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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

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Parte VI Matéria Mole e Fluídos Complexos

Parte VII Materiais Estruturais e Aplicações na Indústria

Parte VIII Métodos e Instrumentação

Parte IX Não se aplica

Parte X Propriedades Estruturais, Eletrônicas e Magnéticas de Sólidos

Parte XI Superfícies, Interfaces e Nanossistemas

Parte I

Plenárias

Advances in small-angle X-ray scattering as a probe to nanoscale structure and dynamics of soft matter

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In recent years, small-angle X-ray scattering (SAXS) has received renewed impetuous as a powerful characterization technique for soft condensed matter and biological systems. This trend is sequel to a combination of several factors, most notably the development of advanced instrumentation at modern synchrotron sources and parallel advancement of data analysis methods. As a result, synchrotron SAXS instruments are in high demand and new facilities are being constructed or planned at upcoming synchrotrons. This talk will give an overview of these developments in SAXS and related scattering and imaging techniques, more specifically for probing the nanoscale structure and non-equilibrium dynamics of soft matter. For instance, a wide range of self-assembly processes in soft matter occurs in the millisecond time range and SAXS can provide unique information in these studies. This will be demonstrated by several representative examples including self-assembly of amphiphilic molecules in solution, protein adsorption on to a charged interface, and growth dynamics of dilute aerosols and so on. Quantitative scattering experiments elucidate not only the transient structures and their growth dynamics but also reveal the link between nanoscale thermodynamics and macroscopic properties. These studies can be extended to a wide range of soft matter and biological systems.

Acknowledgements:

High Pressure X-Ray Photoelectron Spectroscopy: A Tool to Bridge the Pressure Gap in Heterogeneous Catalysis

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High pressure XPS became more and more popular for the investigation of heterogeneous catalytic processes within the last years. This soft X-ray in situ technique allows the identification of correlations between the catalytic activity and the electronic structure of the working catalyst surface. By this kind of measurement it is possible to identify metastable electronic states of the catalyst surface which form just under reaction conditions. These states might not be observed ex situ. The application of high pressure XPS at synchrotron radiation facilities is especially appropriate to identify subsurface species involved in the reaction, due to the fact, that the photon energy and therefore the information depth of the emitted photoelectrons can be changed. This new technique was applied to identify different carbon species on active Pd catalysts in selective hydrogenation reaction. It was shown, that the incorporation of C in the surface has a strong influence on the selectivity of the reaction. In this presentation the basics of high pressure XPS will be described. The potential of the method will be demonstrated by some example of recently investigated catalytic reactions. An outlook on the future of the method will be given.

Acknowledgements:

Application of X-ray absorption spectroscopy to the characterization of real surfaces and interfaces: Some industrial case studies

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Synchrotron radiation provides a unique resource for the characterization of real surfaces and interfaces reflecting its unique properties (tunability, penetrability, polarization and intensity) which confer the opportunity to study materials transformation in-situ and in real time, properties which also provide significant added-value for the industrial research community.

X-ray absorption spectroscopy using synchrotron radiation provides the ability to characterize the local structural environment around selective atomic sites and the same following processing. The wide band-width afforded by synchrotron radiation enables most atoms within the periodic table to be accessed for experimental study.

Drawing down on the above perspective the talk will review the basic principles of the technique (XANES and EXAFS) and the associated instrumentation facilities. These will be illustrated via a number of case studies drawn from a range of industrial collaboration projects, e.g.

Studies of platinum and fuel cell electrodes under conditions of potential control (Pt L-edge).

Characterization of surface oxides on compound semi-conductor wafers (Ga and As K-edges).

Structural characterization of anti-corrosion coatings on copper thin films (C and Cu K-edges).

Studies of the flash calcination of kaolinite particulates (Al and Si K-edges)

Structural degradation of anti-wear additives on steel surfaces (Fe and Z L-edges, S, P, Fe and Z K-edges).

Studies of surface melting on thin films of normal alkanes (C-K edge).

Finally the utility of using of absorption spectroscopy in combination with high resolution diffraction will be highlighted.

