
[2] Universidade de São Paulo - São Carlos - São Carlos SP Brazil

En *Escherichia coli*, dos quinasas no homólogas dependientes de ATP catalizan la fosforilación de fructosa-6-fosfato: Pfk-1 que pertenece a la familia PFKA y Pfk-2 que pertenece a la superfamilia riboquinasa de quinasas de azúcares fosfato. Además de la función catalítica, ambas enzimas convergen en presentar inhibición por su sustrato MgATP. En Pfk-2, el efecto inhibitorio esta relacionado con la unión de MgATP a un sitio alostérico y con un cambio en el estado de agregación del dímero nativo hacia una forma tetramérica. Aunque, Pfk-1 y Pfk-2 han sido bioquímicamente caracterizadas, solo la estructura de Pfk-1 ha sido resuelta por difracción de rayos-X. Con el propósito de determinar experimentalmente la estructura de Pfk-2, ésta fue cristalizada por el método de difusión de vapor en gota suspendida usando acetato de sodio 0,1 M pH 5,3, y PEG 6000 12% (p/v) como agente precipitante. Los cristales fueron crecidos en presencia de MgATP y difractaron hasta una resolución de 1.98 Å(usando un detector MAR CCD). Los cristales del complejo Pfk-2-MgATP pertenecen al sistema ortorrómbico, grupo espacial $P222_1$, con parámetros de celda unitaria a = 42,8 Å, b = 86,8 Å, c = 171,3 Å y $\alpha = \beta = \gamma = 90^o$. El modelo de la estructura se resolvió por el método de reemplazo molecular usando como modelo la proteína 2abq (fructosa-1-fosfato quinasa de *Bacillus alodurans*, no publicado). Como se esperaba, Pfk-2 forma tetrámeros cuando está acomplejada con MgATP. El plegamiento de la subunidad de la Pfk-2 está constituida por dos dominios: el dominio mayor tiene una hebra-β central rodeada por dos α-hélices y un dominio menor con cuatro hebras-β que forman parte de la interfaz monómero-monómero. Por otra parte, la interfaz dímero-dímero involucra contactos entre residuos del dominio mayor. Uno de los motivos de secuencia conservado entre los miembros de la superfamilia riboquinasa de quinasas de azúcares es el motivo NXXE, el que ha sido asociado a la unión de ligandos al sitio activo. La densidad electrónica en el sitio activo de la Pfk-2, muestra que los residuos N187 y E190 del motivo, interactúan con dos moléculas de ATP y dos iones de Mg^{2+}. Se compara la superposición estructural del motivo NXXE con otros miembros de la superfamilia riboquinasa dependientes de ATP y ADP. (Fondecyt 1040892).

Acknowledgements
Laboratório Nacional de Luz Síncrotron (LNLS, Campinas/SP), Linha D03B- MX1.

19

Structural studies of Xylellain, a cysteine protease from *Xylella fastidiosa*

Leite, N.R.[1], Oliva, M. A. V.[1], Nogaroto, V.[2], Gianotti, A.[2], Oliva, G.[1], Henrique-Silva, F[2], and Thiemann, O. H.[1]

[1] Universidade de São Paulo - São Carlos - São Carlos SP Brazil
[2] Universidade Federal de São Carlos - São Carlos SP Brazil

Xylella fastidiosa is a xylem-limited, Gram-negative bacterium responsible for a large number of economically important plant diseases, such as Pierces disease in grapevines, citrus variegated chlorosis (CVC) in sweet oranges and leaf scorch diseases in other plants, including almond, plum, oleander, mulberry and coffee. In all cases, *X. fastidiosa* infects the plant xylem and impairs fruit production. Proteins such as proteases, cellulases and lipases may be involved in the infection process by disrupting plant tissue and allowing the spread of bacteria throughout the vascular system. The interest in cysteine proteases as chemotherapeutic targets stems from the recognition that they are critical to the life cycle or pathogenicity of a large number of parasites. The gene coding to xylellain was cloned into pET28a (Nogaroto, V. *et al*, 2006), and transformed into *Escherichia coli* (BL21-DE3). The recombinant protein was purified by nickel-NTA affinity column. Crystals of xylellain formed at 18 ^{o}C by hanging drop vapor diffusion using PEG8000 as precipitantion agent. X-ray diffraction data were collected on a MAR345 image plate using osmic mirror focused CuK-α X-rays, generated by a RIGAKU ultra X-18 rotating anode operating at 90 mA and 50 kV, with completeness of 95%, the crystal belongs space group P1 and a resolution of 1.65 . Attempts to solve structure by molecular replacement did not resulted in clear solutions. Heavy atoms quick cryo-soacking did not result in heavy-atom containing crystals. Seleno-methionine containing xylellain crystals were produced and collected at Brookhaven National Laboratory (BNL). Eight selenium sites were found and the structure was solved by single-wavelength anomalous dispersion (SAD). The final structure was refined against the best native data set (1.65) showing R/Rfree= 17/19 and FOM=86 % and one intriguing ribonucleotide with unknown function was found outside the active site. Mutants of xyllelain have been produced to study the effect of this ribonucleotide in the structure.

Acknowledgements
This work was supported by FAPESP and CNPq

20

Structural Studies of glyoxalase II from *Salmonella typhimurium* LT2

Leite, N.R.[1], Campos Bermudez, V. A.[2], Krogh, R[1], G.OLIVA[1], Costa, AJ; Costa-Filho, AJ;da Costa, AJ[1], Soncini F[3], and Vila, A.J.[4]

[1] Universidade de São Paulo - São Carlos - São Carlos SP Brazil
[2] Universidad de Rosario - Rosário Argentina
[3] Instituto de Biología Molecular y Celular de Rosario - Rosario St.Fe Argentina
[4] Universidad de Rosario - Rosario Argentina

The glyoxalase system consists of two enzymes, lactoylglutathione lyase (glyoxalase I, Glx 1) and hydroxyacylglutathione hydrolase (glyoxalase lI, Glx 2) that act coordinately to convert a variety of α-keto aldehydes into hydroxyacids in the presence of glutathione. GLX2 is part of the metallo-β-lactamase (MBL) superfamily. The members of this superfamily are characterized by the presence of an αβ/αβ fold and a conserved motif able to bind up to two metal ions in their active sites. Variations on the sequence elements of this motif have been correlated with the selectivity towards different metal ions, for instance *Arabidopsis thaliana* cytoplasmic GLX2 (GLX2-2) can bind zinc, iron, and manganese, its mitochondrial isoform (GLX 2-5) is a iron/zinc protein, while the human enzyme was reported to bind two zinc ions. We have identified in the *Salmonella typhimurium* LT2 genome an ORF showing a significant homology sequence with glyoxalases II, containing the putative metal binding motif and protein fold of MBL superfamily. This ORF was PCR-amplified from chromosomal DNA and cloned in a pET32 expression vector to generate a fusion protein to thioredoxin (Trx-tag) and His-Tag sequence. The resulting protein (GloB) was overexpressed and purified. GloB was able to hydrolyze S-D-lactoylglutathione, dependent on the presence of divalent metal ion. This protein was able to bind iron, zinc as well as manganese in its bimetallic center, as revealed by atomic absorption measurements, H1-NMR and EPR. Diffraction data were collected until 1.45 resolution, at bean line MX1 in Brazilian National Light Source, crystal belongs P21 space group with dimensions of cell A=43.37 , B=57.17 , C=53.9 and β= 111.90^{o}. Data were integrated and reduced with Mosflm and intensities were scaled with Scala, from the CCP4 suite. One clear solution was found by molecular replacement, using *A. thaliana* GLX2 (PDB 1XM8) as search model. Structure of *S. typhimurium* GloB showed that the protein presents the predicted fold αβ/αβ with the putative metal binding ligands involved in the coordination of the metal ions in a bimetallic center. The final structure showed Rfactor/Rfree=14.8/18.5, FOM= 93%. Ramachandran analysis showed that 92% of the residues are located in most favored regions while the 8% were in additional and general allowed regions.

21

Solution Structure of the *L. major* and *T. brucei* Selenophosphate Synthetase (SELD) by Small Angle X-Ray Scattering

Pimenta Jr., A. A.[1], Sculaccio S. A.[1], Rodrigues, E. M.[1], Oliveira, C. L. P.[2], Torriani, I.[2], and Thiemann, O. H.[1]

[1] Universidade de São Paulo - São Carlos - São Carlos SP Brazil
[2] Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil

The translation processes play a central role in the general metabolism of the cell. In particular the pathway of synthesis and incorporation of the amino acids selenocysteine and pirrolysine, that results in the expansion of the genetic code to a total of 22 amino acids. Selenocysteine represents the main biological form of the element selenium incorporated into selenoproteins at an in phase termination codon (UGA). In *Escherichia coli* the main proteins involved are: Selenocysteine Synthase (SelA), Specialized Elongation Factor (SelB or EFSec), Selenophosphate Synthetase (SelD), a specific tRNA (tRNAsec - SelC) and a Selenocysteine Insertion Sequence (SECIS). The protein SelD, subject of this work, catalyses the formation of selenophosphate from selenite and ATP. Recent studies have verified the presence of the gene *selD* in *Leishamania* and *Tripanosoma*. These genes, of 1197 and 1179 base pairs encode for proteins of 399 and 393 amino acids, respectively, with a molecular mass of 43 kDa. The *L. major* and *T. brucei selD* genes were PCR amplified and cloned into the expression vector pET28a. An effective expression and purification protocol was established for the recombinant proteins. Small angle X-ray scattering 2D data was collected at the SAXS-2 beamline at the Brazilian Synchrotron Light Laboratory (LNLS) at 407 and 1620 mm for each enzyme. SAXS is being analyzed using the programs DATASQUEEZE, IGOR and GNOM. Models will be build by chain modeling using GASBOR. The molecular characterization for the *L. major* and *T. brucei* SELD is also presented.

Acknowledgements
This work was supported by FAPESP, CNPq and USP.

22

Crystal structure of the periplasmic molybdate-binding protein (ModA) from the plant pathogen *Xanthomonas axonopodis* pv. *citri*

Santacruz, C. P.[1], Balan, A.[1], Moutran, A.[2], Neshich G.[3], Ferreira, L.C.S.[1], and Barbosa, J.A.R.G.[4]

[1] Universidade de São Paulo - São Paulo - São Paulo SP Brazil
[2] Universidade de São Paulo - São Paulo - SP Brazil
[3] Empresa Brasileira de Pesquisas Agropecuárias - Campinas SP Brazil
[4] Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil

We report the crystal structure of the periplasmic molybdate-binding protein (ModA) of the plant pathogen *Xanthomonas axonopodis* pv. *citri* (*Xac*) responsible for the canker disease affecting citrus plants. Structures of molybdate transporters have been solved in other species including *Escherichia coli* (*Eco*) and *Azotobacter vinelandii* (*Azo*), however, no ortholog derived from plant-associated bacteria has been reported so far. X-ray diffraction data were collected to a maximum resolution of 1.75 at the D03B-MX1 beamline of the LNLS. The structure was solved with the molecular replacement method, where the *Eco* ortholog was used as a template. The *Xac* ModA structure is ellipsoidal with dimensions of approximately 33 x 48 x 62 and it is composed of two nearly symmetrical domains separated by a hinge region where the substrate-binding site lies. Each domain is an α/β sandwich designated as N- and C-domains. The N-domain is formed by residues 1-82 and 196-234 and contains a region defined by one β-sheet with 5 strands that are surrounded by 5 α-helices, while C-domain consists of residues 83-195 and is also formed by one β-sheet with 5 strands that are surrouded by 7 α-helices. Comparisons between the structures of *Xac* ModA and the *Eco* and *Azo* orthologs have been done. Alignments of ModA amino acid sequences revealed three groups of molybdate-binding proteins described as phytopathogens, enterobacteria and soil bacteria, respectively. Structural alignment of the three proteins revealed that *Xac* ModA is closer to *Eco* ModA, not only in its amino acid sequence (56% of similarity), but also in its structure. The relationship between the conservation patterns of each of the three groups allows for the suggestion of characteristics common to all ModAs and those that are specific to each group.

Acknowledgements

Financial support by SMolBNet-FAPESP and ABTLuS

23

Cloning, expression and purification of the human septin 2 and the GTPase domain of the human septin 6

Souza, T.A.C.B.[1], Rampasio, R. R.[1], Zanchin, N. I. T[1], and Barbosa, J.A.R.G.[1]

Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil

Septins are a family of conserved proteins that are essential for cytokinesis in a wide range of organisms including fungi, Drosophila and mammals. So far, human septins comprise a family of 13 genes that encode GTP-binding proteins. They are involved in other cellular processes, such as vesicle trafficking and exocytosis. An increasing body of data implicates the septin family in the pathogenesis of diverse disease states including neoplasia, neurodegenerative conditions and infections. All septins share a highly conserved domain related to those found in small GTPases, and septins have been shown to bind and hydrolyze GTP. Human septin 2 has been cloned in expression vector pET28a, expressed in *Escherichia coli* BL21(DE3) and purified, but suffers from severe aggregation. A screening among different buffers shows that septin 2 purified in a solution containing Tris-HCl 200 mM, NaCl 150 mM, Gycerol 5% and GTP 40 μM has a much lower degree of aggregation. Septin 2 was purified using this solution by affinity chromatography followed by gel filtration chromatography. The purified protein appears to crystallize in MPD 40% and Cadmium Chloride 0.2 M. Some refinements of the conditions are under way in our laborotatory in order to achieve good diffraction quality crystals. The GTPase domain of septin 6 was cloned, expressed and purified in the same way as septin 2. Septin 6 also suffers from severe aggregation, which was avoided by purifying it in the following buffer: Tris-HCl 50 mM, Glycerol 5% and GTP 40 μM. Septin 6 has been submitted to initial screenings using the following kits: Classic-Nextal, MPD-Nextal, Ion-Nextal, Cation-Nextal, AmSO4-Nextal, PEGs-Nextal, Wizard I e II (Emerald); but until now no crystals were observed.

Acknowledgements

Financial support by FAPESP and ABTLuS.

24

Structural insights into the exosome RNA processing mechanism

Navarro, M.V.A.N.[1], Oliveira, C.C.[2], Zanchin, N. I. T[1], and Guimarães, B.G.[1]

[1] Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil
[2] Universidade de São Paulo - São Paulo - São Paulo SP Brazil

The expression of genetic information and protein synthesis ultimately depends on the maintenance of correct RNA levels. Acting on numerous RNA processing pathways and different RNA substrates, the exosome, a multiprotein complex of 3’ - 5’ exonucleases, emerges as a key component of the RNA-surveillance machinery. In Archea, the exosome core is composed by two RNase PH proteins, aRrp41 and aRrp42, which assemble into a hexameric ring by alternating subunits. Such molecular architecture encloses the exoribonucleolytic active sites within a catalytic chamber and restrict to a narrow channel entry the access of only unstructured RNA. Structural and functional analyses have revealed the exosome catalytic mechanism, however important issues concerning how the RNA is progressively processed remain unclear. Here we show, through a series of crystal structures of the RNase PH core from *Pyrococcus abyssi* exosome, the complete picture of the RNA processing mechanism by the exosome. We found three 10-mer RNA strands assembled in a triple helix within the catalytic chamber of the RNA-bound structure. The five inner-most 3’ end bases occupies an specific RNA bind cleft, while the remaining nucleotides of each strand extend to the back entry of the core channel. Furthermore, the structure complexed with CDP have revealed that residues from both aRrp41 and aRrp42 subunits form the phosphorolitic active sites and the ADP bound structure surprisingly showed the nucleotide occupying an unexpected pocket, which was postulated to be exit way after catalysis. Our results suggest that RNA translocation and processivity within the exosome requires the interaction between three RNA strands, which are processed concomitantly.

25

Crystallographic structure of lysosyme 1 from *Musca domestica* complexed with chitotetraose

Valério, A. A.[1], Cançado F.C.[2], Marana, S.R.[2], and Barbosa, J.A.R.G.[1]

[1] Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil
[2] Universidade de São Paulo - São Paulo - São Paulo SP Brazil

Lysozymes (EC 3.2.2.27) catalyze the hydrolysis of 1,4-β-linkages between N-acetylmuramic acid and N-acetylglucosamine residues in peptideoglycan of the bacteria wall. Lysozymes from family 22 are usually part of defense system against bacteria. However, some lysozymes have a different biological function: in some animals, like mammals and insects, they are involved in the digestion of bacteria. Here, we report the first structure of a complex with a digestive lysozyme. Lysozyme 1, found in the gut of *Musca domestica*, was expressed as a recombinant protein in *Pichia pastoris* and purified. Samples of purified enzyme (9.6 mg.ml^{-1}) were submitted to crystallization using the sitting-drop vapor-diffusion method and previously found conditions. The complex of lysozyme 1 from *Musca domestica* with chitotetraose was prepared by soaking and diffraction data were collected at the protein crystallography beam line D03B-MX1 of the LNLS. The data set was processed using HKL-2000 and CCP4 package to a maximum resolution of 1.9 . Molecular replacement was performed with the MOLREP program using one monomer of the lysozyme 1 native structure, deposited in PDB with code 2FBD, as a search model. Initial crystallographic refinement was performed with one cycle of simulated annealing using CNS. Subsequent cycles of refinement were carried out with REFMAC. Model building was done with the programs O and Coot by inspecting the 3Fo-2Fc and Fo-Fc electron density maps. The ligand was copied and adjusted from the coordinates of tryacetylchitotriose obtained via the Hic-Up database. We shall present an analysis of the active site and its interactions with the ligand that intends to contribute for the comprehension of the molecular adaptations of this lysozyme to the digestive function.

Acknowledgements
Financial support by FAPESP and ABTLuS.

26

Three-dimensional structure of *Saccharomyces cerevisiae* Glutaredoxin2 - glutathione mixed disulfide complex

Discola, K. F.[1], Oliveira, M.A.[1], Guimarães, B.G.[2], and Netto, L.E.S.[1]

[1] Universidade de São Paulo - São Paulo - São Paolo SP Brazil
[2] Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil

Glutaredoxins are small (9-12 kDa) heat stable proteins with at least one cysteine at their active sites that are highly conserved throughout evolution. The ubiquitous distribution of glutaredoxins is probably related to the fact that these proteins are involved in many cellular processes, including protein folding, regulation of protein activity, reduction of dehydroascorbate, repair of oxidatively damaged proteins and sulphur metabolism. In the yeast *Saccharomyces cerevisiae* five glutaredoxin genes (GRX1-5) were identified. The Grx1 and Grx2 isoforms are dithiol proteins with a Cys-Pro-Tyr-Cys motif in their active site, whereas Grx3, Grx4 and Grx5 are monothiol proteins that contain Cys-Gly-Phe-Ser in their active site. The importance of glutaredoxin is classically related to the fact that these proteins possess the ability to reduce disulfide bonds. Changes in the thiol-disulfide redox status of proteins are important not only for the reactivation of enzymes and for protein folding and stability, but also for the control of protein function. Our objective is the functional and structural characterization of the yeast glutaredoxins by biochemical assays and X-Ray crystallography. We already had determined the crystallographic structure of yeast Grx2 at 2.05 resolution in the oxidized state. And we reported here the determination of the three-dimensional structure of yeast Grx2-C30S mutant with glutathionyl mixed disulfide at 1,91 resolution. We expect that an accurate analysis of the structures of Grx2 may contribute to a better understanding of its enzymatic mechanisms.

27

Crystallization, X-ray diffraction data collection and structure determination of cytoplasmatic thioredoxin peroxidase I, C47S mutant, from *Saccharomyces cerevisiae*

Oliveira, M.A.[1], Genu, V[1], Discola, K. F.[1], Alves, S.V.[1], Guimarães, B.G.[2], and Netto, L.E.S.[1]

[1] Universidade de São Paulo - São Paulo - São Paolo SP Brazil
[2] Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil

Saccharomyces cerevisiae cytoplasmatic thioredoxin peroxidase I (cTPxI) is a bi-functional protein with protective roles in the cellular defenses against oxidative stress and heat shock, exhibiting peroxidase and chaperone activities. The chaperone activity is trigged by specific overoxidation of a cysteine residue (Cys 47) and/or high temperatures, and is conferred through quaternary structural reorganization of dimers in complexes of higher molecular weight. A recombinant mutant of cTPxI from *S. cerevisiae*, carrying the substitution of cysteine 47 by serine, was overexpressed in *Escherichia coli* as a His_6-tagged fusion protein and purified by nickel-affinity chromatography. Crystals were obtained by the hanging-drop vapor diffusion method from the protein previously treated with 1,4-dithiothreithol using PEG 3000 as precipitant and sodium fluoride as additive. The crystals belong to the monoclinic space group C2, with unit cell parameters a = 239.98 b = 51.96, c = 193.43 , *beta* = 92.33^o. Diffraction data were collected to 2.8 resolution using a synchrotron radiation source, crystal structure was solved by molecular replacement methods and structure refinement is in progress.

Acknowledgements
This work was supported by grants from Fapesp (SMOLBnet) and CNPq (Instituto do Milenio-Redoxoma).

28

Expression and purification of mesothelin for structural studies

Santos, C. R.[1] and Barbosa, J.A.R.G.[1]

Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil

Mesothelin is a glycoprotein present in normal mesothelial cells and in a variety of tumor cells, including mesothelioma, ovarian cancer and pancreatic cancer. It is expressed as a 69-kDa precursor protein that is cleaved in megakaryocyte potentiating factor (31-kDa) and mesothelin (40-kDa). The first is released to the medium and the second is glycosylphosphatidylinositol-ancored to the membrane. Mesothelin is a differentiation antigen considered a promising candidate for target therapy of cancer and a potential tumor marker. Even though mesothelin´s biological function is not known yet, anti-mesothelin immunotoxins with antitumor activity have been developed and DNA vaccines studies encoding mesothelin peptides have been carried out. The gene region corresponding to mesothelin was PCR amplified from a human leukocyte library and cloned into modified pET28a vector. Mesothelin (E296-G580) was expressed in *Escherichia coli* BL21(DE3) with a N-terminal His_6-tag. Only small amounts of protein remained soluble while the majority was present in the inclusion bodies. The soluble form was purified by affinity chromatography and gel filtration. The insoluble form was denatured and purified by affinity chromatography and refolded by dialysis. Biophysical characterization was performed for both samples, showing similar results and indicating that the refolded protein is in its native conformation. The refolded protein has been used for crystallization trials after the removal of the His_6-tag with TEV protease.

Acknowledgements
Financial support by FAPESP and ABTLuS.

29

Structural and Functional Studies of the Outer Membrane Lipoprotein (OmlA) from *Xanthomonas citri*

Teixeira, M. M. A.[1], Benedetti C.E.[1], Sforça, ML[1], Pertinhez, T. A.[2], and Spisni, A.[2]

[1] Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil
[2] Università degli Studi di Parma - Parma Italy

Xanthomonas axonopodis pv *citri* (*Xac*) is the bacterium that causes citrus canker, a disease of great impact to the Brazilian citriculture. The *Xac* 1516 gene encodes an outer membrane lipoprotein (OmlA) whose function remains unknown. The OmlA gene is found adjacently to the gene encoding the *ferric uptake regulator* (Fur), the most important regulator of iron homeostasis in bacteria. Since in *Xac* these genes are oriented in opposite directions, they might share promoter regions, suggesting co-regulation of OmlA/Fur as well as a possible role of OmlA on iron metabolism. To study the regulation of OmlA/Fur, green fluorescent protein was cloned downstream from the promoters of OmlA and Fur and these reporter constructs were introduced into *Xac* to infect *Citrus* leaves. Fluorescence microscopy shows that both reporter bacteria recovered from infiltrated leaves exhibited increased fluorescence. Thus, both the OmlA and Fur promoters are up-regulated in *Xac* during infection, which is consistent with the idea of co-regulation of OmlA/Fur. The OmlA protein was detected by western blot in crude extracts of wild type *Xac* grown in the presence of Cl_3Fe, an iron chelator and sodium benzoate. Lower protein levels were observed in the presence of the iron chelator, suggesting that the OmlA gene is not up-regulated by lack of iron. To associate functional and structural data, the OmlA protein was expressed in ^{15}N- ^{13}C enriched media for the resolution of its 3D (three-dimensional) structure by NMR (Nuclear Magnetic Resonance). Multidimensional NMR experiments were then carried out in the presence of phosphate buffer, allowing the complete backbone and side chain resonance assignments. The Chemical Shift Index (CSI) pattern compared with molecular dynamics data shows that the protein has alpha-helical and beta-sheet elements and unfolded N- and C-terminals. NOESY spectra confirm the secondary structure pattern and NOE unambiguous assignments are being used as distance constraints to determine the protein 3D structure. Preliminary modeling calculations reveal a folded core characterized by the presence of two alpha-helical elements and three anti-parallel beta strands and unfolded C- and N- terminal portions. We expect that the OmlA 3D NMR structure will provide us with clues on the biological function of this protein.

Acknowledgements
Supported by CAPES and FAPESP

30

Structural Studies the Hgxprt from *Pyrococcus horikoshii*

Dantas, D.S.[1], Pereira, G. A. G.[1], and Medrano, F. J.[2]

[1] Universidade Estadual de Campinas - Campinas SP Brazil
[2] Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil

Purine phosphoribosyltransferases are involved in the purine bases salvage. They catalyze the reversible transfer of a phosphoribosyl group from 5-phospho- α-D-ribosyl 1-pyrophosphate (PRPP) to a purine base (hypoxanthine, guanine or xanthine) releasing pyrophosphate, resulting in the corresponding nucleotide monophosphate (IMP, GMP or XMP). HPRT from *Pyrococcus horikoshii* (PhHPRT), a hyperthermophylic microorganism, shows significant differences in key residues present in three of the four catalytic loops. The objective of this study is to characterize the thermal stability of PhHPRT to get some insights into the protein sequence rearrangements necessary to enzymatic activity at high temperatures. We have cloned PhHPRT gene in the pET15b expression vector, and expressed this protein in *Escherichia coli* BL21 Star ^{TM}(DE3). The protein was purified by heating (75žC) and precipitating *E. coli* denatured protein, followed by an immobilized metal affinity chromatography. Steady-state kinetic assays showed that phHPRT is a hypoxanthine-guanine-xanthine phosphoribosyltransferase. CD analysis of PhHPRT and HPRT from *Trypanossoma cruzi* resulted in different spectra, which can reflect a different folding at some parts of these proteins. We have also obtained the DLS spectrum of phHPRT, which indicated a hexamer oligomerization of this protein. Further studies will give us some insights on the effect of sequence rearrangements on the final structure of the protein.

Acknowledgements
This work was supported by FAPESP

31

Structural and functional studies of the oxidoreductases DsbA from *Xylella fastidiosa*

Rinaldi, F. C.[1] and Guimarães, B.G.[1]

Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil

The disulfide oxidoreductases (DsbA) are periplasmic proteins involved in disulfide bond formation. The DsbA's assist the correct folding of exported proteins containing disulfide bonds. In *Vibrio cholerae* one member of this protein family is required for the functional maturation of secreted virulence factors. *Xylella fastidiosa* is a phytopathogenic bacterium that causes serious diseases in a wide range of economically important crops. *X. fastidiosa* genome analysis revealed the presence of two different members of DsbA's protein family (for now named DsbA1 and DsbA2). A sequence alignment showed that the active site regions of DsbA1 and DsbA2 differ from each other by one residue, which is considered important for enzymatic activity. We are performing structural and functional studies on these DsbA oxidoreductases from *X. fastidiosa*.

In this work we have solved the crystal structure of DsbA1 by the single-wavelength anomalous diffraction (SAD) method. The DsbA1 labeled with selenomethionine (DsbA1-SeMet) was expressed in *Escherichia coli* C43 cells in a SeMet supplemented medium. Mass spectrometry analysis showed that all three methionines residues were replaced by SeMet. The DsbA1-SeMet protein was crystallized under the same conditions of the native protein. X-ray diffraction data were collected in the X26C protein crystallography beam line at the National Synchrotron Light Source (NSLS). A data set was collected to a resolution of 1.85 Å and belonged to space group C2, with unit-cell parameters: a= 203.16 Å, b= 42.54 Å, c= 81.435 Å, β= 96.15. The selenium substructure (six sites) was solved using SHELXD program. The phases calculated with the program SHARP/autoSHARP were sufficient for automatic tracing of over 93 % of the structure using the program ARP/wARP. Further manual rebuilding was done and the three molecules present in the asymmetric unit had their structural refinement carried out with REFMAC5. The complete model was refined to a final R/Rfree of 0.196/0.233. During refinement procedure a suspicious electronic density was found in the protein surface close to the active site residues. We believe that a peptide, which probably came from the *E. coli* expression system, is responsible for this suspicious density. In parallel, fluorescence experiments are being performed in order to obtain complementary structural and functional data through the analyses of the oxidizing power of DsbA1 and DsbA2.

Acknowledgements
Financial Support: FAPESP and CNPq.

32

Utilização de Técnicas de Espectrometria de Massas para o Estudo de Interação das Proteínas Tif34p/HisTif35N

Iglesias, A. H.[1] and Gozzo F C[1]

Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil

A espectrometria de massas (MS) é hoje uma técnica bastante abrangente com relação à caracterização de estrutura primária de proteínas. No entanto, as grande vantagens da técnica de MS (altas sensibilidade e rapidez e relativa facilidade no tratamento dos dados) a torna bastante atrativa para vários outros campos da caracterização estrutural de proteínas. As técnicas tradicionais de caracterização estrutural de proteínas, como a Cristalografia de Raios-X e a Ressonância Magnética Nuclear podem fornecer dados estruturais de alta resolução, mas apresentam algumas limitações que impedem seu uso irrestrito. O presente trabalho visa demonstrar duas diferentes metodologias baseadas em Espectrometria de Massas (cross-linking e footprinting) com o objetivo de compreender a interação entre as proteínas Tif34p e HisTif35N de Saccharomyces cerevisiae. Essas proteínas estão relacionadas com o fator de iniciação de tradução eIF3 em eucariotos, sendo que este constitui um grande complexo multiprotéico indispensável para a síntese de proteínas. Em experimentos de cross-linking, utiliza-se um reagente químico que promove a formação de ligações covalentes em sítios específicos das proteínas (nesse caso, serão utilizados reagentes que ligam-se a lisinas e grupos amino terminal). A determinação de quais sítios são ligados entre si, aliada ao comprimento do reagente utilizado permite a determinação de restrições espaciais, que podem ser utilizadas para a obtenção de um modelo do sistema de interesse. Nesse estudo foram utilizados reagentes comerciais e sintetizados no laboratório com diferentes comprimentos. Os peptídeos gerados da digestão dessas proteínas foram então submetidos a análise por LC/MS/MS para determinação dos sítios de ligação dos reagentes. Experimentos de footprinting são baseados no fenômeno de radiólise da água: radiação de alta energia induz a formação de radicais hidroxila em meio aquoso. Esses radicais tendem a reagir com resíduos que se encontram na superfície das proteínas. No caso de complexos protéicos, tanto as proteínas isoladas quanto o complexo nativo são expostos a radiação. Por meio de experimentos de LC/MS/MS, pode-se determinar tanto quais os resíduos específicos são oxidados quanto a cinética de oxidação de cada um destes. Resíduos que se encontram na superfície de interação entre duas proteínas ficam "protegidos"da oxidação e, portanto, apresentam menor cinética de oxidação. Neste trabalho, o complexo Tif34p / HisTif35N foi irradiado utilizando-se a linha de radiólise D06B do LNLS e os peptídeos oxidados analisados por ESI-MS/MS.

Acknowledgements
Os autores agradecem a FAPESP e ao LNLS.

33

Molecular and Structural Analysis of Maltose-binding Protein of *Xanthomonas citri*

Souza, C. S.[1], Balan, A.[1], Barbosa, J.A.R.G.[2], Ramos, C.H.I.[3], and Ferreira, L.C.S.[1]

[1] Universidade de São Paulo - São Paulo - São Paulo SP Brazil
[2] Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil
[3] Centro de Biologia Molecular e Estrutural - Campinas SP Brazil

The MalE protein of *Xanthomonas axonopodis* pv.*citri* belongs to a family of transporters denominated ABC transporters (ATP-Binding Cassete). The mode gene was cloned and expressed in *Escherichia coli* and the recombinant protein was able to bind maltose in vitro experiments. Three-dimentional structures of maltose/maltotriose transporters have been solved in other species including *Escherichia coli* K12, *Thermococcus litoralis*, *Alicyclobacillus acidocaldarius* and *Pyrococcus furiosus* , however, no ortholog derived from plant-associated bacteria have been reported so far and the transport of sugars in *Xanthomonas* is completely unknown. The recombinant purified protein was able to form bipiramidal which have diffracted at low resolution (around 4-10). In this work we report new attempts to crystallization and diffraction. The purified protein was submitted to the crystallization trials with the Jena Biosciences kit and Hampton Research kit, using the hanging drop vapour diffusion method and 10 mg/ml of protein (200 uM) bound to 400 uM maltose at 18°C and 4°C. The crystals were obtained in 12 different conditions and used in the diffraction assays. The best diffraction pattern was obtained for the crystals grown at 0,1M Tris-HCl pH 8,0; 3,5 M Sodium formate at 18°C. X-ray diffraction data were collected to a maximum resolution of 2,6 using a synchrotron-radiation source. Diffraction data were collected for one crystal. Indeed, the binding of the protein to the different sugars was monitored by circular dichroism analysis. Indeed, the thermostability of the protein in the open and closed form (unbound and bound to maltose) in different temperatures was monitored thought the circular dicroism experiments. Structural analysis and biochemical characterization of this protein will be important in the elucidation of the regulation and uptake of maltose in *Xanthomonas*.

Acknowledgements
This work was supported by FAPESP.

Parte III

Biologia Molecular e Química de Proteínas

34

Proteome of phytopathogen Xanthomonas axonopodis pv. citri: Expression of hypothetical, hypersensitive response and pathogenicity genes

SOARES, M.R.[1], Facincani, A. P.[2], De Oliveira, J.C.F.[2], and Gozzo F C[1]

[1] Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil
[2] Universidade Estadual Paulista - Jaboticabal - Jaboticabal SP Brazil

The proteome of Xantomonas axonopodis pv. citri (Xac) was analyzed by liquid chromatography (LC) and tandem mass spectrometry (MS/MS). This approach does not require a gel electrophoresis step and provides a rapidly developed snapshot of the proteome. In order to gain insight into the metabolism of Xac, cells were grown on various media and proteins were proteolyzed with trypsin and examined by 2D LC-MS/MS. Several different experimental approaches were utilized to optimize the proteome coverage and to ensure statistically valid protein identification. Approximately 40% of all predicted proteins (open reading frames) of Xac was identified with high confidence, as their component peptides were unambiguously assigned to tandem mass spectra. The results obtained in this study are generally consistent with those obtained from computational genome analysis. At least 25% genes originally annotated as conserved hypothetical were found to encode expressed proteins and for some of them, functions have been assigned. Although Xac was grown at non infecting conditions, various proteins related with pathogenicity and virulence were found in this work.

Acknowledgements
This work was supported by FAPESP

35

Purification, characterization and cristalization trials of an protein isolated from *Lonomia obliqua* hemolymph with potencialization of replication of the *Ag*MNPV Baculovìrus.

Sousa, A.P.B.[1], Marchi-Salvador, D. P.[2], Fontes, M. R. M.[2], and RZ Mendonça[3]

[1] Instituto Butantan - São Paulo SP Brazil
[2] Universidade Estadual Paulista - Botucatu - Botucatu SP Brazil
[3] Instituto Butantan - São Paulo SP Brazil

The*Anticarsia gemmatalis nucleopolyhedrovirus Ag*MNPV, a member of the family Baculoviridae, has been widely applied as a biopesticide for the control of the velvetbean caterpillar, which is the main soybean. In this work, we investigated the benefits of the Grace's medium supplemented with 3 %(v/v) proteic pool and fraction isolated from *Lonomia obliqua*hemolymph on the *Ag* MNPV baculovirus production. This fraction was obtained by chromatography in HPLC. For this, *Lonomia obliqua* hemolymph was collected from caterpillars in sixth development instar. The collected hemolymph was fractionated by gel filtration chromatography in a Sephacryl S-200 and ionic change chromatography in Resource Q column. The fractions and sub-fractions obtained were analyzed by SDS-Page electrophoresis gel and tested for optimization of replication of the AgMNPV in Sf-9 cells. All experiments were carried out in 100 mL shake flasks with working volume of 13 mL. The cultures were performed in a orbital shaker at 100 rpm and 28^{o}C, starting with a inoculum of 3.5×10^5 viable cells/mL. The cells were infected a MOI (multiplicity infection) of 1. A 611.9-fold increase in baculovirus replication was achieved when employing Grace's medium supplemented with 10%(v/v) of FBS and 3%(v/v) selected fraction chromatography. In addition, a 6443.91-fold increase in baculovirus replication was obtained when using Grace's medium supplemented with 10%(v/v) FBS and 1%(v/v) of the *Lonomia obliqua* hemolymph. Microcrystals and polycrystals of the protein isolated from *Lonomia obliqua* were obtained by hanging-drop vapour-diffusion method in which the protein solution was equilibrated against a reservoir solution number 8 of the Crystal Screen (Hampton Research), 18^{o}C after approximately three weaks, but crystallization trials are being performed to get better crystals.

Acknowledgements
The authors acknowledge the financial support from **FAPESP (01-09040-8 and 04-13292-0)**, LNLS and Fundação Butantan.

36

MudPIT analysis of the *Mycoplasma hyopneumoniae* proteome

Pinto, P. M.[1], Costa, A. P. M.[1], Klein, C. S.[2], Zaha, A.[1], and Ferreira, H. B.[1]

[1] Universidade Federal do Rio Grande do Sul - Porto Alegre RS Brazil
[2] Empresa Brasileira de Pesquisas Agropecuárias - São Carlos SP Brazil

Mycoplasma hyopneumoniae is an important pathogen for pigs, being the causative agent of enzootic pneumonia (EP). Recently the genome sequences of three *M. hyopneumoniae* strains, one non-pathogenic (J) and two pathogenic (7448 and 232), have been reported. A preliminar and complementary proteomic analysis, by two-dimensional gel electrophoresis and MALDI-TOF MS, was also done by our group, for the 7448 strain. In this work, the *M. hyopneumoniae* proteomic analysis has been extended, by the use of multidimensional protein identification technology (MudPIT) to identify proteins from different strains. So far, we have analyzed the 7422 (pathogenic) and J strains, being able to identify 76 and 28 proteins, respectively. Proteins from many different protein families have been identified, including some related to cytoadherence and possibly involved in pathogenicity. At least 15 hypothetical or conserved hypothetical genes have been experimentally validated, with the identification of the corresponding protein products. This proteomic survey will be continued for both 7422 and J strains, and extended to the 7448 strain. After completion, this work will allow comparisons between protein profiles of different *M. hyopneumoniae* strains, which are likely to help in the identification of virulence determinants.

Acknowledgements
This work was supported by MCT/CNPq, FAPERGS and CAPES.

37

THERMODYNAMIC PROPERTIES OF PROLYL OLIGOPEPTIDASE FROM *TRYPANOSOMA BRUCEI*

Lima, M. M.[1], Neves, D.[1], Bastos, I.M.D.[1], Freitas, S. M.[1], Teixeira, A.R.L.[1], Grellier, P.[2], and Santana, J. M.[3]

[1] Universidade de Brasília - Brasília DF Brazil
[2] - Paris France
[3] Universidade de Brasília - Brasília DF

Prolyl oligopeptidase is a ubiquitous serine protease of S9 family that hydrolyses substrates at the carboxyl side of proline and alanine residues. We have demonstrated that the irreversible inhibitors against *Trypanosoma cruzi* prolyl oligopeptidase arrest trypomastigotes entry into nonphagocytic host cells, suggesting a role for this enzyme in the parasite life cycle. In this study we present the biophysical characterization of prolyl oligopeptidase from *Trypanosoma brucei* (POPTb) that present similar molecular properties with its *T. cruzi* counterpart. Aiming at the thermodynamic characterization of this enzyme, we carried on studies of chemical denaturation and quenching of the intrinsic fluorescence. Gdn-HCl and Urea cause alteration on the secondary structure of the protein with a change in wavelength. POPTb is not very stable with deltaG equal 3.6 and 3.7 for Gdn-HCl and Urea, respectively. The presence of CTAB induces a structural alteration that results in loss of activity, whereas that of Sorbitol induces quenching of fluorescence with smaller loss of activity. As for quenching of fluorescence, Stern-Volmer constants show pH-dependence and CsCl more powerful a quencher than Acrilamide. The transition from the native to the denatured state is a two-state one with C equal 3.8 for Gdn-HCl and 5.1 for Urea.

Acknowledgements
Supported by CNPq

38

THERMODYNAMIC PROPERTIES OF METHYLTHIOADENOSNE PHOSPHORYLASE (MTAP) FROM *TRYPANOSOMA CRUZI*.

Neves, D.[1], Lima, M. M.[1], Freitas, S. M.[1], and Santana, J. M.[2]

[1] Universidade de Brasília - Brasília DF Brazil
[2] Universidade de Brasília - Brasília DF

The rational drug design is based on biochemical and physiological differences between pathogens and their hosts. The purine metabolism has been identified as an excellent potential target in trypanosomatids since these organisms lack the molecular machinery to synthesize the purinc ring de novo, obtaining purines through purine salvage pathway or specific transporters. The methylthioadenosine phosphorylase (MTAP) of *T. cruzi* plays a crucial role in this pathway cleaving MTA in adenine and methyl-thioribose-1-phosphate (MTR1P). This pathway is potentially exploitable for chemotherapy target in protozoan parasites because of the needs of pre-formed purines and the high cost of methionine synthesis. We report on the obtaining of fully active recombinant MTAP that allowed us to study its pH dependence unfolding process, thermal and chemical stability through circular dicroism and fluorescence emission. The secondary structure content was predicted using the data from the circular dicroism. The *T. cruzi* MTAP showed a high thermal stability, over the pH range from 4 to 8.6, with a transitional temperature (Tm) between 75 and 80 ^{o}C The protein was also very resistant to chemical denaturation since its unfolding with guanidinium chloride occurred with more than 3 M. In addition the protein kept folded when treated with a concentration as high as 8 M of urea. The thermal denaturation data were also used to calculate the ΔG and the ΔH. The physicochemical characterization of MTAP can help establish a better condition to perform biological assays, to understand its interactions with the environment and to facilitate its structural analysis.

Acknowledgements
Supported by CNPq.

39

Molecular characterization of *Citrus sinensis* proteins that interact with *Xanthomonas citri* effector protein PthA.

Souza, T. A.[1], Cernadas, R. A.[1], and Benedetti C.E.[2]

[1] Centro de Biologia Molecular e Estrutural - Campinas SP Brazil
[2] Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil

Citrus canker disease, caused by *Xanthomonas axonopodis pv. citri* (Xac), affects most citrus species and represents a major threat to the Brazilian citriculture. Plants are infected through natural openings like stomata or wounds in the surface of leaves, stems and fruits. Once in the plant tissue, the bacteria use a type 3 secretion system to inject effector proteins into the plant cell. These effector proteins, including PthAs, alter transcription of the cell host to the benefit of the pathogen, leading to the development of the cancer lesions, such as hypertrophy and hyperplasia. A number of studies have shown that members of the AvrBs3/PthA family function as transcriptional factors in plant cells. To elucidate how PthA activates transcription and to establish its molecular mode of action, a two-hybrid approach was used to identify host proteins that interact with PthA and therefore could be important for the development of the canker lesions. Among the proteins of *Citrus sinensis* identified we selected for further studies an ubiquitin conjugating enzyme and an auxin response factor protein, both involved in the control of cell division by auxin signaling pathway. These genes were amplified by PCR and fused with the activating domain of the pOAD vector. The DNA fragment encoding PthA isoform 4 and 2 were cloned in pOBD vector. Subsequently, the interaction between these proteins was verified by auxotrophic markers and LacZ reporter gene, in a two-hybrid system. The results show that PthA interacts weakly with the auxin response factor and ubiquitin conjugating-enzyme genes, relative to an α-importin clone (positive control), indicating that auxin signaling is likely to play a role in the plant injuries caused by Xac.

Acknowledgements
This work was supported by CNPq, FAPESP and LNLS.

40

Validation of Stanniocalcin-1 (STC1) as a putative microenvironment marker in childhood leukemia and its expression for structural and functional studies

Trindade, D.M.[1], Yunes, J. A.[2], and Kobarg, J.[1]

[1] Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil
[2] Universidade Estadual de Campinas - Campinas SP Brazil

The advances of modern biomedical sciences through sequencing of the human genome, improvements in the methods of protein and nucleic acids analysis, and synthesis of drug libraries through combinatorial chemistry, opened intriguing possibilities for a better understanding, diagnosis and treatment of cancer. Here we investigated some potential target genes associated with the bone marrow (BM) microenvironment of childhood acute lymphoblastic leukemia (ALL). Interaction of leukemia cells with BM microenvironment contributes for acquisition of proliferative advantages by leukemia cells. To identify microenvironment genes modulated by leukemia, we stimulated BM stromal cells by co-culturing them with primary leukemia cells or by addition of ALL patient's plasma to the culture medium; and then performed microarray analysis. Leukemia-induced expression of these candidate stromal genes, and other candidates genes from the literature, was evaluated by quantitative RT-PCR analysis. STC1 was among the genes that showed, in vitro, higher levels of activation by leukemia, and thus was chosen for further functional and structural analyses. This up-regulation will be validated by immunohistochemical expression analysis in BM biopsies from ALL patients or normal donors. STC1 is an endocrine hormone originally discovered in bony fishes but also identified in mammals where is widely expressed in various tissues but neither its receptor nor its exact functions are known. Evidences suggest that STC1 altered expression could be involved in human cancer. STC1 cDNA was amplified from cells from healthy BM stromal cells and cloned into vectors for heterologous protein expression and yeast two-hybrid assays. STC1 protein showed insoluble expression in bacteria but was expressed in soluble form in the baculovirus system. We are currently optimizing the purification for both crystallization trials and spectroscopic assays. Simultaneously, yeast two-hybrid system is being used to screen human cDNA libraries from fetal brain, bone marrow and leucocytes for interacting proteins.

Acknowledgements

This work was supported by FAPESP, CNPq and LNLS.

41

Expression and purification of proteins that interact with FEZ1 for functional and structural studies

Alborghetti, MR[1], Assmann, E. M.[1], Camargo, MER[1], and Kobarg, J.[1]

Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil

The protein FEZ1 (Fasciculation and Elongation protein Zeta-1) is an orthologue of C. elegans UNC-76, necessary for the formation and normal growth axon in this worm. We employed the yeast two-hybrid system in order to identify proteins interacting with FEZ1 and thereby get clues on its cellular functional context. We identified the human proteins BAF60a (BRG1 Associated Factor a), SAP30L (Sin3A Associated Protein 30 Like) and SMC3 (Structural Maintenance of Chromosome 3), and FEZ1 itself among a total of 16 interacting proteins. BAF60a is related to the processes of the chromatin-remodeling activity. BAF60a mediates critical interactions between nuclear receptors and the BRG1 chromatin-remodeling complex for transactivation, mainly by Nuc B remodeling. Moreover, super-expression of FEZ1 induces a post-entry block of retroviruses in cultured cells. SAP30L is homologous to the SAP30, which associates with the transcription repression complex Sin3. A series of functions have been attributed to the protein SMC3 in eukaryotic cells, and its over-expression can induce tumoral cell growth. The cDNA fragments from the yeast two-hybrid prey vectors were cloned in bacterial expression vectors. The expressed proteins were used to confirm the interaction with FEZ1 in in vitro pull-down assay. For a more detailed structural and functional analysis the full lenght cDNAs encoding the interacting proteins were PCR-amplified, cloned and sub-cloned in both bacterial (BAF60a, SAP30L) or baculo virus (SMC3) systems. GST-SAP30L expressed as a soluble protein. It was purified and analyzed by circular dichroism spectroscopy and submitted to crystallization trials. The expression and purification of the other two proteins is still being optimized. The availability of pure recombinant proteins will allow a series of functional and structural studies in vitro. Furthermore, the proteins will be utilized in co-crystallization trials with FEZ1 and analytical gel-filtration studies for the characterization of the protein-complexes

Acknowledgements
Supported by: FAPESP, CNPq and LNLS

42

PRETY, a TATA-binding transcriptional repressor from *Xylella fastidiosa* regulates transcription of an operon conserved in plant-associated bacteria

Barbosa, R.L.[1] and Benedetti C.E.[1]

Laboratŕio Nacional de Luz Síncrotron - Campinas SP Brazil

The protein named PRETY (protein repressor of TATA element from *Xylella*) controls the expression of five genes of unknown function arranged in a single operon. This operon is conserved in some plant pathogenic bacteria including *Xylella fastidiosa*, *Agrobacterium tumefaciens* and other root-associated bacteria. The aim of this project is to elucidate the biological function of PRETY and its target genes. PRETY shows similarities to metal-responsive transcriptional repressors ArsR and SmtB, which control tolerance and detoxification of heavy metals in prokaryotes. However, the PRETY operon differs remarkably from the ArsR and SmtB types of operon since it does not contain the same effector proteins like thioneins and ATPases. Instead, the PRETY operon contains, in addition to PRETY, three predicted membrane permeases and a putative glyoxalase II/beta-latamase (BLH), a member of the beta-lactamase super family. In this work we show that PRETY binds to a TATA box-like element comprising a 9-4-9 palindrome in the BLH promoter and repress transcription of a reporter gene under the control of the BLH promoter providing evidence for its role as a transcriptional repressor in *X. fastidiosa* and *A. tumefaciens*. Although binding of PRETY to its target DNA was diminished in the presence of cadmium, copper and iron, the regulation of the operon by PRETY in response to these metals could not be demonstrated *in vivo* using *Xylella* and *Agrobacterium* cells carrying a reporter plasmid. Structural studies show that PRETY multimerizes in solution and changes its secondary structure in the presence of the target DNA. The use of subtracts for beta-lactamase, lactonases and glyoxalases, as well as hypoxia and nutrient deficiency did not alter the expression of the operon. Similarly, the activity of the reporter genes in *Agrobacterium* and *Xylella* did not change when the bacteria were in contact with the plant or with plant extracts. On the other hand, both *Agrobacterium* and *Xylella* reporter cells showed a significant increase in the operon activity during the biofilm formation indicating a possible function related to a quorum-sensing system.

43

Analysis of the interaction of the hepatitis B virus onco-protein HBx with the human protein p120E4F and with RNA.

Gonçalves, K.A.[1], Rui, E.[2], Moura, P.R.[1], Rooney, R. J.[3], and Kobarg, J.[1]

[1] Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil
[2] Universidade de São Paulo - São Paulo - SP Brazil
[3] Duke University Medical Center - Durham CN United States of America

Infection with hepatitis B virus (HBV) has been associated with development of liver cancer (HCC), one of the most prevalent malignant diseases worldwide. A large body of experimental work points to a central role for the virally encoded protein HBx in this form of carcinogensis. Our discovery that HBx binds to RNA sequences that are rich in A and U (1), brought about the question of the specificity of this interaction and whether it is possible to identify and define a sequence binding motif on the mRNAs target for HBx. In order to identify mRNA sequences that can bind to HBx we employed the technique SELEX (Systematic Evolution of Ligands by EXponential enrichment). We were able to identify several potential target RNA sequences that we are currently testing in quantitative and competitive gel-shift experiments. Furthermore, HBx when expressed in HBV-infected liver cells, interacts with a wide range of cellular proteins, thereby interfering in cellular processes including cell signaling, cell cycle regulation and apoptosis (2). In order to identify possible new protein targets of the HBx protein, we performed a yeast two-hybrid screen using a truncated protein mini-HBx(18-142) as the bait. In addition to known interacting partners, such as RXR and UVDDB1, we identified several new candidates including the human transcriptional regulatory protein p120E4F, which has been implicated in the regulation of mitosis and the cell cycle (3). The interaction of HBx and E4F was confirmed by pull down experiments in vitro. Further transcription activation assays in the yeast one-hybrid system showed that HBx can repress the expression of a reporter gene under the control of both E4F binding site and the HBV enhancer region II. The interaction of HBx and E4F may be of functional importance in the light of cellular transformation and a host-virus co-evolution.

1- Rui et al., Virus Research, 74: 59-73 (2001) 2- Moura et al., Virus Research, 108: 121-131 (2005) 3- Rui, E, Moura, P.R., Gonçalves, K.A., Rooney, R.J. and Kobarg, J.; Virus Research 115(1):31-42 (2006)

Acknowledgements
Supported by: LNLS and FAPESP

44

The characterization of Selenocysteine-Selenomethionine metabolic conversion in biosynthesis of Thioredoxin 1 from Saccharomyces cerevisiae

ALMEIDA FILHO, H. A[1]

Universidade Federal do Rio de Janeiro - Rio de Janeiro RJ Brazil

Almeida Filho, H.A.1; Lery, L. M. S.; Soares, M.R.1,2; Netto, L. E. S.3; Valente AP 4; . and Almeida FC, 1*

Thioredoxins are ubiquous proteins with two cysteines at the active site. The replacement of cysteines by selenocysteines can be performed by heterologous expression in Selenocysteine containing culture medium. A system was devised here which allows the efficient substitution of cysteine residues at thioredoxin 1 from Sacchamyces cerevisiae by selenocysteine. It involves overexpression of the respective gene with the aid of the T7 promotor/polymerase system. The induction of the T7 polymerase formation was performed in cysteine and Selenocysteine-supplemented medium followed by wash-out of the cysteine and production of the desired gene product in the presence of selenocysteine. The SDS-PAGE from culture medium revealed later protein production times to cells harvested from selenocysteine supplemented medium. However the addition of cysteine don't affect the thioredoxin expression. The Maldi-TOF spectra of Thioredoxin 1 expressed at a selenocysteine supplemented medium revealed six component peaks with 46-48 Da range between them, that is the same between Seleno-Sulfur isotopes, indicating the replacement between Cysteine and Selenocysteine and possibly selenocysteine to selenomethionine metabolic conversion during translation. The peptide mass fingerprint of Trx1 expressed in selenocystein enriched medium compared to cysteine enriched medium shows the selenocysteine and selenomethionine containing peptides. The same was not observed in cysteine added medium demonstrating that cysteine was exchanged by Selenocysteine and forward converted in Selenomethionine.

Acknowledgements

This work was supported by Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES), International Centre for Genetic Engineering and Biotecnology (ICGEB), Programas de Núcleos de Excelência (PRONEX) e Fundação de Amparo à Pesquisa do Estado do Rio de Janeiro(FAPERJ).

45

Conformational changes between reduced and oxidized states of the Reductase Thioredoxin (TrxR1) from Saccharomices cerevisae: Insights in Thioredoxin system evolution.

ALMEIDA FILHO, H. A[1], Almeida F.C.L.[1], Valente, A. P.[1], Lima, L. M. T. R.[1], and Netto, L.E.S.[2]

[1] Universidade Federal do Rio de Janeiro - Rio de Janeiro RJ Brazil
[2] Universidade de São Paulo - São Paulo - São Paolo SP Brazil

The E. coli reductase thioredoxin (TrxR) reaction mechanism occurs by electron transfer from NADPH to FAD cofactor, and so forward to the active site disulphide, which reduce the substrate. Kinetic and spectroscopic measurements, redox properties and X-ray structure have supported the conclusion that TrxR undergoes a large conformational change between oxidized (FO) and reduced (FR) forms to enable the NADPH substrate to exchange electrons with flavin ring. In present work the his-tagged TrxR1 from Saccharomyces cerevisiae obtained by heterolog expression in E.coli BL21-DE3 and purified by affinity chromatography and HPLC size exclusion chromatography was submited to reductive and oxidative enviroments. The size exclusion chromatography shown the dimeric state of TrxR1. A large conformational change was supposed between FO and FR through tryptophan fluorescence spectroscopy measurements of emission tryptophan wavelength spectra between 300 to 400nm, using a fixed excitation wavelength from 280nm. The tryptofan fluorescence quenching in FR spectra revealed a high level of tryptophan solvent exposition, which could be generated by the high mobility of NADP domain. The same was not observed to oxidized protein. The fluorescence ressonance energy transfer (FRET) data from reduced TrxR1 collected between NADPH-FAD cofactor was monitored using excitation wavelength of NADPH fluorescence at 340nm and measuring FAD emission spectrum between 400 to 600nm. It revealed that under reductive conditions NADPH and FAD cofactor were able to transfer fluorescence ressonance energy between them, suggesting that these cofactors are very close in tertiary structure under reductive enviroment . Together these data are suggesting that the same large conformational change observed at E. coli TrxR1 during catalytic mechanism , occurs to yeast TrxR1. It add new insights in thioredoxin system evolution between eukaryotes and prokaryotes.

Acknowledgements
This work was supported by Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES), International Centre for Genetic Engineering and Biotecnology (ICGEB), Programas de Núcleos de Excelência (PRONEX) e Fundação de Amparo à Pesquisa do Estado do Rio de Janeiro(FAPERJ).