Acknowledgements:

Parte II

Biologia Estrutural

Conformational Stability of MRJP-1 from *Apis mellifera*

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Major royal jelly protein 1 (MRJP-1) is the main protein component of honey bee (*Apis mellifera*) royal jelly, and is also present in its brain. MRJP-1 function in the brain is still unknown. The physicochemical and structural characterization of MRJP-1 is fundamental to understand its function. It is a glycoprotein of $\sim$57 kDa coded by a single gene, and presents 8 isoforms. Amino acid sequence analysis shows a secondary structure with 20% α-helix and 17.6% β-sheet. In this work we analyzed the conformational stability of MRJP-1 under different conditions of temperature and pH. MRJP-1 was purified from royal jelly by anion-exchange FPLC, dialyzed and lyophilized. Different aliquots were used for the unfolding process analyses using circular dichroism and fluorescence spectroscopy. The thermal unfolding process revealed that MRJP-1 is a highly stable protein at different pHs and less stable in the presence of calcium ion.

Acknowledgements: Supported by CAPES, CNPq and ABTLus.

BIOPHYSICAL CHARACTERIZATION AND CRYSTALLIZATION OF HFQ RNA CHAPERON PROTEIN FROM *Herbaspirillum seropedicae*

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Hfq, an RNA chaperone, has recently been recognized as an important protein involved in the post-transcriptional regulation in several bacteria. This protein was isolated from *Herbaspirillum seropedicae*, a diazotrophic bacterium found associated to important agricultural crops. This protein has a role in the post-transcriptional regulation of nitrogen fixation process. In previous studies, this protein was purified to 99% purity and the purified protein bound specifically to DsrA sRNA. In this work, we analyzed the Hfq protein under a biophysical point of view using circular dichroism (CD) spectroscopy and dynamic light scattering (DLS). The far-UV CD spectrum profile of Hfq protein indicates the predominance of beta-sheet secondary structure. The DLS experiment showed a monodisperse molecule with 48 kDa of molecular mass indicating a hexameric final conformation in accordance with gel-filtration experiments. Automated crystallization trials by sitting drop vapor diffusion method resulted in crystals in several conditions after three days. X-ray diffraction, using an in-house X-ray generator from Rigaku, confirmed that most of the crystals were indeed protein crystals. The crystallization conditions are being refined and soaking experiments with ATP are planed.

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Purification, crystallization and preliminary X-ray analysis of CMS1MS2: a cysteine proteinase from *Carica candamarcensis* latex

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The cysteine proteinases from Caricaceae latex are widely used industrially as well as in pharmaceutical preparations. The purposes of the present work were to isolate the enzyme with the greatest catalytic activity present in *Carica candamarcensis* latex and to determine its tridimensional structure in order to enhance our understanding of the structure-activity relationship of plant proteases. A 23 kDa purified cysteine proteinase (designated as CMS1MS2) displaying approximately four-fold the enzymatic hydrolysis of BAPNA substrate comparing to papain was obtained after three chromatography steps. The purified enzyme inhibited with E-64 [N-(3-carboxyoxirane-2-carbonyl)-leucyl-amino(4-guanido)butane] was crystallized by hanging-drop vapour difusion using Hampton Research Crystal Screens I and II. Crystals suitable for difraction experiments with 0.25 x 0.1 x 0.01 mm appeared in drop solution within weeks. Crystallization drops were prepared in the ratio 1:1 from two stock solutions; (i) 0.2 M ammonium sulfate and PEG 4000/8000 30% (w/v) and (ii) protein at 10 mg/ml. Crystals belong to monoclinic system (space group $P2_1$) and difracted up to 1.80 resolution at a synchrotron source (MX1-LNLS). The unit cell parameters are $a = 53.26$, $b = 75.70$, $c = 53.23$ and $\beta = 96.80$. The calculated Matthews coefficient indicated the presence of two molecules in the asymmetric unit. Initial phases were determined by molecular replacement using a model constructed by SWISS-MODEL server based on the primary structure of CMS1MS2. After manual rebuilding of the model and cycles of refinement the values of R_{factor} and R_{free} obtained were 0.23 and 0.31, respectively. Further refinement is in progress. Due to the large difference between R_{factor} and R_{free} and also to the difficulty to improve the refinement of the atomic model, an alternative data set indexation is being evaluated (in space group P1).