46

Functional characterization of SBDS, the Shwachmann-Diamond Syndrome associated human protein

Hesling, C.[1], Oliveira, C.C.[2], Castilho BA[3], and Zanchin, N. I. T[1]

[1] Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil
[2] Universidade de São Paulo - São Paulo - São Paulo SP Brazil
[3] Universidade de São Paulo - São Paulo - SP Brazil

The Shwachman-Diamond Syndrome (SDS) is an inherited marrow failure disorder with complex pleiotropic phenotypes including predisposition to myelodysplasia and acute leukemia. SDS-associated mutations were described in the SBDS gene that encodes a member of a highly conserved protein family of unknown function. Indirect evidences support the hypothesis that it may function in pre-rRNA processing and ribosome biogenesis. In order to obtain functional information on the human SBDS protein we have used the siRNA technique to down-regulate SBDS in HEK293 cells. Stable inhibition of SBDS expression was achieved, however, cell survival and proliferation were only slightly affected. Quantitative analysis of polysome profiles and pre-rRNA processing did not reveal any striking defect in ribosome biogenesis in the siRNA knock down cells. Nevertheless, pull-down and in yeast two-hybrid assays indicated that SBDS is found in complexes containing HsNip7, providing further data for the implication of SBDS in ribosome biogenesis. Since SBDS may be involved in rRNA covalent modifications such as methylation and/or pseudourydilation, which may affect ribosome function, we will perform experiments based on global gene expression analyses to screen for mRNAs that may require SBDS function for efficient translation. Together, these analyses should contribute to increase our knowledge about SBDS functions and establish whether there is a relationship between a protein involved in non coding RNA biosynthesis and a human genetic syndrome.

Acknowledgements
This work is supported by a fellowship from the "Ministério de Ciências e Tecnologias"(MCT) and by the "Fundação de Amparo à Pesquisa do Estado de São Paulo"(FAPESP).

47

The human regulatory protein Ki-1/57 interacts with RNA binding proteins and 25-mer poly-U RNA

Bressan, G.C.[1], Passos, D. O.[1], and Kobarg, J.[1]

Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil

The human nuclear and cytoplasmatic 57 kDa protein Ki-1/57 was firstly identified in Hodgkin‘s lymphoma analogous cell lines through the Ki-1 monoclonal antibody cross-reactivity. Ki-1/57 shares 41% of sequence identity and 67% of sequence similarity with the human protein CGI-55, suggesting that both proteins could be paralogs. The CGI-55 protein has already been described as a RNA binding protein that binds to 3‘-region of the RNA encoding the type-1 plasminogen activator inhibitor (PAI-1). In recent studies, we explored the yeast two-hybrid system and found that both Ki-1/57 and CGI-55 interact with the several common proteins involved in transcriptional regulation, including CHD3, Topors, Daxx and PIAS. Furthermore, several of the identified Ki-1/57 interacting proteins are involved in RNA metabolism (CIRBP, SFRS9, SF2/p32 and PRMT1). Although neither Ki-1/57 nor CGI-55 posses any classical RNA binding domains, they both share two conserved RGG box motifs, which have been predicted as motifs involved in RNA binding and as PMRT1 methylation sites. Moreover, the Ki-1/57 and CGI-55 were found as PRMT1 interacting protein among several others known RNA binding proteins in our two-hybrid study using PRMT1 as bait, suggesting an involvement of Ki-1/57, as well CGI-55, in RNA metabolism. In this way, to access the RNA binding properties of Ki-1/57, we performed several experiments using the EMSA (Electrophoretic Mobility Shift Assay) technique with 25-mer homo polymers poly-U, poly-A, poly-C, poly-G and poly-AU as ^{32}P probes. We found that the recombinant fusion protein GST-Ki-1/57 binds selectively to the poly-U probe. When we used several truncated protein constructions of Ki-1/57, we observed that the larger fusion construction 6xHis-Ki-1/57(122-413), which contains two RGG box motifs, binds with higher affinity to the U-rich probe than two smaller constructs, which contain only one RGG-box motif each. Furthermore, when we pre-incubated the GST-Ki-1/57 protein, coupled to glutathione beads, with nuclear or cytoplasmic fractions of human L540 cells, we observed different interaction profiles for the five RNA probes in the EMSA. This could suggest that Ki-1/57 may bind to other proteins or RNA binding protein complexes in vivo. In summary, our findings point to a possible role in RNA metabolism for the regulatory protein Ki-1/57.

Acknowledgements
FAPESP, CNPq and LNLS.

48

Expression and characterization of the human protein ISG95: a probable RNA-methyltransferase and RNA-guanylyltransferase that responds to interferon and viral infection.

Vaz, T. H.[1], Silva TCL[1], and Zanchin, N. I. T[1]

Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil

The main mechanism of single-cell resistance to viral infection involves several genes from the interferon signaling pathway, called ISGs (interferon stimulated genes). Some of these genes can also be induced by alternative pathways. ISG95 responds to INF and CpG treatment and to HCV (hepatitis C virus) and VV (vaccinia virus) infection and is also over expressed in leukemic samples. Primary sequence analysis of ISG95 revealed four conserved domains that include: Gpath (RNA binding), FtsJ (RNA methylation), DNA ligase/mRNA capping family domain and WW (protein-protein interaction). ISG95 was expressed in insect cells using a Baculovirus-derived system. Two days after infection the expressed protein was purified and used in functional assays. ISG95 showed triphosphatase activity, but did not show guanylyltransferase nor methyltransferase activity, which are also expected for a capping enzyme. The biochemical characterization of ISG95 is in progress. Functional analysis of ISG95 was performed using *Saccharomyces cerevisiae* conditional strains. Diploid heterozygote deletion strains from the essential genes involved in each step of mRNA cap formation named *ABD1*, *CET1* and *CEG1*, were obtained from the *Saccharomyces Genome Deletion Project*, transformed with a vector encoding the respective wild type gene and sporulated. Complementation assays on medium containing 5-FOA showed negative results both with ISG95 protein and with a ISG95 fused to a mutated form of the *S. cerevisiae* CEG1 gene. In order to better understand ISG95 function, a yeast two-hybrid screen was performed using ISG95 as bait but only self activating preys were isolated. A new screening will be performed using only the C-terminal of the protein (region containing the WW domain, related to protein-protein interactions). To verify whether the ISG95 promoter is induced by interferon and the minimal promoter region, a SEAP (secreted alkaline phosphatase) reporter gene was placed under control of four constructions of the ISG95 promoter in the pTAL-SEAP plasmid (Clontech). The resulting plasmids will be transfected into Vero cells, which will be treated with interferon and will have the SEAP expression levels analyzed.

Acknowledgements
Supported by CNPq/ FAPESP/ LNLS

49

Identification of non-zein proteins in BR473 maize protein bodies by LC-nanoESI-MS/MS

Bicudo, R. C.[1], Bicudo, T. C.[2], Forato, L.A.[2], Colnago, L.A.[2], and Lanças, F.M.[1]

[1] Universidade de São Paulo - São Carlos - São Carlos SP Brazil
[2] Empresa Brasileira de Pesquisas Agropecuárias - São Carlos SP Brazil

The nutritional value of maize seed is limited due to its high content of storage proteins (zeins), which are deficient in essential amino acids as lysine and tryptophan. Because of this, Embrapa (Brazilian Agricultural Research Corporation) developed the BR473 maize variety, which has excellent energetic value and higher proteic content than the normal maize. BR473 maize variety has 0.9 and 4.0 g/kg of grain of tryptophan (trp) and lysine (lys), respectively, against the 0.5 and 2.6 from normal maize. The high lysine content in some maize varieties as opaque-2 (o2), for example, has been related to the presence of cytoskeleton proteins, that are non-zeins. In order to identify these non-zein proteins, which could explain the high proteic content of BR473 maize variety, we analyzed the protein bodies of these grains. For this purpose, liquid chromatography coupled to nanoelectrospray ionization tandem mass spectrometry (LC-nanoESI-MS/MS) was used, since mass spectrometry has become a powerful tool for protein sequencing and identification. We have identified the following non-zein proteins: Brittle-1 protein (chloroplast precursor), Legumin-1, GAPC, and eEF1A.

Acknowledgements
The authors thank FAPESP (Fundação de Amparo à Pesquisa do Estado de São Paulo, process 02/08407-8) for the financial support. We also thank LNLS (Brazilian Synchrotron Light Laboratory, research proposals: MAS3906 and MAS4540) for its support in mass spectrometry experiments.

50

Gene expression analysis in orange leaves in response to the citrus canker pathogen *Xanthomonas* pv *citri*

Cernadas, R. A.[1], Camillo, L. R.[2], and Benedetti C.E.[2]

[1] Centro de Biologia Molecular e Estrutural - Campinas SP Brazil
[2] Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil

The Citrus canker disease caused by the bacterial pathogen *Xanthomonas axonopodis* pv *citri* (Xac) is considered a threat to the Brazilian citriculture because of its easy dissemination and the absence of commercial resistant cultivars. Cell hypertrophy and hyperplasia are the first microscopic symptoms of the disease. Recently we reported the gene expression profile of orange (*Citrus sinensis*) leaves 48hs after inoculation with a suspension of Xac and *Xanthomonas axonopodis* pv *aurantifolii* (Xaa) (RAU 2006 - LNLS). Noteworthy, Xaa is not pathogenic to orange but causes canker in Mexican lime (*Citrus aurantifolia*) indicating an ongoing host defense mechanisms against it. Differentially expressed genes were grouped into functional categories (i.e. cell wall remodeling, vesicle trafficking and transport, auxin signaling elements, gibberellins synthesis and disease response among others). Results were elegantly presented with special enfaces on cell wall remodeling genes and auxin response elements that are induced by Xac in respect to Xaa and account for cell enlargement (hypertrophy). This kind of host manipulation by Xac could explain its capacity to break the leaf epidermis and disseminate. In order to trap early key regulators or signal transducers, we decided to investigate transcriptional changes occurring earlier during infection. In this context, we used Affymetrix GeneChip array for citrus (Affymetrix, Santa Clara, CA) to determine the pathogenic and defense-associated transcriptional responses 6hs after pathogen inoculation. Preliminary results show that ethylene signaling and glucanase inhibitors are specifically induced by Xaa early during the interaction. Also, we expect that these undergoing analyses provide us some clues to understand citrus basal defenses against Xanthomonas.

Acknowledgements
This work was supported FAPESP and LNLS

51

Characterization of the interaction of the human orthologue of yeast Tip41p, (TIPRL) with the catalytic subunits of type 2A phosphatases and the transcription factor MafB

Smetana, J. H. C.[1], Scapin, S. M. N.[1], and Zanchin, N. I. T[1]

Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil

Tip41p is a yeast phosphoprotein which acts as a negative regulator of the rapamycin-sensitive signaling pathway by binding to Tap42p, a regulator of type 2A phosphatases. In this study, we performed a yeast two-hybrid screening with the human orthologue of Tip41p, TIPRL (TIP41, TOR signaling pathway regulator-like), in order to find a functional context for this protein. We found that TIPRL interacts directly with the catalytic subunits of type 2A phosphatases (PP2Ac, PP4c and PP6c), and with the bZIP transcription factor MafB, but not with $\alpha 4$, the mammalian orthologue of Tap42p. The interactions were confirmed in vitro in GST pull-down assays using recombinant, his-tagged TIPRL, and also the endogenous protein from HEK293 cells. The region responsible for the interactions was mapped to the C-terminal third of PP2A and the bZIP domain of MafB. Binding of TIPRL to the bZIP domain of MafB prevented its interaction with the DNA target sequence in an eletrophoretic mobility shift assay (EMSA), which suggests that it might function as an inhibitor of MafB activity in vivo. TIPRL and $\alpha 4$ interact with distinct sites on PP2A, and the simultaneous binding of TIPRL and $\alpha 4$ on PP2A was demonstrated in vitro using a GST pull-down assay. Both TIPRL and $\alpha 4$ inhibited PP2A activity in vitro using a phosphorylated peptide as substrate. These data suggest that TIPRL is a novel common regulator of type 2A phosphatases, and regulates their activity directly, rather than via $\alpha 4$. The regulation of type 2A phosphatases by TIPRL will be further characterized in vivo by down-regulation and over-expression experiments.

Acknowledgements
We thank Adriana C. Alves, Tereza C. Lima Silva and Zildene G. Correa for technical assistance. This work was supported by CNPq, LNLS and FAPESP

52

Identification of interaction-deficient mutants of TIPRL using a reverse two-hybrid screening

Razolli, D.S.[1], Smetana, J. H. C.[2], KOSCKY-PAIER, C. R.[3], and Zanchin, N. I. T[2]

[1] Universidade Estadual Paulista - Rio Claro - Rio Claro SP Brazil
[2] Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil
[3] Universidade Federal de Viçosa - Viçosa MG Brazil

Tip41p is a yeast phosphoprotein which acts as a negative regulator of the rapamycin-sensitive signaling pathway by binding to Tap42p, a regulator of type 2A phosphatases. We performed a yeast two-hybrid screening with the human orthologue of Tip41p, TIPRL (TIP41, TOR signaling pathway regulator-like), in order to find a functional context for this protein, and found that TIPRL interacts directly with the catalytic subunits of type 2A phosphatases (PP2Ac, PP4c and PP6c), which are the major soluble serine/threonine phosphatases in animal cells and regulate a variety of cell functions. We then used the yeast two-hybrid system to find TIPRL mutants which had lost the ability to interact with type 2A phosphatases, which could provide invaluable tools to better characterize this interaction both structurally and functionally. A library of TIPRL mutants was generated in a mutagenic PCR using primers specific for the TIPRL cDNA. The products resulting from the mutagenic PCR were co-transformed with the linearized pTL1-TIPRL vector into the yeast strain L40 containing the pACT2-PP2Ac vector. The cotransformants were selected on minimal medium lacking leucine and triptophan and interaction-deficient mutants were selected by replica-plating on minimal medium lacking leucine, triptophan and histidine, and containing the HIS3 inhibitor 3-aminotriazol (3-AT). These mutants were subjected further selection by testing the activity of the reporter gene lacZ in X-Gal filter assays and expression of the full length fusion protein lexA-TIPRL by Western blot. The mutant plasmids were extracted, transformed into E. coli and sequenced. To confirm the loss of interaction, the mutant pTL1-TIPRL plasmids were retransformed into the L40 strain with the prey plasmids pACT2-PP2Ac, pACT2-PP4c and pACT2-PP6c, respectively. The interaction-deficient mutants isolated in this study will be used in over-expression experiments to understand the functional relevance of the interaction between TIPRL and type 2A phosphatases.

Acknowledgements
We thank Adriana C. Alves, Tereza C. Lima Silva and Zildene G. Correa for technical assistance. This work was supported by CNPq, LNLS and FAPESP

53

PROTEOMA DE VIBRIO CHOLERAE EL TOR CULTIVADA NA PRESENÇA DE N-ACETILGLICOSAMINA.

Santos, E. O.[1] and Coelho, A[1]

Universidade Federal do Rio de Janeiro - Rio de Janeiro RJ Brazil

V. cholerae é capaz de sobreviver em ambientes diversos, como o intestino humano, onde secreta fatores de virulência provocando a cólera, e reservatórios aquáticos, onde é encontrado na forma livre ou em associação com plâncton e invertebrados. Em ambientes aquáticos, esta bactéria tem como principal fonte de carbono, nitrogênio e energia, monômeros e oligômeros da quitina, o segundo polissacarídeo mais abundante na natureza, encontrada na parede de fungos e nas carapaças de invertebrados marinhos e plâncton. V. cholerae apresenta um regulon nag (regulon nagC) envolvido na assimilação e processamento de N-acetilglicosamina e que é induzido por este aminoaçúcar. O objetivo deste trabalho é analisar a expressão de proteínas de V. cholerae cultivada em meio mínimo M9 suplementado com N-acetilglicosamina. Foram estudadas proteínas intracelulares e de superfície, utilizando-se espectrometria de massas para a identificação. Dentre as proteínas de superfície, foram encontradas proteínas de membrana externa, flagelinas e duas proteases. Na análise de proteínas intracelulares obtivemos fatores traducionais, proteínas ribossômicas, chaperoninas, transportadores ABC, proteínas conservadas e diversas outras proteínas envolvidas com vias bioquímicas básicas da célula.

Acknowledgements

Apoio: CAPES, CNPq, FAPERJ, LNLS.

54

Caracterização de proteínas extracelulares de V. coralliilyticus associadas com o branqueamento de corais

Santos, E. O.[1] and Coelho, A[1]

Universidade Federal do Rio de Janeiro - Rio de Janeiro RJ Brazil

O branqueamento de corais, isto é, a ruptura da associação simbiótica entre o coral e a alga zooxantela é uma das doenças mais sérias e prevalentes. Por várias décadas o processo de branqueamento em corais foi tido como um efeito do aumento da temperatura da água do mar. Mais recentemente foi demonstrado em laboratório que o branqueamento é, de fato, uma doença infecciosa. O aumento da temperatura da água do mar funcionaria apenas como um gatilho. Foi sugerido que sob tais condições, as toxinas extracelulares são expressas, bloqueando a fotossíntese e causando a lise da zooxantela e do coral. Até o presente momento não se sabe exatamente qual o conjunto de proteínas expressas por V. coralliilyticus sob altas temperaturas. O objetivo deste trabalho é estabelecer o mapa proteômico deste vibrio em diferentes temperaturas sob condições padronizadas de tempo e cultivo. Análises preliminares por meio do sistema QTOF indicam que uma variedade de fatores de virulência, incluindo lisinas, TTSS, e metaloproteases, são expressas pelo vibrio cultivado por 24 horas a 28°C. Concluímos que a patogenicidade de V. coralliilyticus é provavelmente multifatorial envolvendo fatores de colonização e sistemas de secreção.

55

Comparative analysis of possible type IV secretion system chaperone (XACb0033) and its co-expressed and co-purified target protein (XACb0032) from *Xanthomonas axonopodis pv citri* (*Xac*)

Lopes, T.P.[1], Borin, P. F. L.[1], Aoki,P.S[1], Ramos, C.H.I.[2], da Silva, J.C.[1], Torriani, I.[3], and Tasic, L.[1]

[1] Universidade Estadual de Campinas - Campinas SP Brazil
[2] Centro de Biologia Molecular e Estrutural - Campinas SP Brazil
[3] Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil

Xanthomonas axonopodis pv citri (*Xac*) causes citrus canker in citrus plantations around the world and is of particular significance in Brazil where its incidence has risen exponentially over the past decade. Approximately one third of the predicted *Xac* ORFs show no homology, or homology with very low score with known sequences. Our targets were two of these ORFs: a possible type IV secretion chaperone XACb0033 and its two-hybrid target XACb0032. We have amplified and cloned the hypothetical *Xac* ORFs XACb0033 and XACb0032 by standard molecular biology techniques. The proteins encoded by these ORFs were expressed and purified by standard methods including anion exchange and gel filtration chromatography. As XACb0032 was insoluble, we have co-expressed and co-purified it with its potential chaperone (XACb0033). The XACb0033 and its complex with the XACb0032 were characterized applying fluorescence and circular dichrosim (CD) spectroscopy. Also the structural analysis by small angle X-ray scattering (SAXS) as well as preliminary crystallization assays will be performed in collaboration with the National Laboratory for Synchrotron Light (LNLS, Campinas, Brazil). All spectroscopic data, ellipticities in CD and fluorescence maximums and life times, indicate that XACb0033 by binding to XACb0032 has significantly changed its secondary and tertiary structure features. Preliminary SAXS results also indicated the size and shape differences of two investigated proteins. The functional studies of XACb0033 and its complex with XACb0032 were initiated in collaboration with Prof. Anita J. Marsaioli group and the preliminary STD NMR results indicate the strong binding of complex with ATP and very mild and probably unspecific binding between XACb0033 and ADP. As these proteins have not known homologs in the protein structural databases, the protein structures obtained should contribute to the current knowledge of protein fold and structure-based functional studies will provide important clues to the biochemical functions of these proteins.

Acknowledgements
This work was supported by FAPESP

56

Functional analysis of Nip7p, a conserved protein involved in pre-rRNA processing in *S. cerevisiae*

Coltri,P.P.[1], Guimarães, B.G.[1], Granato,D[2], Silva TCL[1], Oliveira, C.C.[2], and Zanchin, N. I. T[1]

[1] Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil
[2] Universidade de São Paulo - São Paulo - São Paulo SP Brazil

The machinery of ribosome biogenesis is extensively conserved in eukaryotes. More than 170 factors required for eukaryotic ribosome biogenesis have already been identified, including several non-ribosomal proteins that associate transiently with the pre-rRNA. *S. cerevisiae* Nip7p is a 21 kDa non-ribosomal nucleolar protein required for proper 27S pre-rRNA processing and 60S subunit biogenesis. Nip7p orthologs are found in all eukaryotes suggesting the protein plays a conserved and important role in the cell. Previous studies described Nip7p interaction with the nucleolar protein Nop8p and with the component of the exosome complex Rrp43p. In this work, we investigated the molecular function played by Nip7p during pre-rRNA processing through the analysis of Nip7p interactions with proteins and RNA. We showed Nip7p interacts with the proteins Nop53p and Rrp15p, both involved in 60S subunit biogenesis. In addition, protein A-pull down assays confirmed that Nip7p interacts with the core components of the box H/ACA pseudouridylation complex. Interestingly, all the interactions were mediated by the conserved C-terminal domain of Nip7p named PUA. Despite its interaction with the box H/ACA core proteins, functional analysis using primer extension in Nip7p-depleted cells resulted in only a moderate defect in pre-rRNA pseudouridylation. In contrast, cleavage of 27S pre-rRNA was severely affected in Nip7p-depleted cells. RNA-binding assays revealed that Nip7p can bind directly to 5.8S RNA. Further analyses are being performed to determine the 5.8S RNA region that binds to Nip7p. These results suggested that Nip7p plays a central role in 27S pre-rRNA processing, possibly regulating ITS2 cleavages. In order to investigate the functional conservation of Nip7p throughout evolution, we also intend to verify Nip7p human ortholog interaction with ribosomal RNA. Structural analysis was performed using the *Pyrococcus abyssi* Nip7p ortholog (PaNip7). PaNip7 structure is composed of two alpha/beta domains and the C-terminal region corresponds to the PUA domain.

Acknowledgements
The authors are grateful to Adriana C. Alves and Zildene Correa for technical support. Financial support: FAPESP, LNLS

57

PKR protein kinase activator (PACT) interacts with Dengue virus RNA 3’SL region

Alves, B.S.C.[1] and Zanchin, N. I. T[1]

Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil

Dengue virus genome is composed by a single stranded RNA of positive polarity. The viral 5´ untranslated region (UTR) is similar to the 5´UTR of eukaryotic mRNAs, possessing about 100 bases and a cap structure. The 3´UTR is long, without a poly(A) tail, containing stable secondary structures which are conserved among the different Flaviviruses. Deletion studies have demonstrated that 3´UTR secondary structures and the 3´ Stem-Loop (3´SL) are essential both for synthesis of the viral proteins and for virus viability. The 3´SL mediates anchoring of viral proteins responsible by viral replication and also some human proteins whose function on the Dengue virus biology is unknown. In this work, we have used the yeast three-hybrid system to screen for novel proteins that interact with the dengue virus 3´SL. This screen identified PACT, the PKR cellular protein activator, as a putative 3´SL interacting protein. PKR is an interferon-inducible double-stranded RNA activated protein kinase, which is activated by most viral infections and plays a key role in viral infection resistance mechanisms. Activated PKR phosphorylates the translation initiation factor eIF2α, inhibiting translation of cellular mRNAs. The PACT cDNA was amplified by PCR using the plasmid isolated from the yeast three-hybrid system and subcloned into the *E. coli* expression vector pET-TEV. The protein was expressed using *E. coli* BL21(DE3)$slyD^{-}$ cells incubated at 37^{o}C, which resulted in production of a insoluble protein with the expected molecular weight of approximately 34 kDa. PACT domains M1, M2 and M3 and the combinations of M1M2 and M2M3 were also subcloned into pET-TEV. With the exception of M3, the domains were also insoluble. The his-tagged recombinant proteins were renaturated and their interaction with 3´SL was tested in vitro. As expected, the full length protein and the M1M2 construct were able to interact with 3´SL whereas the M3 PKR activating domain interacted poorly with 3´SL. The assays to determine the role of PACT activation of PKR in a context of Dengue virus infection will be conducted.

Acknowledgements

The authors are grateful to Tereza C. L. Silva and Zildene Correa for technical support.

Financial support: FAPESP, LNLS

58

Cloning, purification and cristallization of the PthA protein of *Xanthomonas axonopodis* pv *citri*

Perez N.T.[1] and Benedetti C.E.[1]

Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil

The Citrus canker disease, caused by the pathogen *Xanthomonas axonopodis* pv *citri* (Xac), is one of the major threats to the Brazilian citriculture.*Xac* is easily spread and can attack all the commercial varieties of citrus. The molecular mechanism by which *Xac* induces canker is not fully understood. However, it is known that *avr* protein delivered to the host plant cell by the type III secretion system play a major role during bacterial infection. One of the best studies *avr* proteins from *Xac* is PthA, which has been demonstrated to be required for the induction of hypertrophy and hyperplasia. PthA isoforms are composed of an N-terminal region required for the type III secretion system transfer, a central region consisting of many repeats of a 34 residue peptide, which confers host selectivity and a C-terminal region with DNA-binding characteristics. PthA isoforms differ by the number of repeats in the central domain and the way by which the repeats are folded may dictate how the protein dimerizes and is successfully transported to the nucleus, where it may act as a transcriptional factor. As the three-dimensional structure of PthA and related proteins are unknown we are attempting at crystallizing PthA for protein structure resolution. To accomplish that, different constructs of the PthA2 isoform were obtained, including Ptha2-6xHis, PthA2ΔN-Terminal-6xHis (carrying only 5,5 34 aa repeats) and PthaC-Terminal-6xHis. This constructs were subcloned into pET vectors for *E.coli* expression. As most of the proteins were found in the insoluble fraction, they were purified from inclusion bodies using guanidine hydrochloride. Proteins were subsequently refolded by gradual removal of the denaturant. Refolded proteins analyzed by Circular Dichroism (CD) and Dynamic Light Scattering (DLS) showed high contents of α-helix, which is consistent with secondary structure predictions. These proteins have been subjected to crystallization trials.

Acknowledgements

This work was supported by CNPq, FAPESP and LNLS.

Parte IV

Ciência Atômica e Molecular

59

Ionic fragmentation of molecules of astrophysical interest: CH_3CN and CH_2CHCN

Ferreira-Rodrigues, A. M.[1], Rodrigues, F. N.[1], Coutinho, L. H.[1], Boechat-Roberty , H.M.[1], and de Souza, G.G.B.[1]

Universidade Federal do Rio de Janeiro - Rio de Janeiro RJ Brazil

Chemistry in Interstellar clouds is strongly modified by the photons coming from the nearby young stars. Therefore, knowledge of photoabsorption, photoionization and photodissociation processes in the UV and X-rays regions is extremely important. We have shown that the low abundance of acid formic (HCOOH) in star-forming regions is due almost totally by soft x-rays that destroyed it (Boechat-Roberty, H.M., et al. Astron. and Astroph. 438, 915, 2005). In the study of interstellar gas phase organic molecules, the Nitriles (or CN compounds) are relevant in the context of the astrobiology since they are precursors of biomolecules like glycine, the most simplest amino acids (Mita, H., et al. Advances in Space Research 33, 1282, 2004). In this work we present laboratory data for the acetonitrile (CH_3CN) and acrylonitrile (CH_2CHCN) molecules, both present in star forming regions. The Time Of Flight Mass Spectrometry (TOF MS) technique was employed to study the dissociation using electrons (1keV incident energy) and photons (energies around C 1s edge, 280 eV, and N 1s edge, 400 eV) performed at the Federal University of Rio de Janeiro (UFRJ) and Brazilian Synchrotron Light Laboratory (LNLS) respectively. The excellent signal to noise ratio has allowed the observation of the reactive ions of astrochemical interest, $H_2{}^+$ and $H_3{}^+$. New branching ratios for the ionic dissociation have been determined. Kinetic energy distributions and abundances for each ionic fragment have been obtained from the analysis of the corresponding peak shapes in the mass spectra.

Acknowledgements
This work was supported by LNLS, CNPq and CAPES.

60

Determination of Resonant Raman Scattering Cross-Sections on Pure Samples of Mn, Fe, Cu and Zn

H. J. Sánchez[1], Valentinuzzi, M. C.[1], Abraham, J. A.[2], and Pérez, C. A.[3]

[1] Universidad Nacional de Cordoba - Córdoba Cba Argentina
[2] Universidad Nacional de Cordoba - Cordoba Argentina
[3] Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil

X ray fluorescence spectra present singular characteristics produced by the different scattering processes. When atoms are irradiated with incident energy lower and close to an absorption edge, scattering peaks appear due to an inelastic process known as resonant Raman scattering. It constitutes an important contribution to the background of the fluorescent line. The Resonant Raman Scattering must be taken into account in the determination of low concentration contaminants, especially when the elements have proximate atomic numbers. The values of the mass attenuation coefficients experimentally obtained when materials are analyzed with monochromatic x ray beams under resonant conditions differ from the theoretical values (between 5% and 10%). This difference is due, in part, to the resonant Raman scattering. Monochromatic synchrotron radiation was used to study the Raman effect on pure samples of Mn, Fe, Cu and Zn. Energy scannings were carried out in different ranges of energies near the absorption edge of the target element. As the Raman peak has a non-symmetric shape, theoretical models for the differential cross section, convoluted with the instrument function, were used to determine the RRS cross section as a function of the incident energy.

Acknowledgements
This work was partially supported by the Laboratorio Nacional de Luz Síncrotron (LNLS, Brazil)

61

Dinâmica de Fotoionização das Bases do RNA

Castilho, R.B.[1], Coutinho, L. H.[1], Lago, A. F.[2], Pilling, S.[2], Cavasso Filho, R. L.[2], Barroso, A. S.[1], de Souza, G.G.B.[1], Almeida, S.M.[1], and Freitas, G.N.[1]

[1] Universidade Federal do Rio de Janeiro - Rio de Janeiro RJ Brazil
[2] Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil

A interação da radiação eletromagnética com o material genético constitui um dos campos mais intrigantes da ciência, e um dos mais importantes, por ser este o código-chave para manutenção da vida [1]. Apesar dos muitos estudos relacionando dano biológico com exposição à radiação, não há ainda uma descrição completa e inequívoca dos mecanismos subjacentes, no tocante as espécies iônicas formadas e sua interação com os alvos celulares. Por exemplo, estima-se que cerca de 2/3 do dano ao material genético, seja desencadeado por radicais livres formados por ionização das moléculas de água circunjacentes, por elétrons altamente energéticos, isto é, suficientes para causar ionização. Por outro lado, nos últimos anos foi demonstrado que elétrons de baixa energia (que não produzem ionização), podem sofrer captura eletrônica pelas bases nitrogenadas ou pelos açucares-fosfato, levando à formação de espécies transientes capazes de amplificar esse efeito em uma ou em ambas as fitas do DNA, resultando no aparecimento de lesões múltiplas [2]. A dinâmica de fragmentação das bases Adenina e Uracila foi determinada por espectrometria de massas por tempo-de-vôo (TOF-MS), no modo de coincidência fotoelétron-fotoíon (PEPICO) [3]. Foi utilizada radiação síncrotron monocromatizada (12 a 21 eV) da linha TGM do Laboratório Nacional de Luz Síncrotron (LNLS). Foram determinados os rendimentos iônicos e as curvas de aparecimento dos principais íons, decorrentes da fragmentação do íon molecular. Os resultados demonstram que a estabilidade do íon molecular é bem acentuada na adenina, enquanto que na uracila, este íon é pouco estável. A energia mínima para dissociação do íon-pai da adenina é de 14 eV; enquanto que para a uracila, em 12 eV já ocorre fragmentação do íon molecular.

Referências:

[1] E. Scrödinger. O que é a vida? O aspecto físico da célula viva. UNESP/Cambridge, São Paulo, 1997.

[2] Michael et al. A sting in the tail os electron tracks. Science (2000) 287, 1603-04.

[3] Guilhaus, M. Principles and instrumentation in time-of-flight mass spectrometry. J.Mass.Spectrom. (1995) 30, 1519-32.

Acknowledgements

Capes, LNLS, CNPq e FAPERJ

62

Dissociative Photoionization of FC(O)SCl, ClC(O)SCl and ClC(O)SCH_3, Following Sulfur 1s and Chloride 1s Excitations

Geronés, Mariana[1], Erben, Mauricio F.[1], Romano, Rosana M.[1], and Della Védova, Carlos O.[1]

Universidad Nacional de La Plata - La PLata B.A. Argentina

In recent years, a number of investigations have been performed in the LNLS concerning the compounds belonging to the sulfenylcarbonyl family. These studies have included the elucidation of photo-dissociation channels upon VUV and soft X-ray irradiation and search for site-specific fragmentation. Thus, FC(O)SCl [1], ClC(O)SCl [2], $CH_3C(O)SH$ [3], $CH_3C(O)SCH_3$, CH3OC(O)SCl [4], ClC(O)SCH_3 and FC(O)SCH_3 has been studied in this context. The use of a wide photon energy range (100-1000 eV) allowed studies of shallow-core levels S 2p and Cl 2p and inner-shell level C 1s, O 1s and F 1s of this molecules. In this work, we present results obtained for the study of FC(O)SCl, ClC(O)SCl and ClC(O)SCH_3 following S 1s (E =2480 eV) and Cl 1s (E=2875 eV) excitations.The use of the SXS beamline (790 y 4000 eV) was necessary to excite and ionized these electrons. From PEPICO and PEPIPICO spectra possible dissociation mechanisms involved in the fragmentation of the followed the electronic ionization were deduced.

[1] M. F. Erben, R. M. Romano, C. O. Della Védova, J. Phys. Chem. A, 108, 3938 (2004). [2] M. F. Erben, R. M. Romano, C. O. Della Védova, J. Phys. Chem. A, 109, 304 (2005). [3] M. F. Erben, M. Geronés, R. M. Romano, C. O. Della Védova, J. Phys. Chem. A, 110, 875 (2006). [4] M. F. Erben, M. Geronés, R. M. Romano, C. O. Della Védova, J. Phys. Chem. A, submited (2006).

Acknowledgements
SXS staff, LNLS, CONICET, CIC, UNLP, ANPCyT, DAAD, Antorchas Foundation

63

Ionic Fragmentation and Dissociation Channels in $ClC(O)SCH_3$, under soft-X-Ray Irradiation

Erben, Mauricio F.[1], Geronés, Mariana[1], Romano, Rosana M.[1], and Della Védova, Carlos O.[1]

Universidad Nacional de La Plata - La PLata B.A. Argentina

In this work, the inner shell C 1s and O 1s electronic regions of $ClC(O)SCH_3$ have been studied by using tunable synchrotron radiation in the range of 200-1000 eV available at the SGM beam line. Studies concerning to this molecule around the S 2p and Cl 2p edges were performed recently by using the TGM beam line. At high photon energies corresponding to shallow- and core-shell electronic levels the quantum yield for molecular ionization is quite likely tending to unity. Consequently, the detection of parent and fragment ions as a function of the incident photon energy (TIY) is a powerful method to be used as a complement to absorption spectroscopy. Thus, the Total Ion Yield (TIY) spectra were measured around the C 1s and O 1s ionization energies. In the O 1s region the TIY spectrum is dominated by an intense resonance at around 532.8 eV and by a second signal with lower intensity at 536.0 eV. Below the threshold, the C 1s region shows an intense transition at 288.7 eV. Naturally occurring isotopomer fragments, mainly due to the presence of ^{35}Cl and ^{37}Cl isotopes, are clearly observed due to suitable mass resolution of the experiments. We recorded several PEPICO spectra of $ClC(O)SCH_3$ at photon energy values around the C 1s and O1s regions.The most intense peak in the PEPICO spectra around the two energy regions involved is observed at m/z = 1 amu/q, corresponding to the H+ ion. The molecular ion, M^+ , cannot be observed in any PEPICO spectra measured. The $C(O)SCH_3{}^+$ ion can be seen as a very low-intensity signal in the PEPICO spectra obtained around the C 1s energy region. In the C 1s region, the intensity of the $CH_3{}^+$ ion is higher than the intensities of the remaining ions of this group, evidencing a different behavior than that observed in the O 1s region, where the C^+ ion showed a higher intensity. PEPIPICO spectra were measured at several photon energies around the C 1s edge and O 1s edge. Possible mechanisms involved in the fragmentation of $ClC(O)SCH_3{}^{2+}$ ion was deduced from the shape of the PEPIPICO double coincidence peaks.

Acknowledgements
SGM staff, LNLS, CONICET, CIC, UNLP, ANPCyT, DAAD, Antorchas Foundation

64

Electron-ion coincidence studies of epichlorohydrin molecule following core-level excitation

Lago, A. F.[1], Naves de Brito, A.[1], and Davalos, J.Z.[2]

[1] Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil
[2] Consejo Superior de Investigaciones Científicas - Madrid Spain

Electron-ion coincidence techniques (PEPICO, PEPIPICO) and synchrotron radiation have been used in the elucidation of the ionic fragmentation pathways following core excitation of epichlorohydrin (C3H5OCl) molecule. Total Ion Yield and mass spectra have been recorded for the first time for this molecule in the vicinity of the C 1s, O 1s and Cl 1s core excitation edges. The experimental set up has been previously described [1,2]. Briefly, total ion yield and mass spectrometry measurements were performed using a Wiley-McLaren type TOF spectrometer and synchrotron radiation from the x-ray spectroscopy beamline at the Laboratório Nacional de Luz Síncrotron (LNLS), Campinas, Brazil. Several dissociation channels have been identified and the fate of the multiply charged fragments is discussed. We have found evidences of site selective fragmentation upon core excitation, as well as indication of molecular quasi-alignment in the photoexcitation and dissociation at the Cl 1s resonance.

References: [1] A.F. Lago, A. C. F. Santos, G. G. B. de Souza, J. Chem. Phys. 120, 9547-9555 (2004) [2] R.R.T. Marinho, A.F. Lago, M.G.P. Homem, L.H. Coutinho, G.G.B. de Souza and A. Naves de Brito, Chem. Phys. 324, 420-424 (2006) .

Acknowledgements
The authors thank the LNLS staff for the assistance, FAPESP (Brasil) and Ministerio de Educación, Cultura y Deporte (Spain) for the financial support.

65

Production of H_3^+ Via photodissociation of organic molecules in interstellar clouds

Pilling, S.[1], Neves, R.[2], Ferreira-Rodrigues, A. M.[2], ACF Santos[2], and Boechat-Roberty , H.M.[2]

[1] Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil
[2] Universidade Federal do Rio de Janeiro - Rio de Janeiro RJ Brazil

The H_3^+ ion plays an important role in diverse fields from chemistry to astronomy. As discussed by Herbst & Klemperer (1973) it initiates the chains of reaction that lead to the production of many of complex molecular species observed in the interstellar medium (see also www.astrochemistry.net). It was recently discovered both in molecular clouds (Geballe & Oka 1996) and in the diffuse interstellar medium (McCall et al. 1998). Drossart (1989) and Geballe et al. (1993) have also reported the presence of this ion in the ionosphere of gaseous planets and it was even suggested that the 3.7 micron H_3^+ emission might be detectable form Jupiter-like planets orbiting other stars (Connerney & Satoh 2000).

We present experimental results obtained from photoionization and photodissociation processes of abundant interstellar CH_3-X type organic molecules like, methanol (CH_3OH), methylamine (CH_3NH_2) and acetonitrile (CH_3CN) as alternative route for the production of H_3^+ in interstellar and star forming environments. The measurements were taken at the Brazilian Synchrotron Light Laboratory (LNLS), employing soft X-ray photons, inside a high vacuum chamber. Mass spectra were obtained using the photoelectron photoion(s) coincidence techniques (Pilling 2006). Absolute cross sections for H_3^+ release were determined. We have found, among the channels leading to dissociation that the H_3^+ yield could reach values up to 0.7% for single photoionization process and up to 4% for process involving double photoionization (Auger process).

The H_3^+ photoproduction cross section due to the dissociation of the studied organic molecules by photons over the C1s edge (200-310 eV) were about $0.2\text{-}1.4 \times 10^{-18}$ cm^2. The fraction of the produced H_3^+ due to CH_3OH photodissociation over the total observed H_3^+ amount could reaches up to 4%, as in the case of dense molecular cloud AFGL 2591. Despite the small value, this represent a new source of H_3^+ into molecular clouds and it is not been considered yet in interstellar chemistry models.

References: Connerney J. E. P. & Satoh T. 2000, T. Phill. Trans. R. Soc. Lond. A385, 2359; Drossart P. et al., 1989, Nature, 340, 539; Geballe T. R. & Oka T.1996, Nature, 384, 334; Geballe T. R., Jagod M. -F. & Oka T., 1993, ApJ, 408, L109; Herbst E. & Klemperer W., 1973, ApJ, 185, 505; McCall B. J., Geballe T. R., Hinkle K. H., Oka T., 1998, Science, 279, 1910; Pilling S., 2006, PhD thesis (http://www.sergiopilling.oi.com.br/Artigos/Tese.pdf)

66

Fragmentação Iônica da molécula do Isopreno na região do Ultravioleta de Vácuo

Bernini, R.B.[1], Castilho, R.B.[1], Coutinho, L. H.[1], Nunez, C. V.[2], and de Souza, G.G.B.[1]

[1] Universidade Federal do Rio de Janeiro - Rio de Janeiro RJ Brazil
[2] Instituto Nacional de Pesquisas da Amazônia - Manaus AM Brazil

O isopreno ($C5H8$) é membro fundamental de uma família imensa de compostos, os terpenos, encontrados em grande quantidade no meio ambiente [1]. Além de sua importância na química atmosférica [2], também é um monômero utilizado em grande escala na indústria [1]. Neste trabalho, a fragmentação desse composto foi estudada nas proximidades da borda do carbono 1s (270 a 310 eV) e radiação síncrotron (linha TGM) foi usada como fonte de excitação. A técnica experimental [3] fornece informações sobre novas rotas de fragmentação de moléculas poliatômicas associadas à excitação de elétrons de camada interna, através da análise de coincidências duplas e triplas. Um espectrômetro de tempo de vôo [4] foi empregado na caracterização dos fragmentos iônicos. Neste estudo, os diferentes padrões de fragmentação (rendimentos iônicos parciais) foram obtidos tanto em simples (PEPICO) quanto duplas coincidências (PEPIPICO) e comparados abaixo e acima da borda do carbono 1s. Além disso, os mecanismos de fragmentação, incluindo a formação de dicátions, e a estrutura dos íons principais são propostos. Um maior grau de fragmentação é observado acima do potencial de ionização do carbono 1s, comparado com a fragmentação obtida abaixo desse potencial.

Referências:

[1] Sharkey, Endeavour 20(2), 74 (1996)
[2] Kesselmeier J. et al, Atmospheric Environment 34, 4063 (2000)
[3] Coutinho, L.H. et al, Brazilian Journal of Physics 35 (4A), 940 (2005)
[4] Marinho, R.R.T et al, Chemical Physics 324, 420-424 (2006)

Acknowledgements

LNLS, FAPERJ, CNPq e CAPES

67

Ionization and dissociation of adenine by VUV photons

Pilling, S.[1], Lago, A. F.[1], Coutinho, L.H.[2], Castilho, R.B.[2], de Souza, G.G.B.[2], and Naves de Brito, A.[1]

[1] Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil
[2] Universidade Federal do Rio de Janeiro - Rio de Janeiro RJ Brazil

We present data from valence excitation, ionization and dissociation of adenine with syncrotron radiation. The measurements were taken ant the Brasilian Syncrotron Light Source (LNLS) employing high purity vacuum ultraviolet photons (12-21 eV) from a toroidal grating monocromator (TGM) beamline. The experimental set up consists of a high vacuum chamber with a time-of-flight mass spectrometer TOF-MS. Mass spectra were obtained using photoelectron-photoion coincidence technique (PEPICO). Mean kinetic energy and abundances for each ionic fragment have been obtained from the analysis of the corresponding peak shapes in the mass spectra. A comparison with photoelectron spectrum (Trofimov et al. 2006) and previous measurements using other techniques allowed the assignment of most broad features in the spectra. A discussion about the dissociation channels is included.

The parental ion, $C_5H_5N_5^+$, remains the most abundant fragment (40% at 15 eV; 20% at 20 eV) which indicates the strong survival of adenine to VUV photons. The other intense released ions were $C_4H_4N_4^+$, $C_3H_3N_3^+$, $C_2H_2N_2^+$ and $HCNH^+$. The neutral HCN could represent up to 40% of the dissociative channels and, taking into account that some of these channels have 2, 3 or even 4 neutrals HCN (Jochims et al. 2005), the total amount neutral HCN released could reach up to 70 times the HCN^+ production on the photodissociation of adenine by VUV.

References: Jochims H. -W., Schwell M., Baumgartel H. & Leach S., 2005, Chem. Phys., 314, 263; Trofimov A. B., Schirmer J., Kobychev et atl., 2006, J. Phys. B: At. Mol. Opt. Phys., 39, 305.

Acknowledgements

The authors would like to thank the staff of the Brazilian Synchrotron Facility (LNLS) for their valuable help during the experiments. We are particularly grateful to Dr. R. L. Cavasso. This work was supported by LNLS, CNPq, FAPESP and FAPERJ.

68

Study of Inner shell photofragmentation of bithiophene in gas phase

Mundim, M.S. P.[1], Mocellin,A.[2], Makiuchi, N.[2], Naves de Brito, A.[3], Attie, M.R.P.[4], and Correia, N.[4]

[1] Universidade de Brasília - Brasilia DF Brazil
[2] Universidade de Brasília - Brasília DF Brazil
[3] Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil
[4] Universidade Estadual de Santa Cruz - Ilhéus BA Brazil

This investigation is part of a general study of fundamental aspects of inner shell excitation followed photo-fragmentation relaxation of molecules containing sulfur. We present the photofragmentation of bithiophene around sulfur 2p edge. We investigated the molecule in gas phase using monochromatic synchrotron radiation and ion time-of-flight mass spectroscopy. Except thiophene itself, the bithiophene is the smallest building block of polythiophene polymer [1]. Working with small oligomers is possible to get insights to understand electronic structure of more complex systems [2]. The sample was heated inside the vacuum chamber to avoid polymerization through the admission system. Analysis of mass spectra will be reported on the main resonances as well as the total and the partial ion yield spectra. The measurements were done at LNLS facilities using the TGM beamline for S 2p edge and SGM beamline for C1s edge

Reference: [1] M. Rubio, et al., J. Chem. Phys. 102, 3580 (1994). [2] C. Majumder, , et al, J.Chem. Phys. 117, 2819 (2002).

Acknowledgements
We are grateful for financial support from the LNLS-Brazil. We also thank the help from LNLS staff.

69

PLASMA DESORPTION MASS SPECTROMETRY AND PHOTON STIMULATED DESORPTION OF FORMIC ACID CONDENSED IN ASTROPHYSICAL ENVIRONMENTS

Andrade, D. P. P.[1], Boechat-Roberty , H.M.[1], Rocco, M.L.M.[1], Homem, M. G. P.[2], Martinez, R.[3], P. Iza[3], and E. F. da Silveira[3]

[1] Universidade Federal do Rio de Janeiro - Rio de Janeiro RJ Brazil
[2] Universidade Federal de Sã Carlos - São Carlos SP Brazil
[3] PUC - Rio de Janeiro - Rio de Janeiro RJ Brazil

It is known that planetary magnetosphere retain electrons and populations of ions bound by its magnetic field lines, forming plasma. These ions can arise from the ionized upper atmosphere, ionosphere, from the solar wind, cosmic rays and from volcanic activity like the Jupiters' satellite Io. These ionic species interact with the icy surfaces of satellites producing several fragments, which can form new molecules. The same processes can also occur in comets and asteroids. New chemical species are formed, since some species are implanted into the ice and cause chemical reactions with themselves, while others break chemical bonds and re-sort the atoms in the molecules that are present.

Formic acid (HCOOH) is a possible product from radiolysis of H_2O/CO ices, and may occur from methanol/water radiolysis. Moreover, HCOOH is formed from $H_2O + CO_2$ irradiated by fission fragments. The simplest amino acid, glycine, (NH_2CH_2COOH), was recently detected in the molecular clouds SgrB2, Orion KL and W51. In these objects the precursor molecules like ammonia, formic acid and acetic acid have already been observed. One suggest that the preferential path for the glycine formation via formic acid may go through ice. Therefore, the study of icy formic acid is extremely important in order to clarify all these questions. In this work, we have performed Plasma Desorption Mass Spectrometry ($^{252}Cf - PDMS - TOF$) and Photon Stimulated Desorption (PSD) of formic acid condensed at 50 K. Mass spectra of positive and negative desorbed ions were obtained. PDMS spectrum showed several series of clusters of the type $X_nY_mR^{\pm}$, where X and Y are the neutral ice molecules, such as HCOOH or H_2O, and $R^{\pm}$ is either an atomic or a molecular ion, such as H^+ or H_3O^+. PSD results with energy about C 1s and O 1s edge are also analyzed.

Acknowledgements
The authors would like to thank the staff of the Brazilian Synchrotron Facility (LNLS) for their valuable help during the experiments. We are particularly grateful to Dr. A. Naves de Brito for the use of the Time-of-Flight Mass Spectrometer and of the vacuum chamber. This work was supported CNPq, Capes and FAPERJ.

70

Characterization of $N^+_{n=2-18}$ clusters produced by ^{252}Cf fission fragment impact on a N_2 ice target

F.A. Fernandez-Lima[1], C.R. Ponciano[2], Faraudo, G. S.[2], M. Grivet[2], E. F. da Silveira[2], and M.A. Chaer Nascimento[1]

[1] Universidade Federal do Rio de Janeiro - Rio de Janeiro RJ Brazil
[2] PUC - Rio de Janeiro - Rio de Janeiro RJ Brazil

The structures and abundances of $N^+_{n=2-18}$ clusters produced by ^{252}Cf fission fragment (FF) on N_2 ice target are analyzed. A systematic search for the more stable conformers at the DFT/B3LYP level and a new methodology for a proper taxonomic description (D-plot) of the cluster isomers in series are presented. The clusters stability and ionization potential analysis showed that the ^{252}Cf FF exponential dependence of the cluster yield with its mass is rather a consequence of the production mechanism than that of the cluster structure.

Acknowledgements
The authors would like to acknowledge the Brazilian Agencies CNPq, Faperj and CLAF for their support and the LNLS laboratory.

71

High resolution K$_\beta$–spectroscopy and chemical environment in Cr compounds

Tirao G.[1], Torres Deluigi, M.[2], Stutz, G.[1], and Riveros, J. A.[1]

[1] Universidad Nacional de Cordoba - Cordoba Argentina
[2] Universidad Nacional de San Luis - San Luis Argentina

The K$_\beta$ spectrum of several Cr compounds exhibiting different oxidation state was measured using a high resolution spectrometer [1] at the XRD1 beamline. The energy difference between the K$_\beta 1,3$ and the K$_\beta 2,5$ lines varies with the oxidation state according to $\Delta E(\mathrm{Cr}^{III}) > \Delta E(\mathrm{Cr}^0) > \Delta E(\mathrm{Cr}^{VI})$. We found that this energy difference is very sensitive with the oxidation state, so that it could be used to experimentally determine oxidation states with an accuracy higher than using the absolute position of the K$_\beta 1,3$ peak, as suggested in previous works [2,3,4]. The linewidht of the K$_\beta 1,3$ peak increases linearly with increasing oxidation state (from 1.81 eV for Cr^0 to 2.68 eV for Cr^{VI}). The K''_β satellite line was measured to be shifted about 16 eV from the K$_\beta 2,5$ line, which is in agreement with the type of ligand atom (oxygen) in the investigated Cr compounds. The normalized intensity of the K''_β line decreases exponentially with the Cr–O distance, as previously found in Mn compounds [5]. This relation could be used as a tool to determine bond lengths with an accuracy better than 0.1 Å.

[1] G. Tirao, G. Stutz, C. Cusatis, J. Synchrotron Rad. **11**, 335 (2004)

[2] S. Gamblin, D. Urch, J. Elect. Spec. Rel. Phenom. **113**, 179 (2001)

[3] J. Iihara, T. Omori, K. Yoshihara, K. Ishii, Nucl. Instr. and Meth. B **75**, 32 (1993)

[4] M. Torres Deluigi, G. Tirao, G. Stutz, C. Cusatis, J.A. Riveros, Chemical Physics **325**, 477 (2006).

[5] U. Bergmann, C.R. Horne, T.J. Collins, J.M. Workman, S.P. Cramer, Chem. Phys. Lett. **302**, 119 (1999)

Parte V

Geociência, Meio-ambiente e Aplicações em Materiais Biológicos

72

DIFFERENT METHODS IN ATMOSPHERIC AEROSOLS ON POLYCARBOTE FILTERS ANALYSIS BY XRF DIRECT AND TRXRF USING SYNCHROTRON RADIATION

Figueroa R.[1] and Bongiovanni, G.A.[2]

[1] Universidad de La Frontera - Temuco Chile
[2] Universidad Nacional de Cordoba - Córdoba CO Argentina

Different sample preparation procedure was compared. Until now the digestion acid method for sample preparation is one of the used ones in TXRF. Recently a thin-film sample procedure is described which requires minimal sample preparation, this involves first bringing the oil into solution with a volatile solvent. In this work different sample preparation procedure was compared. Monitoring campaigns was carried out in Temuco city and other cities by collecting the PM10 fraction and the total suspended particulates (TSP) of the airborne dust particles, entrapping element on polycarbonate filters. Each set comprised two polycarbonate membrane filters, one of which was 0.4 μm, and other 8 μm. Controls were unloaded filters each. The sample preparation was carried out by three procedures: a) digestion: this involves bringing the adsorbed elements into solution by a mixture of strong acids and heating; b) dissolution: this involves bringing the filter into solution with a volatile solvent; c) without treatment. After a and b treatments, micro liter amounts were pipetting on to the reflector substrate followed by evaporation of the solvent and the heavy metal concentration was determined by total reflection x-ray fluorescence (TRXRF). The conventional X-ray fluorescence (XRF) analysis was used to the elemental measures on non-treated filters. In TXRF, quantification was carried out by internal standardization adding Rb to the samples and a separate calibration curve were set up with Rb. Accuracy of each sample preparation procedure was checks by analysis of reference material. Results by application of the different sample preparation procedures for TRXRF and different energy excitation XRF method will be reported and compared in this work.

Acknowledgements
We want to be grateful to the personnel of the sample preparation laboratory and the manager of the line of XRF sinchrotron light of LNLS This work was supported by the Laboratorio Nacional de Luz Sincrotron LNLS (Brasil), and the Universidad de La Frontera (Chile).

73

Potential Application of Low Angle X-Ray Scattering on Bone Mineral Density Measurement

Lima, J.C.[1], Barroso, R.C.[2], Oliveira, L. F.[2], C.J.G.Pinheiro[1], Droppa Jr., R.[3], and Braz, D.[1]

[1] Universidade Federal do Rio de Janeiro - Rio de Janeiro RJ Brazil
[2] Universidade do Estado do Rio de Janeiro - Rio de Janeiro RJ Brazil
[3] Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil

X-ray computed tomography and x-ray coherent scattering can be attractive for noninvasive quantification and to provide complementary information to discriminate between cortical and trabecular tissue. The potential applications of coherent x-ray scattering for tissue characterization are nowadays of great interest among the medical physics community. The combined usage of tomography and x-ray scattering techniques opens new possibilities in separating the response of the marrow tissue from that of the bone tissue in order to obtain accurate quantitative results for the mineral content in trabecular bone. The technique of scatter bone imaging needs basic data for the x-ray scattering properties in order to relate scattering intensity and mineral content in bone samples. Phantoms have been constructed to simulate trabecular bone mineral loss which consist of a mixture of dry, fat-free cortical bone and swine fat in various quantities. The fat peak is at 0.1804 $Å^{-1}$. For the cortical bone, the peaks are at 0.1448 $Å^{-1}$ and 0.1782 $Å^{-1}$. The ratio of the heights of both bone peaks is 0.43. Changes in the ratio of adipose tissue to bone mineral in the studied samples can be used to predict changes in bone mineral density. A relationship exists between the ratio of the intensities of the two diffraction peaks due to each component in a two component mixture and the relative concentration of one of the components. The correlation of the measured relative coherent intensity with the mineral content in the samples was then investigated. A plot of bone-fat peak ratio against bone (mineral) volume produces a calibration curve for mixtures of those two components, to which scattered intensity ratio measurements of unknown mineral concentrations can be compared in order to determine the mineral concentration. A good agreement was found ($r = 0.98$). The high photon flux x-ray beam provided by a synchrotron facility allows high signal-to-noise ratio imaging which demonstrate the potential of use the coherent scattering to obtain quantitative information for the mineral content in trabecular bone.

Acknowledgements
Research (partially) supported by Laboratório Nacional de Luz Síncrotron (LNLS/CNPq), Brazil. Projects XRD1 - 4765 and XRD1 - 5369.

74

Coherent Scattering Signature for Lyophilized Human Blood Components

Filgueiras R.A.[1], Barroso, R.C.[2], Pinto, N.G.V[1], Lima, J.C.[1], C.J.G.Pinheiro[1], and Braz, D.[1]

[1] Universidade Federal do Rio de Janeiro - Rio de Janeiro RJ Brazil
[2] Universidade do Estado do Rio de Janeiro - Rio de Janeiro RJ Brazil

Over the last decade, many authors have carried out measurements of the low-angle X-ray scattering (LAXS) profiles of biological samples, as blood and its components. Blood is a variety of conjunctive tissue that works as an efficient system of transport of great variety of substances that are essential to the operation of the human organism. The blood is formed by a liquid part, the plasma, in which is mixed the solid part (composed by the red blood cells, white blood cells and platelets). The plasma is a clear yellowish liquid that represents about 55% of the total volume of the blood. It is constituted for approximately 90% of water, where one finds dissolved proteins, fats, mineral salts, hormones, etc. The corpuscles or formed elements (red blood cells, white blood cells and platelets) represent about 45% of the total volume of the blood. The red blood cells (RBC) exist in larger amount in the blood. The hemoglobin (Hb) is the protein found inside the RBC that it is responsible for the transport of the oxygen. The blood samples were collected of patients of a clinical analysis laboratory by vein puncture. The samples were packed in tubes containing the anticoagulant EDTA. Formed elements were separated from plasma by aspirating. All the samples were lyophilized for 48 hours in a freeze drier (60^{o}C and 780 mmHg) in order to remove the water and then, powdered. The coherent scattering signatures for lyophilized whole blood; formed elements, plasma and hemoglobin show two broad peaks. Some characteristic parameters obtained from the profiles were studied: peaks positions, FWHM and relative intensities. Each parameter was analyzed for each blood component in function of age, gender and diabetes mellitus. Preliminary results showed that the age is the main factor to distinguish scattering signatures for blood and its components ($p = 0.04$).

Acknowledgements
The authors thank to the Laboratory of Clinical Analyses Eliel Figueiredo, Faperj and CNPq. We also thank Dr. Gunther Gehlen for technical support during the experiment. Research partially supported by National Synchrotron Light Laboratory (LNLS) in Campinas, São Paulo, Brazil. Project XRD1 - 4842.

75

CARACTERIZACIÓN DE PIGMENTOS ARQUEOLÓGICOS EN SITIOS DE LA PATAGONIA ARGENTINA POR TECNICAS DE DIFRACCION DE RAYOS X

Vazquez,C[1], Maury, A. M.[2], Alnornoz, Ana[3], and Hayduk, Adam[3]

[1] Comisión Nacional de Energia Atôica - Buenos Aires B.A. Argentina
[2] Universidad de Buenos Aires - Buenos Aires CapFe Argentina
[3] Consejo Nacional de Investigaciones Cientficas y Técnicas - Buenos Aires Argentina

Este trabajo presenta los resultados preliminares obtenidos a partir del análisis por Difracción de Rayos X en la estación XRD2 del LNLS de los componentes inorgâicos presentes en muestras de pinturas rupestres procedentes del Abrigo El Trébol en San Carlos de Bariloche, Río Negro, Argentina. El conocimiento qumico composicional de la fracción inorgânica presente en muestras de pinturas rupestres es indispensable para identificar la fuente y modalidad de preparación de los pigmentos, la correlación con otros hallados en capas arqueológicas coherentes en temporalidad en diferentes sitios e identificar fuentes potenciales de aprovechamiento y aprovisionamiento de materia prima. Estos ambientes en épocas históricas fueron ocupados por dos "etnías"diferentes y que se habrían manifestado mediante modalidades estilísticas diferenciadas. El análisis permitirá detectar posibles variantes culturales y de sesgo temporal.

76

A Comparison between Elemental and Structural Analyses of Dental Tissues and Fluids using XRF Spectroscopy with Synchrotron Radiation and Micro-Infrared Spectroscopy

H. J. Sánchez[1], M. S. Grenón[2], Abraham, J. A.[2], Pérez, C. A.[3], C. Marcelli[4], M. Piccinini[5], M. Cestelli[6], and Valentinuzzi, M. C.[1]

[1] Universidad Nacional de Cordoba - Córdoba Cba Argentina
[2] Universidad Nacional de Cordoba - Cordoba Argentina
[3] Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil
[4] - Orsay Cedex France
[5] - Paris France
[6] - Toulose France

It has been well demonstrated that the different oral tissues, including dental calculus and fluids are excellent descriptors and sentinels of, not only oral diseases, but also many other general diseases from cancer to osteoporosis or diabetes.

Human dental calculus is a result of dental plaque calcification. Calculus is composed by several calcium phosphate phases containing a number of elements at very low concentration. When it first appears on the surface of dental pieces, the primary phases suffer gradual crystalline-structure changes. The formation process of calculus is not well understood yet.

It has been suggested that saliva and gingival fluid contains locally-derived and systemically-derived markers of periodontal disease and, through this, the basis of a specific diagnostic tests for many other diseases.

In previous works, conventional and microXRF analyses with synchrotron radiation were carried out on calculus and dental tissues in order to determine trace concentrations giving insights into the growing process and their relation with several diseases. In addition, using SR-TXRF, traces and ultra traces were studied in saliva and gingival fluids to determine several chemical indicators of developing periodontal disease by comparison of elemental concentrations between two groups of individuals, systemically healthy and periodontal-care required patients.

Recently, similar samples of dental calculus, tooth tissues, saliva and gingival fluids were studied using micro-IR spectroscopy which provided information about structures and phases in those samples.

In this work we present a compilation of the data collected after x-ray spectroscopy studies using synchrotron radiation and using micro-IR spectroscopy. In addition we present a comparison of common and comparable results obtained with both techniques and the future perspectives of linked experiments.

Acknowledgements

This work was partially supported by the LNLS.

77

Multielemental analysis and arsenic determination in renal cortex of rats by μ-SRXRF

R.D. Pérez[1], Rubatto Birri, P.N.[2], Pérez, C. A.[3], Rubio, M.[4], and Bongiovanni, G.A.[2]

[1] Consejo Nacional de Investigaciones Científicas y Técnicas - Rosario Argentina
[2] Universidad Nacional de Cordoba - Cordoba Argentina
[3] Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil
[4] Centro de Excelencia de Productos y Procesos de Córdoba - Cordoba Argentina

Arsenic is an environmental toxicant and a human carcinogen. The kidney's proximal tubules are known to be especially sensitive to injury, primarily because of their characteristically high reabsorptive activity (Robertson, 2000). However, a histological examination of As distribution has not been made. In order to determinate As accumulation in urinary system-related organs, a multielemental mapping was performed by μ-SRXRF at the Synchrotron Light National Laboratory (Brasil). For that, the kidneys and bladder from rats drinking arsenical water (50 ppm) during 0 or 60 days were removed, snap frozen in liquid nitrogen and then cut in slices of 200 μm thickness. The slices were adhered to Ultralene film and were scanned with a collimated white synchrotron spectrum (30 μm x 30 μm). We found the highest arsenic concentration in peri-glomerular region from kidney, but not As was found in bladder tissues. Additionally, the proportion of other elements also was altered by the chronic exposures to As. The results revealed a tissue-specific arsenic accumulation and suggest a proximal tubule altered reabsorption.

References: Robertson, W. O. (2000). Chronic poisoning: Trace metals and others. In Cecil Textbook of Medicine (L. Goldman and J. C. Bennett, eds.), pp. 72-77, W. B. Saunders Company, Philadelphia.

Acknowledgements

The authors would like to thank LNLS - Brazilian Synchrotron Light Source, Campinas, Brazil, under proposal D09B-XRF-5185. This work was supported by CONICET and Agencia Córdoba Ciencia.

78

Synchrotron Radiation TXRF analysis of titanium concentrations in oral fluids of subjects with dental implants.

Abraham, J. A.[1], H. J. Sánchez[2], M. S. Grenón[1], and Pérez, C. A.[3]

[1] Universidad Nacional de Cordoba - Cordoba Argentina
[2] Universidad Nacional de Cordoba - Córdoba Cba Argentina
[3] Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil

With regards to their biological and physicochemical properties, titanium-based biomaterials and other metals have been successfully used in orthopedic, dental and maxillo-facial surgery mainly as osseous implants.

Metal ion release from metallic implants is known to occur, but conflicting data have been reported in the literature as well as the levels of trace elements released and their potential consequences. In spite of the rapidly growing use of such implants, there is a poor knowledge of the intake of trace elements *in-vivo* as a consequence of dental implant materials.

With the aim of studying the increasing degree of elemental concentration in some body fluids, concentration of relevant elements in saliva and gingival fluids were analyzed on samples obtained from two sets of ten patients with and without (control set) dental implants. The analyses were performed by total reflection of x-rays technique using synchrotron radiation in the XRF beamline of the LNLS. The measured spectra were analyzed specific programs fro spectrum analysis and the levels of concentrations were determined using internal standard.

A discussion about the results obtained in this work and the possible systemic implications is presented.

Acknowledgements
This work was partially supported by the LNLS

79

Mapeamento de íons metálicos ligados a proteínas de soja empregando fluorescência de raios-X com radiação síncrotron

Sussulini, A.[1], Pérez, C. A.[2], and Arruda, M. A. Z.[1]

[1] Universidade Estadual de Campinas - Campinas SP Brazil
[2] Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil

Os íons metálicos possuem um papel importante na atividade biológica. A maioria deles é encontrada ligada a proteínas ou enzimas específicas e exercem suas funções como uma parte inerente de seus centros ativos ou estruturais.

Devido à composição complexa e à concentração muito baixa em que os íons metálicos se encontram em amostras biológicas, uma técnica de alta resolução para a separação das proteínas e outra com boa sensibilidade para a identificação e/ou determinação dos metais são requeridas. A eletroforese em gel de poliacrilamida na presença de dodecil sulfato de sódio (SDS-PAGE) é uma técnica de alta resolução e foi empregada na separação e análise das proteínas de soja, de acordo com suas massas molares. A fluorescência de raios-X com radiação síncrotron (SR-XRF) é uma técnica muito sensível, que possui as vantagens de evitar a etapa de preparo da amostra e ser considerada uma técnica não-destrutiva, e foi empregada no mapeamento dos metais ligados às proteínas de soja.

Para os experimentos, as bandas dos géis contendo as proteínas foram previamente recortadas do gel com o auxílio de um bisturi, secas em estufa a 40 ^{o}C por cerca de 5 h (até massa constante). Para a realização das medidas, as bandas foram fixadas em uma plataforma de Al, usando fita adesiva. Na linha de fluorescência de raios-X, um sistema de fendas, controlado por computador, foi utilizado para colimar o feixe branco, de forma a se obter um microfeixe de 200 x 200 μm. Durante os experimentos, foram utilizadas folhas de Al para reduzir a energia de alguns componentes dos raios-X incidentes na amostra. O detector utilizado para coletar o sinal de radiação proveniente da amostra foi de HPGe. Após serem estabelecidas as condições de análise, o mapeamento foi realizado irradiando-se a banda por 100 s em um único ponto. Tal procedimento foi realizado em triplicata.

Os metais encontrados nas bandas de proteínas foram o Ca, Co, Cr, Cu, Fe, K, Mn, Ni, e Zn, que são macro e micronutrientes comumente encontrados em plantas e estes ligam-se às proteínas de maneira específica. A partir destes resultados, foi possível estabelecer um método mais adequado para a extração das proteínas de soja, de modo a preservar mais efetivamente as ligações metal-proteína.

Acknowledgements
FAPESP (processo 04/11960-6)

80

ESTUDO SOBRE A ENERGIA DE LIGAÇÃO DO $CaC_2O_4.H_2O$

L. Kuplich[1], Depianti, J. B.[1], Souza, D.O.[1], DeMedeiros, E. F.[1], Cruz,P.C.M[1], Martinez, L. G.[2], Orlando, M. T. D.[1], and Ortiz, R.[1]

[1] Universidade Federal do Espírito Santo - Vitória ES Brazil
[2] Instituto de Pesquisas Energéticas e Nucleares - São Paulo SP Brazil

Neste trabalho investigamos a estabilidade da molécula de água contida no cristal de oxalato de cálcio monohidratado presente em cálculos renais antes e depois de submetê-los a um tratamento térmico em atmosfera inerte. Os cálculos renais utilizados neste estudo foram previamente submetidos à difração de raios X de pó, que identificou sua composição em 100% de oxalato de cálcio monohidratado. Foi verificado que a total eliminação da molécula de água acontece em torno de 400^oC e não em torno de 180^oC, como relatado na literatura. Durante o tratamento térmico, observamos que alguns picos do espectro de raios X sofreram variação na largura e altura, sugerindo uma mudança de composição e estrutura do cristal: de oxalato de cálcio monohidratado para oxalato de cálcio (sem água). Verificamos, também, que a estabilidade hídrica do composto só foi alterada quando fornecemos mais energia ao processo (aumentando a temperatura e mantendo constante o tempo de tratamento). Pelos resultados obtidos neste trabalho podemos inferir que a molécula de água está fortemente ligada à estrutura do cristal.

Acknowledgements
CAPES, CNPq, UFES, IPEN, FACITEC.

81

Estrutura cristalográfica de esmalte de dentes irradiado com laser de Nd:YAG e Er,Cr:YSGG

Rosa,K.[1], Bachmann, L.[1], Craievich AF[2], Kellermann, G.[3], Ana, P.A.[4], and Zezell D. M.[4]

[1] Universidade de São Paulo - Ribeirão Preto - Ribeirão Preto SP Brazil
[2] Universidade de São Paulo - São Paulo - São Paulo SP Brazil
[3] Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil
[4] Instituto de Pesquisas Energéicas e Nucleares - São Paulo SP Brazil

1.Objetivos

O objetivo deste trabalho foi identificar as alterações na estrutura cristalográfica de esmalte irradiado com laser de neodímio (Nd:YAG) e com o laser de érbio (Er,Cr:YSGG).

2.Material e Métodos

As amostras de esmalte foram confeccionadas a partir de dentes pré-molares humanos. A irradiação foi conduzida utilizando dois lasers: com o laser de Nd:YAG, emissão em 1,064 μm, largura temporal de 100 μs e densidade de energia de 115J/cm^2; e com o laser de Er,Cr:YSGG, emissão em 2,79 μm, largura temporal entre 140 e 200 μs e densidade de energia de 12,5J/cm^2. A determinação dos padrões de difração foi conduzida na linha de difração (XRD-2) do Laboratório Nacional de Luz Síncrotron (LNLS).

3.Resultados e discussão

O esmalte irradiado apresentou picos de difração de raios X que não estão associados à hidroxiapatita. No esmalte irradiado com o neodímio observou-se, além dos picos associados à hidroxiapatita, novos picos em 0,284nm, 0,290nm, 0,299nm e 0,378nm; enquanto o esmalte irradiado com o laser de érbio apresentou novos picos em 0,260nm, 0,287nm 0,304nm e 0,320nm. Os picos observados estão associados a uma nova fase cristalográfica que se formou após a resolidificação do esmalte irradiado. Por outro lado, esses picos não estão associados às fases formadas após a irradiação com outros lasers ou parâmetros de irradiação, que são observados na literatura [1], [2], [3] e [4]. A indexação dos picos foi realizada utilizando o banco de dados PDF2-Release 2005 do "International Centre for Diffraction Data"(ICDD). Para confirmar a identificação da fase formada será necessário estudar um volume maior de tecido resolidificado. Dessa forma espera-se detectar um número maior de picos de difração e aumentar a intensidade de todos eles, incrementando-se assim a sensibilidade do procedimento de análise.

Referências bibliográficas: [1] Hashiguchi, K., Hashimoto, K., Okajimas Folia Anat. Japonica 67:271-281 (1990). [2] Kantola, S., Laine, E., Tarna, T., Archives of Oral Scandinava 31(6):369-379 (1973). [3] Kuroda, I., et al. Caries Res., 26:165-169 (1992). [4] Nelson D. G. A., et al. Caries Research, 21:411-426 (1987).

82

Análise de material particulado por SR-TXRF

Melo Jr, Ariston[1] and Moreira, S.[1]

Universidade Estadual de Campinas - Campinas SP Brazil

Existe atualmente uma preocupação por parte de pesquisadores e governantes com a atmosfera, pois é o meio na qual ocorrem transformações e/ou alterações e estas podem trazer danos significativos para o clima de todo o planeta. Na atmosfera têm sido observadas alterações devido ao crescimento da população e o conseqüente desenvolvimento dos parques industriais das grandes cidades, tornando evidente a existência da emissão de gases poluentes para a atmosfera.

Uma das principais fontes de poluição presente na atmosfera é o material particulado, que não constitui uma espécie química definida, mas um conjunto de partículas no estado sólido ou líquido, capaz de permanecer em suspensão. A presença no ar de algumas substâncias na forma de material particulado tende a agravar os efeitos de certos gases. O caso mais comum é o dióxido de enxofre (SO2), cujo efeito nocivo é maior na presença do material particulado. As relações do material particulado com o meio ambiente são bastante complexas, pois para descrever seu comportamento é necessário determinar a concentração, o tamanho, a composição química, a fase e a morfologia.

Este trabalho tem como objetivo quantificar os elementos químicos presentes na fração grossa e fina do material particulado. Para tanto postos de coleta de PM10 foram instalados no centro urbano da cidade de Campinas, no distrito de Barão Geraldo (UNICAMP) e no município de Paulínia e durante o período de outubro de 2005 à março de 2006 foram realizadas as coletas semanalmente. As amostras foram analisadas pela técnica de SR-TXRF para determinação dos elementos químicos presentes.

O PM10 variou de 43,04 μg/m^3 no posto de Paulínia até 183,55 μg/m^3 para posto localizado no centro urbano de Campinas, enquanto no posto de Barão Geraldo o PM10 chegou a 107,29 μg/m^3.

Foram detectados nas amostras 19 elementos químicos entre eles: Al; Si; P; S; Cl; K; Ca; Ti; V; Cr; Mn; Fe; Co; Ni; Cu; Zn; Se; Br; Pb.

Acknowledgements
Os autores agradecem ao LNLS (projeto D09B-XRF 4659/06) pelo auxílio e a CAPES pela concessão da Bolsa de Doutorado.

83

Utilização dos anéis de crescimento de espécies arbóreas para o monitoramento da poluição ambiental por SR-TXRF

Moreira, S.[1], Vives, A. E. S.[2], and Faria,B. F.[1]

[1] Universidade Estadual de Campinas - Campinas SP Brazil
[2] Universidade Metodista de Piracicaba - Santa Bárbara Dt'Oeste SP Brazil

Neste trabalho foram analisados os teores de elementos traço em uma seqüência de anéis de crescimento anuais de árvores da espécie *Copaifera langsdorfii L.*, coletadas nas proximidades da desativada Indústria de Acumuladores Ajax Ltda, município de Bauru, SP, localizada no km 229 da estrada Jaú-Ipaussu, previamente datados, usados como bioindicadores da poluição ambiental.

Foram selecionadas 12 árvores de Copaíba, em um gradiente de distância a partir da referida indústria, totalizando 4 sítios, distantes 50 m entre si. Em cada sítio foram coletadas 03 árvores. O método de coleta consiste na retirada de cilindros do lenho (10 mm de diâmetro) pela introdução de uma sonda de Pressler no tronco das árvores na altura do DAP, até atingir a região da medula. As amostras de lenho foram submetidas a digestão por via úmida (HNO_3 $+H_2O_2$). A um volume de amostra definido foi adicionado Ga como padrão interno e uma pequena alíquota da mistura foi pipetada sobre o suporte.

Dentre os elementos analisados vamos destacar os elementos Pb e o Cr, para os quais foram encontradas concentrações acima dos valores de referência e de alerta estabelecidos pela CETESB. O valor de referência de qualidade estabelecido pela CETESB para o elemento Pb é de 17 μg.g^{-1} e 33,0 % das amostras do sítio 1, 37,9 % do sítio 2, 21,6 % do sítio 3 e 22,9 % do sítio 4 apresentaram concentrações acima deste valor. No que se refere ao valor de intervenção (72 μg.g^{-1}) menos de 1 % das amostras ultrapassaram este valor.

Para o elemento Cr o valor de referência segundo a CETESB é de 40 μg.g^{-1}. A porcentagem de amostras que ultrapassaram este limite foi de 57,6 % para o sítio 1, 48,3 % para o sítio 2, 46,0 % para o sítio 3 e 35,3 % para o sítio 4. A mesma tendência foi observada para o valor de intervenção (75 μg.g^{-1}), onde 57,6 %, 31,0 %, 24,3 % e 23,5 % das amostras dos sítios 1, 2, 3 e 4 respectivamente, apresentaram concentrações acima deste valor.

CETESB - Companhia de Tecnologia de Saneamento Ambiental. Relatório de estabelecimento de Valores Orientadores para Solos e Águas Subterrâneas no Estado de São Paulo, 2005.

Acknowledgements

Os autores agradecem ao Prof Mário Tomazello Filho da ESALQ/USP pelo auxílio na datação dos anéis de crescimento e ao LNLS - Projeto 5372/06 (D09B-XRF).

84

Evidences from X-ray Absorption Spectroscopy for As(III) selective immobilization by a thiol chelating resin

Duarte, G.[1], Ciminelli, V.S.T.[1], and Teixeira, M.C.[2]

[1] Universidade Federal de Minas Gerais - Belo Horizonte MG Brazil
[2] Universidade Federal de Ouro Preto - Ouro Preto MG Brazil

The conventional techniques for arsenic retention usually require a previous oxidation of As(III) to As(V) due to the higher mobility of the trivalent arsenic species when compared to the pentavalent (Teixeira and Ciminelli, 2005; Smedley and Kinniburgh, 2002). A promising option for immobilization of arsenic in the trivalent form arose from the work of Teixeira and Ciminelli (2005), who demonstrated the large affinity of thiol groups by As(III) in acid and circumneutral environments using X-ray Absorption Spectroscopy (XAS). The results obtained by Teixeira and Ciminelli (2005) led to the hypothesis that trivalent arsenic species could be similarly sorbed by thiol chelating resins containing the functional sulphydril (-SH) group. Thus, the main objectives of the present work were: (i) to verify the As(III) immobilization by thiol chelating resin, determining the equilibrium time and arsenic loading capacity at batch systems; (ii) to identify the oxidation state of the arsenic loaded onto the Amberlite GT73 resin through XANES analyses; and (iii) to obtain the coordination parameters for As(III) immobilized by Amberlite GT73 resin using EXAFS analyses. With the aim to elucidate the performance of this resin for As(III) retention, the experiments were carried out at three different pH conditions. The Amberlite GT73 resin was shown to be able to efficiently retain the trivalent arsenic species at all of the pH values assessed, and room temperature. Under saturation conditions, corresponding to an equilibrium time of approximately 6h, the resin showed an arsenic loading capacity of 30mg of As(III) per gram of dried resin. XANES analyses showed that the arsenic loaded onto the Amberlite GT73 resin was not oxidized during the sorption process, remaining in its trivalent form. EXAFS analyses indicated that only at pH 5.0 the mechanism of the As(III) immobilization onto the Amberlite GT73 resin is similar to the As(III) adsorption onto the cystein-rich biomass studied by Teixeira and Ciminelli (2005), where the arsenic species are coordinated to three sulfur atoms in the resin's thiol groups. For the pH 7.5 experiments, it was found that the As(III) is bound to two sulfur atoms. In the pH 10.0 tests, besides the different coordination, where each arsenic atom is bound to only one sulfur atom, it was also observed the presence of the oxygen atom in the first coordination shell.

Acknowledgements
We thank the National Synchrotron Light Laboratory (LNLS) in Campinas, São Paulo, Brazil, for the use of XAS facilities.

85

Removal of chromium ions from test solutions by *Eicchornia crassipes*, *Pistia stratiotes* and *Salvinia auriculata*

Espinoza Quiñones, F.R.[1], Palacio, S.M.[1], Szymanski, N.[1], Rossi, F. L.[1], M.A. Rizzutto[2], Castro, J. K. D.[1], Dotto, J.[1], Pavan, G. L.[1], and Silva, E.A.[1]

[1] Universidade Estadual do Oeste do Paraná - Toledo PR Brazil
[2] Universidade de São Paulo - São Paulo - São Paulo SP Brazil

Aquatic macrophytes are known to remove metals by surface adsorption and/or absorption and incorporate them into their own system or store them in a bound form. The uptake of trace metals by the root systems of aquatic plants depend both on the kind of metal and on the species of plant absorbing the metal. The aquatics macrophytes Eicchornia Crassipes, Pistia Stratiotes and Salvinia auriculata were evaluated for theirs chromium removal potential. The uptake study by the aquatics macrophytes species were carried out using a Clark solution containing macro- and micro-nutrients. To obtain the test liquids loaded with chromium ions, $5\,mgL^{-1}$ standard solutions of Cr-III (as chromium nitrate) and Cr-VI (as chromium oxide) were added to each nutritive solution. For the uptake of Cr(III) and Cr(VI), fresh aquatic plants were grown in plastic containers containing $7\,L$ test liquids into a greenhouse for 35 days. For each chromium ion and each aquatic macrophytes specimen, a total of 15 containers with test liquids was used to growth aquatic plants. The collecting time was fixed at 7 days. During five weeks, both plants and test liquids were collected from three replicate containers of each test solution. For trace element analysis, a $2\,mL$ aliquot of each water sample was taken and $20\,\mu L$ standard solution of Ga (1000 mgL^{-1} gallium) was added as an internal standard. Aliquots of $5\,\mu L$ were deposited on a pre-cleanned $3\,mm$ thick acrylic disks and dried at room temperature. Elementary concentrations in test water were obtained using SR-TXRF techniques. Polychromatic X-ray beam was used to irradiate the water sample. X-ray spectra were analyzed using the AXIL program and the chromium concentrations were obtained using the sensitivity curve for K X-ray series. To determine the adsorption kinetics parameters, a bioaccumulation process model was applied to the experimental data, according to the Langmuir Law. The absorption rate constants in the experiment with living aquatic macrophytes as absorbents decreases from Pistia Stratiotes to Eicchornia Crassipes and Salvinia. The absorption rate constant values are very different, revealing that the absorption kinetics of Cr-III and Cr-VI cannot be explained by specific adsorption mechanisms on the cell wall or the uptake mechanism for chromium ions.

Acknowledgements
This work has been supported by the Brazilian Synchrotron Light Laboratory (LNLS) under proposals D09B - XRF - 4652.

86

Avaliação da água e do sedimento nos ribeirõess Graminha e Águas da Serra na cidade de Limeira (SP) por SR-TXRF

Moreira, S.[1] and FAZZA, E. V.[1]

Universidade Estadual de Campinas - Campinas SP Brazil

O município de Limeira está localizado no Estado de São Paulo, na segunda região do Estado com o maior crescimento econômico e demográfico. Como a cidade possui galvanoplastias voltadas para a produção de jóias, semi-jóias e bijuterias as descrições e interpretações das concentrações de metais pesados, na água e nos sedimentos, são indicadores para elucidar a influência antropogñica e o carreamento destes compostos para o rio Piracicaba. Como os ribeirões Graminha e Águas da Serra apresentam suas nascentes na zona urbana do município de Limeira, atravessam parte da zona rural e se unem desaguando no rio Piracicaba, há probabilidade destes sofrerem ou já terem sofrido os impactos relacionados à poluiçõ ambiental, causada por fatores antrópicos.

A fluorescência de raios X por reflexão total com radiaçõ síncrotron (SR-TXRF) foi utilizada para a determinaçõ de metais nas amostras de água e sedimento destes mananciais. Amostras de água e sedimento foram coletadas em 06 pontos ao longo dos ribeirões, em dois períodos, seco e úmido. As amostras de sedimento foram digeridas pelo método USEPA 3050 B, enquanto que as amostras de água não foram submetidas a nenhum tratamento.

Os limites de deteçõ nas amostras de água foram iguais a 0,11 μg.L^{-1} para Cr, para Fe, Ni e Zn 0,05 μg.L^{-1} enquanto que para Pb o valor foi 0,24 μg.L^{-1}. Nas amostras de sedimento os limites de detecçõ foram iguais a 0,04 mg.kg^{-1} para Cr, 0,02 para Ni e 0,10 para Pb.

Para as amostras de água coletadas no ribeirão Águas da Serra e Graminha foram observadas concentrações de Al, Fe, Zn, Mn, Cr, Cu, Ni, Pb acima dos valores estabelecidos pela CETESB.

As concentrações obtidas para as amostras de sedimento foram comparadas com os Valores de Referência de Qualidade (VRQ) estabelecidos pela CETESB, cujos valores são iguais a 40, 13 e 17 mg.kg^{-1} para Cr, Ni e Pb respectivamente.

Nas amostras de sedimento coletadas no ribeirão Águas da Serra foram observadas concentrações acima do VRQ para Pb em todos os pontos de amostragem nos períodos seco e úmido. O mesmo ocorreu para Cr, mas apenas em 03 pontos de amostragem. Para o ribeirão Graminha valores acima do Valor de Referłncia de Qualidade foram observados para o elemento Cr em 02 pontos de coleta no período seco, para o Ni em apenas 01 ponto no mesmo período, enquanto que para o elemento Pb valores acima do VRQ foram observados em 01 ponto no período mido e 02 no seco.

87

SYNCHROTRON RADIATION X-RAY FLUORESCENCE ANALYSIS OF PM_{10} AND $PM_{2.5}$ IN LONDRINA, BRAZIL

Lopes, F.[1], Appoloni, C. R.[1], and Nascimento Filho, V. F.[2]

[1] Universidade Estadual de Londrina - Londrina PR Brazil
[2] Centro de Energia Nuclear na Agricultura - Piracicaba SP Brazil

This article presents the first measurement of the elementary chemical composition evaluation of the suspended particulate matter in the atmosphere of Londrina city (Paraná state, Brazil). The sampling was accomplished in the summer of 2003 and winter of 2002, with a stacker filter holder, which allowed the simultaneous collection of fine particulates ($PM_{2.5}$) and coarse particulates (PM_{10}). The excitation and detection of the characteristic X-rays were done in vacuum and air atmosphere, quantifying 08 chemical elements in the particulate matter. The accuracy of the analytical method was assessed by the use of the National Bureau of Standards (NBS) thin glass film Standard Reference Material. The concentration of Ca, Ti, V, Fe, Ni, Cu, Zn and Br associated with particulate matter were determined using synchrotron radiation x-ray fluorescence. The results of the analysis revealed that the elements in the aerosol particles came basically from two sources: soil re-suspension and industrial or anthropogenic activities.

Acknowledgements

We thank to C.A. Perez and Brazilian Synchrotron Light Laboratory (LNLS) for support of the D09-XRF.

88

Estudo da remoção de metais por leitos cultivados empregando a SR-XRF

Moreira, S.[1] and Avelino Neto, Sebastião[1]

Universidade Estadual de Campinas - Campinas SP Brazil

A poluição dos recursos naturais por metais, resulta de diferentes atividades econômicas, a maioria delas industriais, em função das suas características intrínsecas, são intensivamente poluidoras, embora fontes agrícolas e a disposição de rejeitos domésticos também contribuam para a liberação de metais no meio ambiente. Os metais são liberados ou transportados em ambientes aquáticos ou terrestres, principalmente sob a forma dissolvida ou como particulados, e podem alcançar altas concentrações, particularmente próximas ao ponto de lançamento dos efluentes.

Dentre as diferentes opções de sistemas tratamento de efluentes, encontra-se o sistema de tratamento com leitos cultivados (LC) também denominados wetlands um sistema simples, que, com o auxílio de macrófitas, promovem a depuração da água residuária, com mínima geração de biossólidos eliminando boa parte de compostos orgânicos e inorgânicos.

A SR-TXRF foi utilizada com o objetivo de se avaliar o desempenho de LC na remoção de metais no sistema instalado na FEAGRI (UNICAMP).

Com o objetivo de verificar a presença de elementos metais ou não metais na água residuária do leito cultivado, foram realizadas coletas pelo período de 8 semanas consecutivas (janeiro a março de 2005) sendo as coletas realizadas as 10:00 horas.

As amostras foram coletadas no afluente e no efluente do sistema de formato retangular localizado na FEAGRI/ UNICAMP, com as macrófitas *Eleocharis sp.* e *Typha sp.* na fase adulta. O leito cultivado teve a vazão regulada em 1200 L.dia^{-1} para um tempo de detenção hidráulica de 1 dia.

As medidas foram realizadas na linha de XRF na geometria de Reflexão Total. Após o levantamento da concentração dos elementos presentes foi calculada a eficiência de remoção dos elementos pelo sistema de leitos cultivados.

A eficiência na remoção do elemento Cr foi de 89% verificada na 5^a semana de coleta, para o Zn a remoção foi de 73% na 2^a semana, para o Fe 92% na 7^a semana e 88% para o Mn na 8^a semana. Para o P a eficiência na remoção foi de 56% na 4^a semana, para o S, 51% na 7^a semana enquanto que para o Cl foi de 71% na 2^a semana.

Acknowledgements

Os autores agradecem ao Dr. Denis Miguel Toston e José Euclides Paterniane pela disponibilização do sistema. Agradecemos também ao CPNq e ao LNLS (Projeto 5372/06).

89

AN EXAFS STUDY OF THE BINDING OF COPPER, MERCURY AND CHROMIUM ON NATURAL AND CROSSLINKED CHITOSAN FILMS

Vieira, R.S.[1], Aimoli, C.G.[1], Goulart, G. A. S.[1], Meneghetti, E.[1], Paiva, R.G.[1], and Beppu, M. M.[1]

Universidade Estadual de Campinas - Campinas SP Brazil

Chitosan has recently been recognized a biopolymer with significant potential for use in many fields, such as in environmental area, food and medical science, biotechnology and separation processes. It can be molded in several shapes and it is a suitable biosorbent for removal of metal ions from wastewater, since its amino and hydroxyl groups can act as chelation sites. To increase adsorption performance it is possible to chemically modify the structure of the biopolymer. Crosslinking with glutaraldehyde and epichlorohydrin are examples of such chemical modifications. Sophisticated analytical techniques, like XPS, Mösbauer spectrometry, XANES and EXAFS can be used to identify surface groups of adsorbents and metallic species adsorbed. More recently, the technique of X-ray absorption fine structure spectroscopy (EXAFS) has been used to study the mechanism of metal binding by biopolymers. EXAFS provides information on the coordination structure, like the number of atoms in the neighborhood of a determined coordination sphere (-NH2, -OH), and the bond distance between heavy metal and chelation site. This study focused on the determination of the functional groups on chitosan films responsible for heavy metal ions chelation. Mercury, chromium and copper ions were selected, due to their toxic effects, even in low concentrations. Natural and crosslinked chitosan films were mixed with a 1000 mg/L solution of Hg(II), Cr(VI) and Cu(II) at pHs 5.0, 6.0, 4.0 for 60 h at 25°C. The X-ray absorption fine structure spectroscopy (EXAFS) experiments were carried out at Brazilian National Synchrotron Light Laboratory (LNLS), using a channet-cut Si (111) monochromator. All the spectra were performed in transmission mode and were collected around Hg (12284eV) L edge, Cr (5989eV) and Cu (8987eV) K edges. Each spectrum corresponded to an average of 3 independent scans. The spectra were energy calibrated by simultaneous measurements of the transmission spectra of Hg, Cr and Cu,, where the energy of the first inflection point for the reference sample absorption edge, E0, was defined respectively as 12284, 5989 and 8987eV, for Hg, Cr and Cu. As a result of this study it was possible to determine the bond distance from metal ions and N and O atoms and the number of functional groups of chitosan involved in the binding of one metal ion.

Acknowledgements
This work was supported by CAPES and FAPESP

90

Modelamento da biossorção em biomassa vegetal usando XANES e EXAFS

G.C.Silva[1], R.P.de Carvalho[1], and Ciminelli, V.S.T.[1]

Universidade Federal de Minas Gerais - Belo Horizonte MG Brazil

A biossorção consiste na retenção de íons metálicos em solução, em material de origem biológica. Na biossorção, acontecem apenas interações fisico-químicas entre os íons em solução e a biomassa seca. Este fenômeno tem sido estudado como alternativa para a despoluição de efluentes aquosos e recuperação de metais de valor econômico, mas pouca atenção tem sido dada à compreensão dos mecanismos de biossorção.

Em nosso estudo procuramos entender os mecanismos de sorção de ferro e arsênio em biomassa constituída de folhas secas. Estudos preliminares mostraram que a celulose é a responsável pela eficiência da retenção dos metais na biomassa. Por essa razão, foram usadas folhas ricas em celulose, em particular, folhas de alface (*L.sativa*).

As técnicas de Espectroscopia de Absorção Atômica (AAS), Ressonância Paramagnética Eletrônica (EPR), Espectroscopia Mössbauer, XANES e EXAFS, foram usadas para estabelecer modelos para a sorção de ferro e arsênio em folhas secas.

A sorção de ferro em folhas secas se mostrou eficiente tanto para pH=2.0, em soluções onde o íon de metal tem estado de oxidação +3, quanto em pH=4.0, em soluções onde o seu estado de oxidação é +2. O estado de oxidação do ferro dentro da biomassa é sempre FeIII, independente de se ter FeII ou FeIII nas soluções. Observou-se a existência de dois sítios diferentes para o FeIII na biomassa, um de baixa simetria (ao menos rômbica), e outro que parece estar associado a pequenos aglomerados de ferro (2 ou 3 átomos).

A retenção do arsênio pelas folhas de alface só é efetiva na presença de ferro dentro da biomassa. Pela técnica EXAFS, pudemos observar que o primeiro vizinho do íon arsênio não é o FeIII. Além disso, por XANES, pudemos constatar que o estado de oxidação do arsênio dentro da biomassa é sempre AsV, independente de se ter AsIII ou AsV nas soluções.

Dando continuidade à pesquisa do grupo, pretende-se estudar a melhor forma de aplicação das biomassas ricas em celulose na retenção e recuperação de metais de interesse econômico provenientes de rejeitos industriais e de mineração.

Acknowledgements

Agradecemos o suporte financeiro da Capes e do CNPq.

As medidas de EXAFS e XANES foram realizadas no LNLS (Campinas, SP, Brasil).

91

Quantificaçãoo de metais em águas e sedimentos do reservatório Billings por (SR-TXRF)

Moreira, S.[1] and Sampaio, S. A.[1]

Universidade Estadual de Campinas - Campinas SP Brazil

A Represa Billings é o maior reservatório de água da região metropolitana de São Paulo, ao seu redor concentra-se o maior parque industrial da América do Sul e suas margens são ocupadas por quase 1 milhão de habitantes. A qualidade de suas águas é, portanto, motivo constante de preocupação de toda a sociedade.

Neste trabalho foi utilizada a SR-TXRF para a identificação e quantificação de metais em ǵuas e sedimentos da Represa Billings. Foi estabelecida uma comparação dos níveis de metais encontrados com os limites máximos permitidos estabelecidos pela CETESB. A finalidade de contexto social é contribuir para a preservação dos mananciais locais e o aproveitamento racional de suas águas. Foram escolhidos dezoito pontos de coleta, incluídas as margens e a porção central da represa, de acordo com critérios similares aos adotados pela CETESB.

O limite mínimo de detecçã, para as amostras de água, variou de 0,0038 μg.L^{-1} (S) até 0,6347 μg.L^{-1} (Zn). Para as amostras de sedimentos, o limite mínimo de detecçã variou entre 2,8 μg.kg^{-1} (S) até 756,4 μg.kg^{-1} (Zn).

Nas amostras de água o Cr apresentou valores de concentraçã acima dos limites permitidos em dois pontos de amostragem, locais próximos á foz do rio Ribeirão. O mesmo comportamento foi verificado para o Ni. O Cu apresentou valores acima do VMP para todos os locais de amostragem. Tal fato já era esperado, pois o sulfato de cobre é utilizado em larga escala pela SABESP para o controle de algas, já que nesta região, braço do rio grande, a água é captada para fins de tratamento e abastecimento público de bairros da cidade de São Bernardo do Campo. No caso do elemento Fe foram observados valores acima do VMP em todos os locais, especialmente na área urbanizada. O Pb foi detectado em apenas três pontos de amostragem, mas em todos eles com concentrações acima do VMP. Apenas o Mn esteve em concentrações abaixo da VMP em todos os pontos de coleta.

Com relação ás amostras de sedimentos, o Cr apresentou valores acima do PEL (Probable Effect Level) em um ponto de amostragem, indicando desta forma efeitos tóxicos prováveis e o mesmo fato foi observado para Cu e Zn. Por outro lado o Ni apresentou concentrações acima do PEL (Probable Effect Level) em dois pontos de amostragem enquanto que o para o Pb não foram observados valores acima do PEL nos pontos amostrados.

92

Caracterização Estrutural de Gemas da Região Amazônica e de Minas Gerais

Batista, A. C.[1], França, L. A.[1], and Prado, R. J.[1]

Universidade Federal de Mato Grosso - Cuiabá MT Brazil

O Brasil é o maior produtor de gemas coradas do mundo, apresentando uma grande diversidade de espécimes como, por exemplo, Quartzo, Berilo, Turmalinas, Topázio, Crisoberilo, Coríndon, Andaluzita e muitos outros. A maioria dessas gemas são encontradas no Estado de Minas Gerais, que responde pela metade da produção nacional de minerais gemas. O aumento do conhecimento referente às características químicas e físicas dessas gemas é essencial para possibilitar qualquer tipo de análise que tenha como objetivo a certificação de origem, bem como a definição de processos que visem a melhoria de sua qualidade. Nesse sentido foram realizadas inicialmente medidas de Difração de Raios X (XRD) e Espectrometria de Raios X por Dispersão em Energia (EDX), para a obtenção de informações estruturais e químicas. Essas análises estã sendo realizadas no Laboratório Multi-Usuário de Técnicas Analíticas (LAMUTA / UFMT). Foi também utilizada a técnica de Estrutura Fina de Absorção de Raios X (XAFS), que permitiu analisar a estrutura de micro-inclusões presentes nas gemas. Os estudos de XAFS foram realizados com diversas variedades de gemas, na linha XAFS1 do Laboratório Nacional de Luz Síncontron (LNLS). Foram feitas aquisições na borda K de absorção do Fe, Mn, Cr, Ti e V, através da detecção do rendimento de fluoresência de raios X. No momento, esão sendo implementadas medidas de Espectrometria no Infravermelho por Transformada de Fourier (FTIR), Ressonância de Spin Eletrônico (ESR) e Absorção no Visível e Ultra-Violeta (UV-Vis), de maneira a possibilitar uma caracterização mais ampla dessas mesmas gemas. Será apresentado um panorama geral dos dados obtidos por essas diversas técnicas para algumas das variedades de gemas já estudadas, bem como perspectivas para a continuação do trabalho.

Acknowledgements

Este trabalho vem sendo desenvolvido com o apoio do CNPq, CAPES e LNLS.

93

Determination of trace elements concentrations in normal and neoplastic breast tissues

Silva, M. P.[1], Tomal, A.[1], Conceição, A. L. C.[1], Pérez, C. A.[2], and Poletti, M. E.[1]

[1] Universidade de São Paulo - Ribeirão Preto - Ribeirão Preto SP Brazil
[2] Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil

Each year more than one million women are diagnosed with breast cancer around the world. Early screening and diagnosis could certainly increase breast cancer patient's survival rates. Analysis of some trace elements usually present in human breast has gained great interest over the last few years due to the increase in knowledge of their physiological role and of the possible correlations between abnormal concentrations and pathological conditions. In order to determine the K, Ca, Fe, Cu and Zn concentrations present in healthy as well as in neoplastic breast tissues two experiments were performed at the XRF beamline of the Laboratório Nacional de Luz Síncrotron (LNLS). Two different photon energies were used to maximize the X-ray fluorescence by the elements of interest. The energy of 6 keV was chosen in order to detect simultaneously K, Ca while 11 keV for Fe, Cu and Zn. The samples were placed at 45^o from the incident beam whereas the energy dispersive solid state HPGe detector was placed at 90^o from the incident beam, on the plane of the electron storage ring, in order to benefit from the strong polarization of the synchrotron beam thus improving the signal to noise ratio. Eighty samples of breast tissues were analyzed. Pathological information was available for all samples. Metal concentrations in breast tissue specimens were determined using a semi-quantitative method based on calibration curves obtained from aqueous and ethanolic solutions with inorganic salts of well-known concentrations. The accuracy of the semi-quantitative method was checked by the analysis of a set of solutions of urea with known concentrations. This semi-quantitative method is simple and allowed minimizing matrix effects. The results obtained in this work confirm that Fe, Cu and Zn are valuable indicators, to be considered as tracers for the identifications of pathological disorders in breast tissues and show that X-ray Fluorescence analysis using Synchrotron Radiation seems to be a possible helpful diagnostic tool against breast cancer.

Acknowledgements
This work has been supported by the Brazilian agency Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP, process numbers 02/00380-3 and 04/06270-0) and by the Brazilian Synchrotron Light Laboratory (LNLS) under proposal D09B-XRF-4780 and D09B-XRF -5337.

94

Study of the molecular and supramolecular organization of normal and neoplastic breast tissues by WAXS and SAXS

Conceição, A. L. C.[1], Antoniassi, M.[1], Torriani, I.[2], and Poletti, M. E.[1]

[1] Universidade de São Paulo - Ribeirão Preto - Ribeirão Preto SP Brazil
[2] Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil

Wide angle X-ray scattering (WAXS) allows the obtaining of spatial distribution of small structures that constitute tissues, as water for example. Small angle X-ray scattering (SAXS) is a powerful tool that allows the determination of supra-molecular structures characteristics, such as proteins. The combination of the two techniques allows correlating structural changes at atomic level with changes at larger scales. Therefore, WAXS and SAXS experiments can provide structural information on changes in normal human breast tissues due to the presence of the disease (cancer). In this preliminary work both techniques were used to analyze four samples of normal breast tissues and four samples of neoplastic tissues. The experiment was implemented at the SAXS1 beamline of the Laboratório Nacional de Luz Síncrotron (LNLS). A focused monochromator of Si (111) was used in order to provide an X-ray beam of wavelength $1.48\AA$ and to reduce the irradiation area on the sample and allowing to record a range of $6.28nm^{-1} < Q(= 4\pi.sin(\theta/2)/\lambda) < 50.26nm^{-1}$ and $0.15nm^{-1} < Q < 1.90nm^{-1}$ for WAXS and SAXS respectively. The sample to detector distance was fixed at 1.59m and was evacuated in order to minimize air scattering and absorption losses. The detector for both techniques was a Fuji Bas III image plate. Standard samples of alumina (N2O3) and SilverBehenat (AgBr) were used as calibrators to WAXS and SAXS respectively, in order to establish the correct reciprocal space scale of each scattering pattern. The preliminary results of this work show that malignant breast tissues presents different scattering patterns (shape and peaks positions) when compared with normal breast tissues. The WAXS pattern of normal breast tissues showed a sharper peak at $Q = 13.8nm^{-1}$ while neoplastic ones showed a broad peak at $Q = 21.3nm^{-1}$. The SAXS data of normal tissues showed several peaks corresponding to collagen reflections from the 3rd ($Q = 0.29nm^{-1}$) to the 13th ($Q = 1.17nm^{-1}$) order. On the other hand, these peaks seem not to be present in the SAXS patterns from neoplastic tissues. This preliminary study shows that the combination of WAXS with SAXS results provides a potential medical tool for characterizing human breast tissues.

Acknowledgements
This work was supported by the Brazilian agency Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP, process 02/00380-3) and by the Brazilian Synchrotron Light Laboratory (LNLS) under proposal D11A-SAXS1 4783/05.

95

Application of X-ray diffraction in the identification of neoplastic human breast tissues

Conceição, A. L. C.[1], Antoniassi, M.[1], and Poletti, M. E.[1]

Universidade de São Paulo - Ribeirão Preto - Ribeirão Preto SP Brazil

The angular distribution of photons scattered by tissues (scattering profile) gives detailed information of their internal structures and provides an alternative mean to distinguish among pathologies[1,2]. Therefore, it is important to develop an efficient and trustworthy experimental procedure to determine scattering profiles from human tissues. In this work the potential use of X-ray diffraction technique by transmission mode has been investigated to obtain scattering profiles from breast tissues previously histopathologically classified as normal tissues, fibroadenomas and carcinomas. The experiment was implemented at the XRD1 beamline at the synchrotron radiation source of Campinas in Brazil. A double-crystal of Si (111) was used in order to provide an X-ray beam of wavelength $1.128Å$ and to reduce the irradiation area on the sample (5.5mm × 1.0mm) allowing to record the range $0.8° \leq \theta \leq 78.55°$ (corresponding to a momentum transfer interval of $0.7nm^{-1} \leq Q(=4\pi.sin(\theta/2)/\lambda) \leq 70.5nm^{-1}$). The sample was located in the center of a Hubber Diffractometer and the sample-to-detector distance was fixed at 210mm. The detector was a NaI(Tl). The measured angular distribution was corrected by attenuation and geometric effects. The effectiveness of the experimental procedure was validated through the use of water reference data. The preliminary results showed that the scattering profile is an unique impression of each type of tissue, being correlated with their microscopic morphological features. At $Q \leq 25nm^{-1}$, it was statistically verified that the information contained in the scattering profiles allow the differentiation between normal and neoplastic human breast tissues. These initial results show the potentiality of X-ray diffraction technique to provide a rapid diagnostic from human breast tissue with a high sensitivity.

[1] Poletti ME, Gonçalves OD, Mazzaro I. X-ray Spectrom. 2002; 31: 57-61. [2] Cunha DM, Oliveira OR, Pérez CA, Poletti ME, accepted to be published on X-ray Spectrom. 2006.

Acknowledgements
This work was supported by the Brazilian agency Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP, process 02/00380-3) and by the Brazilian Synchrotron Light Laboratory (LNLS) under proposal D12A-XRD1 5300/07.

96

Characterization of osteoporotic bone structures by bidimensional images using X-ray microfluorescence

LIMA, I.[1], Anjos, M. J.[2], Fleiuss, M. L. F.[2], Rosenthal, D.[3], and Lopes, R.T.[3]

[1] Instituto Nacional de Metrologia, Normal e Qualidade Industr - Xerém RJ Brazil
[2] Universidade do Estado do Rio de Janeiro - Rio de Janeiro RJ Brazil
[3] Universidade Federal do Rio de Janeiro - Rio de Janeiro RJ Brazil

Osteoporosis is a pathology that assails the bones, defined as systemic skeletal disease characterized by a decrease in the bone mass and deterioration of the microarquitecture with the increase of the bone fragility and more susceptibly to fractures. The objective of this study was to characterize the bone structures of the femoral head, cortical and trabecular regions, from the bidimensional images by x-ray microfluorescence. The measurements were performed in standard geometry of 45^o incidence, exciting with a white beam and optical capillary with 20 μm of diameter collimation in the XRF beam line. Bone specimens were obtained from 15 Wistar female rats (4 months-old) from femoral head. The animals were separated into three groups: control, OVX and OVX with estrogen replacement (daily subcutaneous doses of 0.7 μg of 17 β estradiol benzoate per 100 g of body weight). The animals were ovariectomized when they were 2 months-old and were killed, when they were 4 months-old, e.g., 2 months-old after OVX. After the sacrifice, the femurs were disarticulated, surrounding tissue manually cleaned to remove soft tissue and the femoral heads were cut with a diamond cutter in 1 mm of thickness. The samples were placed on a XZ table controlled by a microcomputer and scanned as follows: beam size of 30 x 30 μm, a 30 μm /step, counting time of 9 s/point. It was found ten elements: P, S, Cl, K, Ca, Cr, Fe, Cu, Zn and Sr. It was possible to observe that ovariectomy, in a period of two months was able to reduce the percentages of calcium and increase the strontium concentrations. The OVX process (in two months) was able to: a) reduce the thickness of the cortical region in femoral head, while the estrogen replacement increased again this parameter making possible the geometric definition of this bone site; and b) making the internal structure of the bone osteoporotic, in others word, the μXRF images reveals a increase of the porous diameter, representing a high bone porosity with a decrease in trabecular dimensions.

Acknowledgements
Research partially supported by LNLS - National Synchrotron Light Laboratory (projects XRF-4307and XRF-5375) and by the National Council for Scientific and Technological Development (CNPq) and Rio de Janeiro State Research Foundation (FAPERJ).

Parte VI

Matéria Mole e Fluídos Complexos

97

Temperature investigations of water diffusion in synthetic nano-silicates by means of DXAS

da Silva, G. J.[1], Ribeiro, L.[1], Mundim, M.S. P.[2], and Fossum J. O.[3]

[1] Universidade de Brasília - Brasília DF Brazil
[2] Universidade de Brasília - Brasilia DF Brazil
[3] Norwegian University of Science and Technology - Trondheim Norway

In this work we present the results of the study of water intercalation process in a synthetic clay Ni-Fluorohectorite as it progress through the sample utilizing dispersive x-ray absorption spectroscopy [1]. The process of intercalation of water (hydration sphere) in this sample is studied as a function of temperature (parameter responsible for the control of water entrance and exit of the sample) and humidity. Critical values of temperature are related to the stable hydration regime of this sample leading to structures, referred to as having either 0, to 3 intercalated water layers, which are quite well ordered along the stacking direction [2, 3]. The data is analyzed by means of the "Generalized Simulated Annealing"GSA [4], which is a technique of stochastic optimization well adapted to deal with the problem of multiples minima. It is appropriated for simulation of these intercalation processes using experimental data as a stoping criterion.

References:
[1] - LNLS, D06A-DXAS.
[2] - G. J. da Silva, J. O. Fossum, et al, Phys. Rev. B, 67, 94114(2003).
[3] - B. Sandnes, da Silva G. J., Mundim, M S. P., et al, Physica B , 370, 90(2005).
[4] - K. C. Mundim, and C. Tsallis, Int. J. Quantum Chemistry, 58, 373(1996).

Acknowledgements

This work hás been supported by the Brazilian Synchrotron Light Laboratory (LNLS) under proposal D06A-DXAS number 4815/2005, also by the Research Council of Norway (RCN) through funding granted in the framework of the RCN Nanomat Program and the RCN Strategic University Program.

98

Complexos Supramoleculares de PEI (um policátion) e SDS (um surfactante aniônico) investigados por SAXS

Campestrini, I.[1], Felippe, A.C.[1], and Minatti, E.[1]

Universidade Federal de Santa Catarina - Florianópolis SC Brazil

Polímeros e surfactantes podem formar complexos supramoleculares em solução aquosa. O controle morfológico destes complexos permite sua aplicação na nanotecnologia[1]. O PEI (*polietilenoimina*) é um polieletrólito posivitamente carregado, graças ao caráter básico dos grupos aminas. Este polímero é muito usado como ingrediente de fármacos e cosméticos e, recentemente, como *backbone* para *synzimes*[2] (enzimas artificiais). Neste trabalho, investigamos a associação deste políeletrólito com o SDS (*dodecil sulfato de sódio*).

Através de medidas usando as ténicas de SAXS (*espalhamento de raios-X a baixos ângulos). conductivimetria, turbidimetria* e *viscosimetria,* caracterizamos soluções aquosas de PEI nas concentrações de 0,025 a 0,2 % (m/v), garantindo a operação sempre no regime diluto (determinado por viscosimetria). Nestas soluções, observamos uma intensa turbidez no início da adição do SDS. Como o surfactante é aniônico, acreditamos que nesta região ocorra uma intensa ligação específica do DS^- aos íons amônio do políeletrólito, transformando-o em um polímero neutro (PEI-DS). Da conformação estendida, então, o PEI passa a uma conformação mais enovelada. Esta hipótese foi confirmada por experimentos de SAXS, onde observamos um aumento abrupto do R_g médio do polímeros com a adição de surfactante – indicando a transição cadeia estendida – cadeia enovelada. Após uma determinada [SDS], a solução volta a ser translúcida, devido a ressolubilização do PEI-DS pela associação clássica de mais SDS. A partir deste ponto, as curvas de conductivimetria indicam um comportamento clássico de um sistema envolvendo polímero neutro hidrossolúvel + surfactante.

[1] Minatti, E. et al; *Langmuir;* 2005; 21(4); 1180-1186. DOI: 10.1021/la048944f

[2] Shuai, X. et al; *Bioconjugate Chem.*; 2005; 16(2); 322-329. DOI: 10.1021/bc0498471

Acknowledgements

Este trabalho foi possível graças ao auxílio do LNLS.

99

DNA ORGANIZATION IN ORIENTED LECITHIN LAMELLAR PHASE- A REFLECTIVITY STUDY ON SUPPORTED FILMS

Navailles, L.[1], Nallet, F.[2], Grelet, E.[3], and Oliveira, E. A.[4]

[1] Centre National de la Recherche Scientifique - Paris France
[2] Centre national de la recherche scientifique - PESSAC France
[3] Centre National de la Recherche Scientifique - Paris cedex 16 France
[4] Universidade de São Paulo - São Paulo - São Paulo SP Brazil

Synthetic vectors for gene therapy based on cationic lipids/DNA complexes have been proposed as an alternative approach to viral vectors, however toxicity associated to the charges is a limiting factor. Recently it was demonstrated that it is possible to incorporate DNA between non-cationic lipid bilayers due to an entropic interaction1. The advantage of this formulation is the biocompatibility of the lipid used in the vector preparation2. Different organizations of the DNA molecules between the lipid bilyares have been theoretical predicted, with in layer orientational order and positional order with inter layer correlation3, however the identification of such structures requires well oriented samples. In this work we investigate the structure of DNA molecules confined between lecithin bilayers using supported films. The film is placed in a chamber with controlled humidity, which allows us to tune different degrees of lamellar periodicity and explore the effect of confinement in the organization of the DNA. Using the BM-32 line-ESRF facility we identified a lamellar phase (L_α) of lecithin with periodicity D= 6nm, where the peaks related to lamellar structure were localized along the direction of the normal to the layers in the film. Others peaks, were also identified related to the organization of DNA between the membranes. These peaks could be perfectly indexed in a hexagonal structure with a parameter $a = 2D/\sqrt{3}$ =6,9nm. A preliminary phase diagram of the ternary lecithin/DNA/water system will also be presented, where other types of organization of DNA molecules were identified confined between the lecithin bilayers in the liquid phase. We will discuss the influence of the confinement on the DNA organization and the importance of this study in the comprehension of the interactions of biomolecules and membranes.

[1] T. Potts and D. Roux FEBS Lett 511, 150(2002)

[2] P. Chevenier, B. Delord, J. AmÃĺdee, R. Bareille, F. Ichas, D. Roux, Biochm. Biophys. Acta 1593, 17(2002)

[3] L. Golubovic, T. C. Lubensky and C. S. OâĂŹHern, Phys. Rev. E 62, 1069(2000).

Acknowledgements
This work was supported by CNRS.

Parte VII

Materiais Estruturais e Aplicações na Indústria

100

Crystalline structure of M_2C carbide in spray formed AISI M2 high-speed steel

Serna, M.M.[1], Galego, E.[1], and Rossi, J. L.[1]

Instituto de Pesquisas Energéticas e Nucleares - São Paulo SP Brazil

In the spray forming plant the central billet region is submitted to a slow cooling rate allowing the atomic migration and promoting the formation of the M_2C and M_6C carbide network. The M_2C type carbide present a hexagonal structure, which assumed a plate-like shape and are discontinuously precipitated. The conditions used in the spray forming plant to obtain the samples used in this work promote the formation of the unknown phase with M_2C morphology. Since, hexagonal or orthorhombic crystalline structure of the M_2C carbides is function of the ordered or random distribution of the carbon in metallic carbides that is determinate by the cooling temperature, the kinetic of transformation and carbon concentration. The orthorhombic phases can be identified through the distortion of the metallic sublattice, which induces a splitting of some peaks, which may be detectable, by synchrotron measurements. The space group *P b c n* (orthorhombic structure, ξ Fe_2N type) was used for Rietveld refinement of unknown phase. The lattice parameter calculated for the unknown phases is a= 0.4649636 nm, b=0.674553 nm and c=0.5116704 nm. Since, this phase is isomorphs for Mo_2C and W_2C the differences between these parameters are assigned by the mixture of Mo and W atoms in the crystalline structure. The orthorhombic structure of this carbide is commonly accepted as a disordered structure in transition at a hexagonal structure. The presence of this structure in this material is coherent with the thermodynamic history.

101

Role of the SBR Addition to Natural Rubber-based Blends to the Network Formation

Salgueiro, W.[1], Somoza, A.[2], A.J.Marzocca[3], and Torriani, I.[4]

[1] Universidad Nacional del Centro da Provincia Buenos Aires - Tandil B.A. Argentina
[2] Universidad del Centro - Tandil BA Argentina
[3] Universidad de Buenos Aires - Buenos Aires DF Argentina
[4] Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil

The aim of the present work is to go deeper in rubber studies previously developed by the authors on natural rubber (NR) by means of SAXS. In this framework, a systematic SAXS study of blends of NR and styrene-butadiene rubber (NR/SBR) is presented. To this aim, specimens of cured NR and SBR and mixtures with 75/25, 50/50 and 25/75 NR/SBR ratios (in phr) were prepared. In order to get the optimum cure time (t_{100}), these mixtures were experimentally characterized by means of torque curves in a rheometer. After that and to obtain a complete vulcanization process the blends were cured at 433 K during the time t_{100}. Samples with a typical diameter of 10 mm and a thickness of 1.5 mm ca. were cut from the specimens. Using a 1.608 wavelength, SAXS spectra as a function of the scattering vector q were measured in the q range between 0.01 and 0.40 $Å^{-1}$. For all the samples measured and for scattering vector values ranging from 0.1 to 0.2 $Å^{-1}$, a ”shoulder” in the I(q) vs. q curves was observed. To get a more precise localization of the angular positions of the intensity maximum, a representation in Lorentz plots ($I(q)q^2$ vs q) was used. From such representation no variation of the peak position was observed. But, an increment of the intensity of the peak with the increase of the SBR content in the samples was observed. This peak can be associated with a correlation length related to a variety of intramolecular groups present in the vulcanized rubber network. The results obtained are discussed taking account that in the covulcanization the elastomers contain different phases. Furthermore, it was considered that these elastomers should be vulcanized to similar levels with crosslinking across the microdomains intherphases with an interfacial layer of rubber with different state of cure than in the bulk. Bearing in mind that the NR is the matrix phase the influence of the different amounts of SBR on the crosslink structure is also discussed.

Acknowledgements

The support of the LNLS, Brazil (Project: D11A-SAXS 4181/05) is acknowledged. The authors are very grateful to Fernando Queiruga Rey and Tomas Plivelic for the technical help during measurements at LNLS

102

Caracterização Morfológica de Nanoagregados de Poli(óxido de etileno) e Misturas de Surfactantes Aniônicos Investigada Por SAXS

Minatti, E.[1], Felippe, A.C.[1], Zanette, D.[1], Campestrini, I.[1], and DAL-BÓ, A. G.[1]

Universidade Federal de Santa Catarina - Florianópolis SC Brazil

Investigamos a auto-associação de polímeros e biopolímeros com misturas de surfactantes por técnicas tradicionais, como fluorescência, tensiometria e condutivimetria. Este trabalho complementa resultados anteriores através do estudo das mudanças na morfologia de agregados entre poli(óxido de etileno) (PEO), e misturas do biossurfactantes colato de sódio (NaC) com dodecil sulfato de sódio (SDS), investigados por espalhamento de raios-X a baixos ângulos (SAXS). Aqui, apresentamos o efeito da fração molar de SDS na mistura sobre a forma e tamanho dos agregados. Através dos perfis de intensidade de fótons espalhados em função do ângulo de espalhamento para soluções de PEO contendo misturas de SDS/NaC com diferentes χ_{SDS} observou-se um aumento das oscilações nas curvas em função do aumento da χ_{SDS} indicando a formação de agregados esféricos na medida em que estas misturas tornam-se mais ricas em SDS. O diâmetro médio dos agregados micelares ao longo da cadeia do polímero foi obtido pelo ajuste das curvas em acordo com o modelo teórico “colar de pérolas” [2]. Os resultados mostram que em baixas frações molares de SDS ($\chi_{SDS} < 0,2$) os agregados são pequenos (8 nm em diâmetro). Em frações intermediarias de SDS ($0,2 < \chi_{SDS} < 0,7$) os agregados crescem lentamente (10 - 15 nm) mas crescem abruptamente após uma χ_{SDS} de cerca de 0,7, até atingirem cerca de 30 nm em diâmetro para $\chi_{SDS} =1,0$ (tamanho típico de agregados PEO-SDS). Através destes resultados propomos um modelo para estas misturas de SDS-NaC-PEO. Para NaC puro o polímero está livre dos agregados micelares. Em baixas χ_{SDS} micelas mistas são formadas, mas não ocorre agregação com PEO. Para $\chi_{SDS} \approx 0,7$ inicia-se o processo de agregação polímero-surfactante. Os experimentos de SAXS forneceram uma interpretação morfológica para o efeito do incremento de SDS na mistura de surfactantes, reforçando a idéia de que uma transição para uma associação cooperativa ocorre somente após uma determinada fração de SDS na mistura.[3,4] [1] Felippe, A. C.; Zanette, D.; et al. *Macromol. Symp.*, **2005**, 229, 208. [2] Fairclough, J. P. A. et al. J., *Rad. Phys. and Chem.*, **1999**, 56,159. [3] Felippe, A. C.;. Zanette, D.; et al. Colloids and Surfaces A: Physicochem. Eng. Aspects 279, 87–95, 2006. [4] Felippe, A. C.; Zanette, D.; Minatti, E.; et al. Colloids and Surfaces A: Physicochem. Eng. Aspects (in press), 2006.

Acknowledgements

Agradecemos ao LNLS pelo auxílio e instalações.

103

Relation between structure and diisocyanate type in polyurethanes and acrylic/polyurethane hybrids studied by SAXS, WAXS and FTIR.

Peruzzo, P. J.[1], Pardini, O. R.[1], and Amalvy, J. I.[1]

Universidad Nacional de La Plata - La PLata B.A. Argentina

Polyurethanes (PUs) are an interesting class of materials that typically consist of semi-crystalline hard segments and amorphous polyether soft segments. The particular chemical structure of PU is reflected in both their morphology and properties. Due to incompatibility of soft and hard segments phase separation occurs. Linear PUs are prepared using diisocyanates and polyols and the structure in the solid phase depends on the type of diisocyanate. In this work the structure of two PUs prepared using isophorone diisocyanate (IPDI) and m-tetramethylxylene diisocyanate (TXMDI) have been investigated using SAXS and WAXS. TMXDI aliphatic diisocyanate monomer contains two tertiary aliphatic isocyanate groups, providing unique properties as compared to primary and secondary isocyanate groups and morphological changes are expected. Morphology modification by including an acrylic component and by thermal curing is also investigated. SAXS spectrum of IPDI-based PU shows the typical band at $q = 0.1$ Å^{-1} and remains unchanged after curing. A similar peak for the TXMDI-based PU before curing is also observed, but this peak reduces the intensity and shifts slightly to lower q after curing (0.085 Å^{-1}). WAXS curves indicate that the chemical structure of TXMDI changes the local ordering. For IPDI-based PU a peak is observed at 2θ about 16.7 ^{o} and for TXMDI at about 18.2 ^{o}. The incorporation of acrylic component to form hybrids has an influence on the microphase behavior by altering the interaction between chains (1). For IPDI-based hybrid at 90 wt.% of acrylic component microphase separation is observed. After annealing at 60 ^{o}C, the material has a higher tendency to form separated phases and systems with lower acrylic content (approximately 70 wt.%) shows phase separation. TMXDI-based PU seems to behave differently. FTIR experiments have also been carried out to correlate with structural changes observed in SAXS.

1. "Structure of polyurethane/acrylic hybrids films studied by SAXS". P.J. Peruzzo, O.R. Pardini and J.I. Amalvy. 16 RAU, February 20 - 21 2006. Campinas (Brazil).

Acknowledgements

To Brazilian Synchrotron Light Laboratory (LNLS), Campinas, Brazil (proposal D11A-SAXS 4595/05) and T. Plivelic for their cooperation. CICPBA (Grant 694/04), ANPCYT (PICT 14-8709) and CONICET (PIP 2808) are thanked by financial assistance. JIA is member of CIC.

104

SAXS study of nanostructured thin films prepared by pyrosol deposition

Sarmento, V.H.V[1], Hammer, P.[1], Pulcinelli, S.H.[1], and Santilli, C.V.[1]

Universidade Estadual Paulista - Araraquara - Araraquara SP Brazil

A wide variety of methods are available to produce ceramics thin films by chemical routes. Among these, the pyrosol process is interesting as it operates at atmospheric pressure and offers a relatively inexpensive and mature technology for the deposition of oxides thin films over large areas. Depending on the application of the film, the substrate can be metal, glass, silicon wafers or ceramics. The pyrosol apparatus consists of the aerosol generator and the pyrolis chamber. Aerosol of the solution generated in the ultrasonic atomizer is conveyed by the carrier gas through the transport tube to the heated substrate (borosilicate glass, silicon and mica foil). The direction of the flow is perpendicular to the substrate. The deposition mechanism, structure and properties of the deposits depend on a number of experimental parameters, such as the precursor chemistry, the flow rates of the aerosol and the carrier gas, the temperature and the nature of the substrate. The purpose of the present work was to establish a correlation between the process and precursor parameters with the nanostructural properties of the obtained deposits. In order to realize this, oxide films (Sn and Zr) were synthesized by pyrosol process and their morphology and nanostructure studied using scanning electronic microscopy (SEM) and small angle X-ray scattering (SAXS), respectively. Moreover, organic molecules based surfactants were added to the precursor and the effects of these modificators on the nanostructure were studied. In the present case, the precursor solution was prepared using $SnCl_4.5H_2O$ (p. a. 98%) diluted in 90% H_2O DI and 10% ethanol (v/v) with 0.2 mol.dm^{-3} concentration. A non ionic surfactant Tergitol was added to solution (0.04 mol.dm^{-3}) to form nanostructured films. SnO_2 films deposited from the aerosol at 523, 573, 623 and 673 K were characterized by SAXS. The results showed that films deposited at 523 K present a plateau for high q-values ($q > 0.1$ Å^{-1}) indicating the presence of the small particles whereas the SAXS curves of films deposited at higher temperatures do not indicate a continous particle size distribution. These results prove that surfactant affects significantly the film nanostructure.

Acknowledgements

We would like to acknowledgement LNLS for SAXS measurements and CNPQ for financial support.

105

Residual Stress Measurements in Oxyfluoride and Chalcogenide Nano Glass-Ceramics

Serbena, F.C.[1], Souza, G. P.[2], Zanotto, E.D.[2], Lumeau, J.[3], Glebova, L.[3], Glebov, L.B.[3], and Zhang, X.[4]

[1] Universidade Estadual de Ponta Grossa - Ponta Grossa PR Brazil
[2] Universidade Federal de São Carlos - São Carlos SP Brazil
[3] University of Central Florida - Orlando FL United States of America
[4] Université de Rennes I - Rennes France

The residual stresses that arise upon cooling in two glass-ceramics systems were characterized by x-ray synchrotron radiation. One is a photo-thermo-refractive (PTR) glass with sodium fluoride nanocrystals embedded in an oxyfluoride glass matrix, and the other is a chalcogenide glass with nanosized precipitates of cesium chloride. In both glass-ceramics, the crystalline volume fraction is small and the crystals are cubic. Measurements were performed in UV irradiated and non-irradiated PTR samples submitted to heat treatments of 450^{o}C-1h for nucleation and at 520^{o}C-2h or 650^{o}C-20 min. to induce growth of the precipitates. For the chalcogenide glass, measurements were performed on samples heat treated up to 50h at 290^{o}C. Preliminary analyses based on the integral-breadth method reveals reasonable agreement with the stress calculated from the crystalline phase microstrain and the Selsing model, but there is considerable scatter in the particle size and microstrain estimations. At present, residual stresses are being calculated by the integral-breadth and $\sin^2 \psi$ methods and will be compared with the predictions of the Selsing model.

Acknowledgements
The authors acknowledge the financial support of CNPq. The measurements were performed at LNLS - National Synchrotron Light Laboratory, and at Department of Materials Engineering, Federal University of São Carlos, Brazil.

106

Microstructural and superconducting characterization of Nb_3Sn wires with Cu-Nb reinforcement

Sandim, M. J. R.[1], M. P. Cangani[1], and Ghivelder, L.[2]

[1] Escola de Engenharia de Lorena - Universidade de São Paulo - Lorena SP Brazil
[2] Universidade Federal do Rio de Janeiro - Rio de Janeiro RJ Brazil

Nb_3Sn is recognized as one of the most important practical superconducting materials for a high field magnet over 10 T. To fabricate high-field superconducting magnets, high strength Nb_3Sn wires are needed to sustain large electro-magnetic forces (Lorentz force). For this reason, highly strengthened Nb_3Sn composite wires with Cu-Nb reinforcement have been developed [1]. The heat treatment necessary to form the A-15 superconducting phase (650-700^{o}C or higher) can lead to the partial spheroidization followed by coarsening of the Nb filaments in the reinforcement material. Such morphological changes affect the performance of the Nb_3Sn wires. In this work we focus on the microstructural and superconducting characterization of Nb_3Sn wires with different reinforcement positions (at the central or near to the edge part of the wire). The microstructural characterization was performed using scanning electron microscopy in 1450-VP LEO and JSM 6330 F (FEG) microscopes. AC magnetic susceptibility of the wires was measured by a PPMS (Quantum Design) system for a magnetic field of 1 Oe and frequency of 100 Hz, with field applied perpendicular to the wire axis. Noticeable differences were observed among the investigated samples concerning the morphology of niobium filaments in the reinforcement material. Moreover, concerning the Nb_3Sn phase, the samples with reinforcement material in the inner part of the wire presented the broader superconducting transitions [2].

References

[1] P. Badica, S. Awaji, H. Oguro, G. Nishijima, K. Watanabe. Supercond. Sci. Technol. 19 (2006) 323. [2] P. Badica, S. Awaji, G. Nishijima, H. Oguro, M. J. R. Sandim, M. P. Cangani, L. Ghivelder, K. Katagiri, K. Watanabe. Supercond. Sci. Technol, submitted.

Acknowledgements

The authors are grateful to Furukawa Electric Co. Ltd (Japan) for providing samples and to LNLS- National Synchrotron Light Laboratory (Brazil) for technical support. The authors also thank Dr. P. Badica and Dr. S. Awaji (Tohoku University, Sendai-Japan) for collaboration in this investigation.

107

Comparative Study using SAXS and Nitrogen Physisorption in the Textural Characterization of Raney Ni catalyst

Rodella, C. B.[1], Kellermann, G.[1], and Zanchet, D.[1]

Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil

Raney Ni catalyst is widely used as a heterogeneous catalyst for liquid-phase hydrogenation reactions. It is extensively applied in industry for hydrogenation of the d-glucose to sorbitol. The catalyst is produced by alkaline dissolution of aluminum from Ni-Al alloy. The alloy usually contains 50wt.% of the Ni and consist of Ni_2Al_3 and $NiAl_3$ intermetallic phase as well as pure Al. This leaching process leads to nanoparticles of metallic nickel connected in a spongy-like structure highly porous. As shown by many studies, several parameters involved during the preparation stages of Raney Ni can affect its textural and structural characteristics and consequently, its catalytic properties. In this work, the effect of the leaching temperature on textural properties of Raney Ni catalyst was studied by small-angle X-ray scattering (SAXS) and nitrogen physisorption. The catalysts were obtained by a basic dissolution of the aluminum from a Ni-Al alloy. The leaching process was performed in different temperatures: 60, 80 and 110^0C. The textural properties of the Raney Ni were only slightly affected when the leaching temperature was increased from 60 to 80^0C. However, for leaching temperature equal to 110^0C, Raney Ni exhibited a decrease of the surface area, pore volume and an enlargement of the mean pore diameter. The SAXS analyses showed a continuous decrease in specific surface values and an increase in the pores average size for increasing leaching temperatures. These results are in good agreement with the nitrogen physisorption results.

Acknowledgements
GETEC Química Guanabara, ABTLuS and CNPq

108

Inclusions Control in Pearlitic Steel Tyre Cords trough X-Ray Microanalysis (EDS) Automation coupled to Scanning Electron Microscopy (SEM).

Afonso, C R M[1], Arajo,S.R.[1], Biggemann, D.[1], Camparotto, M. R.[1], and Ramirez, A.J.[1]

Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil

The control of level and type of inclusions in special pearlitic steels cords which compose the mesh of automotive tyres is extremely important for the quality warrant of the cord after wire drawing process. Steel cords used to compose the mesh of automotive tyres have initially a diameter of 5.5mm and they can be wire drawn up to 0.15mm. After wire drawing process the cord is transformed in the mesh that composes the structural part of radial tyres (without inner tube). The shear banding is sufficient to generate the delamination crack nuclei, but it should be clear that other external defects such as inclusions, drawing grooves or other surface damage can induce delamination failures. Steel with a high cleanness will prevent problems during drawing and the heat treatment. The studies show that among many defects the most important ones are the non-metallic inclusions and undesirable phases encountered during improper heat treatment. In this study typical wire and cord failures due to non-metallic inclusions are examined. The analysis of the inclusions is made by: (a) atomic weight (Z) contrast in backscattered electrons sign (BSE) in the scanning electron microscope (SEM); (b) chemical composition measured through the X-ray microanalysis (EDS); (c) measurement of the inclusion area trough image analysis using contrast differentiation of dark (lighter) and light (heavier) areas; (d) counting of number, size and type (composition) of inclusions per area in the sample. The current of the electron beam is measures trough a Faraday cup and a picoammeter. The fixed elements to be identified trough the X-ray microanalysis are: Fe, Mn, Mg, Al, Si, Ca, S and O. For the calibration of the automation is necessary, in the beginning of the process, the manual identification of a MnS inclusion. Among the inclusions analyzed MnS (compare to the oxides) have an atomic density closer to the steel matrix. Other inclusions in the same size range, like oxides of cited metals can be detected as well. The analysis of inclusions trough the automation of the EDS microanalysis allows the detection of an average of 50 inclusions per hour and in a total of 5 mountings of 5 tyre cords samples each (25 samples) can be analyzed in a period of approximately 7 hours. This study shows the wide range of possibilities of analysis that can be made trough the automation of EDS X-ray microanalysis via software realizing several combinations of analysis (in this case, BSE image, counting of particles and chemical analysis of each one of them) of many samples in a short time.

109

Investigação do Comportamento Magnético de Aços Inoxidáveis Dúplex por MFM

Santos, F. S.[1], Gheno, S. M.[1], and Kury, S. E.[1]

Universidade Federal de São Carlos - São Carlos SP Brazil

Aços inoxidáveis dúplex são materiais de grande importância tecnológica devido a excelente combinação de propriedades mecânicas e alta resistência à corrosão. Basicamente, esses materiais apresentam microestrutura formada por ferrita, que é ferromagnética, e austenita, que é paramagnética, em frações volumétricas aproximadamente iguais. Neste trabalho, a microscopia de força magnética (MFM), foi utilizada para analisar a microestrutura e investigar o comportamento magnético do aço inoxidável dúplex 2205 solubilizado e envelhecido em baixa temperatura por tempo prolongado. As imagens de MFM do aço inoxidável dúplex 2205 foram obtidas em um microscópio de força atômica (Nanoscope IIIa (LNLS)), através de Tapping/Lift^{TM}, operando no modo força magnética (MFM). Os resultados obtidos mostraram a distribuição de fases sem a necessidade de ataque metalográfico, com a distinção da ferrita por sua configuração de domínios magnéticos

Acknowledgements

Ao laboratório de microscopia de força atômica do LNLS, Campinas e à FAPESP, CNPq e CAPES pelo suporte financeiro.

110

MICROSTRUCTURAL EVOLUTION DURING PLUG FRICTION WELDING OF LOW ALLOY STEEL

Unfried, J.[1], Piza, M.[2], and Ramirez, A.J.[1]

[1] Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil
[2] Petrobrás - Cenpes - Rio de Janeiro RJ Brazil

Plug Friction Welding is recently developed solid state welding process which is recently receiving a lot of attention from the oil and gas industry due to the actual and expected impact on the repair of submerged pipes, offshore platforms and even ships. However, very little is known regarding the microstrutural evolution during this process and its influence on the performance of such joints. Therefore, Petrobras and LNLS have engaged in this project to understand the microstrutural evolution through the welded joint of two different variations of plug friction welding process so-called Friction Taper Plug Welding (FTPW) and Hydro-Pillar Processing Welding (HPPW). Three samples from cold rolled low alloy steel joints processed with different parameters (rotational speed, axial force and plate thickness) were submitted to exploratory evaluation. Optical microscopy, scanning electron microscopy and microhardness were used. It was possible to identify in all samples and evaluated conditions, 6 solid state welding zones: (a) Unaffected plug zone, (b) Mechanically affected plug zone, (c) Partially transformed thermo-mechanically affected zone, (d) Fully transformed thermo-mechanically affected zone, (e) Mechanically affected base material zone, and (f) Unaffected base material zone. Specific microestrutural features that will determine the joint performance where observed on each zone, which depend on chemical composition, processing parameters and previous thermo-mechanical history of the materials. A model for the microstructural evolution has been proposed.

Acknowledgements

The authors would like to acknowledge to Petrobras for the financial support of this project and to CNPq for the technological fellowship.

111

Estudo da Compatibilidade da Mistura de Poliânions com Diferentes Tamanhos e Densidades de Carga por SAXS.

Soldi, V.[1], Lima,A.M.F[1], Soares, R.M.D.[1], Kleinert, J. J.[2], and Villetti, M. A.[2]

[1] Universidade Federal de Santa Catarina - Florianópolis SC Brazil
[2] Universidade Federal de Santa Maria - Santa Maria RS Brazil

Este trabalho visa investigar a compatibilidade e a mudança de conformação local da mistura de polieletrólitos com carga similar (poliânions) mas diferentes tamanhos (Mw) e densidades de carga (ξ). O polieletrólito semi-rígido xantana (XT, ξ=1,0) apresenta um empacotamento do tipo cúbico no regime diluído (domínio q-SLS) e hexagonal/cilíndrico no regime semi-diluído (q-SAXS). A adição de alginato de sódio (Alg, ξ=1,49) ou hialuronato de sódio (Na-Hy, ξ=0,71) a solução de XT desloca o q_{max} para altos vetores de onda. Isto sugere que não ocorre uma mistura efetiva entre os poliânions, levando a uma concentração local de cada componente. Esta incompatibilidade é devido a diferença no tamanho ou densidade de carga dos polieletrólitos, que produz uma assimetria nas interações intermoleculares. Contudo, a adição de plastificantes (sorbitol ou glicerol) a solução de XT não desloca o pico de espalhamento angular indicando que não ocorre segregação das cadeias. A diminuição da altura e aumento da largura do pico com o aumento da concentração de sorbitol ou glicerol pode ser racionalizado pelo aumento das ligações de hidrogênio entre XT/plastificante mudando a conformação local das cadeias do polímero.

Acknowledgements
LNLS e Fapergs

112

Crescimento e caracterização de cristais puros e mistos de KH2PO4 e (NH4)2PO4

C. J. Franco[1]

Universidade Federal de Ouro Preto - Ouro Preto MG Brazil

KH2PO4 NH4H2PO4 são cristais ferroelétricos com excelentes propriedades ópticas não-lineares, possuindo grande potencial de aplicações tecnológicas como, por exemplo, na construção de dispositivos geradores de segundo harmônico. Estes materiais são os únicos que estão sendo utilizados para crescerem grandes cristais 50x50x60cm3 de volume. O domínio do processo de crescimento destes cristais com qualidade ótica é o primeiro passo para a construção de dispositivos eletro-óticos baseados nestes materiais, o que permite visualizar a relevância deste projeto no contexto tecnológico. Bons cristais de KH2PO4 com volume de 2x3x5cm3 estão sendo crescidos pelo método de solução em um recipiente com aproximadamente 3l de solução em períodos que variam de 1 a 3 semanas. Para se ter um bom acompanhamento do processo de crescimento foi feito um estudo de saturação para poder inserir a semente dentro da solução. Os cristais obtidos estão sendo estudados por Difração de raios-X, Análise térmica, XPS e AFM e microscopia óptica. Através da análise dos vários resultados apresentados podemos caracterizar os monocristais de KH2PO4 e cristais mistos de KH2PO4 NH4H2PO4 obtidos por crescimento por solução. Através de medidas de raios-x podemos confirmar a estrutura obtida e caracterização de emissão de segundo harmônico confirmou a propriedade do material que o torna muito importante para aplicações em óptica não linear.

Acknowledgements
CNPq, FAPEMIG, UFOP

113

Investigação do desenvolvimento da morfologia semicristalina em blendas poliméricas de poliésteres termoplásticos, PET/PBT e PET/PC, através de experimentos de microscopia ótica, DSC e SAXS/WAXD/DSC com radiação síncrotron

Barbosa Jr, I. B.[1], Larocca, N.M.[1], Plivelic T.S.[2], Torriani, I.L.[3], HAGE Jr., E.[1], and Mantovani, GL[4]

[1] Universidade Federal de São Carlos - São Carlos SP Brazil
[2] Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil
[3] Universidade Estadual de Campinas - Campinas SP Brazil
[4] Universidade de São Paulo - São Carlos - São Carlos SP Brazil

As cinéticas de cristalização em blendas poliméricas de poliésteres termoplásticos, poli(tereftalato de etileno) (PET) com o poli(tereftalato de butileno) (PBT), PET/PBT, e PET com policarbonato (PC), PET/PC, foram investigadas através de calorimetria exploratória diferencial (DSC), microscopia ótica com luz polarizada (MOLP) e SAXS/WAXD/DSC com radiação síncrotron. As blendas foram obtidas em uma extrusora dupla rosca co-rotacional e os corpos de prova foram moldados por injeção. Foi usado um mesmo perfil de isotermas para todos os experimentos. Os parâmetros avaliados por DSC foram Tg (temperatura de transição vítrea), Tm (temperatura de fusão), Tc (temperatura de cristalização), ΔHf (entalpia de fusão), ΔHc (entalpia de cristalização); por microscopia ótica, as imagens de formação e crescimento das estruturas cristalinas e, por SAXS/WAXD/DSC, os picos de difração das estruturas cristalinas do PET e do PBT e os parâmetros lamelares L (longo período) e l_1, l_2 (espessura das camadas amorfa e cristalina). Dos resultados obtidos por WAXD nas blendas PET/PBT observou-se que há a formação isoladamente de estruturas cristalinas características do PET e do PBT puros. Através dos resultados obtidos por SAXS pode-se observar os momentos iniciais da formação dos esferulitos. Da combinação das três técnicas pode-se avaliar como as variações nas condições de processamento destes materiais, tais como, perfil de rosca (taxas de cisalhamento), tempo de residência e, a adição de catalisador de transesterificação interferem nas cinéticas e na morfologia de cristalização do PET e do PBT.

Acknowledgements

Laboratório Nacional de Luz Síncrotron - LNLS - proposta de pesquisa D11A - SAXS1 - 4820. GE Plastics, Rhodia-Ster e DuPont Brasil pelo fornecimento dos polímeros e catalisadores. FAPESP - programa de inovação tecnológica em pequenas empresas 03/07915-2.

Parte VIII

Métodos e Instrumentação

114

CdZnTe surface analysis by x-rays

Kakuno, E. M.[1] and Mazzaro I.[2]

[1] Universidade Federal do Pampa - Bagé RS Brazil
[2] Universidade Federal do Paraná- Curitiba PR Brazil

CdZnTe material is one of the most promising materials for γ and X -ray detection at room temperature and has a potential application in synchrotrons experiments. Its has a bulk resistivity about 1 E10 ohm-cm, then the surface preparation is an important step for the detector construction, because the surface resistivity could be several orders below the bulk resistivity and dominate the leakage current of the detector. We report an x-ray diffraction characterization of the surface and the gold contacts deposited by electroless from HAuCl4 with 5% gold solution (10 s to 120 s). The previous surface preparation was done by a mechanical polish down to 1 μm diamond powder followed by a chemical polish using 0.5 to 5 % Bromine solution in Methanol. The measurements were done using a Shimadzu XRD-7000 X-Ray Diffractometer, with the thin film attachment, copper target at 40 kV and 20 mA and a graphite monocromator tuned to CuKα line. The x-ray analyze was done with the beam grazing to the surface (from 1^o to 3^o) limited by a 0.3 mm slit. We identify that the peak at 24.16^o is due to substrate and others from surface. The peak at 24.16^o has the peak height direct dependency with the grazing incident beam angle, meaning that the diffraction volume is increasing with the incident angle. The peaks at 38.41^o, 44.65^o, 64.57^o and 77.91^o, has constant height meaning that the diffraction volume is constant, i.e. the beam at 1^o grazing to the surface is enough to penetrate all the thickness of the surface. We identify that peak at 24.16^o corresponds to Cadmium Tellurium Zinc (Cd0.8TeZn0.2 , card no. 50-1440) that is in good agreement with our monocristaline Cd0.9Zn0.1Te (111) sample and we believe that the 111 reflection came from any asymmetric plane or could came from the edge or the surface of sample was damage in the mechanical polishing process. We identify the peaks from 38.41^o to 77.91^o as polycristaline gold and peak at 38.41^o could correspond to gold cadmium (Au1.05Cd0.95 , card no. 3-934). We didn't find any evidence of TeO2 , Cd(OH)2 , Te(OH)6 , AuTe, ZnTe, CdTeO3 , CdTe2O3 on the surface. We demonstrate that with grazing incidence technique is possible identify surface from bulk material and it enhance the sensitivity to the surface by illuminating all the possible diffraction volume. We intend to make surface topography and present the results at the meeting, too.

Acknowledgements
The authors are thankful to Dr. D. Peter Siddons, from Brookhaven Nat. Lab. (BNL-NSLS), to kindly provide the CdZnTe sample.

115

Multibeam X-ray Topographic Method

Almeida, J. M. A.[1], dos Santos, A. O.[2], de Menezes, A. S.[2], L.H. Avanci[3], Cardoso, L.P.[2], and Sasaki, J.M.[1]

[1] Universidade Federal do Ceará - Fortaleza CE Brazil
[2] Universidade Estadual de Campinas - Campinas SP Brazil
[3] Universidade de São Paulo - São Paulo - São Paulo SP Brazil

The purpose of this work is to demonstrate the application of topography in condition of the X-ray multiple diffraction (XRMD) for the study of growth defects in solution-grown L-arginine Hydrochloride (L-AHCl) crystal. We report that by using multiple diffaction we are able to simultaneously obtain more than one topographic image of a crystal. XRMD have been employed to investigate the internal and surface defects in L-AHCl grown by slow evaporation method. Several topographic images were recorded on photographic plate fixed perpendicular to the (500) primary reflected beam and secondary reflected beam at several positions in the peak profile. In this sample it was carried through measured of curve of rocking and Renninger scan. The measurements were carried out using the synchrotron radiation at the XRD-1 station in a geometry developed specially to promote these kinds of experiments. This method provides, for using of special nuclear plate, internal defects image by choosing any diffraction plane inside the sample. The application of the XRMD associate the characteristics special of the synchrotron radiation, amplifies its great potential, which if they detach: High intensity, parallel beam geometry, great length of coherence of the parallel beam, where it comes being used for the study of some materials.

Acknowledgements
The authors acknowledge the support from National Synchrotron Light Laboratory (LNLS) and Brazilian Agencie: CNPq.

116

X-ray fluorescence microtomography analysis of breast tissue samples under various excitation conditions

Pereira, G.R.[1], Rocha, H. S.[1], Anjos, M. J.[2], and Lopes, R.T.[1]

[1] Universidade Federal do Rio de Janeiro - Rio de Janeiro RJ Brazil
[2] Universidade do Estado do Rio de Janeiro - Rio de Janeiro RJ Brazil

The X-ray fluorescence microtomography (XRFCT) is a non-destructive technique to complement other techniques used for samples characterization. The common techniques provide only information on the attenuation coefficients or electronic density and no information on the distribution of the elements inside of the sample can be obtained in these cases. XRFCT is based on the detection of fluorescence photons emitted by the elements in the sample. As the energy of photons of fluorescence has a particular value for each element, is possible to obtain the distribution of all the elements in a sample, since that a minimum of fluorescence signal is detected. The experiments were performed at the X-Ray Fluorescence beamline (D09B-XRF) of the Brazilian Synchrotron Light Source (LNLS), Campinas, Brazil. In this works, it was used a multilayer monochromator at photon energies near 12 keV, a monochromatic beam at 9.8 keV using a Si(111) and a white beam for the excitation of the elements inside the samples. The sample was placed on a high precision goniometer and translation stages that allow rotating as well as translating it perpendicularly to the beam. The fluorescence photons were collected with an energy dispersive HPGe detector (CANBERRA Industries inc.) placed at 90° to the incident beam, while transmitted photons were detected with a fast Na(Tl) scintillation counter (CYBERSTAR-Oxford anfysik) placed behind the sample on the beam direction. In order to study the performance of the system some breast tissue samples have been analyzed in order to verify the efficiency of the system in determination of the elemental distribution in these kinds of samples. The choice for breast tissue samples came together with the world tendency to find diagnostic techniques for cancer and other diseases. The fluorescence mapping of iron, copper and zinc is very important in diagnostics. All the tomographic images were reconstructed using a filtered-back projection algorithm. In the biological tissue samples, the elements of higher concentration were Zn, Cu and Fe.

Acknowledgements
This work was partially supported by Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq), Fundação de Amparo a Pesquisa do Estado do Rio de Janeiro (FAPERJ) and Laboratório Nacional de Luz Síncrotron (LNLS).

117

Coincidência elétron-íon em espectroscopia de massa: uso de um analisador de elétrons

Rodrigues, F. N.[1], Lucas, C.A.[2], and de Souza, G.G.B.[1]

[1] Universidade Federal do Rio de Janeiro - Rio de Janeiro RJ Brazil
[2] Universidade Federal Fluminense - Niterói RJ Brazil

Nos últimos anos, com a construção de novos espectrômetros, os mecanismos de obtenção de espectros de massa em tempo-de-vôo (TDV), de amostras em fase gasosa, em coincidência com elétrons selecionados em energia, apresentaram grandes avanços [1,2,3]. O método de multi-coincidência permite observar a correlação entre o elétrons ejetado e os fragmentos observados, possibilitando o estudo da dinâmica destes processos, ou seja, um estudo estado-a-estado, indicando a origem de formação de cada íon obtido no espectro. Com esta finalidade e utilizando-se da larga experiência na construção de espectrômetros do tipo TDV, o Laboratório de Impacto de Fótons e de Elétrons (LIFE)-Instituto de Química-UFRJ propõe o uso de um analisador eletrostático de velocidade de elétrons do tipo lentes cilíndrica [4,5]. A versatilidade do aparato permite a sua aplicação nas mais diversas técnicas espectroscópica onde a análise em energia dos elétrons se faz necessária.

Referências:

[1] T. Kaneyasu, *et. al.*, *UVSOR Activity Report 2005*, ISSN 0911-5730 UVSOR 33, p. 50, July 2006.

[2] G. Alberti, E. Fainelli,*et al.*, *Rev. Sci. Instrum.* **76**, 073101 (2005).

[3] D. Céolin *et. al.*, *J. electron Spectrosc. Relat. Phenom.* **141**, 171 (2004).

[4] F. N. Rodrigues, *Dissertação de Mestrado*, IQ-UFRJ, 2006.

[5] H. M. Boechat-Robety and G.G.B. de Souza, *J. Phys. B: At. Mol. Opt. Phys.* **25** (1992) 4641-4647.

Acknowledgements

Este trabalho é financiado pelas agêcias CNPq e Faperj.

118

Aplicação da transformada de wavelet no sinal de EXAFS

Fabbris, G. F. L.[1] and Azevedo, G. de M.[2]

[1] Universidade Estadual de Campinas - Campinas SP Brazil
[2] Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil

EXAFS é uma técnica poderosa e bem estabelecida de caracterização da estrutura de curto e médio alcance em materiais desordenados. Devido ao comportamento oscilatório do coeficiente de absorção, a transformada de Fourier (TF) é uma ferramenta essencial para analise de dados, permitindo a partir do sinal localizado em k, obter um gráfico que permite distinguir cada camada de vizinhos do átomo absorvedor.

A modelagem e interpretação dos dados utilizando a TF, é simples quando as camadas de coordenação contém apenas um tipo de átomo espalhador. Porém, a analise torna-se mais complicada quando dois ou mais tipos de átomos espalhadores estão a distâncias interatômicas semelhantes.

Para resolver este problema, propomos o uso da transformada de wavelet (TW). Com a TW é possível analisar o espectro no espaço k e r simultaneamente. Além de analisar as distancias aos retroespalhadores a TW identifica em que posição no espaço k o retroespalhamento ocorre. Portanto, a TW permite reconhecer vizinhos com diferentes números atômicos, embora estejam localizados a distancias parecidas do átomo absorvedor. Criamos um algoritmo que utiliza as Wavelets, de Morlet e de Cauchy, exploradas anteriormente em trabalhos de outros autores [1-2]. Até o momento, fizemos diversas análises qualitativas comparando sinais simulados e com experimentais. Algumas dessas análises serão apresentadas a fim de mostrar a utilidade e potencialidades deste método.

Não há na literatura um estudo quantitativo do uso da TW no sinal de EXAFS. Com este objetivo, desenvolvemos um algoritmo que, a partir de cálculos ab initio feitos pelo programa FEFF, calcula a função de EXAFS teórica para o composto em estudo e aplica a TW no sinal teórico e experimental. A partir disso, estamos em fase final de implementação do algoritmo de Levenberg-Maquardt para extrair parâmetros estruturais da TW. Esperamos obter resultados com menor correlação entre os parâmetros estruturais, já que o ajuste da curva experimental leva em conta informações no espaço k e r simultaneamente.

1 - Funke H. et al, Wavelet analysis of extended x-ray absorption fine structure data, Phys. Rev. B 71, artigo número 094110;

2 - Muñoz M. et al, Continuous Cauchy wavelet transform analyses of EXAFS spectra: A qualitative approach, American Mineralogist 88, páginas 694 a 700.

Acknowledgements
Este trabalho foi financiado pelo LNLS e CNPq.

119

The new D02A-SAXS2 beamline of the LNLS

Torriani, I.L.[1], Plivelic T.S.[2], Rey, J.F.Q.[2], and da Silva, J.C.[1]

[1] Universidade Estadual de Campinas - Campinas SP Brazil
[2] Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil

In the present work results of the commissioning and the first six months of operation as an open facility of the new D02A-SAXS2 beamline are discussed. Major improvements were obtained with respect to the photon flux, vertical focusing and wavelength range when compared to the D11A-SAXS1 beamline. Due to the use of a Rh-coated ULE glass-ceramic mirror for vertical focusing and shorter source-monochromator distances the photon flux increased almost a factor of 10 at the sample position. Good mechanical repeatability and movement precision have been attained with the cylindrical Si 111 crystal monochromator and the 2θ arm. All the system is PC controlled using 3-WINDCM software. Wavelength range is from 1 to 2 and can be easily changed. Two dimensional detection with a CCD detector from MAR-USA lead to important improvement in the SAXS data quality. Lower acquisition times, better statistics in higher q ranges and real time (or shorter exposures) SAXS patterns are some of the advantages of this system. Experimental results from protein solutions and oriented polymers will be presented. For the first subject, SAXS curves of reference samples (Lysozyme) measured in the two beamlines are compared. Preliminary results of the structural characterization of Melanine pigments in DMSO measured at λ=1.045 $^{-1}$ will also be reported. The anisotropic scattering from thin films was studied for MEHPPV and other PPV-derivative polymers. Changes in the morphology or the local packing of the nanoaggregates induced by the polymer structure or the sample temperature for in situ experiments will be discussed. New instrumentation for several combined techniques are in progress. Among them we can mention: i) a new sample-holder with multiple positions (12) for samples in vacuum; ii) SAXS/WAXS experiments with Debye-Scherrer geometry; iii) temperature controlled cell for liquid samples with heating rates of up to 10 ^{o}C/min and maximum temperatures up to 200 ^{o}C; iv) time resolved experiments using the CCD detector and/or one-dimensional gas detectors and v) high velocity mixed liquid reactions using stopped flow equipment.

120

High pressure CuBe cell for small- and wide-angle x-ray scattering

Orlando, M. T. D.[1], J.L.Passamai Jr[1], Orlando, C. G. P.[1], Martinez, L. G.[2], Melo, F. C. L.[3], Garcia, F.[4], Granado, E.[5], Ferreira, F. F.[4], Corrêa, H. P. S.[6], and Tamura, E.[4]

[1] Universidade Federal do Espírito Santo - Vitória ES Brazil
[2] Instituto de Pesquisas Energéticas e Nucleares - São Paulo SP Brazil
[3] Centro Técnico Aeroespacial - São José dos Campos SP Brazil
[4] Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil
[5] Universidade Estadual de Campinas - Campinas SP Brazil
[6] Universidade Federal do Mato Grosso do Sul - Campo Grande MS Brazil

A high pressure CuBe cell with B_4C anvil have been developed since 2004 for small- and wide-angle x-ray scattering experiments under hydrostatic pressure up to 2GPa, at room temperatures is described. This cell was applied to investigate solid samples behavior under external hydrostatic pressure. Moreover, it might also be used to investigate biological system as lipid-water dispersions without changes in its design. Magnetic field up to 1.6 kGauss can be applied together the hydrostatic pressure in this cell, taken into account there is no magnetic signal from de CuBe, B_4 anvil, and CuBe gasket used. Investigations about ReO_2 behavior under hydrostatic pressure up to 1.6 GPa were performed at LNLS-XPD Synchrotron beam line, and the results reveals to the ReO_2 a good inner gauge pressure for 8keV-13keV energy range. We are developing a new control system for the sample local temperature from the $-10C^o$ up to $+150C^o$ using a CO_2 laser. This project was developed by LNLS, UNICAMP, UFES, IPEN/CNEN and IEA/CTA collaboration

Acknowledgements

We would like to thank CNPq Grant 471536/2004-0, CT-Energ 504578/2004-9, and CAPES for financial supports. Thanks also to Cia Vale do Rio Doce (CVRD), Cia Siderurgica de Tubarao (CST), and National Laboratory of Synchrotron Light - LNLS, Brazil (XPD 2950/04, DXAS 2950/04, DXAS 2952/04).

121

Recent developments at XRD2 beamline of LNLS

Kellermann, G.[1] and Zanchet, D.[1]

Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil

Grazing incidence small-angle x-ray scattering (GISAXS) and anomalous small-angle x-ray scattering (ASAXS) are powerful and widely used techniques for structural investigation in materials science. These techniques developed fast in the last years as a consequence of the availability of synchrotron radiation sources which beside the high intensity provide photons over a wide energy range. A setup for GISAXS and ASAXS experiments recently developed at the XRD2 beamline of the LNLS and some examples in which these techniques were successfully applied will be presented. Other improvements in beamline instrumentation will be also presented.

Acknowledgements

Research supported by Brazilian Synchrotron Light Laboratory (LNLS), FAPESP and CNPq.

122

Focal Series Restoration

Biggemann, D.[1] and Ramirez, A.J.[1]

Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil

New developments and challenges in nano-science world require improvements in spatial high resolution. New techniques were developed to improve the performance of Transmission Electron Microscopes (TEM). Spherical Aberration Correctors are now a reality. Nevertheless, new mathematical methods are also applied to obtain aberration-free images. These methods, using a set of focal series images, are able to obtain a exit-plane wavefunction of electrons. In this work we present an algorithm developed by Meyer et. al. for focal series restoration (FSR) applied on a TEM Jeol JEM 3010 URP installed at LME. This method allowed us to improve the actual spatial resolution from 1.7 at Scherzer defocus to $\sim$ 1.3 . Different materials are being successfully tested. FSR technique will be available for external users briefly in our JEM 3010 URP and our two new TEMs.

123

Recent improvements on the X-ray powder diffraction (D10B-XPD) beamline

Ferreira, F. F.[1] and Granado, E.[2]

[1] Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil
[2] Universidade Estadual de Campinas - Campinas SP Brazil

The X-ray powder diffraction (D10B - XPD) beamline of the LNLS has been operating for external users since March 2004 [1]. Improvements on this beamline are being continuously made in order to optimize its performance, reliability, automation, ease of operation, as well as to expand the sample environment possibilities. For investigations involving high temperatures, a recently installed system, based on an automated imaging plate arrangement attached to a home-made furnace (293 - 1273 K) is available. This system permits the fast acquisition of full-pattern diffractograms. At the exit Kapton window of the furnace, a variable slit controls the width of the exposed region of the image plate. By translating the stage where the image plate is located, one can obtain several diffractograms in a few minutes. The conversion from pixels to degrees can be obtained directly by measuring a Standard Reference Material and taking the distance from sample-to-image plate. Another point which is of great concern is the energy stability of the beamline. To quantify any possible deviation along the day, several measurements of the (111) reflection of a silicon powder Standard Reference Material (SRM 640c) were taken. It could be inferred that the peak position did not change along the several acquisitions, indicating that any possible change in energy is negligible.

References

[1] F.F. Ferreira, E. Granado, W. Carvalho Jr., S.W. Kycia, D. Bruno, and R. Droppa Jr., J. Synchr. Rad. 46-53, 13 (2006).

Acknowledgements

Thanks are due to the LNLS technical staff which has been contributing to the progress of the beamline and to FINEP for partial financial support.

124

NEW BUILDING FOR THE ELECTRON MICROSCOPY FACILITY AT LNLS

Afonso, C R M[1], Bettini J.[1], Silva, P. C.[1], Biggemann, D.[1], Araújo,S.R.[1], Ramirez, A.J.[1], and Ugarte, D.[1]

Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil

An expansion of the Electron Microscopy Laboratory (LME) is on course by the installation of two new Transmission Electron Microscopes (TEM): a 200 kV TEM oriented to materials science imaging and diffraction studies (JEOL JEM-2100 HTP) and a 200 kV FEG-TEM oriented for nano-analysis and Electron Energy Loss Spectroscopy (JEOL JEM-2100F URP, FEG-STEM/TEM). At present, the High-Resolution Transmission Electron Microscope (HRTEM) room reaches the necessary specifications and the microscope attains full performance, so we have acquired reasonable experience for TEM installation. However, for the FEG STEM/TEM is necessary a new site due to the new STEM and EELS capabilities. The FEG-STEM/TEM microscope room must reach mechanical vibration, sound vibration and magnetic field, among other specifications to allow the microscope to deliver its design performance. A new building for electron microscopy facility at LNLS has been designed and is under construction. This building has special characteristics as: Building in a building concept to reduce external disturbances; minimization of steel reinforcement and conductor loops within the concrete structure; Inertial concrete blocks (60 tons for TEMs, 35 tons for SEMs). In this building a desirable vibration and magnetic field environment at an installation site is required. However, the mechanical stability (vibration) conditions may be degraded by ground-propagated waves coming from a variety of sources such as vehicle and people traffic, construction, and other research facilities. In addition, the presence of high power AC sources such as generators, high-tension lines may degrade the magnetic environment around the microscopes. Therefore, a detailed mechanical vibration and magnetic field assessment regarding the electron microscopes installation in the new building is ongoing. The mechanical vibration evaluation of the new building site has also been evaluated, especially the effect of nearby buildings and large equipment. The identification of possible vibrations and magnetic field sources, such as complementary equipment, is extremely important in order to minimize their effects. The previous knowledge of site and equipment conditions and possible sources will reduce the time and cost in the new building design and construction.

Acknowledgements

This work was supported by LME/LNLS.

125

Photon Stimulated Gas Desorption from Welds

Seraphim, R. M.[1], Ferreira, M. J.[1], Ierardi, F. M.C.[2], and Ramirez, A.J.[1]

[1] Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil
[2] Universidade Estadual de Campinas - Campinas SP Brazil

The Brazilian Synchrotron Light Laboratory (LNLS) has engaged on the continuous improvement of the synchrotron radiation source since it was built back in the 90s. One of the key technical areas has been the ultrahigh vacuum (UHV) system of the machine, because of its paramount effect on the beam lifetime. As part of this effort has been built a dedicated experimental station attached to one of the source dipoles to study photon stimulated desorption (PSD). The studies performed at this new station (beam-line) will provide new insights into PSD within particle accelerators and storage rings, and will allow the improvement of fabrication processes for UHV chambers. The research now started at this beam-line focuses on the study of PSD from vacuum chamber welds, which are produced using gas tungsten arc welding (GTAW) process. This study will help to identify the sources of gases contributing to LNLS storage-ring residual atmosphere, which it is strongly dependent of radiation induced gas desorption during operation. Particularly, it is paramount to identify the source of high levels of argon in such chambers. The first results have revealed that the weld joints contribute to the vacuum residual atmosphere if they are exposed to synchrotron radiation. This was verified when weld joints prepared using different mixtures of shielding gases were compared with unwelded samples. It was also verified that the mixture of shielding gas used to weld did not significantly affected the species desorbed. The most relevant conclusion at this stage of the study is that the level of desorption during synchrotron irradiation strongly depends on the level of surface oxidation caused by the welding process and is not apparently affected by the shielding gas used to weld.

Acknowledgements
The authors would like to acknowledge the Brazilian Synchrotron Light Laboratory (LNLS) for the financial support, and the CNPq and FAPESP for the master scholarship.

126

Survivability of extremophile microorganisms under simulated extraterrestrial environments

Lima, I. G. P.[1], Pilling, S.[2], Naves de Brito, A.[2], and C. Lage[1]

[1] Universidade Federal do Rio de Janeiro - Rio de Janeiro RJ Brazil
[2] Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil

Extremophile microorganisms are known to survive and proliferate in extreme environmental conditions on our planet and even beyond, as part of scientific experiments in Eartht's orbit (Rettberg et al., 2004). Therefore, they are suggested to be the first life forms to arrive or emerge here. The goal of this work is to investigate the survivability of extremophile microorganisms, and its biologic responses, under different extraterrestrial environments. In an attempt to simulate the conditions presents in other planets and moons inside the solar system, we submit the microorganisms to different kind of stresses like radiation exposure (Lyman alfa lamp; synchrotron light), planetary atmosphere compositions, low pressure and low temperature. Deinococcus radiodurans, a bacteria well known to survive high doses of ionizing radiation, psichrophile microorganisms (adapted to cold conditions) and methanogenic microorganisms (methane-producing archaea) are the most probable extremophile microorganisms to survive under these extraterrestrial conditions (Cavicchioli, 2002; Rothschild and Mancinelli, 2001). We present the preliminary results concerning the different kinds of culture medium tested, the methodological adjustments and technical adaptations necessary to coordinate the biological and physical parameters. After exposition in different treatments, we will conduct molecular analysis of the DNA repair genes of the surviving mutants. The results of this work could be important to the biological products industry, by the isolation of biotechnological interesting compounds. Moreover, the results could support origin-of-life theories such as panspermia and could also contribute to the development of planetary engineering projects.

References

CAVICCHIOLI, R. Extremophiles and the search for extraterrestrial life. Astrobiology, v. 2, p. 281-292, 2002.

RETTBERG, P.; RABBOW, E.; PANITZ, C.; HORNECK, G. Biological space experiments for the simulation of Martian conditions: UV radiation and Martian soil analogues. Advances in Space Research, v. 33, p. 1294-1301, 2004.

ROTHSCHILD, L. J.; MANCINELLI, R. L. Life in extreme environments. Nature v. 409, p. 1092-1101, 2001.

Acknowledgements

CNPq - National Counsel of Technological and Scientific Development

127

Current Status of New Developments Facilities at the XRF Fluorescence Beamline of the LNLS

Pérez, C. A.[1]

Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil

This work pretends to describe the status of two new facilities, currently under commissioning at the XRF fluorescence beamline, which will be available for users in the near future. One facility consists of an optical element, able to monochromatize the white beam with the energy bandwidth of about 3% in an energy range between 8 keV to 20 keV. It is composed by one multilayer crystal of W/Si (2d=3nm, 75 periods) placed in a small low vacuum chamber and designed to be near the sample holder, minimizing the beam shift at the sample position. This device is being adapted for signal to background ratio improvements in TXRF spectra as well as for micro-XRF and XRF microtomography experiments, in which a combination of a large energy bandwidth of monochromatic beam and moderate spatial resolution are required.

Another facility consists of a set-up to carry out X-ray reflectivity experiments in an energy dispersive mode. It is composed by a sample goniometer (theta), coupled to a small vacuum chamber, and a 2-theta goniometer which has an arm to attach a silicon drift detector (KETEK-GmbH). The sample holder was initially designed to be able to perform *in situ* thermal treatment of the sample up to 150^{o}C. One prototype has been constructed and it is now under commissioning.

Acknowledgements

The author would like to thank Dr. Ângelo Malachias for his support in the development of the energy- dispersive X-ray reflectivity set-up, as well as to Thiago Silva from the LNLS project group (PRO) for the mechanical design. This work was supported by the LNLS.

128

New end station to study high pressure liquids such as water on the atomic scale

Naves de Brito, A.[1], Mundim, M.S. P.[2], Mocellin,A.[3], and Campos,J.A[3]

[1] Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil
[2] Universidade de Brasília - Brasilia DF Brazil
[3] Universidade de Brasília - Brasília DF Brazil

A new end station especially design to investigate liquids with vapor pressure up to several mili bars at room temperature will be presented.

This new end station is aimed to operate at the forcoming high performance undulator beamline. The study of solvent effect on molecules is of highest scientific interest. For example, in nano-medice the electronic and geometrical properties of amino acids as well as peptides in water and solutions are of growing interest since this will help to synthesize new products such as bleeding stopping agents. We aim to obtain more realistic information of small molecules of biological interest in the environment they are found in leaving organisms.

The small spot size of our undulator beamline will allow ion collection 1 millimeter from the sample by our specially designed time of flight spectrometer. Usually, liquids with high vapor pressure pose serious vacuum compatibility problems. We have circumvented this problem by using a micro-jet source with 10-micrometer diameter, which is ejected very close to the spectrometer entrance. A nozzle collects the liquid beam, which is trapped by liquid nitrogen cold fingers. The ions produced on the surface are collected into a 1 millimeter aperture. Careful ion path simulations where carried out. As a result we obtained a high ion collections efficiency while care was taken to minimize contributions from unwanted surrounding vapor molecules. To the best of our knowledge, there is no other spectrometer with these capabilities reported in the literature so far.

Acknowledgements
This work was supported by FAP-DF/CNPq (Brasília) Brazil via a PRONEX grant. The authors also are in debit with LNLS project design under Regis T. Neuenshwander lidership.

129

High Pressure Facilities at the D06A-DXAS Beam-line

E. J. Carvalho[1], Orlando, M. T. D.[2], Azevedo, G. de M.[1], and Garcia, F.[1]

[1] Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil
[2] Universidade Federal do Espírito Santo - Vitória ES Brazil

High pressure conditions associated with the X-Ray techniques such XAFS and diffraction, can be used to study many physical or chemical systems. The kinetic of chemical reactions, electro-magnetic and structural properties of materials are examples of parameters that can be affected under high pressure conditions characterizing it as an interesting tool in the material science. In the last edition of the RAU was also realized the first workshop about experiments over high pressure conditions, that grouped the scientific community to discuss about the necessities and to present the facilities available at the LNLS. As a result of this workshop, approximately 20% of the researcher projects submitted to the DXAS beam line for the first semester of 2007 were related with High Pressure conditions, that shows the great demand for this kind of experiment. The instrumentation available at the DXAS beam line count with a diamond anvil cell specially designed to *in situ* high pressure experiments. The diamonds are mounted in two pistons aligned with the symmetry axes of the cell. In this axe, a window allows that the X-Ray pass through the diamonds and the sample placed between them. The increment in the pressure is given by the ratio between the area of the face of the diamond and the area of the piston where a force is applied. With this cell, pressures up to 10GPa can be obtained. Beyond the interesting sample, is placed inside the cell a small ruby chip that is used as a pressure indicator thought their photoluminescence signal. We will present an overview about the high pressure experiments at the DXAS beam-line as well as showing the results about the pressure measurements through the ruby photoluminescence signal. We will hope also discuss with the community about the necessary improvements to be implemented for the high pressure facilities at the DXAS beam line.

130

Caracterização de cintiladores cerâmicos de Y_2O_3 dopados com íons lantanídeos através da técnica de XEOL

Valerio, M.E.G.[1], Macedo, Z.S.[1], Alcântara, M. C.[1], and Azevedo, G. de M.[2]

[1] Universidade Federal de Sergipe - São Cristóvão SE Brazil
[2] Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil

Uma técnica de detecção da estrutura fina de absorção de raios-X (XAFS) que ainda permanece relativamente inexplorada é a detecção da luminescência óptica induzida por raios-X, mais conhecida por XEOL (X-ray Excited Optical Luminescence). Diversos materiais emitem luz visível quando excitados com raios-X. A luminescência óptica que é emitida após a excitação de um nível de caroço pode ser utilizada como um método alternativo de detecção de XAFS. Esta é uma idéia muito interessante visto que permite capacidades adicionais à espectroscopia XAFS, impossíveis de obter com outra técnicas experimentais, mais especificamente, a seletividade ao sítio do átomo excitado, além da já bem conhecida seletividade química. Neste trabalho, demonstramos a viabilidade da realização de experimentos de XEOL nas linhas de absorção de raios-X do LNLS. Neste experimento inédito no Brasil, utilizamos amostras de Y_2O_3 dopado com íons terras. A ítria dopada com terras raras é um cintilador com aplicação potencial em tomografias PET e CT e na física de altas energias. As amostras foram produzidas na forma de cerâmicas nanoestruturados pela rota de sol-gel protéico. Os materiais apresentaram fase cristalina única, confirmada por medidas de difração de raios-X (DRX) de pó, com tamanho de partícula em torno de 50 nm. As medidas de XEOL foram realizadas na linha XAFS-2 do LNLS, nas bordas K do Y e LIII das terras raras e comparadas com espectros obtidos na linha XAFS-1 pelos métodos tradicionais de detecção. Nas medidas de XEOL, a luz emitida pela amostra era coletada por uma fibra óptica acoplada a um espectrômetro equipado com rede de difração fixa e câmara CCD. Para cada valor de energia do feixe incidente de raios-X, um espectro de luminescência completo no intervalo de 200 e 1100nm era obtido. O espectro de XEOL era obtido analisando-se a área sob o espectro completo de luminescência (ou uma dada linha de emissão) como função da energia dos raios-X. A comparação dos resultados de EXAFS/XANES com os resultados de XEOL e de fotoluminescência permitem um estudo completo dos processos de geração, transferência e recombinação de cargas no material. Discutiremos as melhorias necessárias para que o arranjo experimental permita a detecção de XEOL em outros materiais de grande apelo tecnológico, mas fracamente luminescentes, como nanoestruturas semicondutoras, por exemplo.

Acknowledgements
Este trabalho tem apoio financeiro do CNPq/PADCTIII, PIBIC/CNPq, FINEP.

131

The LNLS XAFS-2 beam line: first commissioning results

Oliveira, J.J.[1], Sotero, A.P.S.[1], Neueschwander, R. T.[1], Rodrigues, F[1], and Azevedo, G. de M.[1]

Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil

Currently only XAFS-1 beam line, which yields a modest photon flux in the intermediate 10^8 photons/mm^2/second range, is available at LNLS for conventional (i.e. sequential) XAFS measurements in the hard X-ray domain. With the ever-increasing request for beam time and maturity of the XAFS community, which demands more complex and sophisticated experiments, there is an urgent need for more beam time and better performance.

To suit these demands, a new beam line will be available to the XAFS community in 2007. It has been planned aiming at a maximization of the photon flux impinging at the sample position. To this purpose, the optics is comprised of a vertically collimating and a toroidal focusing mirror before and after, respectively, the Si 111 double crystal monochromator. The new beam line will cover the 4-16 keV energy range, with better energy resolution and a 20 to 60-fold increase in photon flux, as compared to XAFS-1. With the higher flux, the detection limit in fluorescence mode will be lowered down to a few tens of ppm, enabling a number of experiments which are either impossible or extremely difficult in XAFS-1. The higher signal-to-noise ratio will permit EXAFS scans up to higher wave numbers, improving in the spatial resolution. In this contribution we report the first commissioning results, present the potentialities and discuss the planned facilities for this new beam line.

Acknowledgements
This work was supported by FINEP and LNLS.

Parte IX

Microfabricação

132

CARACTERIZAÇÃO DE FOTORRESISTE NEGATIVO PARA ELETRODEPOSIÇÃO

G. Coletti[1], Piazzetta,O.M.H[1], Moreira NH[1], Almeida, A.L.J.[1], and Gobbi, A. L.[1]

Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil

A fabricação de microestruturas com alta razão de aspecto (HARMST) possui extrema importância no desenvolvimento de sistemas microeletromecânicos (MEMS). Esta tecnologia é crucial para o sucesso da integração de componentes, permitindo a fabricação de microdispositivos para diferentes aplicações. Para tanto, as resinas fotossensíveis utilizadas devem apresentar algumas características especiais, tais como baixa absorção óptica na região do UV e alta viscosidade, o que torna possível a realização de fotogravações em camadas espessas, além de elevadas resistências mecânica e química, que viabilizam sua aplicação como material estrutural ou sua utilização como molde em processos de eletrofomação. Dentre as opções existentes para processos de litografia UV, a resina fotossensível SU-8 da Microchem Inc, é certamente a opção de escolha quando a aplicação exige estruturas de alta razão de aspecto. Entretanto, apesar de apresentar características físico-químicas extremamente adequadas para litografia UV, estruturas gravadas em resina SU-8 são de difícil remoção, o que pode ser um inconveniente, principalmente quando são utilizadas como molde para processos de eletroformação, incentivando a busca de alternativas para a sua utilização. Neste trabalho, será apresentada a carcterização de um fotorresiste negativo, que aparece como alternativa ao SU-8, a NR2 20000P da Futurrex Inc., com o atrativo de ser facilmente removida em acetona. As variáveis de processo da resina NR2 20000P, tais como espessura, tempos de exposição e de tratamento térmico, foram investigadas, e seus efeitos sobre a qualidade das fotogravações estudadas por microscopia óptica e eletrônica de varredura (MEV). Comportamentos anômalos da resina frente ao processo de fotogravação foram abordados com base em análises termogravimétricas(TGA) do material, que apontaram o tratamento térmico pré-exposição como uma etapa crítica do processo. Faz também parte deste projeto a exposição da tecnologia de fotogravação de estruturas espessas em SU-8, que se encontra a disposição dos usuários do LMF/LNLS.

Acknowledgements
LNLS

133

CONSTRUÇÃO E SELAGEM DE ESTRUTURAS MICROFLUÍDICAS UTILIZANDO PDMS E CORROSÃO EM VIDRO

Almeida, A.L.J.[1], Piazzetta,O.M.H[1], Moreira NH[1], G. Coletti[1], and Gobbi, A. L.[1]

Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil

Atualmente, componentes microfluídicos vêm sendo amplamente estudados, principalmente em função de seu alto potencial de aplicação em áreas de intensa atividade científica, como as de química analítica, microbiologia e ciências médicas por exemplo. A execução de processos químicos e biológicos em micro-estruturas complexas, conhecidas pelas siglas LOC (lab-on-a-chip) ou μ-TAS (micro-total-analytical-system) vêm apresentando vantagens significativas com relação às técnicas convencionais de laboratório, especialmente no que diz respeito à economia de tempo e à diminuição das quantidades de reagentes e resíduos envolvidas.

Esse trabalho reporta o desenvolvimento de circuitos microfluídicos construídos em vidro e em poli-dimetil-siloxano (PDMS), um polímero de silicone extremamente barato e versátil. Serão apresentadas as técnicas utilizadas no LMF/LNLS para a gravação de micro-canais nesses dois tipos de substrato, bem como os processos de integração e selagem de dispositivos neles fabricados. Canais de 10 a 50 μm de profundidade e 50 μm de largura foram obtidos através das técnicas de fotolitografia UV, corrosão por via úmida e impressão por micro-contato. A integração dos dispositivos foi feita através da ativação de suas superfícies por ação de plasma de oxigênio, seguida da aplicação de pressão.

Fatores como as condições de oxidação do PDMS e a natureza dos substratos tiveram sua influência sobre o processo de selagem avaliada por técnicas instrumentais, como microscopia eletrônica e espectroscopia de infravermelho.

Acknowledgements
LNLS

134

Micro-Sistemas de Análise Eletroforética com Detecção Eletroquímica Integrada.

Moreira NH[1], Piazzetta,O.M.H[1], G. Coletti[1], Almeida, A.L.J.[1], and Gobbi, A. L.[1]

Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil

Atualmentente, a busca por altas freqüências analíticas, portabilidade e reduções dos volumes de reagentes e rejeitos tem, ao menos em parte, orientado o desenvolvimento de novas técnicas instrumentais de análise química. Nesse contexto, a miniaturização de métodos de separação, em especial os eletroforéticos, tem se mostrado uma alternativa bastante promissora.

Esse trabalho reporta nossos avanços no desenvolvimento de micro-sistemas de análise química por eletroforese capilar com detecção eletroquímica integrada, cujo objetivo aponta para obtenção de dispositivos funcionais e de custo reduzido, com apreciável potencial de aplicação tecnológica-comercial. Serão apresentados dispositivos micro-fluídicos com sistemas de canais gravados em material polimérico (PDMS), através da técnica de litografia suave, e integrados, através de selagem ativada por oxidação em plasma de Oxigênio, à micro-eletrodos de Ti-Au gravados sobre vidro.

Diversas alternativas de processo foram testadas e serão apresentadas, discutindo-se criticamente os resultados de cada uma. Parâmetros experimentais relevantes, como as condições de oxidação do PDMS e a influencia dos substratos utilizados sobre a selagem dos dispositivos, foram investigados com auxílio de técnicas instrumentais de análise, como microscopia óptica e espectroscopia de infra-vermelho, bem como de ensaios específicos de resistência e selagem. Da mesma forma, o desempenho geral dos dispositivos foi avaliado por técnicas eletroquímicas de análise, como a de voltametria cíclica.

O design do dispositivo, com uma estrutura de múltiplos canais microfluídicos acoplados a um único sistema de detecção eletroquímica, confere-lhe um recurso de calibração interna que potencializa sua utilidade para fins de análise quantitativa.

Acknowledgements
FINEP/CNPq e LNLS

135

Caracterização morfológica e eletroquímica de compósitos PPi/AC

Canobre, S. C.[1], Luz, J. A.[1], C. Polo Fonseca[1], and Neves, S.[1]

Universidade São Francisco - Itatiba SP Brazil

Polímeros condutores são materiais alternativos para aplicação em catodos de baterias secundárias e supercapacitores. Vários trabalhos na literatura relatam a síntese destes materiais na presença de matrizes *template* inorgânicas e orgânicas (membranas poliméricas, óxidos de metais de transição e nanotubos de carbono), contendo poros ou espaços vazios com dimensões variando de nanômetros a alguns mícrons. Seguindo o princípio do método *template*, utilizamos uma membrana de acetato de celulose (AC) como matriz *template* para a síntese de polipirrol (PPi) visando a aplicação dos compósitos obtidos em dispositivos de armazenamento e conversão de energia. Os compósitos PPi/AC foram sintetizados por meio da eletropolimerização do pirrol no interior dos poros da matriz hospedeira de acetato de celulose. Após a caracterização eletroquímica por voltametria cíclica, testes de carga/descarga e espectroscopia de impedância eletroquímica, constatou-se o melhor desempenho eletroquímico em compósitos obtidos através da síntese potenciodinâmica do polipirrol em membranas AC com 4,31 μm de espessura. Em todos os casos a resposta eletroquímica dos compósitos foi superior àquela obtida para o polipirrol sintetizado sem restrição espacial, exatamente nas mesmas condições. Através da microscopia eletrônica de varredura foi possível observar a variação da porosidade das membranas de acetato de celulose em função da espessura, e constatar que membranas com espessura acima de 1,55 μm, apresentaram morfologia mais compacta. Pôde-se também concluir que o acetato de celulose atuou como uma boa matriz *template*, pois observou-se que o polipirrol cresceu no interior de seus poros, adquirindo assim, a sua forma, tamanho e orientação espacial. Como o compósito polipirrol/acetato de celulose apresentou uma boa reversibilidade eletroquímica em meio orgânico à base de carbonato de propileno, este meio foi escolhido para montagem de um dispositivo eletroquímico. O comportamento predominantemente capacitivo, evidenciado em todas as caracterizações eletroquímicas, definiu a aplicação do compósito como eletrodos em supercapacitores. Capacitâncias específicas na ordem de 240 F.g^{-1} foram obtidas aplicando-se uma densidade de corrente de 10 μA.cm^{-2} durante 250 ciclos, com eficiência coulômbica de, aproximadamente, 100%.

Acknowledgements
This work was supported by FAPESP processo 05/54578-7, CNPq, CAPES, LNLS

136

Pulse electroplating of Gold-Tin eutectic alloy applied in the welding process for the optoelectronic industry

Piazzetta,O.M.H[1], G. Coletti[1], Almeida, A.L.J.[1], Moreira NH[1], Avendano, E.[1], and Gobbi, A. L.[1]

Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil

The substitution of the environment pollutant Led-Tin alloys in the welding processes for optoelectronic applications have been challenged by the incorporation of the Gold-Tin alloys, specifically, the eutectic composition Au70Sn30 (%at). This alloy apart of being environment compatible, has optimal mechanical properties, low melting point combine with a lower cost with respect to the Au80Sn20 (%at) commercially available.

Different deposition techniques have been used in the thin film production of those alloys. The more representative are sputtering, and co-electroplating. However, there are disadvantages associated to these deposition techniques. For example, sputtering involves high costs of implementation and in the case of co-electroplating the solutions have short term (few weeks) durability. To overcome those problems the use of pulse electroplating from gold and tin solutions with long durability and low cost is an alternative for the growing of multilayer Au-Sn that includes a post annealing treatment to form the alloy.

Preliminary results in samples grown with 2 to 17 bi-layers of Au-Sn are reported. Thermal treatment in an inert gas (i.e. Ar or N2) was done after the deposition. A dependence of the morphological and structure properties of the samples with respect to the number of bi-layers was found and will be describe in detail. Series of inter-metallic compound were form during the thermal treatment and an optimum deposition conditions was found for samples with more than seven bi-layers. Tests of welding in industrial conditions are presented as function of the deposition condition of the samples.

Acknowledgements

We are grateful with the LME-LNLS for the support in the characterization.

137

Consolidação do Processo de Fabricação de Chave MEMS-Shunt para linhas CPW

A.Tavora, A. S.[1] and Kretly, L. C.[1]

Universidade Estadual de Campinas - Campinas SP Brazil

Este trabalho apresenta o novo processo de microfabricação elaborado para estabilizar o processo das chaves MEMS, bem como introduz uma grande diversidade de geometrias de chaves e os procedimentos de projeto, considerando tanto as características eletromecânicas, quanto as eletromagnéticas. A principal modificação feita no processo foi substituir a formação da membrana suspensa por um processo de metalização por evaporadora e-beam, ao invés de deposição eletrolítica, reduzindo assim os riscos envolvidos. O processo de metalização e-beam garante uma melhor qualidade de grão do metal e não agride a camada de sacrifício, portanto é um processo bem mais confiável e seguro do que a deposição eletrolítica. Várias etapas foram modificadas para ajustar o processo de acordo com o projeto e material e equipamentos disponíveis nas facilidades do LNLS. As características eletromecânicas foram obtidas por meio de hand calculation e verificadas através de simulação no software ANSYS. Para a obtenção do acoplamento eletromagnético foi utilizado o modelo descrito em literatura para o cálculo das características da chave e simulações no ADS fornecem dados sobre o funcionamento do dispositivo como chave de RF. Os resultados de cada etapa do processo, bem como a descrição detalhada do método utilizado estão descritos neste trabalho.

Etapas de Fabricação - Novo processo

1 - Deposição de Ti/Au sobre alumina - camada semente (400/600);
2 - Litografia das linhas;
3 - Corrosão;
4 - Deposição de dielétrico SiO2 / Si3N4 - camada isolante;
5 - Fotolitografia do dielétrico;
6 - Corrosão do dielétrico;
7 - Fotoresiste para camada de sacrifício (1,5 μm);
8 - Fotogravação dos postes de sustentação da ponte;
9 - Crescimento dos postes de Au (1,5 μm);
10 - Fotolitografia das pontes, para lift off posterior;
11 - Flash de Ti (0,05 μm) + Deposição de Al para formar as pontes (0,5 μm);
12 - Lift off para definição das pontes e remoção da camada de sacrifício com Acetona e Plasma de oxigênio.

Acknowledgements

Laboratório de Microfabricação (LMF) do LNLS. Especialmente: Ângelo Gobbi e Maria Helena. CNPq.

138

MODIFICAÇÃO POR PLASMA E CARACTERIZAÇÃO DA SUPERFÍCIE DO PHBV OBTIDO VIA FUSÃO

Ferreira, B. M. P.[1], Pinheiro, L. M. P.[2], Nascente, P. A. P.[2], Ferreira, M. J.[3], and Duek, E. A. R.[4]

[1] PUC - São Paulo - Sorocaba SP Brazil
[2] Universidade Federal de São Carlos - São Carlos SP Brazil
[3] Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil
[4] Universidade Estadual de Campinas - Campinas SP Brazil

O poli(hidroxibutirato-co-hidroxivalerato) - PHBV é um dos materiais poliméricos mais estudados como biomateriais, nos últimos tempos. Apesar das aplicações, o PHBV é hidrofóbico, o que dificulta a interação deste com as células humanas. A modificação da superfície desse polímero se torna importante quando o mesmo está em contato com componentes fisiológicos. Os plasmas de baixas temperaturas são amplamente empregados para modificar muitas propriedades das superfícies de materiais poliméricos, tais como adesão, penetrabilidade, molhabilidade, facilidade de pigmentação e biocompatibilidade. Neste trabalho, a superfície do PHBV foi tratada a plasma de nitrogênio, com o objetivo de se obter um material com as características normais do polímero puro, porém com maior hidrofilicidade na superfície, promovendo uma melhora na adesão celular e, conseqüentemente, uma possível melhora na interação polímero-tecido. O PHBV foi moldado em uma mini-injetora e as amostras foram submetidas ao tratamento por plasma, a uma potência de 50 W ou 100 W, até atingir a pressão desejada (20 a 80 Pa), quando foi introduzido o gás (N2), por até 600 s. As amostras foram caracterizadas por ângulo de contato, microscopia eletrônica de varredura (SEM), microscopia de força atômica (AFM) e espectroscopia de fotoelétrons excitados por raios-X (XPS). O tratamento a plasma sobre o polímero PHBV promoveu uma diminuição nos ângulos de contato e um aumento na energia de superfície das amostras estudadas. Este aumento está relacionado aos parâmetros de tratamento utilizados. O tratamento de plasma também alterou a morfologia das superfícies estudadas, tornando as amostras mais ou menos rugosas, conforme os parâmetros de plasma utilizados. Foi possível observar um aumento dos grupos polares nas superfícies, deixando as superfícies dos polímeros mais hidrofílicas. Os resultados mostraram que o tratamento a plasma melhora várias propriedades importantes das superfícies do polímero PHBV, mostrando-se promissor na área de engenharia de tecidos.

Acknowledgements
Este trabalho contou com o apoio do Laboratório Nacional de Luz Síncroton, FAPESP e CNPq.

139

Produção de dipositivos microfluídicos em polidimetilsiloxano (PDMS) e medida da mobilidade do fluxo eletroosmótico.

Duarte, G. R. M.[1] and Carrilho, E.[1]

Universidade de São Paulo - São Carlos - São Carlos SP Brazil

Dispositivos microfluídicos tradicionalmente são fabricados em vidro, quartzo e silício. O processo de fabricação é caro e consome muito tempo. A utilização de materiais poliméricos para a produção de microdispositivos tem crescido nos últimos anos, e a popularidade desse material é resultado do baixo custo, simples fabricação e suas propriedades elastoméricas. Muitos tratamentos na superfície têm sido desenvolvidos para tornar o PDMS mais hidrofílico e aumentar a mobilidade do fluxo eletroosmótico. Este trabalho propõe produzir microdispositivos em PDMS e medir o fluxo eletroosmótico em microcanais. Os microcanais foram produzidos em PDMS a partir do Sylgard 184. O pré-polímero e o catalisador foram misturados na proporção de 10:1 (m/m) e a bolhas foram retiradas por aplicação de vácuo. A mistura foi depositada sobre um molde metálico, e. o polímero foi curado sob o molde a 75 °C durante 1 hora. Depois da cura o polímero foi removido do molde e furos de acesso foram confeccionados nas regiões dos reservatórios. Os microcanais foram vedados contra uma superfície planar feita em PDMS. Antes da vedação as duas partes foram submetidas a dois tratamentos diferentes: 1)oxidação das superfícies com plasma de oxigênio e 2) as duas partes foram lavadas com solventes orgânicos para retirar oligômeros livres e posteriormente oxidados com plasma de oxigênio, segundo o método desenvolvido por Henry[1]. Antes da medida da mobilidade do fluxo eletroosmótico μeo os microdipositivos foram caracterizados, com relação aos efeitos eletroforéticos. Um gráfico de Ohm foi obtido através da medida da corrente sob diferentes valores de campo elétrico aplicados. O procedimento utilizado para a medida do fluxo eletroosmótico foi o de monitoramento da corrente adaptado por Locascio [2]. Pode-se observar que a corrente foi proporcional à voltagem aplicada até 300 V/cm, a partir desse valor há um desvio resultante do aquecimento provocado pelo efeito Joule. Os valores medidos da μeo no dispositivo que passou apenas pela oxidação da superfície com plasma de oxigênio foi de 3,7x10^{-4} cm^2/ s^{-1}V^{-1} e no dispositivo que passou pela lavagem com solventes orgânicos foi de 4,3x10^{-4} cm^2 /s^{-1}V^{-1}, demonstrando um pequeno aumento na μeo nos canais que passaram pelo processo de retirada dos oligômeros livres.

1 - Locascio, L. E., Perso, C. E.; Lee. J. Chromatogr. A 1999, 857, 275. 2 - Henry, C. S., Vickers, J. A. , Caulum, M. M. Anal. Chem. 2006, 78, 7446.

Acknowledgements

FAPESP e Laboratório de Microfabricação - LNLS

Parte X

Propriedades Estruturais, Eletrônicas e Magnéticas de Sólidos

140

Growth and characterization of iron silicides thin films on Si (111)

Miquita, D.R.[1], Gonzalez, J. C.[1], M. I. N. da Silva[1], M.V.B. Moreira[1], Andrade, R.R.[1], Carvalho, M. A. D.[1], Magalhaes-Paniago, R.[1], Paniago, R.[1], and A. G. de Oliveira[1]

Universidade Federal de Minas Gerais - Belo Horizonte MG Brazil

In the last years the orthorhombic iron disilicide β-$FeSi_2$ has been pointed out like a promising candidate to integrate with Si technology because it can be synthesized by several techniques in silicon substrates, exhibits an indirect band gap that under strain transforms to a direct band gap material (0.85 - 0.89 eV) and efficiently emits light at 1.5 μm. In this work, the growth of iron silicides thin films by Solid Phase Epitaxy (SPE) and Reactive Deposition Epitaxy (RDE) methods are investigated in a systematic way. The influence of different growth conditions such as growth temperature, annealing temperature, and annealing time are investigated. Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM) were used to investigate the correlations between growth conditions and the morphology of the samples. X-ray Diffraction (XRD), Magnetic Force Microscopy (MFM) and Conversion Electron Mössbauer Spectroscopy (CEMS), were used to identify and quantified the different iron silicide phases present in samples. A transition from iron rich phases to silicon rich phases was observed as a function of the growth temperature. These phase transitions are followed by significant changes in the morphology of the samples and a redistribution of the crystallographic orientations of the iron silicide grains in each phase. It was observed that for the formation of a uniform β-$FeSi_2$ film a larger thermal budget is needed for SPE growth than for RDE growth. However, both techniques are suitable for the production of β-$FeSi_2$ thin films.

Acknowledgements
This work was supported by CNPq, CAPES, FAPEMIG and LNLS

141

Estudo da incorporação de Co a fase magnética $Pr_2Fe_{14}B$ em imãs permanentes de Pr-Fe-B-Nb .

Galego, E.[1], Barbosa, L. P.[1], Serna, M.M.[1], and Faria, R.N.[2]

[1] Instituto de Pesquisas Energéticas e Nucleares - São Paulo SP Brazil
[2] Instituto de Pesquisas Energéticas e Nucleares - Sao Paulo SP Brazil

A substituição de átomos de ferro por átomos de cobalto na fase magnética $Pr_2Fe_{14}B$, de estrutura tetragonal (P_{42}/mnm), resulta no aumento da temperatura de Curie desta fase sem perda significativa das propriedades magnéticas. Estudos anteriores mostraram que esta substituição ocorre preferencialmente nos sítios k_2. Neste trabalho foram estudados os compostos com estequiometria atômica $Pr_{13,7}Fe_{79,9-x}Co_xB_6Nb_{0,1}$, onde x = (0, 4, 8, 12 e 16) % atômico, representa o teor de cobalto adicionado em substitução ao ferro. As micrografias obtidas por microscopia eletrônica de varredura conjuntamente com as análises por dispersão de energia (EDX) mostram a formação de fases de Laves quando a adição de cobalto é igual ou maior de 12% atômico. Com a adição de 16% atômico de cobalto, ocorre o surgimento das fases de Laves, demonstrando que o limite de solubilidade foi ultrapassado. Os resultados obtidos com as anlíses realizadas por difração de raios X mostraram que em todas as amostras houve a substituição de átomos de ferro por átomos de cobalto na fase $Pr_2Fe_{14}B$ levando a alterção nos parâmetros de rede da célula unitária ocorrendo a diminuição dos parâmetros de rede, sendo que a diminuição do parâmetro de rede c foi mais acentuada que no parâmetro de rede a. A utilizção da técnica de espalhamento anômalo com energia 20eV abaixo da borda de absorão do ferro e energia 1keV acima desta borda utilizando luz sincrotron sintonizadas nestas energias permitiu-se determinar que para as condições de processamento HDDR utilizadas na preparação das amostras não induziu substituição do cobalto em sítios preferenciais diferente aos determinados em estudos anteriores.

142

Magnetic and structural effects of Kr irradiation on FeCo/Cu multilayers

I. L. Graff[1], Teixeira, S.R.[1], AMARAL L.[1], and A. Traverse[2]

[1] Universidade Federal do Rio Grande do Sul - Porto Alegre RS Brazil
[2] Université Paris-Sud - Orsay France

In this work we investigated the structural and magnetic effects on $\mathrm{Fe_xCo_{100-x}/Cu}$ multilayers after Kr ion irradiation. Two thicknesses of Cu were studied, 25 and 50 Å, keeping fixed on 15 Å the thickness of FeCo. The irradiations were carried out at room temperature with 600 keV ions and fluences ranging from 1×10^{15} to $5 \times 10^{15} \mathrm{ions/cm^2}$. The structural evolution of the samples, specially around Fe and Co atoms, was followed by XAS. In order to complement the data obtained from XAS, two kinds of magnetic measurements were performed: magnetization versus applied field (AGFM) and magnetization versus temperature (SQUID).

The XAS data show that the structure of FeCo suffers a transformation from bcc, in the as-depsited state, to fcc after irradiation. This structural transition depends on the Cu thickness and on Fe concentration. The XAS data were fitted considering some models and the fittings outcome were evaluated through statistical analysis in order to verify the atomic environment around Fe and Co atoms before and after irradiation. The results indicate that ion irradiation induced atomic level mixing, even being the system composed of positive heat of formation elements.

The data from magnetization versus applied field showed a large decrease of M_s magnitude, for 50 Å Cu, after irradiation. In this case the FC/ZFC curves develop from a continuos-like magnetic film behaviour to small clusters. When the thickness of Cu is 25 Å, M_s does not decrease considerably. The FC/ZFC curves show a small change when compared to the case of 50 Å. Both structural and magnetic data are consistent with an atomic mixture promoted by irradiation in case of largest Cu thickness. The driving force for mixing comes from the energy deposited in the lattice by the incident ions and from the excess of interface free energy stored in the multilayer, which enhances the initial energetic state of the system.

Acknowledgements
This work was supported by CNPq and CAPES brazilian scientific agencies. The authors are very grateful to LNLS staff for their help during the experiments.

143

Structural characterization of $Pb_{1-x}Ba_xZrTiO_3$ ferroelectric ceramics by XRD and XANES: Cation substitution and temperature dependence.

Doriguetto, A.C.[1], Neves P.P[2], Mastelaro, V.R.[2], Mascarenhas, Y.P.[2], Rocha, J. A. L.[2], Garcia D[3], Lente, M. H.[3], Michalowicz, A.[4], and Eiras, J.A[3]

[1] Universidade Federal de Alfenas - Alfenas MG Brazil
[2] Universidade de São Paulo - São Carlos - São Carlos SP Brazil
[3] Universidade Federal de São Carlos - São Carlos SP Brazil
[4] Université Paris XII - Val de Marne - Creteil cedex France

Many properties of the $PbZr_xTi_{1-x}O_3$ (PZT) ceramics, which has been applied in a variety of piezoelectric, pyroelectric and ferroelectric devices, could be improved by adding appropriate dopants. In the present work we are studying the structural changes introduced by insertion of Ba^{2+} to the PZT system: $Pb_{1-y}Ba_yZr_xTi_{1-x}O_3$ (PBZT). We have used X-ray absorption near edge structure (XANES) and X-Ray Diffraction (XRD) as a probe to respectively the short and long range-order of PBZT ferroelectric ceramics. The samples, $Pb_{1-x}Ba_xZr_{0.65}Ti_{0.35}O_3$ with x= 0.0, 0.1, 0.2, 0.3 and 0.4 (abbreviated as PBZTx from PBZT00 to PBZT40) were prepared by the conventional mixed oxide method. The XRD measurements were done at LNLS (D10B-XPD beam line) and the titanium K-edge X-Ray absorption spectra were collected at the LNLS using the D04B-XAS1 beam line. According to XRD-Rietveld refinements, the rhombohedral-to-cubic (R3m:r-to-Pm$\bar{3}$m) phase transition for the PBZT samples occurs increasing the barium content. The phase transition seams to be place after 20 at% of barium (PBZT20). The rhombohedral structural model R3m:r fitted well to the three lower barium content samples, PBZT00, PBZT10 and PBZT20. For the highest barium content sample, the fitting obtained in the cubic phase Pm$\bar{3}$m is significantly better than in R3m:r. XANES measurements indicate that the local structure around Ti atoms has a different compositional dependence from that one obtained from XRD. According to XANES data, the local structure around Ti remains distorted at all barium concentrations, including the PBZT30 and PBZT40 samples, for which XRD highlighted a cubic structure. This result suggests that the local structure is weakly dependent on crystallographic phase. The results observed with the XRD refinements agree with that one observed by electric measurements (temperature dependence of the relative dielectric permittivity).

Acknowledgements
This work has been supported by LNLS under proposal D10B - XPD - 3354. We are grateful to FAPESP and CNPq. The authors wish to thank Prof. Eduardo Granado and Dr. Fabio Furlan Ferreira for their help during the data collection.

144

STRUCTURAL RIETVELD REFINEMENT OF MAGNETITE AND HEMATITE OF A STEATITE AND ITS FORMING SOIL FROM QUADRILÁTERO FERRÍFERO, MG, BRAZIL

Silva, F. D. da[1], Goulart, A.T.[1], FABRIS, J. D.[1], COUCEIRO, P.R.C.[2], and Viana, J.H.M.[3]

[1] Universidade Federal de Minas Gerais - Belo Horizonte MG Brazil
[2] Universidade Federal do Amazonas - Manaus AM Brazil
[3] Empresa Brasileira de Pesquisas Agropecuárias - São Carlos SP Brazil

Magnetite (ideal formula, Fe_3O_4; cubic system, space group Fd3m) is a ferrimagnetic iron oxide with inverted spinel structure. In the soil, magnetite may be oxidized to hematite (αFe_2O_3, hexagonal system, space group R3c), which is a thermodynamically a more stable iron oxide , either directly or via the intermediate formation of maghemite (γFe_2O_3, also with the spinel structure). The aim of this work was characterize by XRD and Mössbauer spectroscopy the mineralogical phases of a parent rock and its corresponding soil developed on steatite (Quadrilátero Ferrífero area, state of Minas Gerais, Brazil) in order to propose mineralogical pathways involved on the iron oxides transformation in the natural environment. The diffraction pattern shows narrow, characteristic peaks of magnetite, in the magnetic fraction of the steatite (rock) sample and characteristics peaks of magnetite and hematite, in the magnetic fraction of the steatite (soil). The Rietveld analysis was performed for both samples. For magnetite, a = 0.83964 nm (rock) and a = 0.83959 nm (soil) are in good agreement with the indexed a = 0.8390 nm (JCPDS card 07-0322). Similar agreement between determined and indexed values was also observed for the soil-hematite: a = 0.50380 and c = 0.137720 nm. The room-temperature Mössbauer spectrum for this soil revealed two superposed six-line patterns. The hyperfine parameters indicating a well crystallized magnetite. The Mössbauer parameters for the soil reveals three six-line patterns and a paramagnetic Fe^{3+} doublet. The found hyperfine parameters are characteristic of magnetite and hematite.

Acknowledgements

This work has was supported by the Brazilian Synchrotron Light Laboratory (LNLS) under proposal D10B - XPD 4157, by the Federal University of Minas Gerais, the University of Patos de Minas (MG), CNPq and FAPEMIG.

145

KDP:Mn piezoeletric coefficients obtained by X-ray diffraction

C. M. R. Remedios[1], Cardoso, L.P.[2], dos Santos, A. O.[2], de Menezes, A. S.[2], and Moreira, S. G. C.[1]

[1] Universidade Federal do Pará - Belém PA Brazil
[2] Universidade Estadual de Campinas - Campinas SP Brazil

Crystals menbers of the KDP-family exhibit piezoelectricity in both the paraeletric and ferroelectric phases. The KDP undergoes a ferroelectric phase transition at 122K. In addition, the influence of doping introduced into the crystal lattice has been studied extensively in various ferroelectrics, in particular because they can improve physical properties of materials for technological applications. Crystals of pure KDP and Mn-doped KDP (KDP:Mn) heve been grown from a water solution by slow-cooling method. KDP:Mn crystals were grow from solutions containning $KMnO_4$ of 1, 3 and 5 mole % relative to KH_2PO_4, respecftively. Their piezoelectric coefficients were measured by X-ray multiple diffraction phenomenon in the room temperature.These crystals were cut in parallelepipeds with the dimensions (0.87 x 3 x 5) mm^3. The parallelepipeds faces were orthogonal to the a, b and c crystallographic directions of the tetragonal structure. Electrodes of silver were placed in the area of both surfaces perpendicular to the c axis where the electric field was applied. A Keithley instruments high voltage supply, model 246, was used as DC voltage source. The high-resolution Renninger Scan of KDP crystals was carried out at beam line XRD1 (D12A) of the Brazilian Synchrotron Light Laboratory (LNLS) using the Huber three-axes goniometer. The minimum step sizes of the ω and ϕ axes are 0.0004^0. In this work, we investigated the influence of the Mn doping on the piezoelectric propierties of the KDP crystal. In conclusion, we reported on the experimental verification based on x-ray measurements, the piezoelectric coefficients increased with increasing doping concentration of the MN in the solution.

Acknowledgements
We acknowledge the LNLS staff for valuable help during the experiments of multiple diffraction and the financial support from the Brazilian agencie CNPq.

146

Electronic energy-loss spectra of MgB_2 by inelastic X-ray scattering spectroscopy

Stutz, G.[1], Tirao G.[1], Granado, E.[2], García-Flores, A.F[2], and Pagliuso, P.G.[2]

[1] Universidad Nacional de Cordoba - Cordoba Argentina
[2] Universidade Estadual de Campinas - Campinas SP Brazil

Soon after de discovery of superconductivity in magnesium diboride [1], much theoretical effort was devoted to studying collective electron excitations in this compound [2,3]. Those investigations were based on first principles calculations of the frequency- and wave-vector-dependent density response function. Besides the free-electron-like plasmon at $\sim$ 20 eV, a long-lived plasmon mode at lower energies ($\sim$ 2.5 eV) was predicted by the theoretical models. This novel collective mode was ascribed to strong coherent charge fluctuations between parallel Mg and B sheets. Recently, by means of high-resolution measurements of inelastic X-ray scattering spectra at low momentum transfers ($q < 0.78$ a.u.) [4], the low-energy plasmon, including its energy dispersion and anisotropy, was experimentally verified. Due to the negligible contribution of multiple-scattering processes, and thus to the negligible distortion of the X-ray energy-loss spectra, and to the enhanced X-ray scattering cross-section at high momentum transfers, inelastic X-ray scattering spectroscopy (IXSS) has become a well-suited technique to investigate electron excitations in the range of intermediate and high momentum-transfers (single-particle excitation domain). In this work we extend the experimental IXSS study of electron excitations in MgB_2 beyond the plasmon domain, where besides lattice effects, exchange and correlation effects should play an important role in the shape of the energy-loss spectra. Measurements were performed using a high-resolution X-ray spectrometer [5] installed at the XRD1-beamline. Energy-loss spectra were measured for a wide range of momentum transfers, going from 0.55 a.u. to 2.4 a.u. At low momentum transfers a good agreement with the previous experimental and theoretical works was found. Though the measurements were made on a polycrystalline sample, some momentum-dependent, lattice-effect induced fine-structure is noticeable at high momentum transfers. A significantly broadening of the energy-loss spectra for increasing momentum-transfer was observed. A high-energy tail in the spectra, caused by band structure and dynamical correlations effects, evolves at large momenta.

[1] J. Nagamatsu et al, Nature (London) **410**, 63 (2001)
[2] V.P. Zhukov et al, Phys. Rev. B **64**, 180507(R) (2001)
[3] W. Ku et al, Phys. Rev. Lett. **88**, 057001 (2002)
[4] S. Galambosi et al, Phys. Rev. B **71**, 60504 (2005)
[5] G. Tirao, G. Stutz and C. Cusatis, J. Synchrotron Rad. **11**, 335 (2004)

147

MULTIVARIATE ANALYSIS ON THE INTERPRETATION OF DYNAMIC XANES SPECTRA

Ambrosio, R. C.[1] and Nascimento, M. A.[1]

Universidade Federal do Rio Grande do Norte - Natal RN Brazil

A complete kinetic study consists on the investigation of chemical reactions and encompasses the identification of the correct reaction mechanism and the associated rate constants. The determination of reaction rate constants should be accomplished by fitting of experimentally determined concentration profiles of reactants, intermediates and products as a function of time to kinetic models. The analysis becomes complicated when the responses of the reactants and the products overlap and cannot directly determine their concentration over time. This is the case on large amount of XANES spectra collected at DXAS beam line. To circumvent this difficult, multivariate curve resolution with alternating least squares, MCR ALS, was employed. MCR ALS permitted to deconvolve the spectra of pure factors and its correspondent concentration profiles. During the iterative process of MCR ALS, non-linear kinetic parameters were fitted to the optimized concentration profiles. Generalized 2-D correlation analysis was also applied. The 2 D correlation analyzes the behavior of the system during the influence of the perturbation. The principal aspects explored on 2 D correlation analyses was better resolution of overlapping peaks, revealing features not readily observable in regular plots, determining the spectral intensities that change as an effect of the perturbation and setting up a sequence of order of changes that occurs in the spectra. All this multivariate techniques was employed on kinetic modeling of dynamic XANES spectra collected during the NiCo alloy formation supported on MCM 41. Data analysis was performed on our home-made MULTIPHOTON software.

148

Wide Angle X-ray Scattering characterization of SBS / Pani.DBSA blends

Souza Jr, F. G.[1], Soares, B.G.[1], and Mantovani, GL[2]

[1] Universidade Federal do Rio de Janeiro - Rio de Janeiro RJ Brazil
[2] Universidade de São Paulo - São Carlos - São Carlos SP Brazil

In this work, electrically conductive blends based on polyaniline-dodecylbenzene sulphonic acid (Pani.DBSA) / styrene-butadiene-styrene (SBS) block copolymer have been prepared by two methods namely melt mixing and polymerization of aniline in the presence of SBS using in situ polymerization method. A great reduction in volume resistivity values with increase in Pani content was noticed for in situ polymerization method compared to melt mixing method. The microstructural parameters were also computed using Wide Angle X-ray Scattering (WAXS). The results are compared with mechanical and electrical properties. WAXS experimental results showed the influence of synthetic routes on the microcrystalline behavior of SBS/Pani blends. The number of unit cells increases with increase in crystalline Pani content in the amorphous SBS matrix, as expected. The tensile strength and volume resistivity decrease with increase in Pani content, whereas number of unit cells increases. This is due to increase in high crystalline Pani phase in SBS matrix. The changes in physical properties are attributed to the crystal imperfection, wherein parameters like number of unit cells and surface-weighted crystal size increase with increase in Pani content. Blend prepared by in situ polymerization resulted in lower resistivity because of a favorable morphology characterized by the formation of interconnected microtubules, seen by MEV, which form the conducting pathway with lower amount of Pani. In spite of lower resistivity, the crystallinity level of these blends was lower than the corresponding mechanical mixing blends. Blends prepared by in situ polymerization method can be considered a physical interpenetrating network. Therefore, there was no formation of large aggregates constituted by Pani chains in large extent because of the interconnection of SBS chains. The absence of large aggregates decreases the crystallinity level but promotes the formation of conducting pathway at lower Pani concentration.

Acknowledgements
We would like to acknowledge the Conselho Nacional de Desenvolvimento Cientíco e Tecnológico (CNPq), Coordenação de Aperfeiçoamento de Pessoal de Ensino Superior (CAPES) and Fundação de Amparo a Pesquisa do Estado do Rio de Janeiro (FAPERJ-26/150.351/2004), for the financial support for this project. The authors would like to thank Laboratório Nacional de Luz Sincontron for the technical support on the WAXS experiments (Research proposals D11A-SAS 2934/04 and D11A-SAXS No.3406/05).

149

XAFS study of Co, Ni, Cu or Zn doped TiO_2 films

Rodríguez Torres, C. E.[1], A.F. Cabrera[1], L. A. Errico[1], F. Golmar[2], Duhalde, S.[2], M. Rentería[1], and F.H. Sánchez[1]

[1] Universidad Nacional de La Plata - La Plata Bs.As Argentina
[2] Universidad de Buenos Aires - Buenos Aires CapFe Argentina

A variety of semiconducting materials, called diluted magnetic semiconductors (DMS) combine two properties: semiconductivity and magnetism. Many research groups have focused their efforts on doping TiO_2 with transition metals. Much of the work has been concentrated on Co-doped TiO_2 films, in which ferromagnetism at room temperature has been confirmed first for anatase and later also for rutile phase films. On the other hand some authors have reported remarkable room temperature ferromagnetism on pure TiO_2, HfO_2 and In_2O_3 oxides films and also in films doped with non-magnetic impurities. All the theoretical and experimental results point out the important role of oxygen vacancies on the origin (or presence) of magnetism, then it is crucial to know the local environment of the impurities in the films.

In this work we present an XAFS characterization of the local environment of the M atoms (M=Co, Ni, Cu or Zn) in doped anatase TiO_2 thin films. All these films present ferromagnetism at room temperature. We did not found evidences of metallic clusters in any case. The oxidation state is +2 and the local oxygen coordination is similar to MO (CoO, NiO, CuO or ZnO) but, with the exception of Cu, the similitude with these oxides is only in the short range.

150

X ray diffraction and electrical resistivity analyses on granular (Hg,Re) - 1223 superconductors

Passos, CAC[1], Orlando, M. T. D.[1], J.L.Passamai Jr[1], Cruz,P.C.M[1], Mello, E. V. L. de[2], Corrêa, H. P. S.[3], and Martinez, L. G.[4]

[1] Universidade Federal do Espírito Santo - Vitória ES Brazil
[2] Universidade Federal Fluminense - Niterói RJ Brazil
[3] Universidade Federal do Mato Grosso do Sul - Campo Grande MS Brazil
[4] Instituto de Pesquisas Energéticas e Nucleares - São Paulo SP Brazil

Hg,Re-1223 polycrystalline samples were prepared with different three oxygen partial pressure. The Rietveld refinement of the XRD measurements have shown that the better spectrum fit was obtained including an extra Hg-1223 phase (poor oxygen) additionally to the main (Hg,Re)-1223 phase (rich at oxygen). The lattice parameter a has indicated that the extra Hg-1223 phase is underdoped (poor at oxygen). Scanning Electron Microscopy (SEM) images and Energy Dispersion X-ray Spectra (EDS) analysis were done. The results have shown that the samples have similar morphology of the grains and average junction sizes. Moreover, the intergrain region of samples were investigated by ac magnetic susceptibility (χ_{ac}) using these samples in pellet form. The results indicated that the in-phase component χ'_{ac} of the ac susceptibility has two transitions towards lower diamagnetic screening. As intergrain morphologies are similar for all samples, the second transition in χ'_{ac} susceptibility is associated with the presence of Hg-1223 phase on grain boundary. It is known that the HTSC exhibit complex behavior, which is related to thermodynamic fluctuations of the superconducting order parameter. For the polycrystalline samples case there are two models which can give a picture of fluctuations in intergrain and intragrain regions. Therefore, dc electrical resistivity of the samples was measured using the four-point probe method. The analysis of these measurements was possible to estimate single crystal average size which was order of 1500 Å.

Acknowledgements
We would like to thank CNPq Grant CT-Energ 504578/2004-9, CNPq 471536/2004-0, CNPq-FAPERJ Pronex E26/171168/2003, and CAPES for financial supports. Thanks also to Companhia Vale do Rio Doce (CVRD), Companhia Siderúgica de Tubarão (CST). We gratefully acknowledge to National Laboratory of Light Synchrotron - LNLS, Brazil.

151

Structural and magnetic study of nanostructured $(Fe_{79}Mn_{21})_{1-x}Cu_x$ alloys

M. Mizrahi[1], A.F. Cabrera[1], and Desimoni J.[2]

[1] Universidad Nacional de La Plata - La Plata Bs.As Argentina
[2] Universidad Nacional de La Plata - La PLata B.A. Argentina

Although the magnetism of fine particles has been widely studied during the last years, there are a rich variety of phenomena, which remain to be understood in the nanoscale granular systems. A complete understanding of the magnetic properties of these nanoscopic systems is hindered by their inherent complexity, involving broad size distributions, different structural and/or magnetic phases and interparticle magnetic interactions. In order to get deeper insight into the nanoestructurated metallic systems, allowed powders of $(Fe_{79}Mn_{21})_{1-x}Cu_x$ (x = 0.1 to 0.35) were prepared by milling the elemental species in a horizontal vibrating device with steel ball and vial, under Ar atmosphere during 15h at 33Hz. The structural analysis has been obtained by X-ray diffraction (XRD) and X-Ray Absorption Fine Structure (EXAFS-XANES) at the Fe K-edge and at the Cu K-edge at RT. Mössbauer spectroscopy (MS) and magnetic measurements (AC-susceptibility, ZFC-FC and M vs H) were performed to magnetic characterized the samples. Preliminary XAFS results show changes in the amplitude of the Fourier transformation. The amplitude increases when decreases the Cu content in the sample. XRD and MS results suggest the presence of two FCC-phases with different ordering temperatures. The AC-susceptibility measurements indicate the existence of a characteristic temperature T_c ($\sim$ 150 K) which shifts to lower temperatures with increase the Cu content. These results, associated with magnetization measurements as function of temperature and applied field, provide evidence for a highly disordered magnetic system with spin-glass-like behavior.

Acknowledgements
This work was partially supported by LNLS.

152

Fe K-XANES study of Fe_xO_y in Ultrathin Nanostructured Melanin Films on Au(111)

FERNANDEZ BALDIS, F. J.[1], Andrini, L. R.[2], Salvarezza R C[3], and Requejo, F. G.[1]

[1] Universidad Nacional de La Plata - La Plata Bs.As Argentina
[2] Universidad Nacional de La Plata - La PLata B.A. Argentina
[3] Instituto de Investigaciones Fisicoquimicas Teoricas y Aplic - La Plata BA Argentina

Melanins are complex biopolymers widely distributed in living organisms. The secondary structure of melanins is still under debate. There are strong evidence that melanin is formed by small nanometer-sized particles that aggregate forming a hierarchical structure. Moreover, melanin exhibits interesting properties such as photoactivity, semiconductor behavior, and electrochemical activity; and is interesting from the point of view of material science [1].

In this work we explore by XANES experiments the nature of the sities of of Fe-containing nanostructured ultrathin melanin films electrochemically self-assembled on Au(111). The X-ray absorption spectra were measured at the D04B-XAS beamline of the LNLS, Laboratorio Nacional do Luz Síncrotron, Campinas, Sao Paulo, Brazil. XANES spectra at the Fe K-edge for pure melanin sample were recorded in air at room temperature in transmission mode. X-ray absorption data for supported melanin on Au(111) was obtained by total electron-yield mode.

The analysis of the relative concentration of Fe-species in melanin film on Au(111) by XANES indicates that the main Fe-species in Au-supported melanin corresponds to magnetite like-species (Fe_3O_4 nanoparticles) ($\sim$ 80 %) being Fe-species remaining in melanin nanoparticles just a minor component ($\sim$ 20 %).

Acknowledgements
Acknowledgements: ANPCyT (PICT02-11111 and PICT03-17492), LNLS (project D04B - XAFS1 - 4642). P.D acknowledges a grant from Conicyt-Chile and a fellowship from MECESUP-REDES project.

[1] Y. Gimeno, P. Dip, P. Díaz, A. González Orive, P. Carro, A. Hernández Creus, G. Benítez, P. L. Schilardi, L. R. Andrini, F. G. Requejo, R. C. Salvarezza. Electrocatalytic and Magnetic Properties of Ultrathin Nanostructured Iron-Melanin Films on Au(111). Chemistry - A European Journal (2006) ISSN: 0947-6539 (print), 1521-3765 (online).

153

Relationship between Oxygen Coordination Environment and catalytic properties in Grafted Ti-Calixarenes catalysts probed by Ti-K XANES studies

Andrini, L. R.[1], Notestein, J. M.[2], Iglesia E.[2], and Requejo, F. G.[3]

[1] Universidad Nacional de La Plata - La PLata B.A. Argentina
[2] University of California at Berkeley - Berkeley CA United States of America
[3] Universidad Nacional de La Plata - La Plata Bs.As Argentina

Highly dispersed Ti centers dispersed onto or within SiO_2 frameworks are active catalysts for selective oxidations and other molecular rearrangements catalyzed by Lewis acids because the resulting four-coordinate Ti centers are electron-deficient and can expand their coordination to bind oxidants or substrates and to activate oxidants towards attack by electron-rich substrates.

We report here the use of X-ray absorption methods on surface-grafted Ti-SiO_2 catalysts based on calixarene-Ti complexes, which catalyze epoxidation reactions with turnover rates independent of Ti surface density. Ti K-edge X-ray absorption near-edge spectroscopy (XANES) allow us the determination of the Ti coordination number and density of unoccupied electronic states at Ti 3d-level in these materials as a function of treatment temperature, Ti surface density, Ti precursor ($TiClS_4$ or TiO^iPr_4), and catalyst use in epoxidation reactions.

The Ti K-XANES experiments were realized in the D04B-XAS beamline of the LNLS (Laboratorio Nacional do Luz Síncrotron, Campinas, Brazil). Ti K-edge XANES spectra of all dried materials based grafting calix[4]arene-Ti complexes indicate $^{[4]}$Ti with increased Ti 3d occupancy based on comparison to known Ti-SiO_2 catalysts and soluble calixarene-metal species with known single crystal X-ray diffraction structures. In contrast to the similar catalytic activity and structure of materials based on calix[4]arene-Ti, materials based on homoxacalix[3]arene-Ti possess an average Ti coordination number of 5 and this coordination number is persistent to 523 K eliminating the possibility of simple coordination sphere expansion by a physisorbed species.

Acknowledgements

The authors acknowledge the financial support of the U.S. DOE Office of Basic Energy Sciences (DE-FG02-05ER15696), ANPCYT (PICT 06-17492), Argentina; CONICET (PIP 6075), Argentina; CONICET-CNPq-NSF collaborative research agreement (CIAM program), and LNLS, Campinas, Brazil (project D04B - XAFS1 - 3492). VIK acknowledges the financial support from the Science and Technology Center in Ukraine Grant 3655. JMN acknowledges the National Science Foundation for a graduate fellowship.

154

Wide-angle X-ray Diffraction (WAXD) simultaneously with Thermal Analysis and Scanning Electronic Microscopy (SEM) applied to study different polymorphs of pharmaceutical drugs: Chlorpropamide

Cuffini, S. L.

Centro de Excelencia de Productos y Procesos de Córdoba, Córdoba-Argentina

Chlorpropamide (CPD) is a drug used to treat diabetes type II (non-dependent of insulin), especially when the diabetes can not be controlled by a diet. The polymorphism of this drug is widely documented exhibiting several crystalline forms. Unfortunately, Thermal techniques (Differential Scanning Calorimetry - DSC) can not reveal completely the identity of the transforming phases and the identification of each peak is often difficult without the aid of techniques that give information regarding structures and reactions. In the last decades, phase transitions between polymorphs (drug substances which exist as two or more crystalline phases that have different arrangements and/or conformations of the molecules in the crystal lattice) have been the focus of much attention, mainly their characterization. In this work, we present a morphology characterization of four CPD polymorphs I, II, III, IV by SEM. The electron microscopy work has been performed with the JMS-5900LV microscope of the LME/LNLS (Campinas-Brazil). DSC and WAXD is a very powerful methodology with can have many applications for the pharmaceutical solids and the experimental measurements were carried out using the D11A-SAS (LNLS-Brazil) station. In, the present work we also present, the temperature phase transitions of the different polymorphs of CPD, achieving an interpretation of thermal behavior of these type of compounds. In the case of Pol. II was determined solid-solid transition to Pol. I before melting point and Pol. IV presented a solid-solid transitions to Pol III-Pol.I.

Acknowledgements
The authors thank to LNLS, Agencia Córdoba Ciencia SE and Conicet for the financial support.

155

Cationic exchange in nanosized ZnFe_2O_4 spinel revealed by experimental and simulated near-edge absorption structure

Figueroa, S. J. A.[1], S.J. Stewart[1], Ramallo-López, J. M.[1], Prado, R. J.[2], Marchetti, S. G.[1], Bengoa, J. F.[1], and Requejo, F. G.[1]

[1] Universidad Nacional de La Plata - La Plata Bs.As Argentina
[2] Universidade Federal de Mato Grosso - Cuiabá MT Brazil

The non-equilibrium cation site occupancy in nanosized zinc ferrites (6-13 nm) with different degree of inversion was investigated using Fe and Zn K-edge x-ray absorption spectroscopy XANES and EXAFS, and magnetic measurements. The very good agreement between experimental and ab initio calculations on the Zn K-edge XANES region clearly show the large Zn^{2+}(A)Zn^{2+}[B] transference without altering the long-range structure. We also demonstrate that the mechanical crystallization on nanocrystalline spinel causes a significant augment of the inversion. XANES spectra as a function of the spinel inversion were shown to depend on the configuration of the ligand shells surrounding the absorbing atom. Both experimental XANES spectra and their theoretical simulations confirm that Zn at the tetrahedral sites. Good agreement between theory and experiment has been obtained.

Acknowledgements
We appreciate financial support by LNLS synchrotron, Campinas - SP, Brazil (project D04B - XAFS1 4148/05); ANPCyT, Argentina (PICT03 06-17492); CONICET, Argentina (PIP 6524 and PIP 6075). We thank E. D. Cabanillas for TEM microscope operation and F. Sives for fruitful discussions.

156

Refinamento da estrutura cristalina de $Y_3Al_5O_{12}$ (YAG) obtido a partir de óxido misto de ítrio e de terras raras

Santos, C.[1], Suzuki, P. A.[2], and Souza, R. C.[1]

[1] Faculdade de Engenharia Química de Lorena - Lorena SP Brazil
[2] Escola de Engenharia de Lorena - Universidade de São Paulo - Lorena SP Brazil

A sinterização de materiais cerâmicos à base de carbeto de silício, nitreto de silício e SiAlONs é usualmente feita com a utilização de aditivos tais como: Y_2O_3, Al_2O_3 e SiO_2, num processo envolvendo o aparecimento de uma fase líquida transiente. Durante a sinterização, observa-se a formação de fases intergranulares como: Y_2SiO_5, $Y_3Al_5O_{12}$ (YAG), Y_2SiO_7, $YSiO_2N$ e $Y_2Si_3N_4O_3$. A presença da fase YAG (yttrium aluminum garnet) tende a melhorar as propriedades mecânicas dos materiais cerâmicos a temperatura ambiente e em altas temperaturas. Na síntese de cerâmicas estruturais, a substituição da ítria (Y_2O_3) pura por um óxido misto (E_2O_3) contendo óxido de ítrio e de terras raras (Yb_2O_3, Er_2O_3, Dy_2O_3 e outros) no aditivo tem sido considerada. A principal vantagem da utilização deste óxido misto, produzido a partir do minério xenotima, é a redução do custo de obtenção dos materiais cerâmicos na ordem de 70 % quando comparado com a utilização de Y_2O_3 pura. O objetivo deste projeto foi o refinamento da estrutura cristalina de $Y_3Al_5O_{12}$ (YAG) preparada a partir de Y_2O_3-Al_2O_3 e E_2O_3-Al_2O_3. As medidas foram realizadas no difratômetro Hubber da linha $XRD1-D12A$ na geometria Bragg-Bretano, com o acoplamento dos eixos ω e 2θ. Foi utilizado o cristal analisador de germânio (111) e detetor de cintilação para a coleta dos raios difratados. A energia de $10,9952$ keV $(\lambda = 1,1276\ )$ foi escolhida para diminuir os efeitos de absorção pelo Yb, presente no óxido misto. As amostras de YAG foram produzidas a partir da mistura de Al_2O_3 e Y_2O_3 (ou E_2O_3), seguido de tratamentos térmicos a 1400 e 1525 ^oC em ar. As amostras foram moídas na forma de pó, selecionando partículas com tamanhos inferiores a 50 μm. O pó foi mantido sob rotação para minimizar efeitos de orientação preferencial. A partir dos dados coletados, a estrutura cristalina de YAG e fases secundárias (quando presentes) foram refinadas pelo método de Rietveld. A baixa contribuição da largura instrumental nos difratogramas contribuiu para concluir que YAG produzido a partir de Al_2O_3 e óxido misto forma uma solução sólida. Os parâmetros estruturais (parâmetros de rede, posições atômicas) estão sendo refinados e comparados com as de YAG obtido com ítria.

Acknowledgements
Ao LNLS por possibilitar a execução do projeto $XRD1-5391/06$, ao Dr. Roosevelt Droppa Jr. pelo auxílio na condução do experimento e à FAPESP (C. Santos) pelo apoio financeiro.

157

Evaluation of precursor on the Hg,Re-1223 polycrystalline samples

J.L.Passamai Jr[1], Passos, C. A. C[1], Cruz,P.C.M[1], Orlando, M. T. D.[1], Orlando, C. G. P.[1], Corrêa, H. P. S.[2], and Martinez, L. G.[3]

[1] Universidade Federal do Espírito Santo - Vitória ES Brazil
[2] Universidade Federal do Mato Grosso do Sul - Campo Grande MS Brazil
[3] Instituto de Pesquisas Energéticas e Nucleares - São Paulo SP Brazil

Samples of $Hg_{0.82}Re_{0.18}Ba_2Ca_2Cu_3O_{8+d}$ were prepared by solid-vapour reaction technique. Firstly, preparation of the ceramic precursor typical began with a mixture of $Ba_2Ca_2Cu_3O_x$ and ReO_2 in powder form with the molar relationship 1 : 0.18. It is known that the oxygen stoichiometry may be modified and controlled through the thermal treatment. Then, the obtained precursor material was then submitted to an annealing with three different partial pressure of oxygen: 5% of O_2 and 95% of Ar (sample A), 10% of O_2 and 90% of Ar (sample B) and 15% of O_2 and 85% of Ar (sample C). X-ray powder diffraction pattern (XRD) analysis of each precursor preparation step was done in order to evaluate the oxygen content of the ceramic precursor. The identified phases were $BaCuO_{2+x}$, $Ba_2Cu_3O_{5+x}$, $Ba_4CaCu_3O_{8+x}$, Ca_2CuO_3 and $Ca_5Re_2O_{12}$. The $BaCuO_{2+x}$ phase was found 64%, 33% and 50% from the XRD spectra for sample A, B and C, respectively. The $Ba_2Cu_3O_{5+x}$ phase was found 10%, 34% and 14% for sample A, B and C, respectively. While the $Ca_5Re_2O_{12}$ phase was found 5%, 7% and 10% for sample A, B and C, respectively. On the other hand, the peaks associated with the $BaCuO_{2+x}$, $Ba_2Cu_3O_{5+x}$ phases, which has oxygen stoichiometry variation, are slightly displaced to low angles. This is an indication that there was a oxygen increment of the precursors ceramics B and C, as compared with ceramic A. Finally, the precursors prepared with different O_2 partial pressure were blended with HgO at molar relationship 1 : 0.82. XRD measurements indicated that the main phase was Hg,Re-1223 (93% Wt %), residues of $HgCaO_2$, $BaCO_3$, $CaCuO_2$ and $BaCuO_2$ were also found. The phase Hg,Re-1223 was very crystalline as shown by the small broadening of their peaks. The XRD spectra of all samples were quite similar and the cell parameters did not show important differences. These samples were also investigated by ac electrical resistivity measurements. Our results showed similar T_c (133.6, 133.9 and 133.7 K for sample A, B and C, respectively).

Acknowledgements
This work was supported by Laboratório Nacional de Luz Síncrotron. (D12A-XRD1, D06-DXAS) and CNPQ 504578/2004-9.

158

Tetragonal-to-cubic phase transition in nanostructured ZrO_2-CeO_2 solid solutions

Acuña, L. M.[1], Fábregas, I. O.[1], Lamas, D. G.[1], Fuentes, R. O.[1], Fernández de Rapp, M. E.[1], Walsoe de Reca, N. E.[1], Fantini, M. C. A.[2], Craievich AF[2], and Prado, R. J.[3]

[1] Consejo Nacional de Investigaciones Científicas y Técnicas - Buenos Aires Argentina
[2] Universidade de São Paulo - São Paulo - São Paulo SP Brazil
[3] Universidade Federal de Mato Grosso - Cuiabá MT Brazil

ZrO_2-CeO_2 ceramics are widely investigated due to their excellent mechanical and catalytical properties. Compositionally homogeneous ZrO_2-CeO_2 solid solutions exhibit 3 tetragonal forms (*P4$_2$/nmc* space group). The stable tetragonal form is called the t-form and is restricted to the solubility limit predicted by the equilibrium phase diagram. The t'-form has an expanded solubility but is unstable against the mixture of t-form and cubic phase. Finally, the t"-form has an axial ratio c/a of unity but with the oxygen atoms displaced along the c axis from their ideal sites of the cubic phase (8c sites of the *Fm3m* space group). If CeO_2 content is further increased, the cubic phase is retained. In previous works carried out at LNLS, we investigated the crystal structure and the local order at room temperature of compositionally homogenous ZrO_2-CeO_2 nanopowders synthesized by gel-combustion routes. By means of XPD, we determined the crystal structure of the solid solutions as a function of CeO_2 content and found that the tetragonal/cubic boundary is located at 85 mol% CeO_2 (D.G. Lamas et al., J. Appl. Cryst. 38 (2005) 867). In addition, EXAFS study showed that this tetragonal-cubic transition is associated to a symmetry change in the Zr-O coordination sphere, while the Ce-O one has a cubic symmetry in the whole compositional range (I.O. Fábregas et al., J. Phys.: Condens. Matter 18 (2006) 7863).

In this work, we investigated the crystal structure and the local order of compositionally In this work, we investigated the crystal structure and the local order of compositionally homogeneous, nanocrystalline ZrO_2-CeO_2 solutions by XPD and EXAFS as a function of temperature for compositions between 50 and 65 mol% CeO_2. ZrO_2-50 and 60 mol% CeO_2 solid solutions, that exhibit the t'-form of the tetragonal phase, transform into the cubic phase in two steps, t'-to-t" followed by t"-to-cubic. Differently, the ZrO_2-65 mol% CeO_2, which exhibits the t"-form, directly transforms to the cubic phase. The results suggest that t'-to-t" transition is of first order, while the t"-to-cubic one seems to be of second order.

Acknowledgements

This work was supported by LNLS, CAPES/SECyT, CNPq/CONICET, CNPq (PROSUL program), ANPCyT and CONICET.

159

Crystal structure of compositionally homogeneous, nanocrystalline ZrO_2-Sc_2O_3 powders synthesized by gel-combustion

Abdala, P. M.[1], Lamas, D. G.[1], Fernández de Rapp, M. E.[1], Walsoe de Reca, N. E.[1], Craievich AF[2], and Fantini, M. C. A.[2]

[1] Consejo Nacional de Investigaciones Científicas y Técnicas - Buenos Aires Argentina
[2] Universidade de São Paulo - São Paulo - São Paulo SP Brazil

ZrO_2-Sc_2O_3 ceramics are very important from a technological point of view because they exhibit a very high ionic conductivity and, therefore, can be used as solid electrolytes in intermediate-temperature solid-oxide fuel cells.

Compositionally homogeneous ZrO_2-based solid solutions exhibit three forms of the tetragonal phase, all belonging to the *P4₂/nmc* space group. The stable tetragonal form is called the t-form, which is restricted to the solubility limit predicted by the equilibrium phase diagram. There is also a t'-form with a wider solubility, but unstable in comparison with the mixture of the t-form and cubic phase. Finally, the t-form has an axial ratio c/a of unity, but with the oxygen atoms displaced along the c axis from their ideal sites of the cubic phase (8c sites of the *Fm3m* space group). If the dopant content is further increased, the cubic phase is retained. For ZrO_2-Sc_2O_3 solid solutions, the existence of a β -phase with a rhombohedral structure has also been reported.

In this work, we have investigated the crystal structure of nanostructured ZrO_2-Sc_2O_3 solid solutions with Sc_2O_3 contents up to 12 mol% by synchrotron X-ray powder diffraction. This study was carried out in the D10B - XPD beamline of the LNLS, operated in the high-intensity (low resolution) mode. These materials were synthesized by a nitrate-citrate gel-combustion route. The crystallite size was about 10 nm for all the compositions. The tetragonal/cubic compositional boundary was determined by following the evolution of small peaks related to the oxygen anions displacement, as a function of Sc_2O_3 content. The β -phase was not observed in this work, probably due to the high compositional homogeneity of the materials synthesized by gel-combustion and/or their small crystallite size.

Acknowledgements

This work was supported by LNLS, CAPES/SECyT, CNPq/CONICET, CNPq (PROSUL program), ANPCyT and CONICET.

160

ReO_2 as a inner pressure gauge used in X-ray Diffraction under external pressure up to 1.8 GPa

Orlando, M. T. D.[1], J.L.Passamai Jr[1], Martinez, L. G.[2], Ferreira, F. F.[3], Tamura, E.[3], Granado, E.[4], Garcia, F.[3], Melo, F. C. L.[5], and Cruz,P.C.M[1]

[1] Universidade Federal do Espírito Santo - Vitória ES Brazil
[2] Instituto de Pesquisas Energéticas e Nucleares - São Paulo SP Brazil
[3] Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil
[4] Universidade Estadual de Campinas - Campinas SP Brazil
[5] Centro Técnico Aeroespacial - São José dos Campos SP Brazil

A new B_4C anvil cell has been developed and tested by UFES, IPEN, IAE-CTA and LNLS since 2004. This pressure cell will be used to study the behavior of X-ray diffraction patterns of materials under hydrostatic pressure. In order to measure and calibrate the pressure inner the gasket hole, we have investigated the effect of the hydrostatic pressure on the monoclinic ReO_2 using X-ray diffraction and XANES under hydrostatic pressure up to 1.8 GPa. The X-ray transparency of the B_4C anvil above 9 keV has guaranteed a satisfactory signal/noise ratio. The $La_{0.85}Sr_{0.15}MnO_3$ magnetic transition and ReO_3 octahedral distortion were used as second inner pressure gauge, which were used in the XANES under hydrostatic pressure measurements.

Acknowledgements
We would like to thank CNPq Grant CT-Energ 504578/2004-9, CNPq 471536/2004-0, and CAPES for financial supports. Thanks also to Companhia Vale do Rio Doce (CVRD), Companhia Siderúgica de Tubarão (CST). We gratefully acknowledge to National Laboratory of Synchrotron Light - LNLS, Brazil (XRD1, XPD and DXAS)for providing the authors acces to its facilities.

161

Caracterização Estrutural de Nanoparticulas de TiO_2 Através das técnicas de XAS e SAXS

Mastelaro, V.R.[1], Mascarenhas, Y.P.[1], Ribeiro C.T.M.[1], Leite,E.R.[2], Vila, C.[2], Sanches M[1], and Longo, E.[3]

[1] Universidade de São Paulo - São Carlos - São Carlos SP Brazil
[2] Universidade Federal de São Carlos - São Carlos SP Brazil
[3] Universidade Estadual Paulista - Araraquara - Araraquara SP Brazil

Em geral, o crescimento de nanocristais em suspensões coloidais é associado a mecanismos de dissolução-precipitação conhecido como Ostwald-ripening. Recentemente, identificamos outro processo de crescimento baseado no choque entre partículas com ou sem rotação, denominado Oriented Attachment (OA). Este mecanismo foi identificado em óxidos semicondutores (TiO_2 e SnO_2) de grande interesse tecnológico e vem sendo apontado na literatura como o mecanismo mais provavel para promover o crescimento anisotropico de partículas, originando por exemplos nanorods ou nanofitas. Em estudos recentes, identificamos que este mecanismo modifica a cinética de transformação de fases no TiO_2. De fato, a ocorrência do AO acelera a transformação de fase, possibilitando a síntese de nanocristais de TiO_2 (fase rutilo) abaixo do tamanho crítico reportado na literatura (abaixo de 14 nm) O mecanismo de AO acelera a transformação de fase de anatase para rutilo, gerando partículas anisotrópicas (nanorods), com diâmetros de 8 a 10 nm e comprimento de 30 a 60nm. Este trabalho teve como objetivo analisar a estrutura local ao redor do átomo de titânio através da técnica de XAS e acompanhar através da técnica de SAXS o processo de crescimento e transformação de fases de partículas coloidais de TiO_2 em água, submetidas a diferentes temperaturas e tempos de tratamento hidrotermal. Serão apresentados resultados da análise do espectro XANES na borda K do átomo de titânio e da cínetica de crescimento das nanoparticulas em função do tempo de tratamento térmico obtida através da técnica de SAXS.

Acknowledgements
Este trabalho contou com o apoio financeiro da FAPESP e CNPq e do LNLS através do projeto D11A SAXS1 5285/06

162

Strain and interdiffusion of InP islands on Ga(001) studied by resonant X-ray scattering

L. N. Coelho[1], Magalhaes-Paniago, R.[1], Malachias, A.[2], Cotta, M.A.[3], Zelcovit, J.G.[3], and Iikawa, F.[3]

[1] Universidade Federal de Minas Gerais - Belo Horizonte MG Brazil
[2] Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil
[3] Universidade Estadual de Campinas - Campinas SP Brazil

Semiconductor islands or quantum dots have been intensely studied for their opto-electronic properties and the quantum confinement effects they present. X-ray scattering has proven to be a very efficient tool to probe the structural and compositional profile of the islands. By tuning the X-ray photon energy to an absorption edge of a chemical element, its composition profile along the island can be determined. Near an absorption edge, the intensity scattered by an atom is strongly dependent on the photon energy. At an atomic K edge, the atom scatters as if it had fewer electrons than it would for photon energies far from the edge. If two scans are done at the edge and below it, the contrast in intensities will be due to the presence of the chemical element corresponding to that edge. We have studied samples of InP islands grown on GaAs(001) by CBE. Three samples were grown, at T = 470°C, 500°C and 530°C. In order to determine the concentration of all four elements present in the sample, we have measured resonant X-ray scattering at 4 different energies, 10268eV, 10368eV (Gallium K-edge), 11751eV and 11871eV (Arsenic K-edge) at beamlines XRD1 and XRD2 of LNLS. All measurements were done in grazing incidence geometry to maximize the islands/substrate signal ratio. Radial scans near the GaAs(220) peak were done in all four energies to obtain contrast due to element concentration profile. The substrate peak is very intense and sharp, but the strained small islands produce a broad peak, spanning different lattice parameters present at the structure as the InP relaxes from the strained lattice parameter at the base equal to the substrate (5.65) to its bulk lattice parameter of 5.86. At different positions of the radial scan, that is, at different lattice parameter values, angular scans were done to determine the island lateral size corresponding to that lattice parameter. Associating these values of lateral size with the height profile from AFM images it was possible to determine the dependence of the lattice parameter as function of height for all samples. From this and the contrast profiles from the radial scans, concentration maps were built for all elements present in the sample.

163

A carbon supported Pt-Co (3:1) alloy as improved cathode electrocatalyst for direct ethanol fuel cells.

Lopes,T.[1], Antolini, E.[1], Colmati, F[1], and Gonzalez, E. R.[1]

Universidade de São Paulo - São Carlos - São Carlos SP Brazil

In direct alcohol fuel cells, ethanol crossover causes a less serious effect compared to that of methanol because of both its smaller permeability through the Nafion membrane and its slower electrochemical oxidation kinetics on a Pt/C cathode. The main objective in the development of direct ethanol fuel cells (DEFCs) is to find an anode catalyst with high activity for the oxidation of ethanol. However, due to the low activity of pure platinum for the oxygen reduction reaction (ORR), research on cathode electrocatalysts with improved ORR and the same or improved ethanol tolerance than that of Pt are also in progress. In this work a commercial (E-TEK) carbon supported Pt-Co (3:1) electrocatalyst was investigated as cathode material in DEFCs and the activity compared to that of a pure Pt electrocatalyst. In the cathodic potential region (0.7-0.9 V vs. RHE) Pt/C and Pt-Co/C have the same activity for the ethanol oxidation. But the performance of Pt-Co/C as cathode material in DEFCs in the temperature range 60-100 ^{0}C is better than that of Pt/C both in terms of mass activity and specific activity. This was ascribed to the improved activity of the alloy for oxygen reduction.

Acknowledgements

The authors thank. the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq, Proc. 142266/2003-5, Proc. 300477/2005-8 and Proc. 142097/2005-5), for financial assistance to the project. Thanks are also due to the Brazilian Synchrotron Light Laboratory (LNLS, Campinas, SP, Brazil), for the XRD analysis.

164

Incipient Orbital Order in Half-Metallic Ba_2FeReO_6

Azimonte, C.[1], Granado, E.[2], and Criginski, J.[3]

[1] Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil
[2] Universidade Estadual de Campinas - Campinas SP Brazil
[3] European Syncrotron Radiation Facility - Grenoble Cedex France

The overwhelming majority of studies on orbital ordering and its relationship with magnetism and crystal structures has been done in 3*d* or 4*d* oxide systems such as manganites, vanadates, and ruthenates. 5*d* elements, on the other hand, are generally non-magnetic and orbitally-inactive in the solid state, being nonetheless at the verge of magnetism. For this reason, hybridization of 5*d* electrons with 3*d* magnetic electrons of nearby ions, or even particle size effects may trigger the 5*d* magnetism. A particularly interesting case is the A_2FeReO_6 (A = Ca, Sr, Ba) double perovskites. This structure is characterized by a three-dimensional network of alternating FeO_6 and ReO_6 octahedra, with the A^{2+} ions being charge donors outside the octahedra. The Re moments are found to define a periodic ferromagnetic sublattice that is antiferromagnetically coupled to the Fe 3*d* moments. The system is half-metallic for A= Sr and Ba and the spin-polarized conduction electrons show primarily Re 5*d* character, while showing semiconducting transport behavior for A = Ca. In addition, this family has been attracting increasing interest due to the potential use in spintronics devices. A marked feature of this particular system is the presence of large magnetic anisotropy effects associated with unquenched Re 5*d* orbital magnetic moments due to strong spin-orbit coupling. Here, we investigate in detail the crystal structure and local magnetism of Ba_2FeReO_6 (BFRO) by means of T- and H-dependent high-resolution synchrotron x-ray powder diffraction (s-XPD), neutron powder diffraction (NPD), and Re and Fe $L_{2,3}$-edges x-ray magnetic circular dichroism (XMCD) experiments. Our results indicate an incipient orbital ordering transition of Re 5*d* orbitals in the metallic phase. This appears to be characteristic of the 5*d* magnetism, since the orbital degree of freedom tends to be much less pronounced, or completely quenched, in the metallic state of 3*d* or 4*d* systems.

Acknowledgements
This work was supported by FAPESP, CNPq and ABTLuS

165

Investigation of the local Re and Fe magnetic moments in Ca_2FeReO_6 double perovskite through the metal-insulator transition

Azimonte, C.[1], Granado, E.[2], Criginski, J.[3], and H.C.N.Tolentino[4]

[1] Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil
[2] Universidade Estadual de Campinas - Campinas SP Brazil
[3] European Syncrotron Radiation Facility - Grenoble Cedex France
[4] Centre National de la Recherche Scientifique - Paris cedex 16 France

The local ferromagnetic (FM) moments of the Re and Fe ions in Ca_2FeReO_6 double perovskites were investigated by means of x-ray magnetic circular dichroism (XMCD) spectroscopy at the Fe and Re $L_{2,3}$ edges. A large orbital moment was detected for the Re ions (m_L/m_s=0.3μ_B), in contrast to the spin-only moment of Fe ion indicating an unquenched orbital magnetic moments for Re. The Re FM moments decrease significantly in the insulating phase ($T < T_{MI} \sim 150$ K) with respect to the metallic one ($T > T_{MI}$).This is interpreted in terms of a canting of the ferrimagnetic structure below T_{MI}. Based on these results, this system is suggested to be on the border of a magnetically-driven transition, in which the following ground states would compete through a first-order transition: (i) a phase with collinear Fe and Re spins that facilitates carrier hopping between neighboring transition-metal sites (half-metal), and (ii) a state with non-collinear Re spins and a reduced Re 5*d* bandwidth (Mott insulator) that satisfies crystal-field and spin-orbit interactions for the Re ions in monoclinic double perovskite structure.

Acknowledgements
This work was supported by FAPESP, CNPq and ABTLuS

166

SAXS and EXAFS Studies of Ordered Mesoporous Silica

Fantini, M. C. A.[1], Martins, T. S.[1], Cides Silva L.C.[1], and Matos, J. R.[1]

Universidade de São Paulo - São Paulo - São Paulo SP Brazil

Ordered mesoporous silica has been developed for different applications, ranging from adsorbent, catalyzer and luminescent material. The LNLS D11A-SAXS1 and D04B-XAFS1 beamlines were used to investigate the meso-pores long range order and local atomic arrangement of incorporated elements (Fe, Ce and Eu) in the silica walls. Cubic FDU-1 samples, heat treated in microwave, were studied by SAXS. A factorial planning was performed in order to check the dependence on the heat treatment temperature and acid concentration (HCl) on the structural properties of the mesopores. Also, iron was incorporated during the synthesis of cubic FDU-1 and the SAXS data revealed a better ordering, which depends on the amount of iron inside the silica network. The formation of iron oxide is confirmed by XANES and EXAFS analysis. The catalytic behavior of these samples was also checked. In order to improve the stability of lanthanide compounds of Eu and Ce, this work also developed and analyzed the encapsulation of these compounds in ordered mesoporous silica. SAXS and EXAFS measurements were used to characterize the samples. The aim of this research was to check the influence of the lanthanide complex on the pores ordering and to analyze the coordination of different Eu and Ce complexes encapsulated into cubic mesoporous silica FDU-1 and, Ce into hexagonal (MCM-41) phase.

Acknowledgements
Thanks are due to CNPq and FAPESP for supporting this research.

167

Study of the structural properties of the PECVD SiO_xN_y dielectric layers obtained with different RF powers by XANES and EXAFS analysis

Albertin, K.F.[1], Criado, D.[1], Fantini, M. C. A.[1], and I. Pereyra[1]

Universidade de São Paulo - São Paulo - São Paulo SP Brazil

Research is now directed to the substitution of SiO_2 by high - k materials making possible the use of thicker films. An alternative material, in spite of its relatively low dielectric constant (4 to 7), is SiO_xN_y because it is totally compatible with the silicon MOS technology and has some improved properties, such as enhanced resistance to high field stress, enhanced hot carrier immunity, resistance against boron penetration, higher dielectric strength and higher dielectric constant, over conventional SiO_2. In previous works we demonstrated the possibility of producing higher dielectric constant SiO_xN_y films with good interface state density with silicon, comparable to those of thermally grown SiO_2 and SiO_xN_y. Some these films were deposited from SiH_4, N_2O and He mixtures, at 120 mTorr, the inert gas is added to the gaseous mixture in order to prevent gas phase reactions and to obtain films with good structural and electrical properties. However, the effective charge density for these films is worst than the obtained for thermally grown SiO_2 films. This result was attributed to the high RF power utilized, which generates many ions that can be incorporated, as fixed charge, in the films. In this work, we fabricate and characterize SiO_xN_y films deposited from SiH_4, N_2O and He mixtures, with 120 mTorr at different RF powers (50,100 and 200 Watts). These films are characterized by Fourier Transformed Infrared Spectroscopy (FTIR), Rutherford Backscattering Spectroscopy (RBS), X-Ray Absorption Near-Edge Structure at the N-K and Si-K Edges (XANES) and EXAFS (Extended X-Ray Absorption Fine Structure) at the Si-K Edge. In order to approach the electrical characteristics (interface state density and effective charge density), MOS capacitors fabricated using these films as gate dielectric, are characterized.

Acknowledgements

Thanks are due to CNPq and FAPESP for supporting this research.

168

Structural Instabilities at the Ferroelectric Transition of Multiferroic $BiMn_2O_5$

Eleotério, M.[1], Granado, E.[2], and García-Flores, A.F[2]

[1] Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil
[2] Universidade Estadual de Campinas - Campinas SP Brazil

Multiferroics, also termed magnetoelectrics, are materials where (anti)ferromagnetism and (anti)ferroelectricity coexist. Such rare effect attracts steady attention due to the interesting physics involved as well as relevant potential applications in devices with new functionalities. In multiferroics, a coupling between magnetic and electric properties may in principle occur, leading to concrete possibilities of realizing the long-sought control of the electric polarization by a magnetic field or vice-versa. Among other interesting systems, promising candidates for this purpose may be found within the RMn_2O_5 family ($R =$ rare earth, Y or Bi), which are isostructural insulators. Members of this family undergo a ferroelectric transition at (or slightly below) the antiferromagnetic (AFM) transition temperature for the Mn spin sublattice, $T_N = 39 - 45$ K.

A detailed understanding of the multiferroic properties of the RMn_2O_5 family is challenged by the complex crystal and magnetic structures. In fact, $Mn^{4+}O_6$ octahedra form edge-sharing infinite linear chains along the z direction, while $Mn^{3+}O_5$ square pyramids interconnect the $Mn^{4+}O_6$ octahedra. The magnetic structures depend strongly on R and T. It was suggested that the lattice geometry causes an inherent magnetic frustration in the system, which is lifted by small shifts of the Mn^{3+} cations. This would lead to a canted antiferroelectric phase that would be strongly coupled to the magnetic structure, providing a hint for the strong magnetoelectric coupling in this system. Nonetheless, despite extensive efforts in this direction, the structural distortion associated with the ferroelectric phase was never observed by diffraction techniques, preventing a detailed knowledge of the origin of this phase.

In this work, we performed high-resolution synchrotron x-ray powder diffraction of $BiMn_2O_5$ in the XPD beamline of LNLS. A flat-plate geometry using photon energies of 9 keV, a Ge(111) analyser crystal, and a closed-cycle He cryostat was employed. We found that, for temperatures below $T_N \sim 40$ K, coexistence of two or more phases, with the same *Pbam* space group but slightly different lattice parameters, starts to take place, suggesting the formation of ferroelectric domains. This would be the first reported structural manifestation of the ferroelectric phase in this family of materials.

Acknowledgements
This work was supported by Fapesp and CNPq.

169

Metallic Au nanoparticles embedded in electrochromic hydrated NiO matrix

Ferreira, F. F.[1] and Avendano, E.[1]

Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil

Electrochromic materials show a reversible optical modulation in a wide range of wavelengths that goes from ultraviolet to infrared, when, by means of an external applied electric field, ions are electrochemically intercalated. Nanoparticles (NP's) embedded in electrochromic matrices have attracted the attention of the scientific community due to the possibility of combining the optical modulation of the matrix together with the selective absorption of the metallic NP's embedded on it. Preliminary results on the coloration mechanism of NiO-Au have been studied with the aim of understanding the correlation between Au and NiO geometric and electronic structures in different intercalation states. Samples were grown by reactive DC sputtering in a multilayer system of NiO-Au. Some samples were post annealed using a Rapid Thermal Annealing (RTA) system prior cycling in a 0.1 M KOH solution and compared with others without heat treatment. The HRTEM images had shown a nanostructured material consisting of fcc gold NP's embedded in an also fcc hydrated NiO matrix. EXAFS measurements on the Ni K edge had shown a small decrease in the Ni-Ni interatomic distance and an increase of the structural disorder due to the incorporation of gold as NP's in the matrix. Analyses on the Au L_{III} edge revealed a mixture of metallic and oxidized gold, the latter is presumed to be located in the surface of the NP's. The presence of gold oxide slightly increases upon de-intercalation of the films that is consistence with the electrochemical response of the films. Finally, optical characterization shown the predicted absorption band around 550 nm wavelength calculated using the Maxwell Garnett's effective medium theory.

Keywords: Electrochromic, nickel oxide, metallic gold nanoparticles, synchrotron radiation, sputtering

Acknowledgements

We are grateful to the LNLS for beamtime to realize the experiments, the LME-LNLS, LMF-LNLS and the Solid State Physics Department at the Uppsala University, Sweden through The Angstrom Laboratory, for the support in the characterizations.

170

EXAFS-cumulant study of nanoparticles: differentiating real thermodynamics from artifacts.

Caruso M.G.[1], Giovanetti, L.[1], Ramallo-López, J. M.[1], and Requejo, F. G.[1]

Universidad Nacional de La Plata - La Plata Bs.As Argentina

The standard treatment of the thermal disorder in EXAFS trough the harmonic Debye-Waller factor $exp^{-2k^2\sigma^2}$ has become inadequate with respect to the increasing accuracy of experimental data and analysis techniques. Recent works have shown that enharmonic effect can not be neglected even in the case of bulk material like Ge[1] when trying to obtain structural information as a function of temperature. In the case of nanoparticles, the effects of not including the third order cumulant in the analysis routine, gives a non physical distance contraction in metallic system when increasing the temperature. In this work Pt nanoparticles (NP) of about 2-3 nm were synthesized by seeded growth and direct ethylene glycol reduction methods and stabilized with poly-(vinylpyrrolidone) (PVP). EXAFS experiments were performed at seven different temperatures to investigate the thermal behavior of these nanoparticles. We shown the different trend observed when the third order cumulants in the interatomic distance is introduced. To correlate the distance distribution moments with temperature we parameterize the near-neighbor interaction in our material as a one-dimensional enharmonic potential in interatomic distances[2].

Referências

1. G. Dalba, P. Fornasini, M. Grazioli and F. Rocca Phys Rev B 52 11034 (1995).
2. Edward A. Stern, et. al Phys Rev B 43 8850 (1991).

Acknowledgements

We would like to acknowledge the financial support received from projects PICT 06-17492 (ANPCyT, Argentina), PIP 6075 (CONICET, Argentina), CIAM collaborative project (CONICET, NSF and CNPQ), D04B - XAS1 - 4246/05, D11A - SAXS1 - 4719/05 (LNLS, Brazil), Lawrence Berkeley Nationanal Laboratory Materials Science Division, the University of California,Berkeley and the Swiss National Science foundation.

171

Magnetic structure and enhanced T_N of the $TbRhIn_5$ antiferromagnet

R. Lora-Serrano[1], Giles, C.[1], Granado, E.[1], D. J. Garcia[1], and Pagliuso, P.G.[1]

Universidade Estadual de Campinas - Campinas SP Brazil

In this work the physical properties of the intermetallic compound $TbRhIn_5$ were investigated by means of temperature dependent magnetic susceptibility, electrical resistivity, heat-capacity and resonant x-ray magnetic diffraction experiments. $TbRhIn_5$ is an intermetallic compound that orders antiferromagnetically at T_N = 45.5 K, the highest ordering temperature among the existing $RRhIn_5$ (1-1-5, R = rare earth) materials, which in in contrast to what is expected from a de Gennes scaling along the $RRhIn_5$ series. The X-ray resonant diffraction data have allowed us to solve the magnetic structure of $TbRhIn_5$. Below T_N, we found a commensurate antiferromagnetic (AFM) structure with a propagation vector ($\frac{1}{2}$ 0 $\frac{1}{2}$) and the Tb moments oriented along the *c*-axis. Strong (over two order of magnitude) dipolar enhancements of the magnetic Bragg peaks were observed at both Tb absorption edges L_{II} and L_{III}, indicating a fairly high polarization of the Tb 5*d* levels. Using a mean field model including anisotropic first-neighbors exchange interaction, J_{R-R} (R= Rare Earth), and the tetragonal crystalline electrical field (CEF), we evaluate the influence of the CEF effects in the physical properties of $TbRhIn_5$. The results reported here seems to corroborate to a general trend of CEF driven effects on T_N along the $RRhIn_5$ series.[1]

[1] R. Lora-Serrano *et al*. Acepted to be published in Phys. Rev. B. Cond-Mat/0602612.

Acknowledgements

This work was supported by FAPESP (SP-Brazil) Grants No. 03/09861-7, 04/08798-2, 05/00962-0, 00/08649-6 and CNPq(Brazil) Grants No. 140613/2002-1, 307668/03, 04/08798-2 and 304466/20003-4. LNLS at Campinas is also acknowledged for beamtime at XRD2 beamline.

172

Electrical conductivity and X- ray diffraction studies of $(Ba_xR_{1-x})_2In_2O_{5-\delta}$ Solid Solutions.

Rey, J. F. Q.[1], Ferreira, F. F.[1], and Muccillo, E. N. S.[2]

[1] Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil
[2] Instituto de Pesquisas Energéticas e Nucleares - São Paulo SP Brazil

$(Ba_xR_{1-x})_2In_2O_{5+\delta}$ (x=0, 0.01, 0.1, 0.15 ; R= Gd and Er) mixed oxides were synthesized by the solid state reaction method. The crystalline structure of powdered materials was studied by X-ray Diffraction (XRD), and the electrical conductivity was used to determine phase transition temperatures of sintered specimens. The phase assemblage in sintered specimens was determined by Rietveld refinement of high-intensity X-ray diffraction patterns. Electrical conductivity results evidenced a dependence of the phase transition temperature with the type and the amount of additive. The specimen with x=0.001 of Er shows the lowest phase transition temperature along with higher electrical conductivity. For x=0.25 of Er or Gd different crystalline structures and high electrical conductivity values at lowest temperatures were observed.

Acknowledgements
FAPESP, CNPq and LNLS

173

Influência da Morfologia na Fotoluminescência de Filmes de Polifluorenos

Faria, G. C.[1], Plivelic T.S.[2], Mantovani, GL[1], Torriani, I.[2], Atvars, T.D.Z.[3], Bonagamba, T. J.[1], and deAzevedo, ER[1]

[1] Universidade de São Paulo - São Carlos - São Carlos SP Brazil
[2] Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil
[3] Universidade Estadual de Campinas - Campinas SP Brazil

Diodos poliméricos emissores de luz PLED's (do inglês Polymer lighting emitting diodes) apresentam diversas vantagens frente aos diodos inorgânicos convencionais como : flexibilidade, simplicidade na deposição do filme, baixo custo de produção, entre outros. Entretanto, eles também apresentam uma desvantagem no que se refere à sua estabilidade. Sabe-se que em contato com oxigênio, luz excessiva e/ou em ambientes com temperatura relativamente elevada o polímero sofre alterações em sua morfologia, podendo implicar na mudança ou perda de suas características desejáveis (propriedades óticas e elétricas). Esses processos são, freqüentemente, abordados na literatura, entretanto é um consenso que não são completamente compreendidos. Na realidade, o que se procura entender é a influência de mudanças morfológico-estruturais nas propriedades de emissividade. Neste contexto, procuramos realizar este estudo na tentativa de elucidar aspectos desta correlação. No Laboratório Nacional de Luz Sincrotron (LNLS), realizamos medidas de Wide Angle X-ray Scattering (WAXS) em diversas temperaturas em filmes derivados de Polifluorenos. Com isso, pudemos acompanhar a evolução da mudança de morfologia para as temperaturas estudadas. Paralelamente, realizamos estudos da fotoluminescência para cada uma das temperaturas utilizadas na coleta de dados de WAXS. Realizou-se também medidas de DMTA (do inglês Dynamical Mechanics Thermal Analysis). Esta técnica possibilita a determinação das temperaturas das relaxações dos filmes (relaxação beta é relacionada ao início dos movimentos das cadeias laterais; e relaxação alfa é relacionada aos movimentos da cadeia principal). Os resultados revelaram a formação de agregados moleculares em todos os filmes. Observou-se também que o empacotamento das cadeias que formam esses agregados varia com a temperatura, sendo esta variação éespecífica para cada tipo de polímero. Tal variação no empacotamento molecular foi associada com as mudanças observadas na fotoluminescência dos filmes como função da temperatura.

Acknowledgements
Este trabalho é financiado pela FAPESP e pelo IMMP.

174

MORPHOLOGY AND DYNAMICS EVOLUTION UPON ANNEALING OF MEH-PPV FILMS

Souza,A.A.[1], Plivelic T.S.[2], R. F. Cossiello[3], deAzevedo, ER[1], Mantovani, GL[1], Atvars, T.D.Z.[3], Torriani, I.[2], and Bonagamba, T. J.[1]

[1] Universidade de São Paulo - São Carlos - São Carlos SP Brazil
[2] Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil
[3] Universidade Estadual de Campinas - Campinas SP Brazil

The objective of this work was to investigate the influence of the solvent, temperature and one specific annealing process on the microstructure and morphology of poly[2-methoxy-5-(2´-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) films cast from chloroform and toluene, using Wide-Angle X-ray Scattering (WAXS), Nuclear Magnetic Resonance (NMR) and Fluorescence Spectroscopy (PL). The annealing was done at 363 K for 12 hours under dynamic vacuum. The NMR results showed that the dynamics of side-chains in MEH-PPV films tend to be less hindered in films cast from toluene than in chloroform, which suggested looser side-chain packing in former case. This was attributed to the differences in the polarity and vapor pressure of these two solvents. Besides, it was also showed that these differences tend to disappear when the films are annealed, proving that the distinct dynamics is indeed due to solvent memory effects. Corroborating the NMR measurements, WAXS results showed presence of molecular aggregation and suggested that in films cast from chloroform the aggregate structures tend to be such that the side-chains are more organized, contributing to the increase of the in plane distance between adjacent chains. From de WAXS curves, it is possible to calculate parameters associated with an idealized orthorhombic unit cell, with the characteristic cell parameters: *a* (distance between two aggregation planes), *b* (distance between two backbones) and *c* (distance between two phenyl rings inside the same macromolecule). The *b* parameter tends to increase with the annealing process, indicating that the aliphatic side-chains are more organized in that condition, while the *a* and *c* parameters do not show significant differences. The photoluminescence measurement indicates that the emitting backbone chains in films cast from toluene exhibit a more planar configuration, producing narrower PL lines. In fact, chloroform solvates side-chains, extending it and impeding an efficient packing of the backbone. On the other hand, toluene prefers to solvate backbones, what facilities the planarity among the phenylene-vinylene rings, producing a loosely packing in the side-chain, and so shifting the spectrum to red edge.

Acknowledgements
LNLS (D11A - SAXS1 4247), FAPESP, CNPq, CAPES and IMMP.

175

Study of Pure and Ba-doped L-Histidine Hydrochloride Monohydrate by Synchrotron Radiation Renninger Scan

de Menezes, A. S.[1], dos Santos, A. O.[1], Almeida, J. M. A.[2], C. M. R. Remedios[3], and Cardoso, L.P.[1]

[1] Universidade Estadual de Campinas - Campinas SP Brazil
[2] Universidade Federal do Ceará - Fortaleza CE Brazil
[3] Universidade Federal do Pará - Belém PA Brazil

The L-Histidine Hydrochloride Monohydrate crystallizes in the orthorhombic structure with 4 molecules for cell, space group $P2_12_12_1$ and cell parameters determined by Rietveld refinement method (Rwp= 8.88%) for powder samples as a= 15.312(5) , b= 8.929(3) e c= 6.852(2) in good agreement with the literature [J. Donohue et al., Acta Crystallogr., 9,655 (1956)]. Also, Ba^{2+} doped (2% in weight) powder samples were prepared and characterized by Rietveld method (10.86%) providing the unit cell parameters a= 15.298(2) , b= 8.921(1) and c= 6.846(1) . In this work, x-ray multiple diffraction technique was applied to determine the lattice parameters of pure and doped $L-Histidine.HCl.H_2O$. In this technique a set of crystallographic planes, normally parallel to the crystal surface, called primary planes (h_p, k_p, l_p), are aligned to diffract the incident beam. By rotation ϕ around the primary reciprocal vector, several other planes (h_s, k_s, l_s), called secondary, with arbitrary orientation inside the crystal also diffract simultaneously with the primary reflection. The intensity interaction between the primary and the several secondary reflections is established through the so-called coupling reflection $(h_p - h_s, k_p - k_s, l_p - l_s)$. The $I_{(primary)}$ versus ϕ plot is the Renninger scan (RS) that presents 2n mirrors of symmetry throughout the pattern coming from the n-fold symmetry of the chosen primary vector and the two diffraction conditions represented by the entrance and exit of the secondary reciprocal lattice point on the Ewald sphere under rotation. RS presents enough sensitivity to detect small deformations in the crystal lattice which cause symmetry changes in the RS. The RS were performed at LNLS (XRD1 station), using the (10 0 0) and (0 0 4) primary reflection for pure and Ba^{2+} doped $L-Histidine.HCl.H_2O$ crystals, respectively. Regions around the ϕ= 0^o and 90^o symmetry mirrors were carefully measured for both allowing to determine the lattice parameters that agree with the Rietveld obtained values.

Acknowledgements

The authors thank the Brazilian Agencies CNPq, CAPES and the support from the Laboratório Nacional de Luz Síncrotron (LNLS).

176

Crescimento e caracterização de cristais mistos da família do sal de Tutton

C. J. Franco[1]

Universidade Federal de Ouro Preto - Ouro Preto MG Brazil

Cristais da família crsialográfica do sal de Tutton A2B(XO4)2.6H2O, A=K, NH4, Rb, Cs, Tl, B=Mg, Mn, Fe, Co, Ni, Cu, Zn, Cd, V, Cr, X=S e Se têm sido investigados por diversas técnicas experimentais com o objetivo de se compreender suas propriedades físicas e potenciais aplicações tecnológicas. Medidas térmicas mostraram que eles fundem mais ou menos incongruentemente. Investigações sobre o comportamento estrutural têm sido realizadas por difração de raios X e difração de nêutrons com o objetivo de se compreender suas propriedades estruturais, principalmente a distorção Jahn-Teller presentes nos cristais com cromo e cobre. Esta distorção surge quando um elétron desemparelhado, e ou eg, de metal de transição provoca um alongamento ou uma contração de um ou mais dos eixos principais da camada de coordenação. Soluções sólidas destes sais na forma A(1)2xA(2)2(1-x)B(SO4)2.6H2O, A2B(1)xB(2)(1-x)(SO4)2.6H2O, têm sido relativamente pouco investigadas embora possam apresentar distorção Jahn-Teller. Eletrodos negativos para pilhas de estado sólido foram elaborados com mistura de zinco e (NH4)2Zn(SO4)2.6H2O e, demonstrou ser mais eficientes que outros condutores protônicos. A estrutura dos cristais desta série á temperatura ambiente é monoclínica, grupo espacial P22/a com duas moléculas por célula unitária. Os dois íons B estão circundados por seis moléculas de água formando um octaedro que quando distorcido origina a distorção Jahn-Teller. Bons monocristais dos compostos mistos (NH4)2Ni(1-x)Cox(SO4)2.6H2O, K2Ni(1-x)Cox(SO4)2.6H2O, (NH4)2K2(1-x)Znx(SO4)2.6H2O (NH4)2Ni(1-x)Cux(SO4)2.6H2O já foram obtidos pelo método de evaporação isotérmica. A análise de difração de raios x em duas séries mostra que existem grupos de linhas sensíveis a mudança da composição, e que devem estar associadas à formação de um ordenamento cristalográfico com grupo espacial diferente dos compostos puros. Medidas de TG permitem analisar a decomposição dos sais até entre temperatura ambiente e 600°C, sendo proposto um mecanismo de decomposição nesta faixa de temperatura. Medidas de DSC permitiram determinar a temperatura de fusão dos sais sendo que para os sais puros estão de acordo com dados da literatura. Para algumas composições foram feitas medidas desde -150 °C sendo observado picos que sugerem transições de fases estruturais. Para Co=0,7 observa-se um pronunciado pico exotérmico entre 200 °C e 400 °C.

Acknowledgements
CNPq, FAPEMIG, UFOP.

177

Study of the magnetic phase coexistence in manganites

Cerro, M.[1], Garcia, F.[1], A. M. Gomes[2], Ghivelder, L.[2], R. M. Fernandes[3], and Westfahl Jr., H.[1]

[1] Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil
[2] Universidade Federal do Rio de Janeiro - Rio de Janeiro RJ Brazil
[3] Universidade Estadual de Campinas - Campinas SP Brazil

The colossal magnetoresistance in the manganites has attracted considerable attention from researchers. The explanation of this effect is related with coexistence between a metallic ferromagnetic and insulate anti-ferromagnetic phases. However, some fundamental questions about the phase segregation are still without satisfactory responses, such as, the phases stability and the microscopic interfaces structure between the phases [1]. Another phenomenon that has attracting great interest is the Exchange Bias (EB) [2]. Its main macroscopic manifestation is the unidirectional magnetic anisotropy observed in field cooling hysteresis loops, which is closely related to the interfacial magnetic coupling through the FM/AFM interface. Therefore, this effect could be a very powerful tool to better understanding of the nature phase coexistence in the manganites, specially, the interfacial microscopic configuration. We did a systematic magnetic study in the $Pr_{1-x}Ca_xMnO_3$ series with $0.3 < x < 0.4$, which exhibit FM-AFM phases coexistence. In these samples, as a consequence of phase separation, below the Néel temperature, field cooling (FC) loops are shifted towards negative fields, evidencing an exchange biasing mechanism. In contrast with conventional EB systems where the shift decrease as the temperature increase [1], this system shows a combined oscillatory-decreasing behavior. In order to reveal the Pr participation in this phenomenon, XMCD measurements at the Pr $L_{2,3}$ edges were performed in transmission mode, at Brazilian Synchrotron Radiation Laboratory at the D06A-DXAS beamline [3]. The Pr magnetic moment behavior with temperature was different from that observed in the EB behavior, evidencing the no responsibility of the Pr magnetic moment in the results previously obtained.

[1] Daggoto, E., Hotta, T. and Moreo, A. Phys. Rep. 344, 1 (2001) [2] Kiwi. M. Jour. Mag. Mag. Mat. 234, 584 (2001) [3] Funk, T., Deb, A., George, S.J., Wang, H and Cramer, S. Coord. Chem. Rev. 249, 3(2005)

Acknowledgements
This work was supporte by CNPq and ABTLus.

178

Tuning of the Magnetic Anisotropy using Nanomagnetic Caps.

E. De Biasi[1], Medeiros Soares, M.[2], L. N. Coelho[3], M. Cougo dos Santos[4], Knobel, M.[5], Sampaio, L. C.[6], Pimentel, V. L.[2], and Garcia, F.[2]

[1] Centro Atômico de Bariloche - La Plata AC Argentina
[2] Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil
[3] Universidade Federal de Minas Gerais - Belo Horizonte MG Brazil
[4] Universidade Federal do Rio Grande do Sul - Porto Alegre RS Brazil
[5] Universidade Estadual de Campinas - Campinas SP Brazil
[6] Centro Brasileiro de Pesquisas Físicas - Rio de Janeiro RJ Brazil

In a recent work, Albrecht et al. have shown that is possible to tune an out plane arbitrary magnetic anisotropy axis of particular magnetic nano-structure system simply by varying the deposition angle. In the present work, we have carried out a systematic study of the influence of the depositing condition, and the intrinsic anisotropy of the capped film (eg. the anisotropy of the flat film) on the magnetic properties of the auto-organized array of the different sizes latex nano-spheres (50, 200, 500 and 1000 nm). The samples were deposited by dc sputtering machine in two different conditions: the first is with a planetary substrate movement, that stands a well homogeneity of the deposited film; and the second way is in perpendicular deposition. The choused deposited films it were [Co(0.4)/Pd(1nm)]x6 that present a very strong perpendicular anisotropy, [Co(0.8)/Pd(1nm)]x6 that present an insipient perpendicular anisotropy, and Co and Py single layers that present a well defined in plane anisotropy and a isotropic behavior respectively. Theses samples have been analyzed by means of the MOKE, Extraordinary Hall Effect, Scanning Electronic Microscopy, AFM, MFM, SQUID and for to get a better understanding of the micromagnetic behavior of the sping configurations, we performed some simulations. From the magnetic characterization, we have observed the increase of the effective perpendicular anisotropy in the samples [Co(0.8)/Pd(1nm)] as well the sphere size decrease. Two regimens were observed, in the greater spheres there are two regions (domains) that contributed to the planar and perpendicular anisotropies characteristics, however the smaller caps shows one defined perpendicular anisotropy behavior. The interpretation of these anomalous behaviors it was based in the vortex formation, originated by the competition of the magnetostatic and exchange interaction in a particular morphology. This interpretation is corroborated by MFM images and the micromagnetics simulations.

Acknowledgements

We acknowledge the support provided by CNPq (proyect 555216/05), FAPESP, CAPES/SECYT, and LNLS facilities, groups MTA and LME.

Parte XI

Superfícies, Interfaces e Nanossistemas

179

Formation and growth of nanoparticles embedded in a matrix

Sasaki, J.M.[1], Meneses, C. T.[1], and W.H. Flores[2]

[1] Universidade Federal do Ceará- Fortaleza CE Brazil
[2] Universidade Federal do Pampa - Bagé RS Brazil

Nanostructures display many properties which are very exciting from both fundamental and technological points of view. Novel properties arise from the large surface to volume ratio, which leads to new materials and devices. During the past decade, significant progress has been made in preparing nanostructures systems using numerous physical and chemical methods. However, more recently, many studies have been dedicated to bio-inspired methods. In order to manipulate them easily it is required a matrix. In this context, the main goal is to create both new materials and methods of production with specific properties and original behavior. Recently we have reported that pyrolysis of metal/gelatin system yields metal oxide nanoparticles embedded in a carbon matrix. In this process, the gelatin framework is used as a template to disperse the metallic ions. In this work the structural features and the mechanism of formation of NiO nanostructured embedded in a carbon matrix are studied by X-ray absorption spectroscopy (XAS). Besides, Ni K-edge XAS provide information about the structure of the Ni at gelatin framework.

180

In situ X-ray diffraction study of the crystallization of NiO nanoparticle

Meneses, C. T.[1], W.H. Flores[2], and Sasaki, J.M.[1]

[1] Universidade Federal do Ceará - Fortaleza CE Brazil
[2] Universidade Federal do Pampa - Bagé RS Brazil

Nickel oxide has attracted attention of researchers due to its applications, when sizes of the particles are reduced, such as catalysis [1], electrochromic films [2] and others. Large magnetic moments have been observed in NiO nanoparticles and was theoretically explained by multi-sublattice model [3]. Several methods of synthesis have been used to obtain NiO nanoparticles, most of them is sol-gel, which use organometallic precursor, relatively expensive when is compared to others methods. Recently, we have developed a new method using organic precursor and metallic salts to obtain nanoparticles of metallic oxides [4,5]. In this work, we show a new procedure to obtain NiO nanoparticles in which the gelatine, as organic precursor, is used. This procedure consists in mixing controlled of the aqueous solution of gelatine and salts. The xerogels were pre-treated at 300^{o}C for 1 hour (puff state). The XRPD patterns at high temperature were recorded by the use of an image-plate detector in reflection geometry. For such experiments, the samples were heated using two heating rates (5 ^{o}C/min and 10 ^{o}C/min) and the temperature was kept constant in the isothermal at 500^{o}C for 1 hour. These results revealed a sequence of phase transformation during the heat treatment, starting from amorphous to NiO crystalline phase, and confirm the capability of both techniques to follow the early stage of crystallization of NiO nanoparticles. As a result, the particle growth is dependent of carbon matrix concentration, which is produced during the calcinations and act as barrier. High resolution SEM micrographs will be showed for some particles obtained by this method.

References

[1] A. M. Turky, Applied Catalysis A: General, 83-93, 247(1) (2003).

[2] F. F. Ferreira, M. H. Tabacniks, M. C. A. Fantini, I. C. Faria and A. Gorenstein, Solid State Ionics, 971-976, 86-88(2) (1996).

[3] R. H. Kodama, S. A. Makhlouf and A. E. Berkowitz, Physical Review Letters, 1393-1396, 79(7) (1997).

[4] C. T. Meneses, W. H. Flores and J. M. Sasaki, Journal of Nanoparticle Research, Aceito (2006).

[5] M. A. Macedo and J. M. Sasaki, Brazillian Patent PI 0203876-5/BR, (2002).

Acknowledgements

This work was supported by CNPq (projects 470939/2003-6, 308358/2004-0 and 141074/2003-5) (Brazilian funding agency) and LNLS.

181

Effects of the thermal treatments in the formation of NiO nanoparticles

Meneses, C. T.[1], W.H. Flores[2], and Sasaki, J.M.[1]

[1] Universidade Federal do Ceará - Fortaleza CE Brazil
[2] Universidade Federal do Pampa - Bagé RS Brazil

In last years the technique of X-ray absorption near edge spectroscopy (XANES) has been used for characterization in materials nanosize, mainly in studies of catalytic materials. X-ray absorption can also find out the mechanism that provides the formation of nanoparticles. Using a set of samples (precursors of the nanoparticles) prepared by a new method [1], the kinetic of formation of NiO nanoparticles was investigated. The oxidation of this material change its structure initial (amorphous) forming NiO nanoparticles. The results were obtained in real time from dispersive X-ray absorption spectroscopy (DXAS) in the region XANES in the Ni K edge using the DXAS beamline of LNLS and a lamp furnace [2]. We have observed in the experiment the changes in the absorption profile, which allows us to see the beginning of NiO particle. The effects of different heating rate (5, 10 and 20^{o}C) also were studied. These studies provide new insight in the production of nanoparticle by hydrothermal technique, which will be useful for improving the particle size control in the process. We demonstrated that the heating rate in the obtaining nanoparticles is also very important in the process.

References:

[1] C.T. Meneses, W.H.Flores, J.M .Sasaki, Journal of Nanoparticle Research, Aceito (2006).

[2] C.T. Meneses, W.H.Flores, A. P. Sotero, E. Tamura, F. Garcia, J.M .Sasaki, Journal of Synchrotron Radiation, Aceito (2006).

Acknowledgements

LNLS and CNPq

182

Ultra-thin Films of Nickel Deposited on Pd(111): a XPS, LEED, and XPD Study

Carazzolle M.F.[1], Maluf, S.S.[2], de Siervo A.[3], Nascente, P. A. P.[2], Landers R[1], and Kleiman, G.G.[1]

[1] Universidade Estadual de Campinas - Campinas SP Brazil
[2] Universidade Federal de São Carlos - São Carlos SP Brazil
[3] Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil

In the past decade ultra-thin films of transition metals deposited on single crystal metal substrates have been investigated due to their interesting catalytic, electronic, electrochemical, and magnetic properties. The interfacial interactions between the two metals can lead to preferential surface orientations, surface relaxation, surface reconstruction, order/disordered effects, and surface alloying. A better understanding of bimetallic compounds is important for designing new devices that could be employed by the industry. Ni-Pd presents a complete solid solution in the bulk, but significant Pd surface enrichment was found in polycrystalline bulk alloys, alloy films, and single crystal alloys. In this work, we report on the surface composition and structure of nickel ultra-thin films deposited on Pd(111). The films were evaporated in ultra-high vacuum and were characterized by characterized by XPS, LEED, XPD. Up to 3 ML coverage, it is observed a LEED (1x1) pattern with a diffuse background due to the random distribution of Ni atoms on the surface. After annealing at 600C the background reduced drastically and sharp (1x1) spots were observed on the screen, but XPS showed a complete depletion of nickel on the surface, indicating that Ni diffused into the Pd bulk. Annealing at 300C for 30 minutes yielded also a sharp (1x1) LEED pattern, and the Ni/Pd rate obtained by XPS showed a decrease with annealing time. The comparison between experimental and theoretical XPD results indicated that the surface was partially covered by Ni islands and partially formed by random Ni-Pd surface alloy.

Acknowledgements
This work was supported by the Brazilian Synchrotron Light Source (LNLS) under proposal D08A-SGM 2195/03. Grants and scholarships from FAPESP and CNPq are gratefully acknowledged.

183

In situ studies of Pt and PtPd nanoparticles under reaction with sulfur by XAS

Bernardi, F.[1], Alves, M.C.M.[1], C.W. Scheeren[1], Dupont, J.[1], and Morais, J.[1]

Universidade Federal do Rio Grande do Sul - Porto Alegre RS Brazil

In this work, we present the first results of a reactor especially designed for in situ study of the hydrodesulfurization (HDS) process by x-ray absorption spectroscopy. The reactor was used to monitor atomic specific modifications in the chemical environment of catalysts under reactive conditions. We have investigated catalysts consisted of Pt or PtPd nanoparticles that were prepared in the presence of an ionic liquid ($BMI{\cdot}PF_6$). Our main purpose was to study both the reduction and sulfidation processes of the catalysts, which were clearly observed in our experiments and compared to results found in the literature for similar systems.

Acknowledgements

We gratefully acknowledge Agnès Traverse for fruitful discussions and suggestions in the data analysis and the support given by the CNPq, CT-PETRO, CAPES/PROBRAL 167-04, LNLS (DXAS 3385/04, DXAS 3384/05, DXAS 4556/06 and XAFS1 5269/06 projects) and the LNLS staff. F. B. thanks CNPq for his PhD fellowship.

184

Study of SnO Nanobelts and Dentrites by Transmission Electron Microscopy

Orlandi, M.O.[1], Longo, E.[2], Bettini J.[3], Aguiar, R.[4], and Leite,E.R.[4]

[1] Universidade Estadual Paulista - Ilha Solteira - Ilha Solteira SP Brazil
[2] Universidade Estadual Paulista - Araraquara - Araraquara SP Brazil
[3] Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil
[4] Universidade Federal de São Carlos - São Carlos SP Brazil

This work reports on the growth and characterization of tin oxide nanobelts and dendrites. The nanobelts were synthesized by carbothermal evaporation of SnO_2 powder mixed with 5% wt of carbon black in a sealed tube furnace at 1210 ^oC under a N_2 gas flow of 40 cm^3/min. After the synthesis a gray-black wool-like product was collected in a region (downstream) where the temperature was in the range of 400-500 ^oC. The obtained product was characterized by high-resolution field emission scanning electron microscope (FE-SEM), transmission electron microscope (TEM and HRTEM), energy dispersive X-ray spectroscopy (EDS) attached to the TEM and X-ray diffraction (XRD). The XRD result showed that materials in SnO and metallic tin phases form the gray-black product. By SEM analysis it was possible to observe that the gray-black material is composed by one-dimensional nanostructured materials with retangular cross-section; i.e. nanobelts, and that some nanobelts presented dendritic growth. The SEM and TEM images show that the nanobelts are flat, and possesŠ metallic tin drops at their extremities. Using SAD and HRTEM techniques it was possible verify that nanobelts are single-crystallines and that there are no defects in the junction of the nanobelts with the dendrites. The EDS analyses show that nanobelts have stoichiometry close to SnO, which is in agreement with XRD and SAD results, and that the metallic tin drops at the tip of nanobelts and dendrites are supersaturated with oxygen, which means that the growth mechanism for these belts must be the self-catalytic VLS process. In such a process, once the tin droplet is supersaturated and a nucleus is formed, the belt will grow with the same structure of the initial nuclei, since no oxygen is available inside the furnace in order to promote the belt oxidation.

Acknowledgements
We thank the FAPESP and CNPq by the financial support. The TEM facilities were provided by LME-LNLS.

185

KSCN-DOPED SILOXANE-POLY(PROPYLENE OXIDE) HYBRID ELECTROLYTES: STRUCTURE-PROPERTIES RELATIONSHIPS

J.A. Chaker[1], Santilli, C.V.[2], Pulcinelli, S.H.[2], DAHMOUCHE, K[3], Briois, V.[4], and A.F. Craievich[5]

[1] Universidade de Brasília - Brasília DF Brazil
[2] Universidade Estadual Paulista - Araraquara - Araraquara SP Brazil
[3] Universidade Federal do Rio de Janeiro - Rio de Janeiro RJ Brazil
[4] Syncrotron SOLEIL - Orsay France
[5] Universidade de São Paulo - São Paulo - São Paulo SP Brazil

During the past decades, considerable effort has been devoted to the development of solid polymer electrolytes with high ionic conductivity at room temperature for application in rechargeable and high energy density power sources. One of the most successful approaches relies on the preparation of OrMoLytes (organically modified electrolytes). Organic-inorganic nanocomposites composed of silica and poly(ether) are already described in the literature, they could present ionic conductivity comparable to pure polymers. They are several in-depth studies about structure and transport properties of siloxane-poly(propylene oxide) (PPO) nanocomposite, but less attention was been paid to known relationship between the structure and the ionic conduction properties of siloxane- PPO hybrid material. The work reported here is mainly devoted to determine which cation coordinating site of the host matrix is active in the case of KSCN doped, its influence on the nanostructure of the samples and its relation with the thermal and electrical properties. Complementary techniques were carried out to perform this study: small angle X-ray scattering (SAXS), differential scanning calorimetry (DSC), X-ray diffraction and complex impedance spectroscopy. The SAXS parameter ds is related to the distance between siloxane particles in hybrid molecule and it is obtained by the maximum of a SAXS curves. The weak interation between the cations and the polymeric chain is verified by the small variation of ds with increasing Tg values. On the other hand, we observe the decreasing of the correlation length (Lc) with salt content increasing. This SAXS parameter is related to the extension or size of the regions in the material where siloxane particles are spatially correlated. The increase of salt content perturbs the extension of spatial correlation in the system. The conductivity values as a function of doping from the same samples and the origin of the maximum observed for [O]/[K]=15 is consistent with the structural and dynamical changes described below and with the results of the literature of similar hybrids. The incorporation of K+ ions into the initial step of sol-gel synthesis of the siloxane-PPO hybrid host affects the structure and dynamics of both organic and inorganic phases and consequently ionic conductivity.

186

Caracterização de pontos quânticos de CdTe por GID e GISAXS

Ferreira, S. O.[1], Ribeiro, I. R. B.[1], and Suela, J.[1]

Universidade Federal de Viçosa - Viçosa MG Brazil

Este trabalho apresenta os resultados finais da caracterização de pontos quânticos (QD) de CdTe crescidos sobre substratos de Si(111). As amostras investigadas foram crescidas utilizando a técnica de crescimento epitaxial por paredes quentes (HWE), utilizando uma taxa de crescimento de $0,02$ Å/s e temperatura de crescimento entre 150^oC e 300^oC. Foram analizadas amostras crescidas em diferentes temperaturas e diferentes taxas de cobertura. A caracterização foi feita utilizando microscopia de força atômica (AFM), difração de raios-x com incidência razante (GID) e espalhamento de raios-x de baixo ângulo (GISAXS). As imagens de AFM mostram que o CdTe sobre Si segue o modo de crescimento Volmer-Weber, com a nucleação de ilhas tri-dimensionais sobre a superfície do substrato sem a formação de uma camada de molhamento. As medidas de GID e GISAXS realizadas na linha XRD2 mostram que os QD obtidos apresentam-se totalmente relaxados tanto no plano quanto na direção de crescimento, seguindo a orientação [111] do substrato. Apesar dos resultados de AFM indicarem uma morfologia pirâmidal das ilhas, as medidas de GISAXS não permitiram observar o facetamento e a determinação do ângulo das faces.

Acknowledgements
Este trabalho foi financiado pelas agências financiadoras CAPES, CNPq e FAPEMIG

187

XAS spectroscopy of ferritin-encapsulated copper nanoparticles.

Ceolin M.[1], Dominguez-Vera, J.M.[1], and Galvez, N[1]

Instituto de Investigaciones Fisicoquimicas Teoricas y Aplic - La Plata BA Argentina

Ferritin is a widespread mineral storage protein. It is able to harvest up to 4500 iron atoms within its hollow spherical interior forming the iron hydroxide ferrihydrite. Recently the metal-depleted form apo-ferritin (AF) was used as a natural nano-reactor for confined synthesis of nano-structured materials allowing tight control of particle shape. Recently a reductive chemical route for the synthesis of metal nanoparticles within the AF cavity was presented [1,2]. In that study nickel and cobalt nanoparticles (3-3.5 nm) were produced exhibiting superparamagnetic behaviour. Here we present the results obtained from XAS experiments on ferritin-encapsulated copper-nanoparticles produced following the route outlined in [1]. XANES experiments indicate that the precursor before reduction should be a Cu(II) specie. EXAFS experiments indicate that the structure around copper ions is more likely to be the one observed in Cu(OH)2 rather than in CuO. Both, the intensity of the XANES "white line"and the average coordination number obtained for the Cu(II) precursor are compatible with a nanosized structure possibly confined within the apo-ferritin cavity. After NaBH4 reduction the line shape and features around Cu-K edge are the expected for metallic copper indicating fully reduction of the precursor particle. Their EXAFS spectrum resembles the one for bulk copper indicating that the particles are crystalline. An overall reduction of the coordination number of the particles (in comparison with metallic copper) reinforces the conclusion that copper atoms are forming nanometer crystallites. Finally, the temperature behaviour of the EXAFS spectrum render a Debye temperature of 269 K well bellow the one expected for metallic bulk copper (315 K) as expected for finite size nanostructures.

Acknowledgements

Partial financial support by LNLS, Campinas, Brazil is gratefully acknowledged. MC is staff member of CONICET, Argentina.

188

Carbon nanotubes prepared in mesoporous AAO membranes by CCVD

Bertholdo, R.[1], Hammer, P.[1], Pulcinelli, S.H.[1], and Santilli, C.V.[1]

Universidade Estadual Paulista - Araraquara - Araraquara SP Brazil

CNTs can be thought as a layer of graphite rolled-up into a cylinder with a diameter in the range order of the nanometer. Multi-walled CNTs (MWCNT) were discovered by S. Ijima in 1991. Two years later, single-walled CNTs (SWNT) were synthesized. The diameter of SWNTs is $\sim$1nm, and they can be as long as a few tens of nanometers up to several centimeters, making them one of the highest aspect-ratio objects known. SWNT have fantastic electronic and mechanical properties. Depending on their chirality they can behave as semiconductors or metals and their Young's modulus is $\sim$1,2TPa, 5 times that of steel, which makes then the strongest objects in nature. Currently there are three principal techniques to produce high-quality SWNT: laser ablation, electric arc discharge and CCVD. However, the CCVD method is the most interesting, from a technological point of view, mainly for the ability to grow aligned CNTs directly on a substrate. In this way, the combination of CCVD and template synthesis methods can be used to obtain aligned and homogeneous CNTs in porous hosts. AAO has been used for the fabrication of CNTs with very uniform diameter and length, which are of the same dimension of the pores in the AAO template. These characteristics are very important to explore the mechanical stability and anisotropic thermal and electronic transport properties. In this work, we synthesized the CNTs by CCVD method. Firstly, the channels of (AAO) membranes, used as template, were modified by iron particles impregnation using a aqueous solution of $Fe(NO_3)_3.9H_2O$ with different concentrations (0,1-1,0 Mol.L^{-1}) . The solvent was evaporated and the catalyst dried at 100^oC for 12h and 600^oC in air stream for 3h to obtain iron oxide particles. In the next step, CNTS were obtained by catalytic pyrolysis of CH_4 or C_2H_4 as carbon precursors and varying the flow rate, carrier gas and growth temperature. The high-resolution SEM images of the obtained material shows both iron particles and CNTs in the pores of AAO membrane. These CNTs have about 15nm of external diameter and few microns of length. In conclusion, the CNTs were obtained by CCVD method. The SEM results show the high size distribution of catalyst particle. The control of particle size and its abundance it is of crucial importance for a homogeneous CNTs growth in the AAO matrix.

Acknowledgements

This work was supported by the Brazilian Synchrotron Light Laboratory (LNLS) under proposal FEG-4997/06. Authors would like to tank CNPq and EMBRACO for the financial support.

189

Are There Intermediate Phases During Hydrothermal Conversion of Monetite to Hydroxyapatite? An XRD Study.

M. H. Prado da Silva[1], ALBUQUERQUE,SRS[1], Dourado, Erico[1], and Rossi A. M.[1]

Centro Brasileiro de Pesquisas Físicas - Rio de Janeiro RJ Brazil

Monetite, CaHPO4, is a calcium phosphate obtained by aqueous precipitation under acidic conditions. The biological occurrence of monetite is associated to some pathologic calcifications like dental calculi. The study of phase transformation involving calcium phosphates allows the conversion of thermodynamically stable phases under acidic conditions, into those ones stable under alkali conditions. In this direction, monetite coatings were produced on niobium substrates. The coatings were converted to hydroxyapatite, the most similar calcium phosphate to the main component of mineral bone tissue. The conversion monetite-hydroxyapatite was analysed by X-ray diffraction(XRD) using synchrotron light and scanning electron microscopy. XRD with synchrotron light showed to be efficient in the identification of intermediate phases. These phases are seldom detected by conventional X-ray diffraction, using Cu K-alpha radiation.

Acknowledgements
LNLS, CNPq, CBMM for the Nb sheets.

190

PHOTON STIMULATED ION DESORPTION FROM POLY(VINYL CHLORIDE) AND POLY(VINYLIDENE CHLORIDE) PHOTOEXCITED AT DEEP CORE LEVEL

Mendes, L. A. V.[1], Magalhães, S.D.[1], Pinho,R.R.[2], M. Ferreira[1], de Souza, G.G.B.[1], and Rocco, M.L.M.[1]

[1] Universidade Federal do Rio de Janeiro - Rio de Janeiro RJ Brazil
[2] Universidade Federal de Juiz de Fora - Juiz de Fora MG Brazil

Photon stimulated ion desorption (PSID) studies have been performed in poly(vinyl chloride) (PVC) and poly(vinylidene chloride) (PVDC) using synchrotron radiation, operated in a single-bunch mode, at the Cl 1s edge. The PSID experiments were performed at the SXS beamline from the Brazilian Synchrotron Light Source (LNLS). The experimental setup includes a sample manipulator and a time-of-flight mass spectrometer (TOF-MS), which are housed in an ultra-high vacuum chamber with a base pressure of about 10^{-9} Torr. The TOF-MS consists basically of an electrostatic ion extraction system, a drift tube and a pair of microchannel plate detectors, disposed in the chevron configuration. After extraction, positive ions travel through three metallic grids, before reaching the MCP. Photoabsorption spectra were recorded by measuring the total electron yield, TEY (electron current at the sample) simultaneously with a photon flux monitor (Au grid). The final data was normalized by this flux spectrum to correct for fluctuations in beam intensity. Desorption ion yields have been determined for the main fragments as a function of the photon energy. Two different processes mainly the Auger Stimulated Ion Desorption (ASID) and the X-ray induced electron stimulated desorption (XESD) processes were employed to explain the ionic desorption from poly(vinyl chloride) and poly(vinylidene chloride).

Acknowledgements
The authors would like to thank LNLS, CNPq, FAPERJ and IMMC for financial support.

191

AZ1518 Photoresist Analysis with Synchrotron Radiation using High-Resolution Time-of-Flight Mass Spectrometry

Mendes, L. A. V.[1], L. F. Avila[2], Pinho,R.R.[3], Carlos R. A. Lima[3], and Rocco, M.L.M.[1]

[1] Universidade Federal do Rio de Janeiro - Rio de Janeiro RJ Brazil
[2] Universidade Estadual de Campinas - Campinas SP Brazil
[3] Universidade Federal de Juiz de Fora - Juiz de Fora MG Brazil

Positive photoresists are widely used in lithographic process in microelectronics and in optics for the fabrication of relief components. In microelectronics, they are used as masks to transfer geometric patterns by manufactures of the integrated circuits. In optics, the photoresists are used to construct periodic structures with diffractive optics properties. The most popular positive photoresist is composed of the photoactive compound (PAC) denominated diazonaphthoquinone (DNQ) and the matrix material that is a thick resin called novolak. When positive photoresists are exposed to UV light, some physicochemical changes occur which is traduced by some alterations in the complex refractive index of the material. The changes during the exposure process depend on the absorbed energy by the material. Despite the novolak + DNQ films be used by the industry since a long time ago, the details of the breakup process are still being investigated and the changes in their physical and chemical properties are not yet fully understood. With the aim of getting inside into the degradation mechanisms induced by photons in photoresists we have performed Photon Stimulated Ion Desorption (PSID) studies on the AZ1518 photoresist, using high-resolution time-of-flight mass spectrometry (TOF-MS) to observe molecular modifications among photoresists unexposed and previously exposed to the ultraviolet light. Data acquisition was performed at the SXS beamline from the Brazilian Synchrotron Light Source (LNLS), during a single-bunch operation mode of the storage ring, covering the sulphur K-edge. Mass spectra on both photoresists (unexposed and exposed) were obtained as a function of the photon energy. The AZ1518 photoresist presented different PSID spectra, showing characteristic fragments. This work shows preliminary results on the applicability of photon stimulated ion desorption using high-resolution time-of-flight mass spectrometry to observe molecular modifications among photoresists unexposed and previously exposed to the ultraviolet light.

Acknowledgements
The authors would like to thank Dr. Lucila Cescato of the Universidade Estadual de Campinas for furnishing the AZ1518 photoresist. They also like to acknowledge the financial support of FAPEMIG, CAPES, CNPq and IMMC. R. R. Pinho thanks the financial support of the ICE - UFJF and FAPEMIG.

192

Photon Stimulated Ion Desorption from intrinsically conducting polymer films based on polypyrrole

Arantes, C.[1], Rocco, A. M.[1], and Rocco, M.L.M.[1]

Universidade Federal do Rio de Janeiro - Rio de Janeiro RJ Brazil

Intrinsically conducting polymers based on polypyrrole are very attractive materials because of their electrical, optical and redox properties. Polypyrrole have been used for technological applications, such as electrochromic devices, sensors and capacitors. The understanding of the main processes occurring in this class of material as well as the production of stable polymers with high technological potential are topics of great interest. In this work, we have performed NEXAFS and photon stimulated ion desorption (PSID) studies on polypyrrole (PPy) films doped with different counter ions (dodecylsulfate (DS) and $[Ni(dmit)_2]^{2-}$). The experiments were taken at the SXS beam line from the Brazilian Synchrotron Light Source (LNLS) operating in a single-bunch mode following sulphur K-shell photoexcitation and using TOF-MS for ion analysis. At the sulphur K-edge desorption of small and large fragments can be observed for both films. Their partial ion yield curves have been determined for the main fragments as a function of the photon energy. The $PPy/[Ni(dmit)_2]^{2-}$ results showed that S^+ and S^{2+} ionic desorption occurs mainly due to the Auger Stimulated Ion Desorption (ASID) mechanism. An increase in the S^+ ionic yield occurs at the first resonance energy and the production of S^{2+} is induced mainly by higher energy excitations. On the other hand, the PPy/DS results showed an increase in the ionic yield for several fragments at the first resonance energy, but since these fragments are observed below and above the absorption edge we suggest that both ASID and XESD (X-ray induced electron stimulated desorption) processes are importance in the ionic desorption from PPy/DS.

Acknowledgements

The authors would like to thank FAPERJ, CNPq, IMMC and LNLS for financial support.

193

Strain and interdiffusion of InP islands on GaAs(001) studied by resonant X-ray scattering

L. N. Coelho[1], Magalhaes-Paniago, R.[1], Malachias, A.[2], Zelcovit, J.G.[3], and Cotta, M.A.[3]

[1] Universidade Federal de Minas Gerais - Belo Horizonte MG Brazil
[2] Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil
[3] Universidade Estadual de Campinas - Campinas SP Brazil

SEMICONDUCTOR islands or quantum dots have been intensely studied for their opto-electronic properties and the quantum confinement effects they present. X-ray scattering has proven to be a very efficient tool to probe the structural and compositional profile of the islands. The strain along the island can be determined by X-ray diffraction and, combined with height profiles obtained by Atomic Force Microscopy (AFM), the strain as function of island height can be determined. By tuning the X-ray photon energy to an absorption edge of a certain chemical element, its composition profile along the island can be determined. In this work, we have studied samples of InP islands grown on GaAs(001) by CBE. Three samples were grown, at T = 470žC, 500žC and 530žC. In order to determine the concentration of all four elements present in the sample, we have measured resonant X-ray scattering at 4 different energies, 10268eV, 10368eV (Gallium K-edge), 11751eV and 11871eV (Arsenic K-edge) at beamlines XRD1 and XRD2 of LNLS. All measurements were done in grazing incidence geometry to maximize the islands/substrate signal ratio. Radial scans near the GaAs 220 peak were done in all four energies. The substrate peak is very intense and sharp, but the strained small islands produce a broad peak, spanning the different lattice parameter present at the structure as the InP relaxes from the strained lattice parameter at the base equal to the substrate (5.65Å) to its bulk lattice parameter of 5.86Å. At different positions of the radial scan, that is, at different lattice parameter values, angular scans were done to determine the island lateral size corresponding to that lattice parameter. Associating these values of lateral size with the height profile from the AFM images it was possible to determine the dependence of the lattice parameter as function of height for all samples. From this, concentration maps were built for all elements present in the sample.

Acknowledgements

This work was supported by ABTLuS, CNPq, FAPEMIG and FAPESP.

194

XAS and SAXS characterization of the nanoparticles produced by chemical depletion of the ferrihydrite core in holo-ferritin.

Ceolin M.[1], Galvez, N[1], and Dominguez-Vera, J.M.[1]

Instituto de Investigaciones Fisicoquimicas Teoricas y Aplic - La Plata BA Argentina

Ferritin is a widespread mineral storage protein. It is able to harvest up to 4500 iron atoms within its hollow spherical interior forming the iron hydroxide ferrihydrite. The mechanism explaining iron entering, reduction and storage was extensively studied and a comprehensive picture was depicted. However, although we know how iron is harvested, several important questions on how iron is depleted from the ferrihydrite core and made bio-available remain still unanswered. Our aim is to characterize the depletion process studying the overall low-resolution structure of holo-ferritin at different depletion extents (2200, 1200, 500 and 200 Fe atoms) using Small angle X-ray Scattering. Our results indicate that the mineral core remains in one piece during the depletion process discarding alternative models pointing to a fragmentation of the ferrihydrite core during depletion. XAS experiments on Fe-K edge indicate that the mineral core has an EXAFS spectrum very similar to the one observed for artificial ferritins. However, an overall decrease of the mean coordination number around iron was observed compatible with a monotonic decrease of core size. Surprisingly, the Debye-Waller factor for single scattering Fe-O paths has no thermal dependence.

References N.Galvez et al. Inorg. Chem. 44 (2005) 2706 P.Sanchez et al. Dalton Transactions (2005) 811

Acknowledgements

Partial financial support by LNLS, Campinas, Brazil is gratefully acknowledged. MC is staff member of CONICET, Argentina.

195

Nanostructural and local study of the effects of polycondensation of silicon species on the structural features of siloxane-PMMA hybrids sols

Sarmento, V.H.V[1], DAHMOUCHE, K[2], Pulcinelli, S.H.[1], Santilli, C.V.[1], and Craievich AF[3]

[1] Universidade Estadual Paulista - Araraquara - Araraquara SP Brazil
[2] Universidade Federal do Rio de Janeiro - Rio de Janeiro RJ Brazil
[3] Universidade de São Paulo - São Paulo - São Paulo SP Brazil

Siloxane-polymethylmethacrylate (PMMA) hybrids were prepared by the sol-gel process through hydrolysis and polycondensation of methacryloxyproyltrimethoxysilane (MPTS). The effects of water, MMA, methanol contents and of the pH of the initial sol on the nanoscopic and local structural evolution during the advances of polycondensation reactions was followed by Small Angle X-ray Scattering (SAXS) and Nuclear Magnetic Resonance (NMR) spectroscopy. The SAXS patterns of all samples show the presence of an interference peak attributed to the scattering of spatially correlated silicon species present in the sol. For pH 1 and 3 a shift of the peaks position towards low q-range were observed increasing the water content up to [H_2O]/[Si]=2.The peak position remains essentially invariant by increasing the [H_2O]/[Si] ratio above 2, while an increase of the methanol content and monomer (MMA) concentration lead to a shift of the peak position towards low q-range and to the peak broadening. These interpretations were confirmed by the evolution of the condensation degree of silicon species during the reaction, determined by ^{29}Si NMR.

Acknowledgements

We would like to acknowledgement LNLS for SAXS measurements and FAPESP for financial support.

196

Preliminary studies of organic-capped iron oxide nanoparticles: Assessing nanostructure.

Socolovsky, L. M.[1] and Bakuzis, A. F.[1]

Universidade Federal de Goiás - Goiânia GO Brazil

A growing interest in organic-capped magnetic nanoparticles (NP) has arisen as a consequence of their unique properties. These particles, produced by chemical methods, joined several desirable characteristics for both science and technology, like controlled size, small size distribution, regular shapes, and organic capping. This last one prevents from direct contact between NP. We study magnetotransport properties in nanostructured systems, like Magnetoresistance and giant Hall effect, so these NP can provide a good system to test current theories. As a starting point for these studies, assessing the nanostructure is fundamental. We have prepared samples of nanoparticles of magnetite capped with tartaric acid, polyaspartic acid and carboxyldextran. We have carried out Transmission Electron Microscopy to find that the distributions are lognormal, with mean size $d = 7.4 \pm 0.4$ nm ($\sigma = 0.16 \pm 0.1$ nm) for tartaric-acid-covered NP; $d = 8.9 \pm 1.1$ nm ($\sigma = 0.4 \pm 0.3$ nm) for polyaspartic-acid-covered NP; and $d= 10.8 \pm 1.7$ ($\sigma = 0.5 \pm 0.2$ nm) for carboxyldextran-covered NP. We are planning to study our samples by Small Angle X-ray Scattering. With both studies we can have a complete characterization of the mean size, size distribution, crystalline structure, and the width of the organic capping. We will discuss how these capping can affect magnetotransport properties.

Acknowledgements
We acknowledge support from CNPq

197

GRAZING INCIDENCE SMALL ANGLE X-RAY SCATTERING STRUCTURAL CHARACTERIZATION OF ZNO FILMS PREPARED BY THE SOL-GEL DIP-COATING TECHNIQUE

Bojorge, C. D.[1], Cánepa, H. R.[1], Casanova, J. R.[1], Craievich AF[2], Heredia, E.[1], Kellermann, G.[3], Lamas, D. G.[1], and Walsoe de Reca, N. E.[1]

[1] Consejo Nacional de Investigaciones Científicas y Técnicas - Buenos Aires Argentina
[2] Universidade de São Paulo - São Paulo - São Paulo SP Brazil
[3] Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil

The present work deals with the characterization of nanostructured films of pure and Al-doped ZnO deposited on amorphous SiO2 substrate by the dip-coating technique. The properties of sol-gel ZnO films are affected by various processing parameters. The object of this work is to investigate the structural variations of the films related to the number of deposited layers and thermal treatments carried out after the layer deposition to obtain the nanocrystalline ZnO film from the amorphous precursor. X-ray diffraction patterns performed with conventional X-ray equipment in the gracing incidence configuration only showed ZnO peaks after the thermal treatment. Mean crystallite sizes estimated by the Scherrer equation were obtained between 7 and 24 nm. As regards the coating features, atomic force micrographs show that all the samples have very homogeneous surfaces with low roughness, being about 25 nm the typical thickness of two-layer films. Additional studies with grazing incidence small angle x-ray scattering (GISAXS) and X-ray reflectivity (XRR) were performed using a source of synchrotron light (line XRD2). The aims of these experiments were: i) determination of the shape and distribution of sizes of the nanopores, as well as eventual anisotropic effects in the films morphology ii) determination of the thickness of the ZnO thin films and heterogeneity effects in the perpendicular address to the deposition plane in the case of multilayer samples. These studies are currently in progress.

Acknowledgements

The authors thank funding supports provided by LNLS, CAPES/SECyT, CNPq/CONICET, CNPq (PROSUL program), ANPCyT and CONICET.

198

SAXS and XAFS characterization of Pt nanoparticles in SBA-15 mesoporous materials

Giovanetti, L.[1], Figueroa, S. J. A.[1], Ramallo-López, J. M.[1], Requejo, F. G.[1], Craievich AF[2], and Koebel, M. M.[3]

[1] Universidad Nacional de La Plata - La Plata Bs.As Argentina
[2] Universidade de São Paulo - São Paulo - São Paulo SP Brazil
[3] Lawrence Berkeley National Laboratory - Berkeley CA United States of America

Pt nanoparticles (NP) were synthesized by seeded growth and direct ethylene glycol reduction methods and stabilized with poly-(vinylpyrrolidone) (PVP). Different set of nanoparticles with an average size of 1.9 and 9 nm respectively were impregnated into SBA-15. The shape and size distribution of the NP was determined using transmission electron microscopy (TEM) before the impregnation. Complementary, small angle X-ray scattering (SAXS) experiments were performed to estimate the average NP size and size distribution before and after the impregnation. In addition, X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) studies were performed to elucidate the effect of the capping agent and the interaction with the SBA-15 on both shape,geometry and electronic structure of the nanoparticles. While the PVP capping seems to interact only weakly with the Pt atoms on the NP surface, the SBA causes changes in the electronic structure and adds new contributions to the atomic radial distribution function of Pt atoms as determined by EXAFS. This stronger interaction with the substrate could also be responsible for the change in the Pt 5d electronic configuration observed by XANES.

Acknowledgements
We would like to acknowledge the financial support received from projects PICT 06-17492 (ANPCyT, Argentina), PIP 6075 (CONICET, Argentina), CIAM collaborative project (CONICET, NSF and CNPQ), D04B - XAS1 - 4246/05, D11A - SAXS1 - 4719/05 (LNLS, Brazil) and the Swiss National Science foundation

199

Influence of the organic-inorganic hybrid matrix interactions on the controlled encapsulation and release of drugs

Molina, E. F.[1], Chiavacci, L.A.[1], Santilli, C.V.[1], Lopes, L.[1], and Pulcinelli, S.H.[1]

Universidade Estadual Paulista - Araraquara - Araraquara SP Brazil

Siloxane-polyether hybrid materials are ease to prepare, transparent, flexible and present mechanic properties better than the polyether itself . The combination of all these characteristics in a unique material allows it to be suitable for several scientific and technological areas, including the human health ones. In recent work the controlled release of sodium diclophenac from siloxane-polyoxyetylene (POE) or siloxane-polyoxypropylene (POP) hybrid matrix prepared with different polymer molecular weight was analyzed. Results show that the better thermodynamic compatibility between POE polymer chains and water favors the samples swollen during delivery, giving rise to five times faster delivering rates. Moreover, the higher the molecular weight of the polymer chains the faster and more effective the drug delivery. So that, in this work we analyze the possibility of reach a more precise control of the sodium diclophenac delivery rate by using a new hybrid matrix formed either by combining polymer chains of different nature, i.e., varying POP/PEO proportions or different molecular weight, i.e., low and high ones. These matrixes were prepared from a new precursor formed by the simple mixture of non-hydrolyzed siloxane-PEO and siloxane-POP hybrid precursors. The hydrolysis and polycondensation reactions were promoted by addition of water, ethanol and sodium diclophenac aqueous solution. SAXS results, from curves recorded during in-situ delivering tests, revealed a new hybrid structure, that is constituted by correlation distances between the siloxane groups larger than that observed for the original hybrids . The comparison of the delivery ratios from siloxane-POE, siloxane-POP and siloxane-POE-POPhybrid matrixes, containing different POP/POE proportions revealed that the delivery rate is dependent on the polymer chain nature, and that can be controlled by adjusting the POP/POE proportions. In a similar way, the variation of the proportion of low and high molecular weight of the polymer chain has also allowed to the control of the sodium diclophenac delivery rate. Indeed, irrespective of the polymer chain size the sodium diclophenac delivery is always faster and more effective for samples containing higher amounts of POE.

Acknowledgements

CNPQ and Fapesp for finantial support and LNLS for SAXS measurements

200

Cinética de efeitos fotoinduzidos em filmes finos calcogênicos sob irradiação

Moura, P. R.[1], Almeida, D. P.[2], and De Lima, J.C.[2]

[1] Universidade do Estado de Santa Catarina - Joinville SC Brazil
[2] Universidade Federal de Santa Catarina - Florianópolis SC Brazil

Apresentaremos os resultados de medidas das alterações fotoinduzidas ocorridas em filmes finos calcogênicos da liga Ge30Se70 e da liga Ga40Se60, investigadas sob vários regimes de irradiação. Ênfase será dada a descrição das técnicas experimentais, bem como ao aparato construído para as medidas apresentadas. A liga Ge30Se70 e a liga Ga40Se60 foram sintetizadas por moagem mecânica em um moinho de bolas, depositadas na forma de filmes finos em substrato de vidro e posteriormente expostas à luz síncrotron na faixa do visível e ultravioleta, a fontes radioativas como, partículas alfa, partículas beta, radiação gama e raios - X, e a radiação visível. A dependência da transmissão por um feixe de laser de diodo foi determinada como uma função do tempo de exposição à radiação utilizada.

Acknowledgements
Os autores agradeçem ao LNLS. Este trabalho foi suportado pela Secretaria de Educação, Ciência e Tecnologia do Estado de Santa Catarina.

201

Efeito da adição de álcoois no equilíbrio de fases e nas estruturas formadas por CTAPA$_n$ em água

Bernardes, J.S[1] and W. Loh[1]

Universidade Estadual de Campinas - Campinas SP Brazil

Neste trabalho estuda-se a interação entre polieletrólitos e surfatantes de cargas opostas em meio aquoso, analisando a formação de estruturas supramoleculares advindas das propriedades de auto-organização destes sistemas. A forma e o tamanho dos agregados formados dependem de alguns fatores, tais como: concentração de polieletrólito e surfatante, presença de cossolventes, temperatura, entre outros. (Svensson, A.; Piculell, L.; Cabane, B.; Ilekti, P. J. Phys. Chem. B 2002, 106, 1013.) Em uma primeira etapa estudou-se o efeito da adição de diferentes óleos (decanol, p-xileno, ciclohexano) sobre o equilíbrio de fases e a forma de agregados constituídos pelo surfatante CTA^+ e o polieletrólito PA^-. Com os resultados obtidos, foi possível concluir que o decanol se posiciona entre as moléculas de surfatante no agregado, favorecendo dessa maneira estruturas lamelares. No entanto, o p-xileno e o ciclohexano se localizam no core dos agregados, favorecendo estruturas hexagonais que intumescem ao aumentar a concentração de óleo. Em uma segunda etapa analisou-se o efeito do aumento da hidrofobicidade do polímero sobre a auto-organização do sistema, para isso utilizou-se o ácido polimetacrílico em sistemas binários (água-complexo) e ternários (água- complexo -cossolvente). Os resultados obtidos mostram que o equilíbrio de fases e a estrutura dos agregados formados são semelhantes quando comparados com o ácido poliacrílico, no entanto, os tamanhos dos agregados são maiores com o polímero mais hidrofóbico. Na terceira etapa deste trabalho, que ainda está em andamento, estão sendo analisados sistemas ternários contendo água, complexo (poliácido acrílico - $C_{16}TA^+$) e álcoois com diferentes tamanhos de cadeia (octanol, hexanol, butanol, etanol). Com os resultados preliminares, verificou-se que pequena quantidade de álcool é necessária para promover a transição de fase hexagonal para lamelar, como já observado para decanol, e em concentrações superiores de álcool para sistemas contendo octanol e hexanol observou-se a presença de uma outra fase líquido-cristalina que não pode ser determinada, no entanto, devido a sua posição no diagrama de fases estima-se que seja uma estrutura hexagonal reversa. Observou-se também um aumento da fase L_2 com a diminuição da cadeia carbônica do álcool, o que provavelmente está relacionado com o aumento da solubilidade do complexo em álcoois menores.

Acknowledgements

FAPESP e CNPq pelo suporte financeiro e LNLS pelo uso da linha D11A SAXS1

202

Thickness dependence of the structure of iron silicide thin films grown by reactive deposition epitaxy on Si(111)

R.Ribeiro-Andrade[1] , D.R.Miquita[1], M.V.B.Moreira[1], R.Magalhães-Paniago[1], J. C. González[1], M. I. N. da Silva[1] and A.G.Oliveira[1]

Departamento de Física, Instituto de Ciências Exatas, Universidade Federal de Minas Gerais, Caixa Postal 702, Belo Horizonte, MG, CEP 30123-970, BRAZIL

The semiconductor iron silicide beta-$FeSi_2$ has a great potential for technological applications in the field of optoeletronic devices. Different iron silicide compounds and phases can be formed in accordance with the phase diagram of the iron-silicon system. The formation of these phases is strongly dependents of the thermodynamics and kinetic variables of the growth process used to produce iron silicide thin films. The most usual growth techniques are the Reactive Deposition Epitaxy, the Solid Phase Epitaxy and the Molecular Beam Epitaxy. In this work, several characterization techniques are used to study the influence of the initial iron coverage on the growth of iron silicide thin films by Reactive Deposition Epitaxy. Coplanar X-Ray Diffraction is used to identify and quantify the different iron silicide phases, the main growth orientations and the mean grain size of these films. Atomic Force Microscopy is used to analyze the morphology of the samples. Initially we observe the formation of islands predominantly in the beta-$FeSi_2$ phase. Increasing the iron coverage the islands grow in size and coalesce. The epilson-FeSi phase appears in intermediary Fe coverages, but this phase disappears at Fe coverages larger than 20nm. Such results are tentatively interpreted as a strain driven phase transition. The beta-$FeSi_2$ phase is stabilized in Si (111) for small islands with a relatively low elastic energy. However, increasing the iron coverage the elastic energy of the islands increases producing a transition to the epilson-FeSi phase. For larger iron coverages the iron silicide island coalescence produces a relaxed film and the beta-$FeSi_2$ phase is again stabilized.

Acknowledgements
CNPq, CAPES, Fapemig

203

Anaálise da superfície vítrea de fibras ópticas envelhecidas com microscopia de força atômica

de Aragão, B. J. G.[1] and Messaddeq Y.[2]

[1] Fundação Centro Pesquisa Desenvolvimento em Telecomunicações - Campinas SP Brazil
[2] Universidade Estadual Paulista - Araraquara - Araraquara SP Brazil

Fibras ópticas para telecomunicações, fabricadas com sílica vítrea, estão sujeitas à degradação mecânica devido à dissolução da sílica pela água, com formação de ácido silícico e aumento de rugosidade superficial. Esta introduz pontos de concentração de tensões na superfície vítrea, reduzindo a tensão de fratura da fibra. Em laboratório, recorre-se ao envelhecimento acelerado para investigar a degradação de fibras ópticas. No envelhecimento acelerado deste trabalho, uma fibra óptica monomodo de sílica foi envelhecida em água deionizada, com pH = 7,5, temperatura de 85C, razão entre área superficial da fibra e volume e solução de 4,7x10^{-3} cm^{-1}, com dois níveis de tensão mecânica: a) sem tensão e b) com uma tensão de 0,5 GPa. A duração foi de 50 dias, com retiradas de amostra após 7, 14, 25 e 50 dias. Para cada tempo de envelhecimento e nível de tensão, foi avaliada a resistência mecânica da fibra óptica por flexão em dois pontos e a rugosidade superficial da fibra com microscopia de força atômica. A resistência mecânica foi avaliada através da tensão de fratura e o parâmetro de susceptibilidade à corrosão das fibras. Ambos os parâmetros foram relacionados com a rugosidade superficial da fibra óptica, avaliada através da rugosidade média quadrática (RMS). Foi verificado que, devido à baixa razão entre área superficial da fibra e volume de solução, a dissolução da sílica pela água ocorreu muito lentamente durante todo o período de envelhecimento acelerado estudado, sem e com tensão. Logo, tanto a rugosidade superficial e a tensão de fratura não alteraram significativamente durante o envelhecimento acelerado, quando comparado com a fibra não envelhecida. Esse resultado é coerente com cálculos teóricos de mecânica da fratura para o crescimento lento de trinca na superfície vítrea sob tensão constante. Observou-se ainda neste trabalho que o valor de RMS depende do tratamento adequado das imagens da perfície vítrea obtidas no microscópio de força atômica. Além da filtragem dos ruídos de baixa e alta freqüência, foi importante identificar e isolar os restos de revestimento polimérico que reveste a superfície vítrea e que não se logrou remover totalmente antes da medição da rugosidade.

Acknowledgements
Ao Laboratório Nacional de Luz Síncroton (LNLS), pelo uso do microscópio de força atômica, em particular ao Vinícius Pimentel, sempre disponível quando o seu apoio se fazia necessário.

204

Atividade eletrocatalítica de óxidos de manganês preparados por decomposição térmica para a redução de oxigênio.

Lima, F. H. B.[1], de Castro, J.F.R[1], and Ticianelli, E. A.[1]

Universidade de São Paulo - São Carlos - São Carlos SP Brazil

Apesar de muitos estudos envolvendo os óxidos de manganês como cátodos para a reação de redução de oxigênio (RRO) [1,2], a atividade e o mecanismo pelo qual a RRO se processa não é completamente entendido. Tem-se discutido [2] que a reatividade eletroquímica de alguns óxidos de Mn se deve à presença de átomos de H e grupos de OH na superfície do material. Também, tem-se proposto que a eletroredução de O_2 ocorre por mediação da oxidação de Mn(III), ciclicamente produzido por redução de Mn(IV). Em outro trabalho [1], foi mostrado que a RRO ocorre por processos sucessivos de 2 elétrons, tendo-se HO_2^- como intermediário. Neste trabalho, a RRO foi estudada em eletrólito de KOH em diferentes óxidos de manganês em diferentes cargas (em massa) suportados em carbono, mencionado neste trabalho como Mn_yO_x/C. A preparação envolveu a decomposição de nitrato de manganês diferentes condições. A caracterização estrutural dos óxidos de Mn foi feita por XRD na linha D12A-XRD1 do LNLS (Laboratório Nacional de Luz Síncrotron), usando radiação de 1,2403 e velocidade de varredura de 2^o/min. As fases dos óxidos presentes em diferentes potenciais do eletrodo foram investigadas por XANES in situ e realizado na linha D04B-XAFS1. Os resultados de XANES mostraram uma mudança do estado de oxidação no Mn ao longo da faixa de potencial em que a RRO ocorre, envolvendo os pares redox Mn(IV)/Mn(III) e Mn(III)/Mn(II). A comparação das atividades eletrocatalíticas indicou maior atividade para a RRO do catalisador de β-MnO_2. Assim, várias observações foram consideradas: (i) os resultados mostraram que a atividade frente à RRO é maior para os materiais com alto conteúdo de MnO_2; (ii) a RRO se processa por um mecanismo via 2 elétrons; (iii) o coeficiente de Tafel próximo do intervalo de 60 - 80 mV/dec é consistente com um caminho reacional formado por um processo redox rápido, acoplado com um passo químico lento. Esse grupo de observações juntamente com os resultados obtidos por XANES está em concordância com um mecanismo da RRO envolvendo uma mudança do estado de oxidação de Mn (IV) para Mn (III), e transferência de elétrons do Mn (III) para o O_2, que volta a Mn (IV), fechando o ciclo. [1] MAO L.; ZHANG D.; SOTOMURA T.; NAKATSU K.; KOSHIBA N.; OHAKA T., Electrochim. Acta 48: 1015-1021, 2003. [2] CAO Y. L.; YANG H. X.; AI X. P.; XIAO L. F., J. Electroanal. Chem. 557: 127-134, 2003.

Acknowledgements
Fapesp, Capes, CNPq e LNLS

205

Self-assembly in colloidal systems containing silicone compounds

Gurgel, A.[1], Ferreira, M.S.[2], W. Loh[2], and Torriani, I.[3]

[1] Universidade Federal de Viçosa - Viçosa MG Brazil
[2] Universidade Estadual de Campinas - Campinas SP Brazil
[3] Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil

The mechanism of formation of micellar solutions of surfactants and more complex self-assembled systems, such as emulsions and microemulsions, may be initially elucidated from thermodynamic considerations involving different experimental techniques. The complementary utilization of distinct analytical methods may provide direct information on these systems. In view of this, the present work employed the small-angle X-ray scattering (SAXS) technique to provide information on the micellization of so-called "CO2-phillic"commercial silicone surfactants in low cohesive energy silicone solvents. An important aspect of this work regarded the observation of the water uptake capacity of the multicomponent systems prepared, by forming isotropic and/or birrefringent samples in equilibrium. Direct structural evidence, typically shape and size of the aggregates, could be provided by SAXS measurements. In particular, the presence of lamellar and hexagonal structures was identified according to the composition of the systems, and the effect of variation of water content on the size of the aggregates in both isotropic and anisotropic environments was quantified. As a result, an excellent mapping of the corresponding pseudoternary phase diagram was effected. These preliminary results are useful to subsequent researches on the formation of aggregated systems in a non-aqueous solvent with high industrial potential: supercritical CO2 (scCO2).

Acknowledgements
The authors are indebted to FAPESP for financial support and LNLS for allocation of SAXS beam time.

206

X-ray and FTIR-ATR study of *Herbaspirilum Seropedicae* GlnB-Hs protein adsorption on silicon

Lubambo,F.A.[1], Benelli, E. M. ou Machado Benelli, E.[1], Mazzaro I.[1], Yokaichiya, F.[2], Giles, C.[3], Silveira, E.[1], and de Camargo P.C., deCamargo P.C., Camargo P.C.[1]

[1] Universidade Federal do Paraná - Curitiba PR Brazil
[2] Centre National de la Recherche Scientifique - Greboble France
[3] Universidade Estadual de Campinas - Campinas SP Brazil

The investigation of self-assembled protein adsorption on solid surfaces is relevant for both understanding protein properties and its applications. In addition to the nanometric dimensions, proteins naturally self-assemble building functional and spatially controllable supramolecular architectures. These aspects have been explored for applications such as biocompatibility, biosensor design, nanobiofilm templates for protein crystallization and also nanowire formation. This work consists on the investigation of the adsorption of globular protein GlnB-Hs of *Herbaspirilum Seropedicae* on silicon deposited by "spin-coating". GlnB-Hs is a signal transduction protein, involved in the control of nitrogen, carbon and energetic metabolism. It was purified at Biochemistry and Molecular Biology Department - UFPR. Protein adsorption is a complex phenomenon. A single experimental or theoretical approach is not enough in order to depict an overview of it. To characterize the GlnB-Hs, we have combined information from X-Ray at grazing incidence angles, atomic force microscopy (AFM) and Fourier transform infrared attenuated total reflection spectroscopy (FTIR-ATR). X-ray at grazing incidence angles angles was applied to sense any diffraction pattern, comparing the results with the crystallographic data already obtained. Atomic force microscopy was also used in order to access the 2-D conformational protein arrangement. Infrared absorption spectrum provided information about the adsorbed protein secondary structure. GlnB-Hs adsorbed on hydrophilic substrates led to the formation of donut-shaped, with evidences of face-up protein adsorption. FTIR-ATR spectra showed evidence of secondary structure conservation. Reflectivity and diffraction profiles from protein deposits on Si(111) and Si(100) have suggested the formation of ordered domains. The observed domains are stable under the X-ray beam and have d-spacing compatible with protein dimensions already determined.

Acknowledgements
The authors are grateful to LORXI- UFPR, Dr. Cyro Ketzer Saul, Dr. Guinther Kellermann for technical assistance on the beam line and LNLS for financial support.

207

Quantitative characterization of roughness and chemical interdiffusion at interfaces from atomic resolution HRTEM images.

Tizei, L. H. G.[1] and Ugarte, D.[1]

Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil

The constant reduction of microelectronic device size has reached the nanometer scale, creating a demand for experimental techniques to understand novel phenomena involved. New methods of manipulation and characterization at nanometric or atomic level must be developed to fulfill present and future scientific and technological needs. In the nanometer scale, the existence of interfaces or surfaces induces spatial variations on composition, crystal structure and density of electronic states which have important roles in materials functionality. Because of the need of high spatial resolution and low signal level detection, the potential uses of nanosystems require stringent efficiency of experimental methods. Among techniques capable of providing atomic resolution information, Transmission Electron Microscopy (TEM) is a technique very well suited to this purpose. Our main goal in this research is to develop tools to characterize interfaces at the atomic level in order to derive quantitative information on roughness and chemical interdiffusion. Here, we will discuss the analysis interfaces present in of InGaP/GaAs quantum wells 5-10 nm in width. Based on the algorithm QUANTITEM (Ourzmad et. al. 1990) we have implemented a program which allows the quantification of chemical compositional variation through the thorough analysis of contrast variations in of High Resolution TEM images. The derived information is validated by image simulation.

Acknowledgements

The authors would like to thank the LME/LNLS staff for technical support and J. Bettini and M. M. G. Carvalho for providing samples. This project is funded by FAPESP, CNpQ and LNLS.

208

Structural and electronic properties of atomic-size wires at low temperatures

M. Lagos[1], Rodrigues, V[2], and Ugarte, D.[1]

[1] Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil
[2] Universidade Estadual de Campinas - Campinas SP Brazil

We have studied structural and electrical behaviour of gold nanowires generated by mechanical elongation at liquid nitrogen temperature. Real-time observations using a low temperature sample holder in a High Resolution Transmission Electron Microscopy and, an ultra high-vacuum compatible Mechanically Controllable Break Junction modified to cool the sample region has been used. It has been observed that narrowest region of gold constrictions is crystalline and defect-free at room temperature, but this pattern is quite different at 150K. Extended defects(ex. twins) generate defective nanometer constrictions, indicating a very different structural evolution pattern during stretching. The generation of different atomic arrangements can be also deduced from transport measurements at low temperature. Finally, onte-atomi-size nanowires seem to be more stable at 150K, as revealed by very long conductance plateus at one quantum of conductance (lasting about 5-10 times longer than a room temperature).

Acknowledgements
The authors aknowledge FAPESP, CNPq and LNLS. We also thank J. Bettini for helping to process the HRTEM images.

209

COMPLEXOS FORMADOS ENTRE POLIETILENIMINA E DODECILSULFATO DE SÓDIO - UM ESTUDO DO EQUILÍBRIO DE FASES E DE ESTRUTURAS.

Padula, L.[1] and W. Loh[1]

Universidade Estadual de Campinas - Campinas SP Brazil

A associação entre um polieletrólito e um surfatante de carga oposta é proposta como um processo de troca de íons, no qual além da atração eletrostática há uma agregação cooperativa das moléculas de surfatante ligadas. Após todos os grupos carregados do polímero serem neutralizados, as interações hidrofóbicas serão as responsáveis pelo controle das interações, o que induzirá a reestruturação das cadeias de surfatante em agregados de diferentes formas. O objetivo deste trabalho é o estudo das variações estruturais e equilíbrio de fases das fases líquido cristalinas formadas entre polietilenimina (PEI) e dodecilsulfato de sódio (SDS). As variações são observadas utilizando polímeros de diferentes tamanhos, estruturas (ramificado ou linear), grau de ionização e razão $n_{surfatante}/n_{EI}$. As amostras foram caracterizadas por espalhamento de raios-X em baixo ângulo (SAXS) e observação visual. Os diagramas binários dos complexos PEI-SDS foram obtidos para dois polímeros de massas molares distintas, um de 423 g. mol^{-1} e outro de 2000 g. mol^{-1}, com 3 diferentes razões $n_{surfatante}/n_{EI}$ 0,50 , 0,75 e 0,85. Observou-se que o polímero de maior massa molar formou apenas estruturas lamelares e o polímero de menor massa molar formou tanto estruturas lamelares quanto hexagonais. Os parâmetros estruturais das estruturas formadas para o complexo, como a distância entre os planos, *d*, mostrou pequena diferença quando comparado com o surfatante puro o que indica um pequeno efeito de ponte do polímero. Depois de obtido os diagramas binários realizou-se o estudo de um dos complexos em presença de solventes orgânicos, p-xileno ou decanol. O complexo utilizado para obtenção do diagrama ternário foi o obtido com PEI 423 g. mol^{-1} e razão $n_{surfatante}/n_{EI}$ de 0,75. As estruturas formadas foram apenas hexagonais e lamelares, mas a presença do polímero no complexo mostrou grande influência sobre o comportamento das estruturas em presença de água e óleo, quando comparado com o sistema contendo somente o surfatante em água e óleo.

Acknowledgements
Ao CNPq e ao LNLS

210

Comparison of Available Practical Techniques for the Quantitative Analysis of White Lines Associated with Platinum-based Catalysts

Sousa, R[1], Colmati, F[1], Ciapina, E. G.[1], and Gonzalez, E. R.[1]

Universidade de São Paulo - São Carlos - São Carlos SP Brazil

One paramount feature of x-ray absorption is the large peak called “white line“ visible in many L-edge (and K-edge) spectra. The cause to the appearance of white lines has been understood as due to a high density of final states. The s-symmetric portion of the density of states is usually small and spread in energy. However, the d-symmetric portion of the density of states can be large and narrow, being a candidate to produce white lines. Regarding the practical techniques for the quantitative analysis of white lines associated with Platinum-based catalysts, two reasoning methods presented in the literature can be considered: the one proposed by Mansour et al.[1], and the method considered by Shukla et al.[2]. In this work, we apply the two techniques in the analysis of some experimental data from our laboratory and compare the two methodologies. The analysis by Mansour's method gave the following results for the number of unoccupied d states associated with Pt/C E-Tek 1100 mV and Pt_2Sn_1/C 1100 mV (and Pt foil), respectively: 0.3489, 0.3167 (and 0.3 for Pt foil). The analysis by Shukla's method gave some information about the d-band vacancies through the integrated intensity of the Lorentzian, i.e., 0.00794 keV for Pt/C E-Tek 1100 mV, 0.00698 keV for Pt_2Sn_1/C 1100 mV and 0.00397 keV for Pt foil. The main drawback of Shukla's approach seems to be the fact that it does not supply the number of unoccupied d-states themselves, but only some integral values. Regarding Mansour's methodology, it seems to be a more complete one, but there is some uncertainty in scaling and positioning the energy of the edges.[1] Mansour, A.N., Cook, J.W., Sayers, D.E. *Journal of Physical Chemistry*, 88 (1984) 2330-2334. [2] Shukla, A.K., Raman, R.K., Choudhury, N.A., Priolkar, K.R., Sarode, P.R., Emura, S., Kumashiro, R. *Journal of Electroanalytical Chemistry*, 563 (2004) 181-190.

Acknowledgements

The authors thank FAPESP, CNPq, CAPES and LNLS.

211

Plasmonic and Structural Effects in the Growth of Ag Triangular Nanoplates

Rocha, T. C. R.[1], Winnischofer, H.[1], Westphal, E.[2], Dantas, S. O.[3], D. S. Galvao[4], and Zanchet, D.[1]

[1] Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil
[2] Universidade Federal de Santa Catarina - Florianópolis SC Brazil
[3] Universidade federal de Juiz de Fora - Juiz de Fora MG Brazil
[4] Universidade Estadual de Campinas - Campinas SP Brazil

The shape control of metallic nanoparticles has been a subject of intensive research in the past few years because it provides an alternative way, in addition to size, to tune the properties of a metal. In this work, we present solid experimental evidences corroborated by computational simulations of the important role of surface plasmons (SP) and structural defects in the growth mechanism of photochemically synthesized Ag triangular nanoplates (TNPs). The use of incident radiation with different wavelengths revealed that two different growth process are present: an initial slow growth (stage I), when small TNP are formed and a second rapid anisotropic growth (stage II), which begins when the surface plasmon resonance (SPR) peak of the growing TNPs becomes resonant with the incident light. Our results pointed out that SP excitation plays an important role defining the final length of the nanoplates during stage II, and therefore providing an efficient size control mechanism, but it does not seem to be the main driving force of the anisotropic growth. The structural characterizations of the particles at different stages of the synthesis revealed that TNP are formed in the early stages of the synthesis by epitaxial anisotropic deposition of Ag photoreduced atoms over the defective seeds present in the initial solution. The use of Au seeds confirmed the effect of structural defects in the growth process and also provided instructive insights about the role of the capping molecule. Finally, the use of seeds with different distribution of crystalline structures had a striking effect in the final product, pointing out the important role of structure in the shape control mechanism.

Acknowledgements

We thank Prof. Daniel Ugarte for the instructive discussions. LME/LNLS is acknowledged for the use of the TEM (JEM-3010). LNLS is acknowledged for the use XD2 and XPD beam lines.This research was supported by FAPESP procs. 01/07715-8, 02/12720-3 and 04/12581-9. E.W. thanks CNPq for partial funding during the Summer Scientific Program at LNLS.

212

Efeito do pH na condensação de sílica mesoporosa

Martines, M. A. U.[1]

Universidade Estadual Paulista - Ilha Solteira - Ilha Solteira SP Brazil

A descoberta dos materiais cristalinos mesoporosos, em 1992 [1], despertou o interesse dos cientistas que trabalham na área de síntese de zeólitas e materiais relacionados. Materiais mesoporosos são obtidos por método envolvendo micelas de surfactante e de precursores inorgânicos. A natureza do bloco copolímero P123 permite o ajuste do tamanho de poros numa região maior (de 2 nm a 12 nm) do que outros templates e como também a preparação de partículas bastonetes com uma rede porosa hexagonal e tamanho de poros próximos de 10 nm. Neste trabalho investiga-se o efeito do pH de síntese na nanoestrutura de sílica mesoporosa. A síntese de sílica mesoporosa é baseada na formação intermediária de micelas híbridas e é realizada em duas etapas: na primeira ocorre a reunião que é controlada termicamente; a condensação da sílica ocorre na segunda etapa que é controlada cineticamente. A caracterização por MEV mostra que as sílicas apresentam partículas micrométricas do tipo bastonete. A condensação da sílica próxima do ponto isoelétrico (pH 2,0) resulta na fusão dos bastonetes devido ao balanço hidrofílico-lipofílico e ao movimento Browniano que destroem a rede polimérica. Mas as nanoestruturas são mantidas como pode ser observado pelos resultados de isotermas de adsorção de nitrogênio das sílicas mesoporosas que apresentam uma distribuição de tamanho de poros estreita próxima de 7 nm. Esta via de síntese permite o controle das características macroscópicas e microscópicas do material como morfologia e porosidade. Sílica hexagonal hierarquicamente organizada é potencial como material padrão para estudos de aplicações biológicas para macromoléculas.

[1] J.S. Beck et al. Journal of the American Chemical Society, 114, 10834 (1992).

Acknowledgements

FAPESP, LCr/IF/USP, LME-LNLS

213

Interface Delocalization and Buried Modulated Phase in the Extraordinary First-Order Magnetic Transition of $GdIn_3$

Malachias, A.[1], Granado, E.[2], R. Lora-Serrano[2], and Pagliuso, P.G.[2]

[1] Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil
[2] Universidade Estadual de Campinas - Campinas SP Brazil

It is well known that the near-surface region may behave considerably different than the bulk at the vicinity of a phase transition. In some cases, the relevant interaction at the surface may be enhanced, leading to a larger transition temperature in the near-surface layer (NSL) ($T_c^{NSL} > T_c^{bulk}$). The bulk ordering transition at T_c^{bulk} is then termed "extraordinary", as opposed to the "ordinary" transition for which $T_c^{NSL} = T_c^{bulk}$. For first-order transitions, the interface between the bulk and NSL phases is predicted to become delocalized at the bulk transition, implying the possibility of a NSL of macroscopic thickness. Thus, for extraordinary transitions, the ordered phase would be nucleated at the surface at T_c^{NSL}, propagating towards the bulk as T decreases and aproaches T_c^{bulk}.

Direct observations of the interface delocalization phenomenom at first-order transitions are rare, and, in most cases, not related to magnetism. It is then clear that more experimental work on interface delocalization and related phenomena at first order transitions is necessary to test theoretical predictions and, perhaps, reveal new unexplored physics.

In this work, a detailed resonant x-ray diffraction investigation of the magnetic structure and critical behavior of $GdIn_3$ will be presented. A bulk first-order transition to a constant-amplitude antiferromagnetic (CA-AFM) state is observed for all samples, at $T_c^{bulk} = 44.1$ K. The NSL is found to order at $T_c^{NSL} \sim T_c^{bulk} + 0.8$ K, revealing an extraordinary transition. Between T_c^{bulk} and T_c^{NSL}, the depth of the near-surface ordered phase varies strongly with T. Most remarkably, a long wavelength amplitude-modulated (AM) AFM phase develops between the NSL CA-AFM phase and the bulk paramagnetic phase immediately above T_c^{bulk}, defining a natural magnetic multilayer system in a narrow T-interval. This additional phase is not observed samples with partial Cd- and Ga-substitution in the In site, indicating great sensistivity of the AM phase to atomic disorder.

Acknowledgements

This work was supported by Fapesp and CNPq. LNLS is acknowledged for beamtime concession.

214

Study of interactions between cyclodextrin-DNA complex and dioleoylphosphatidylethanolamine by differential scanning calorimetry and X-ray diffraction

Nunes, B. R.[1], Carvalho, W. S.[1], Pesquero, J.L.[1], Kellermann, G.[2], Magalhaes-Paniago, R.[1], and De Oliveira, M.C.[1]

[1] Universidade Federal de Minas Gerais - Belo Horizonte MG Brazil
[2] Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil

DNA-based therapy has emerged in recent years as a promising strategy for a wide range of diseases, such as cancer, cystic fibrosis and Alzheimer's disease. Due to the poor cellular uptake and biological instability of DNA, DNA transfection has been performed using non-viral vectors. We developed a new anionic lipidic system containing DNA. This system is obtained by the previous binding of DNA molecules to cationic cyclodextrins (CD), followed by their encapsulation into pH-sensitive liposomes. These liposomes are composed by DOPE and cholesteryl hemisuccinate (CHEMS). Thus, in order to clarify the structural consequence of the interactions of the CD/DNA complex with the liposomes bilayers, and especially on DOPE, DSC and X-ray diffraction studies were carried out. DOPE showed three transition temperatures centred at -26, 10 and 17°C. Diffraction patterns of DOPE, at -28 and -15°C, showed X-ray spacings in the ratios of 1,2,4, which indicate the occurrence of Lbeta to Lalfa lamellar phase transition. At above 3°C, the diffraction patterns revealed Bragg spacings relative to the hexagonal phase. The addition of CHEMS to DOPE sample did not modify the Lbeta to Lalfa transition temperature, but led to a decrease of the X-rays diffraction peak widths of both Lbeta and Lalfa phases. Moreover, the presence of CHEMS induced an increase of the hexagonal transition temperature of DOPE (above 15°C). The addition of the CD/DNA complex led to the shift of the two peaks corresponding to the gel and liquid-crystalline lamellar phase transitions of DOPE and CHEMS towards higher temperatures (-22 and -14°C). Concerning the X-ray spacings, lower values of the Lalfa phase were obtained in comparison with DOPE/CHEMS sample (53.5 and 52.2 Å). It was not observed a hexagonal phase transition until 60°C. The X-ray diffraction patterns showed only ratios equal to 1,2, indicating the existence of lamellar phase. The peak width was higher, indicating a disorganization of the bilayer provoked by the CD/DNA complex. The knowledge of these interactions is important for the understanding of the efficiency of these carriers in biological studies.

Acknowledgements
The authors would like to thank LNLS, FAPEMIG and CNPq for their financial support and Lipoid GmbH for providing materials.

215

Investigation of the growing mechanism of colloidal iron oxides nanoparticles under thermal treatment

Haddad, P.S.[1], Martins, T. M.[2], Knobel, M.[2], and Zanchet, D.[1]

[1] Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil
[2] Universidade Estadual de Campinas - Campinas SP Brazil

The growing mechanism of iron oxide nanoparticles (NPs) obtained by decomposition of $Fe(CO)_5$ under thermal treatment in excess ligand is investigated. The colloidal Fe NPs were prepared by thermal decomposition of $Fe(CO)_5$ in decalin solution, in the presence of sarcosine ligand and airless conditions. NPs sizes were tuned to 6 nm. Samples containing excess ligand were submitted to thermal treatments in air, after solvent evaporation. The experimental conditions were NP/ligand mass ratios of 2:1; 4:1 and 8:1, temperatures of 100, 150, 230, 300^{o}C and times from 30 min to 24 h. The ligand excess was used to keep the solubility of the NPs. The samples were characterized by X-ray diffraction (XRD), small angle X-ray scattering (SAXS), transmission electron microscopy (TEM) and magnetization curves. The as-prepared sample presented an amorphous partially oxidized iron structure. Depending on the thermal treatment condition, the particles grow and crystallize, leading to a magnetite phase. By increasing the temperature, the crystallization takes place in shorter times. The surfactant addition reduces the degree of crystallinity of the samples. A coarsening process is suggested to these systems. The magnetic properties display a superparamagnetic behavior and there is an increase of the saturation magnetization with increasing temperatures.

Keywords: coarsening, thermal treatment, magnetite, sarcosine, crystalline

Acknowledgements

Thanks are due to ABTLuS and CNPq for financial support.

216

HRTEM Characterization of Nano-Structured Hydroxyapatite

Biggemann, D.[1], Ramirez, A.J.[1], Rossi A. M.[2], and M. H. Prado da Silva[2]

[1] Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil
[2] Centro Brasileiro de Pesquisas Físicas - Rio de Janeiro RJ Brazil

Hydroxyapatite (HA), $Ca_{10}(PO_4)_6(OH)_2$, is one of the most important bioceramics for medical and dental applications such as bone reconstruction and drug delivery systems. Nanostructured hydroxyapatite (nHA) is very similar to bone-like apatite, the apatite precipitated from human plasma on bioactive ceramics surfaces. It is a poorly crystallized, with crystal dimensions similar to those from bioapatite. In order to synthesize nHA with chemical composition, structure, crystal size and morphology similar to bioapatite, a quantitative high resolution transmission electron microscopy (QHRTEM) analysis of such synthetic nanoparticles was performed. Stoichiometric and fully crystallized larger particles of HA were also used as standard for the crystallographic and chemical analyses. Nano-structured HA crystals were quantitatively analyzed by HRTEM using the focal series reconstruction (FSR) technique. This method was employed to correct the objective lens spherical aberration, improving resolution up to 0.13 nm on a LaB_6 gun Jeol JEM-3010 microscope operated at 300 keV. HRTEM images of stoichiometric HA samples revealed large and irregular shape particles (mean equivalent diameter D $\sim$ 100 nm) with almost no amorphous phase. HRTEM images of nHA sample revealed different kind of configurations; i.e., some particles are formed by both amorphous and crystalline HA (see Figure 2a) while other particles are very small (D $\sim$ 2 - 5 nm) isolated HA crystals. A very interesting fact is the presence of nano structures as small as only two times the HA lattice parameter (0.96 nm). This study shows the main differences between stoichiometric HA and nHA. The results can give a strong feedback to optimize the compatibility of nHA with bioapatite.

217

Depth Profiling Surface Analysis of Layered Thin Films Combining Grazing-Exit X-ray Fluorescence and Synchrotron Radiation X-Ray Microprobe

Pérez, C. A.[1], H. J. Sánchez[2], Avendano, E.[1], Gobbi, A. L.[1], and Azevedo, G. de M.[1]

[1] Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil
[2] Universidad Nacional de Cordoba - Córdoba Cba Argentina

Characterization techniques sensitive to the chemical and physical properties of the material surface are of key importance in modern science and technology. The use of grazing-incident (GI) condition, introduced in different x-ray research fields, has enabled surface characterization of materials due to the small penetration depth of x-rays under total external reflection condition. Surface characterization techniques often need spatial resolution in order to be able to analyze their properties in different points. This is actually an intrinsic limitation of the GI excitation condition in which the collected information normally comes from a large area of the sample surface.

Becker et al. have pointed out that grazing-exit (GE) experiments also provides the same information as GI experiments, according to the optical reciprocity theorem. Since in this case the excitation is normal to the sample surface, the combination of GE-XRF and synchrotron radiation x-ray microprobe permits surface-sensitive analysis with spatial resolution.

In this work, we will describe the experimental setup mounted at the LNLS XRF Fluorescence beamline for combined GE-XRF condition with a synchrotron radiation x-ray microbeam. Preliminary results from the measurements of patterns of layered thin films samples deposited by sputtering on silicon substrate will be also reported. Some results on the study of diffusion processes at the layers interface after thermal treatment of the samples will also be discussed.

Acknowledgements
This work was supported by the LNLS.

218

A study by GISAXS of the size and shape of Ag nanoclusters embedded in SiO_2 glass

Kellermann, G.[1], O. Peña[2], Oliver, A.[3], and Rodríguez-Fernández, L.[3]

[1] Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil
[2] Universidad Nacional Autónoma de México - Coyoacán Distr Mexico
[3] Universidad Nacional Autonoma de Mexico - México Mexico

Nanometer-sized metallic particles embedded in glass matrix exhibit peculiar optical properties, and are particularly promising candidates for applications in the fields of nonlinear integrated optics and photonics. However, their optical properties are strongly dependent of the concentration, average size, shape, size distribution, and the interaction of the nanoparticles (NPs) with the host matrix. In order to accomplish several of these requirements, new synthesis methods have been developed. Among these, ion implantation is of large interest for optoelectronic applications. A detailed review of the properties and characterization techniques of metal nanoclusters was reported by Gonella and Mazzoldi [1]. Different techniques like transmission electron microscopy (TEM), x-ray diffraction (XRD) and small-angle x-ray scattering (SAXS) have been used to characterize the structure of NPs embedded in matrices. In particular, due to the surface selectivity, grazing incidence small-angle x-ray scattering (GISAXS) combined with the intense and collimated synchrotron radiation sources is a powerful technique for structural investigation of metallic and semiconductor NPs-glass composites prepared by ion implantation technique. In this work we will present the results from a study by GISAXS of metallic Ag NPs produced in silica by ion implantation followed by thermal treatment at different temperatures, in oxidizing and reducing atmospheres, in order to determine their shape and size distribution.

[1] F. Gonella and P. Mazzoldi, chapter 2, Vol. 4, Handbook of Nanostructured Materials and Nanotechnology, ed. by H.S. Nalwa, Academic Press 2000.

Acknowledgements
Research partially supported by Brazilian Synchrotron Light Laboratory (LNLS).

219

Influence of Ce ions valency on the densification of $Ce_{0.8}Sm_{0.2}O_{2-\delta}$ solid electrolyte

Souza,E.C.C.[1], Rey, J. F. Q.[2], Avendano, E.[2], and Muccillo, E. N. S.[1]

[1] Instituto de Pesquisas Energéticas e Nucleares - São Paulo SP Brazil
[2] Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil

In this work, $Ce_{0.8}Sm_{0.2}O_{2-\delta}$ solid electrolyte was synthesized by homogeneous precipitation. The nanoparticles obtained with and without thermal treatment of the precursor material were studied by thermal analysis, Raman spectroscopy, density, and X-ray photoelectron spectroscopy. Thermal analysis results show that the precursor material decomposes up to 500 ^{o}C, and exhibits an exothermic event at 250 ^{o}C due to the oxidation of residual Ce^{3+} to Ce^{4+}. The Raman spectrum of the dried precursor shows low-intensity bands at relatively higher wavenumbers usually attributed to the oxygen vacancies. This result evidences the formation of the solid solution during the precipitation step. Increasing of the calcination temperature produces a reduction in the full-width half-maximum of the main Raman band, which is characteristic of the triple degenerated mode of the fluorite structure, along with increase in the intensity of secondary mode bands at lower wavenumbers. Apparent density values obtained at a fixed sintering temperature show that those specimens calcined at 700 ^{o}C exhibit higher density than specimens thermally treated at other temperatures. XPS results demonstrate that this effect is related to the relative fractions of Ce^{4+}/Ce^{3+} and consequently in the concentration of oxygen vacancies, which is maximized after thermal treatment at 700 ^{o}C.

Acknowledgements
FAPESP,CNPq and LNLS

220

Síntese de nanoestruturas semicondutoras: pontos quânticos em estruturas verticais e nanofios autosustentados

Zelcovit, J.G.[1], Bortoleto, J. R. R.[1], Bettini J.[2], and Cotta, M.A.[1]

[1] Universidade Estadual de Campinas - Campinas SP Brazil
[2] Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil

Neste trabalho, onde nossas amostras foram obtidas por CBE, estudamos a nucleação de GaP, InP e InAs sobre uma grade de pontos quânticos de InP com ordenamento espacial lateral bi-dimensional. A grade de InP é obtida utilizando uma camada de InGaP com modulação periódica de composição como buffer. As camadas de GaP, InP e InAs foram depositadas a 550^{o}C, 540^{o}C e 500^{o}C, respectivamente. Outra estrutura que estudamos foram nanofios semicondutores autosustentados de InP e InAs e heteroestruturas de InP e InAs, obtidos com nanopartículas de Au como catalisador. Todas as amostras de nanofios foram crescidas à 450^{o}C. todas as amostras foram analisadas por HRTEM com medidas de alta resolução, de campo claro e escuro e EDS. Imagens de FESEM serviram para verificar a uniformidade dos nanofios crescidos sobre a amostra. As amostras com pontos quânticos foram também analisadas por AFM. A análise por AFM das amostras com pontos quânticos mostrou a formação de ilhas com ordenamento lateral similar ao observado no caso das ilhas de InP crescidas sobre a camada InGaP modulada. Nas medidas de HRTEM observamos que as ilhas de InAs e GaP crescem em correlação e anticorrelação vertical, respectivamente, com as ilhas de InP. A distribuição de tamanhos nos dois casos foi drasticamente alterada, um efeito que deve ser levado em conta para a construção de estruturas multi-camadas destes materiais. Para os nanofios, observamos através da HRTEM a presença de deslocações e variações relativamente abruptas de espessura ao longo do nanofio. Medidas de EDS mostraram a incorporação de In no catalisador de Au e presença de As nas proximidades do catalisador mesmo quando o crescimento é terminado em InP (como no caso de fios com camadas alternadas de InP e InAs). Este último resultado sugere que o As pode ter uma concentração de equilíbrio no catalisador durante o crescimento de InP que é eliminada na formação do ŚpescoçoŠ durante o processo de resfriamento. Das medidas de EDS para heteroestruturas InAs/InP, analisamos a composição ao longo dos fios através da determinação da relação As/P, e verificamos que o processo de transporte de material através do catalisador durante o crescimento proporciona uma interface relativamente abrupta entre os dois materiais.

Acknowledgements
A Fapesp e ao CNPQ pelo suporte e ao LME-LNLS

221

Análise do gradiente de espessura em multicamadas magnéticas depositadas sobre nano-esferas

Medeiros Soares, M.[1] and Garcia, F.[1]

Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil

Sistemas ferromagnéticos com anisotropia oblíqua podem ser obtidos da deposição de uma multicamada Co/Pd (que em substratos planos apresentam uma bem definida anisotropia perpendicular) sobre um arranjo bidimensional (densamente empacotado), gerado através de um processo de auto-organização de nano-esferas de poliestireno monodispersas. Este processo dá origem a um sistema de calotas magnéticas, magneticamente isoladas umas das outras, que exibem ciclos de histerese com comportamentos não convencionais. Neste sistema o ângulo de deposição em relação ao plano do substrato determina a direção do eixo de fácil magnetização da amostra. Tal comportamento está relacionado ao gradiente de espessura que a curvatura da esfera impõe ao filme por efeito de sombra. Esta dependência do eixo de anisotropia com o ângulo de deposição ocorre, pois em multicamadas Co/Pd a anisotropia magnética perpendicular é um efeito interfacial, sendo fortemente dependente das espessuras de Co e de Pd, assim como da micro-estrutura da interface. É, portanto, necessário estudar como a espessura da calota varia ao longo da esfera para, então, inferir como varia a anisotropia da calota. Estamos fazendo uma análise por Microscopia Eletrônica de Transmissão (MET) do corte transversal de nossas amostras, de forma a conhecer o gradiente de espessura da calota em função do diâmetro das esferas (50, 100, 500 ou 1000 nm) e da forma de deposição (substrato parado ou girando). Interessa-nos ainda avaliar nas imagens de MET a modulação das interfaces Co/Pd, assim como a continuidade das camadas e outros detalhes da microestrutura da amostra. Grande parte das dificuldades encontradas até o momento está na preparação de amostras adequadas à MET. Os resultados iniciais mostram que há continuidade no filme depositado e sugerem o efeito de sombra previsto pelas medidas magnéticas realizadas nas amostras. As medidas seguem sendo feitas com o constante aperfeiçoamento dos métodos de preparação.

Acknowledgements

Esse trabalho foi financiado parcialmente pelo CNPq, FAPESP e LNLS. Agradecemos especialmente ao LME-LNLS.

222

Estudio de las propiedades termodinàmicas locales de aleaciones nanoestructuradas binarias obtenidas por aleamiento mecànico: Fe-Cu, Fe-Au, empleando XAFS y càlculo de primeros principios

Lede, E. J.[1] and Socolovsky, L. M.[2]

[1] Universidad Nacional de La Plata - La Plata Bs.As Argentina
[2] Universidade Federal de Goiás - Goiânia GO Brazil

Tècnicas de aleamiento mecànico han mostrado ser eficaces en la sìntesis de aleaciones binarias nanoestructuradas metaestables. Presenta gran interès el estudio de sistemas binarios en los cuales la solubilidad mutua de sus componente bàsicos es baja en el equilibrio termodinàmico debido a su calor de formaciòn positivo. En el presente trabajo se investigaron dos sistemas que incluyen hierro en matrices no magnèticas: Fe-Cu y Fe-Au. Propiedades magnèticas y de magnetotransporte compatibles con nanopartìculas de hierro incorporado en ambas matrices (Cu o Au) fueron previamente observadas [1,2]. Estos sistemas muestran efectos de magnetoresistencia gigante (GMR). Esta caracterìstica es muy sensible a cambios en los paràmetros estructurares. Por tanto la caracterizaciòn estructural es imprescindible para comprender los procesos involucrados en tal efecto. XAFS presenta grandes ventajas frente a otras tècnicas de caracterizaciòn como XRD, etc., permitiendo determinar el tipo y número de vecinos pròximos, distancias interatòmicas, estructura electrònica, etc. Otros paràmetros adecuados para estudiar el comportamiento nanotermodinámico local, pueden ser directamente determinados ajustando un modelo teòrico con los resultados experimentales. Se realizaron experimentos XAFS (LNLS) en un conjunto de muestras de Fe_xCu_{100-x} y Fe_xAu_{100-x} (15 % at. $\sim$ x $\sim$ 45 % at.). Los datos experimentales obtenidos fueron analizados (Feff, Feffit) con el fin de determinar las propiedades termodinàmicas, empleando un modelo unidimensional anharmònico para el potencial interatòmico, cuyos parámetros son modulados por una función de densidad de probabilidad. Para el caso del Fe-Cu, los paràmetros estructurales obtenidos por XAFS seràn empleados para realizar càlculos de primeros principios (LAPW), con el fin de determinar el campo magnètico hiperfino en función de la concentraciòn de Fe. Los resultados de los cálculos seràn contrastado con resultados de espectroscopía Mössbauer (MS) previamente obtenidos. [1] L. M. Socolovsky, F. H. S ànchez and P. H. Shingu; Hyp. Interact. 133 (2001) 47-52 [2] L. M. Socolovsky, F.H S ànchez and P.H.Shingu; J.of Magn.Mat.226-230(2001) 736

Acknowledgements
Los autores agradecen el apoyo brindado por el CNPq (Brasil)

223

Caracterizaciòn XAFS de tamices moleculares Ti-MOR sintetizados empleando H_2TiF_6 como fuente de Ti

Lede, E. J.[1], Fernandez, R.[2], and D. Cardoso[2]

[1] Universidad Nacional de La Plata - La Plata Bs.As Argentina
[2] Universidade Federal de São Carlos - São Carlos SP Brazil

TS-1 es un catalizador obtenido incorporando Ti en la red de la silicalita [1]. Este catalizador es activo y selectivo en la oxidación de compuestos orgánicos con bajo impacto ambiental, y los microporos de su estructura MFI son de diámetros medios (5Å) [2]. La mayoría de los compuestos aromáticos, diámetros cinéticos superior a los 6Å, se ven impedidos de alcanzar los centros catalíticamente activos de estas zeolitas. Esta limitación ha motivado el estudio de la incorporación de Ti en zeolitas con microporos grandes, tales como Ti-Beta [3], Ti MCM-41 [4] y Ti-MOR [5]. El objetivo de este trabajo fue la síntesis hidrotérmica de la Ti-MOR utilizando una fuente de Ti mas barata y de sencilla manipulación, ácido hexaflourotitanico en lugar de TEOT. Los catalizadores fueron probados en la oxidación del ciclohexeno usando H2O2 como agente oxidante. Entre los diferentes sitios de Ti presentes, los que se han revelado más apropiados para estas reacciones son los átomos de Ti tetracoordiando de red. Sin embargo, otras especies de Ti pueden estar presentes, como el pentacoordinado, el octacoordinado o también Ti extra-red como anatasa [3]. Para identificar las especies presentes, relacionándolas con los resultados de actividad catalítica, se realizaron experimentos de Espectroscopia de Absorción de Rayos X (XAS). Mediante XAS fue posible estudiar el entorno del Ti obteniéndose información relevante sobre la coordinación de este átomo en la red, su vecindad local y las distancias medias entre vecinos próximos. Los espectros XAS muestran distintas especies de Ti claramente diferentes de TiO2 anatasa. La población de sitios de Ti tetra y octacoordinado varía en función del tenor de Ti. La actividad catalítica es similar a la de los catalizadores sintetizados con TEOT y se observa que los sitios son más activos que en el caso de los sintetizados con TEOT.

1. M. Taramasso, G. Perego, B. Notari, US Patent, 4.410.501, 1983. 2. R. A. Sheldon., Heterogeneous Catalytic Oxidation and Fine Chemicals. Studies in Surface and Catalysis, 1991, 59, 33. 3. M. A. Camblor, A. Corma, J. Pérez-Pariente, Zeolites, 1993, 13, 82. 4. A. Corma, M. T. Navarro, J. Pérez-Pariente, J. Chem. Soc, Chem. Commun., 1994, 147, 147.

Acknowledgements

Los autores agradecen al CNPq y al Programa Pronex por la ayuda económica. A los responsables por la línea XAS del LNLS por el soporte técnico durante las medidas de XANES y EXAFS.

224

APLICAÇÃO DE MEMBRANAS POROSAS DE ALUMINA ANÓDICA COMO FILTROS BIOLÓGICOS

Kisner, A.[1], Aguiar, M. R.[1], Lyra, M.[1], Moshkalyov, S.A.[1], and Kubota, L.T.[1]

Universidade Estadual de Campinas - Campinas SP Brazil

Nos últimos anos, a síntese e o controle de produção de membranas porosas de alumina anódica tem atraído grande interesse devido às características físicas e geométricas observadas nestas. Membranas porosas de alumina contendo poros com diâmetros variando desde 10 nm até 800 nm, podem ser fabricadas pela oxidação anódica de alumínio utilizando-se diferentes voltagens e soluções eletrolíticas. Em função das relativas pequenas dimensões de seus poros, membranas de alumina anódica tem sido sugeridas como excelentes filtros biológicos para bactérias, vírus e algumas outras macromoléculas. Adicionalmente, em função de sua característica eletropositiva, estas apresentam alta capacidade de adsorver espécies carregadas negativamente[1,2].

Baseado nestes, o presente trabalho descreve a síntese e a caracterização morfológica de membranas porosas de alumina produzidas por anodização de alumínio à 25 V em H_2SO_4. Análises por microscopia eletrônica de alta resolução (FEG-SEM), mostram que membranas com poros regularmente distribuídos e apresentando diâmetros entre 20 e 35 nm podem ser produzidos num espaço de tempo relativamente pequeno. A espessura das membranas neste caso, é controlada pelo tempo de anodização e por um pós-tratamento químico para alargamento dos poros com H_3PO_4. Em uma segunda etapa, removeu-se quimicamente o substrato, isolando assim somente a membrana de alumina, a qual foi então aplicada como filtro na purificação de água, contaminada com diferentes concentrações da bactéria *Escherichia coli* cultivada previamente por 24 h à 37 ^oC em meio TYM. Medidas de absorbância utilizando-se um espectrofotômetro de UV-vis, revelaram que o emprego destas membranas porosas como filtros biológicos é capaz de reduzir a concentração de células bacterianas nas amostras analisadas pelo protocolo de detecção utilizado. Adicionalmente, devido as dimensões de seus poros, estas membranas são capazes de filtrar mesmo em baixas concentrações ($< 3 \times 10^5$ células/mL) de células do parasita. Contudo, estes resultados sugerem que a alumina produzida anodicamente é capaz de reter praticamente todas as células, mostrando grande potencial para ser utilizada em filtros para a retenção de espécies de origem biológica consideradas patogênicas e contaminantes da água potável.

Acknowledgements
FAPESP e CNPQ

225

Caracterización mediante XAS, de Ti incorporado como hetero átomo en aluminofosfatos microporósos ALPOs

Lede, E. J.[1], Fernandez, R.[2], and D. Cardoso[2]

[1] Universidad Nacional de La Plata - La Plata Bs.As Argentina
[2] Universidade Federal de São Carlos - São Carlos SP Brazil

TS-1 es un material catalítico , que se obtiene incorporando Ti en la red de silicalita (MFI). Ha mostrado ser activo y selectivo en oxidación bajo condiciones blandas [1] de reaccione, pero los microporos de la red son de diámetros medios impidiendo que moléculas con diámetro cinético superior a 5 puedan reaccionar con sitios activos. Esta limitación ha motivado a estudiar la incorporación de Ti en tamices moleculares con mayor diámetro de micro poros. Los aluminofosfatos microporosos (AlPOs) no poseen carga neta en su estructura (AFI). La sustitución isomórfica de tetraedros $[PO_4^+]$por $[TiO_4]$ en la estructura AFI, puede modificar drásticamente sus propiedades, dependiendo del tipo de sustitución. Estos tamices denominados TAPO-5, pueden presentar propiedades ácidas, además de las redox, dependiendo del tipo de catión empleado [2]. Las especies de Ti que han revelado ser las más apropiadas en reacciones de oxidación, presentan átomos de Ti tetracoordinados. En este contexto, la espectroscopía de absorción de rayos x (XAS), se torna una importante herramienta para caracterizar cualitativa y cuantitativamente las posibles especies de Ti presentes en TAPO-5. El objetivo principal de este trabajo es caracterizar las diferentes especies de Ti en TAPO-5, sintetizadas hidrotermicamente con diferentes tenores de Ti, empleando H2TiF6 como fuente de Ti. Se realizaron experimentos XAS (LNLS), con un conjunto de muestras TAPO-5 con diferentes tenores de Ti. Mediante el análisis de los resultados obtenidos, fue posible confirmar la presencia de Ti como heteroátomo sustitucional en sitios de P tetracoordinados. Mediante simulación de los espectros XAS (Feff 7.02), fue posible determinar la geometría del entorno químico del Ti en red. Esta información fue correlacionada con los resultados de actividad en la reacción catalítica de interés. Además, fue posible confirmar que la incorporación de Ti en TAPO-5, genera sitios ácidos permitiendo explicar los procesos involucrados en la reacción, así como también el mecanismo de la síntesis.

1.- M. Taramasso, G. Perego, B. Notari, US Patent, 4.410.501 (1983). 2.- S.T. Wilson, E.M. Flanigen, US Patent 4,567,029 (1986).

Acknowledgements

Los autores agradecen al CNPq y al Programa Pronex por la ayuda econ ómica. A los responsables por la línea XAS del LNLS por el soporte técnico durante los experimento XAS.

226

Hybrid reciprocal space for x-ray diffractin in epitaxial layers

Morelhão S.L.[1] and Domagala, J.K.[2]

[1] Universidade de São Paulo - São Paulo - São Paulo SP Brazil
[2] Universidade de São Paulo - São Paulo - SP Brazil

Capability of growing thin layers of single-crystals onto one face of another single crystal has made possible many fundamental achievements in semiconductor technology. Epitaxial growth is today one of the most important and basic process used in manufacturing nanostructured devices. Multilayered materials such as superlattices and quantum wells, or even quantum wires and dots, require epitaxy at some stage of their preparation procedures. X-ray diffraction has been the primary tool for structural analysis of epitaxial layers, whose techniques and machineries have followed closely the needs of the semiconductor industry.

A quarter of century ago, when using divergent x-ray source and photographic film to record the layer/substrate diffraction lines —the simplest possible setup to measure lattice mismatch of epilayers — Isherwood and co-authors [J. Cryst. Growth **54**, 449 (1981)] reported the observation of extra features, a kind of short lines, appearing all over the recorded images. Such features were sequences of consecutive Bragg reflections in both single-crystal lattices, named hybrid reflections. Ten years latter, the phenomenon was quantitatively described [J. Cryst. Growth **110**, 543 (1991)] and several methods to exploit its properties were suggested. However, to precisely probe the excitement conditions of hybrid reflections, collimated x-ray beam setups would be necessary, as those commonly found in most synchrotron facilities where the beam can be highly collimated on two orthogonal directions.

Even after several decades of systematic usage of x-ray diffraction as one of the major analytical tool for epitaxial layers, the vision of the reciprocal space of these materials is still a simple superposition of two reciprocal lattices, one from the epilayer and another from the substrate. Diffraction conditions generating any other extra feature have been avoided since they could not be explained by this simplistic vision of the reciprocal space, commercial diffractometers do not have the appropriated optics to investigate them properly and, consequently, the analysis of epilayers by standard x-ray diffraction techniques would be compromised. This scenery is about to change! In this work, the general theory to account for hybrid reflections in the reciprocal space of epitaxial layers is presented. It allows a deep insight on how complex such reciprocal space is in fact, and how many interesting properties it has. Properties that can be exploited even on commercial diffractometers, leading to different, very detailed, and comprehensive analysis of such materials.

227

Synchrotron X-ray Renninger scanning for studying nanostructured seminconductor devices

R.O.Freitas[1], T.E. Lamas[2], Quivy, A. A.[1], and Morelhão S.L.[1]

[1] Universidade de São Paulo - São Paulo - São Paulo SP Brazil
[2] Universidade de São Paulo - São Paulo - SP Brazil

Synchrotron radiation has become an indispensable tool in many fields of Materials Science. Several analytical techniques are so important that most synchrotron facilities have stations optimized for carrying out specific techniques routinely. Systematic procedures for data acquisition and data treatment are also necessary mainly in studies involving large ensembles of samples, as for instance when developing new materials and nanostructured devices for technological applications.

X-ray Renninger scanning (XRS) is one of the most accurate technique for absolute lattice parameter determination in single crystals. However, in despite of this fact, there still are major limitations for systematically using XRS in studying technological materials: *i)* difficults experimented by users not familiar with multi-beam diffraction geometry in choosing suitable *umwegs* for a given purpose — *umweg*, a short name for the multi-beam diffraction peaks in the XRS — ; *ii)* instrumental errors that compromise accuracy in studies where it is really necessary; *iii)* lack of simple line-profile functions capable of measuring peak positions without further reducing accuracy due to the usually asymmetrical profiles of the *umwegs*; and *iv)* the need of a package of standardized procedures to handle quickly and systematically the materials analysis in synchrotron facilities.

In this work, a systematic procedure [Microelectron. J. **36** 219 (2005)] for ultra-precise lattice parameter determination using XRS is optimized and applied to probe the average in-plane strain in series of samples representing the different stages of the growth process of single-buried QDs. This procedure takes advantage of the shallow penetration depth of the X-ray wavefield under Bragg-surface diffraction — a particular type of *umweg* — , to enhance the sensitivity to the in-plane strain closer to the surface. Mechanical imprecisions and residual sample-misalignment errors are treated automatically, and a genetic algorithm plus a phase sensitive line-profile function [Phys. Rev. Lett. **89**, 015501 (2002)] are employed for fast and accurate peak position measurements.

228

Coloration mechanism in Iridium oxide and Iridium tantalum oxide

Avendano, E.[1], J. Backholm[2], Azevedo, G. de M.[1], and Niklasson, G.A.[2]

[1] Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil
[2] Uppsala University - Uppsala Sweden

Ion insertion materials that change color when a voltage is applied across them are called electrochromic (EC) and are found in several organic and inorganic materials. The change of color in an EC layer is caused by the intercalation of ions together with electrons. Thin films of $IrTaO_x$ appear as interesting alternatives to IrO_x as anodic electrode in devices. Due to the high cost of iridium oxide, when used for large area EC applications, additives are often mixed with iridium. The use of tantalum as an additive is promising, because it preserves the high stability of the iridium oxide and improves its ionic conductivity and optical contrast.

We have prepared sputtering deposited films with compositions $IrO_{2.2}$ and $IrTa_{1.4}O_{5.6}$ of an average grains size of 3-4 nm for both films, as measured by HRTEM. XPS results gave valuable evidence concerning the intercalation mechanism. The films need a number of electrochemical cycles in order to become fully charge stabilized. During the stabilization process the oxygen content in the films increases by of the order of 10%. After stabilization the intercalation process is highly reversible and stable, and no changes in oxygen or metal contents were observed. Hence, only protons are intercalated into and drawn out of the stabilized films during electrochemical cycling.

Acknowledgements

E. Avendaño and G. de M Azevedo are grateful with the Brazilian agencies of development FAPESP and CNPq for the support, and to the LNLS for the beam time to perform the experiments. This project was also supported by the Swedish Science Research Council.

229

Estudo da estrutura eletrônica (XPS) e cristalográfica (LEED e PED) da superfície) de CrO(100) e CrO(111) sobre Cu(100)

Pancotti A.[1], de Siervo A.[2], Carazzolle M.F.[1], Rodrigues, G.L.M.P.[1], Landers R[1], and Kleiman, G.G.[1]

[1] Universidade Estadual de Campinas - Campinas SP Brazil
[2] Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil

Hoje em dia, nota-se, pelo número de publicações, um interesse crescente nas propriedades de superfície e de volume de materiais utilizados em filmes finos de óxidos pelas indústrias. Esse forte interesse veio de investigações de reações catalíticas onde os óxidos servem como um material catalítico ou como um suporte para clusters de metais com atividades catalíticas. Óxido de Cromo III (Cr_2O_3) é um óxido cataliticamente interessante com várias aplicações potenciais. Esse tipo de óxido, suportado, é ativo na catálise da de-hidrogenação de Alcanos para Alcenos[1]. Filmes de óxido de Cromo formados pela segregação de Cr, contidos em ligas metálicas, para a superfície também conferem substancial resistência à corrosão de muitos materiais.[2,3]. O entendimento da estrutura da superfície do Cr_2O_3 para essas aplicações é de fundamental importância para que possamos compreender os mecânimos que governam a atividade catalítica desse material. O sistema a ser estudado envolveu a preparação da superfície de um monocristal de Cu(100) (a limpeza será feita in situ por ciclos de bombardeamento de íons de argônio e aquecimento para facilitar a reconstrução da superfície), e a caracterização da estrutura eletrônica (XPS) e cristalográfica (LEED e PED). A segunda etapa correspondeu ao crescimento de filmes de óxidos ordenados sobre monocristais, onde incialmente testamos a formação de Cr_2O_3[4] sobre esse cristal. Neste trabalho pretende-se determinar, por Difração de Fotoelétrons PED e Difração de Elétrons de Baixa Energia LEED quantitativo, a estrutura cristalográfica de camadas de óxido de cromo. Foi utilizado radiação síncrotron da linha SGM do LNLS e radiação convencional (Al/Mg Ka). Com base nos padrões de difração LEED e de PED para fotoelétrons O 1s, Cr 2p e Cu 2p propomos diferentes modelos teóricos para a estrutura de óxido de cromo.

[1] B.M. Weckhuysen, R. A. Schoonheydt, Catal. Today 51 (1999) 223;

[2] P. Marcus, V. Maurice, in: M. Schutze (Ed.), Corrosion and Environmental Degradation: A Comprehensive Treatment, Wiley, New York, 2000

[3] P. Schmuki, J. Solid State Electrochem. 6 (2002) 145;

[4] A. Maetaki, K. Kishi, Surf. Sci. 411 (1998) 35

Acknowledgements
This work was supported by FAPESP, LNLS and CNPQ

230

Pd ultrathin film growth on C(0001): Does it show magnetic behavior?

E. De Biasi[1], de Siervo A.[2], Garcia, F.[2], Vicentin, F.C.[2], Landers R[3], and Knobel, M.[3]

[1] Centro Atômico de Bariloche - La Plata AC Argentina
[2] Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil
[3] Universidade Estadual de Campinas - Campinas SP Brazil

Recently has been increase the interest for the study of some systems that a priory not exhibits a magnetic behavior but, under special condition they should became magnetic. This is the Pd case. Theoretical studies shows if Pd could be grown hcp, there is a possibility that they become ferromagnetic, fulfill the Stoner Criteria. In order to study this subject we gowned ultrathin palladium metal films on C(0001). Their composition, electronic structure and magnetic behavior were studied by synchrotron based techniques (XPS and XAS), LEED and magnetic measurements. The Pd films were deposited in UHV conditions (pressure < $5x10^{-10}$ mbar) with thicknesses ranging from 1-2 ML to 12 ML. Annealing was performed to segregate Pd and to generate a cluster structure, which could induce the system to acquire magnetic properties as has been predicted by theoretical studies. To clarify the existence or not of ferromagnetic behavior in these samples, magnetic measurements were performed using a SQUID Magnetometer. Also, complementary DFT calculations were made in order to study the ferromagnetic ordering possibility.

Acknowledgements
The authors would like to thank the LNLS staff and particularly P.T. Fonseca for his help during beam time. This work was financially supported by CNPq, FAPESP and LNLS under the proposal D08A-SGM-4848. E. D. B. especially would like to thank CNPq for his post-doctorate fellowship.

231

Ultrathin filmes of Pd on Ru(0001): magnetic behavior?

de Siervo A.[1], E. De Biasi[2], Garcia, F.[1], Landers R[3], Martins, M. D.[4], and W. A. A. Macedo[4]

[1] Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil
[2] Centro Atômico de Bariloche - La Plata AC Argentina
[3] Universidade Estadual de Campinas - Campinas SP Brazil
[4] Centro de Desenvolvimento Tecnologia Nuclear - Belo Horizonte MG Brazil

Recently much effort has been done to study induced magnetic properties of ultrathin Pd films grown on different substrates [1]. Many theoretical works, most of them based on Density Functional Theory (DFT) calculations, claim that Pd in an expanded *fcc* structure or in an *hcp* symmetry should display a ferromagnetic behavior. It is well known that the obtained electronic and crystallographic structures of ultrathin films are functions of growth mode and parameters such as substrate temperature, rate of deposition, and mismatch of the lattice parameters. Due the small lattice mismatch between the Pd(111) and Ru(0001) it is expected that Pd can grow in an almost planar fashion on Ru(0001). However, it is not clear if Pd grows in an *hcp* or *fcc* structure on this surface. In this work, Pd films with thicknesses ranging from sub-monolayer up to approximately 15 ML were grown on a Ru(0001) single crystalline substrate, under ultrahigh vacuum conditions. The study was based on x-ray photoelectron spectroscopy and diffraction (XPS and XPD) using conventional Mg Kα and synchrotron radiation sources, low- and high-energy electron diffraction (LEED, RHEED) and magneto-optical Kerr effect (MOKE) measurements. LEED patterns show hexagonal symmetries, which could be interpreted as an indication of an *hcp* Pd film, which would be used to verify the predictions of a ferromagnetic behavior in this system. However, the XPD analysis indicates that our Pd films are formed by *fcc* domains rotated by 60 degrees one in relation to the other. Notwithstanding the fact that Pd films did not grew in *hcp* symmetry, the XPD analysis indicated a strong interlayer expansion, which have been a promise to see magnetism in such Pd films. The electronic structure and crystallography of the Pd films as well as the magnetic behavior of such Pd films will be discussed in details based on the multitechnique measurements and on a comprehensive theoretical approach including multiple scattering calculations for photoelectron diffraction and spin-polarized DFT calculations.

References [1] E. Hüger and K. Osuch, Phys. Rev. B 72, 085432 (2005).

Acknowledgements

This work has been financially supported by FAPESP, CNPq and LNLS. The theoretical calculations for this work were performed at the LNLS PC cluster. The authors would like to thank P.T. Fonseca for his help in the SGM beamline.

232

Morphological study of metal hexacyanoferrate films dispersed on the $SiO_2/ZrO_2/C$-graphite carbon ceramic electrode disk

Marafon, E[1] and Gushikem, Y.[1]

Universidade Estadual de Campinas - Campinas SP Brazil

New generations of materials presenting high electrical conductivity, designated as carbon ceramic materials, have been prepared by the sol-gel processing method and their use as substrate materials to support electroactive species has been a subject of great interest in recent years. Compared to the conventional carbon paste electrodes, where graphite particles are mechanically mixed with silica-zirconia mixed oxide and mineral oil, the great advantage of the carbon ceramic disk prepared by sol-gel method is that in this case graphite particles are uniformly and homogeneously dispersed in this mixed oxide matrix. Transition metal hexacyanoferrates have been subject of widespread interest because of their electrocatalytic, electrochromic, ion exchange, ion sensing and photomagnetic properties. The objective of this work is to characterize morphologically the thin films of copper hexacyanoferrate (CuHCF) and iron hexacyanoferrate (Prussian Blue, PB) formed by an *in situ* reaction on the $SiO_2/ZrO_2/C$-graphite (SZC) carbon ceramic electrode surface. The carbon ceramic disks prepared were analyzed by scanning electron microscopy (SEM), using low vacuum microscopy (JSM 5900LV) from the Laboratory of Electronic Microscopy at the National Synchrotron Light Source Laboratory (LNLS) in Campinas, Brazil, operating at an accelerating voltage of 25 kV. The images were obtained by using the secondary electrons. X-ray emission analysis (EDS) was used for elemental mapping in a Noram Voyager instrument. The disks were fixed onto conducting double faced tape adhered to an aluminum support. SEM images for SZC disk shows a smooth surface, due to the applied pressure to obtain the disk. Otherwise, for the CuHCF and PB modified disks, in both modified disks are possible to observe an increase in the roughness. For the PB modified disk it is observed some structures like fibers presenting agglomerates of PB particles at the end.

Acknowledgements

This work has been supported by the Brazilian Synchrotron Light Laboratory (LNLS) under proposal LV 4551/05. The authors also wish to thank FAPESP for financial supports.

233

ATOMISTIC PROCESSES OF METAL ALLOY NANOWIRES

Bettini J.[1], Silva, P. C.[1], D. S. Galvao[2], and Ugarte, D.[1]

[1] Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil
[2] Universidade Estadual de Campinas - Campinas SP Brazil

Metallic nanowires (NWs) receive huge attention from the scientific and technological communities due to their quantum conductance behavior. Atomic-scale metal wires may be generated by elongating metal contacts. During the elongation and just before rupture, the NW conductance shows flat plateaus and abrupt jumps of approximately a conductance quantum. In these experiments, NW atomic arrangement and conductance change simultaneously, making difficult to discriminate between electronic and atomic structure effects. Most studies have been focused on pure metals such as, Au, Ag, Pt, Cu, etc. and a good understanding has been developed, but many open questions and controversial points remain. Among the important questions are the atomistic mechanism associated with the elongation and rupture of alloy nanocontacts and whether it is possible to obtain one-atom thick wires. In this work, we report an experimental and theoretical study of the stretching of metallic alloy nanocontacts (Ag/Au) and the formation of linear suspended atomic chains. The theoretical data are from tight-binding molecular dynamics using second moment approximation and ab-initio calculations. HRTEM in-situ experiments have revealed that metal (Au, Ag, Pt, etc.) junctions generated by tensile deformation are crystalline and free of defects. In addition, the neck structure is strongly dependent on the surface properties of the analyzed metal. Then, the nanowires preferred atomic structure and elongation behavior is quite distinct for each metal, allowing the definition of a structural pattern for each metal. We have analyzed different Au1-x-Agx alloys and, noted that an Au-like structural behavior of the nanowires is easily identified for most compositions and that a high silver content ($x > 0.9$) is needed to recover silver structural behavior. This fact can be explained if we consider that during the NW elongation, the neck region chemical composition is modified and the region becomes Au enriched. However the validity of this model can not be verified from the analysis of the HRTEM images because they are originated by phase contrast. In order to follow the atomistic and compositional evolution of alloy NWs, we have used theoretical simulations, which have confirmed the Au enrichment on the narrowest contact region during the elongation. Finally, our experimental and theoretical results show that the formation of atomic chains very similar to those obtained from pure metals is also possible from metallic alloys

234

ZnO/Er_2O_3 core/shell nanowires

Mustafa, D.[1], Biggemann, D.[2], and Tessler, L. R.[1]

[1] Universidade Estadual de Campinas - Campinas SP Brazil
[2] Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil

Zinc oxide/erbium oxide core/shell nanowires are very interesting because they may exhibit laser emission in the 1.54 μm range. In this paper we present a convenient technique to obtain such structures. ZnO nanowires were obtained by a vapor-liquid-solid (VLS) method. Gold coated silicon wafers were placed in a tube furnace in the presence of ZnO + C under oxygen flow at high temperatures. By optimizing the oxygen flow, 50-100 nm diameter ZnO nanowires can be obtained on the substrates. Erbium was added by exposure of these nanowires to the the erbium source compound $Er(tmhd)_3$ at elevated temperatures. After annealing at 700°C in air the nanowires presented 1.54 μm emission when excited by any of the lines of an Ar^+ laser. EXAFS analysis revealed that the Er atoms are coordinated to 6 oxygen atoms, exactly as in Er_2O_3 . HRTEM indicated that indeed the outermost layers of the nanowires consist of a cubic compound, most probably erbium oxide. In fact, erbium atoms were not incorporated in the ZnO network and consequently the nanowires have ZnO/Er_2O_3 core/shell structures.

Acknowledgements
This work was partially supported by FAPESP and NSF.

235

ESTUDO DA INFLUÊNCIA DO SISTEMA SUBSTRATO-CATALISADOR NO CRESCIMENTO DE NANOTUBOS DE CARBONO

Aguiar, M. R.[1] and Swart, J. W.[1]

Universidade Estadual de Campinas - Campinas SP Brazil

O presente trabalho, que faz parte de um projeto de post-doc, com bolsa individual de pesquisa do CNPq, refere-se ao estudo da influência do sistema substrato-catalisador na nucleação e crescimento de Nanotubos de Carbono - NTC por CVD térmico à pressão atmosférica, com metano como precursor de carbono. Os substratos utilizados são o Al_2O_3 e o SiO_2. O óxido de silício é obtido por oxidação de lâminas de Si tipo-n, no próprio CCS. Já o óxido de alumínio é obtido de duas formas, a saber, uma delas usa magnetron sputtering com alvo de Al no Instituto de Física-IF, da Unicamp e, a outra, se dá por e-beam com óxido de Al no Laboratório de Microfabricação do LNLS; ambas as deposições são realizadas sobre lâminas oxidadas de silício. Com o intuito de verificar a situação da superfície desses óxidos, tanto antes, como após deposição dos catalisadores e tratamento térmico, uma vez que o substrato pode induzir mudanças no comportamento do catalisador, utiliza-se Microscopia de Força Atômica (AFM) com o microscópio DI Nanoscope IIIa do LNLS. Essa técnica, que permite uma análise topográfica das superfícies, mostra que a rugosidade dos óxidos e a dos sistemas óxidos-metais difere por valores em torno de mil por cento. Os metais catalisadores empregados são o níquel e o ferro. O Ni sobre os óxidos obtidos na Unicamp é depositado no IF. O Ni também é depositado pelo LMF-LNLS imediatamente após a deposição do Al_2O_3. O Fe sobre todos os óxidos é depositado exclusivamente pelo LMF-LNLS. Não somente a verificação da nucleação e o crescimento de nanoestruturas cilíndricas, como também, a distribuição dos clusters metálicos após tratamento térmico, só são possíveis através de microscopia de varredura de alta resolução, como a fornecida pelo FEG-SEM JSM 6330F do Laboratório de Microscopia Eletrônica (LME) do LNLS. Esse tipo de microscopia eletrônica permite a visualização clara das diferentes distribuições das partículas catalisadoras, conforme o tipo de substrato utilizado, possibilitando análises estatísticas. Permite, também, estudar a densidade de nucleação e crescimento dos nanotubos de carbono, que é um dos objetivos do projeto de post-doc. Dessa forma, pode-se verificar como os diferentes sistemas substratos-catalisadores se relacionam com o crescimento das nanoestruturas cilíndricas (nanotubos ou nanofibras) obtidas por CVD com metano e H_2, em diferentes temperaturas e tempos, permitindo-se sistematizar o processo.

Palavras-chave: nanotubos de carbono, nanoestruturas, CVD, metano, catalisadores

Acknowledgements
CNPq e LNLS.

236

Local structure and vibrational dynamics of CdSe quantum dots.

Romano, R.[1], Rodella, C. B.[2], Avendano, E.[2], Alves. O. L.[1], and Azevedo, G. de M.[2]

[1] Universidade Estadual de Campinas - Campinas SP Brazil
[2] Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil

Nanocrystals are an intriguing domain of condensed matter. They exist in an intermediate regime between that of a large molecule and a bulk solid. Their nanometric dimensions and large surface-to-volume ratio give rise to a variety of interesting phenomena such as the quantum confinement of carriers, which enables the tuning of optical properties by varying their size. In this work, we explore the influence of size and surface effects on the thermodynamics of nanocrystalline CdSe through temperature-dependent XAFS measurements.

Samples of CdSe nanocrystals with average diameters varying from 2 up to 10 nm, were prepared by precipitation of CdSe in a high boiling point coordinating solvent and a capping agent. Specific nanocrystal sizes were obtained by means of a rigorous control of the temperature and time of reaction. Samples were extensively characterized with a number of techniques, including optical absorption, X-ray diffraction (XRD), Transmission Electron Microscopy (TEM) and X-ray Absorption Fine Structure (XAFS). Herein, we focus our attention on the dependence of structural and electronic properties on different capping agents.

Temperature-dependent XAFS measurements around the Se K-Edge (12658 eV) were performed at the LNLS D04B XAFS-1 beam line. EXAFS results indicate the core of the nanocrystals has a highly strained bulk-like local structure. A distinct contraction of the Se-Cd interatomic distance, as well as an increase in static disorder, are observed as the size of the nanocrystals is reduced. X-ray Absorption Near Edge Structure (XANES) results show systematic changes in shape and absorption edge position. Analysis of the temperature dependence of thermal disorder yielded the Debye temperature and thermal expansion coefficient as a function of nanocrystal size. As our results demonstrate, both quantities are size-dependent. The influence of different capping agents (such as TOPO and HDA) on the structure of the nanocrystals will be discussed. The Se-Cd radial distribution function and mean interaction potential, reconstructed from a cumulant analysis of the temperature-dependent EXAFS signal, will be presented.

Acknowledgements
This work was partially supported by CNPq and FAPESP.

Índice Remissivo