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Crystallization and preliminary X-ray diffraction analysis of Leucurolysin-A, a non-hemorrhagic metalloproteinase from *Bothrops leucurus* venom

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Snakes of the Viperidae family (vipers and pit vipers) are known to induce hemorrhage as a typical consequence of envenomation. These snake venoms are a rich source of metalloproteinases, known as snake venom metalloproteinases (SVMPs). In Brazil, snakes of the Bothrops (Lanceheads) genus are responsible for 90% of all recorded snakebites in which the snake is identified. Of the 24 currently recognized Brazilian Bothrops species, *Bothrops leucurus* is an important poisonous snake which inhabits the Atlantic forest remnants in valleys of northeastern Brazil, including the States of Bahia and Espirito Santo. The SVMPs are synthesized in the venom gland as large multidomain proteins, including a proenzyme domain and a highly conserved zinc-proteinase domain. The structural differences between these classes are the result of additional carboxy-terminal domains following the metalloproteinase domain. Class P-I includes the small SVMPS (Mr 23 kDa), with lower or no hemorrhagic effect, whereas the P-II, P-III and P-IV classes have disintegrin-like, disintegrin-like and cysteine-rich, and disintegrin-like, cysteine-rich and lectin-like domains carboxy to the proteinase domain, respectively. Leucurolysin-A (Leuc-A), a non-hemorrhagic zinc-metalloproteinase grouped in P-I class, was successfully purified from crude venom of *B. leucurus*. The proteinase was crystallized using the hanging-drop vapour-diffusion method. The X-ray diffraction data showed that the crystal belongs to the orthorhombic system, space group $P2_12_12_1$, with unit-cell parameters a = 43.98, b = 58.36 and c = 76.41 and one molecule in the asymmetric unit. This zinc-metalloproteinase from *B. leucurus* shares 74% amino acid sequence identity with BaP1, a hemorrhagic zinc-metalloproteinase from *B. asper*. Using the Bap1 structure as a model (PDB code 1ND1), the phase problem was solved by molecular replacement. It is expected that our structure will help us to understand the dierences between this non-hemorrhagic enzyme and others hemorrhagic proteinases.

Acknowledgements: This work was supported by CNPq, FAPEMIG and CAPES.

Purification, crystallization, data collection and processing of chymotrypsin-BTCI-trypsin ternary complex

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The black-eyed pea trypsin/chymotrypsin inhibitor (BTCI) is a Bowman-Birk type inhibitor isolated from *Vigna unguiculata* Cowpea seeds a kind of bean that represents an important alimentary source for most of the population in Brazillian northeast region. BTCI is a stable globular protein with 83 amino acid residues, molecular mass of 9.1 kDa and seven disulfide bonds. In this work, we present the crystallization, data collection and processing, and molecular replacement solution of the structure of BTCI in ternary complex with trypsin and chymotrypsin. The ternary complex was obtained by mixing BTCI and enzymes at 1:1:1 molar ratio in 50 mM Tris-HCl, 0.2 M KCl pH 7.5 for 30 minutes. It was purified by size-exclusion chromatography and corresponds to a band of approximately 55 kDa on native polyacrylamide gel electrophoresis. This ternary complex was crystallized by the sitting-drop vapor-diffusion method with 0.1 M Hepes pH 7.5, 10% polyethylene glycol 6,000, 5% 2-metil,2,4-pentanodiol as precipitant. X-ray data were collected from a single crystal of ternary complex under cryogenic conditions to 2.7 resolution. The crystal belong to the space group $P12_11$, with unit-cell parameters a = 49.56, b = 93.26 and c = 70.81 , angles $\alpha = \gamma = 90.00$ and $\beta = 95.91^o$. The structure of the ternary complex has been solved by molecular replacement using the crystal structure of the BTCI-trypsin binary complex (PDB code 2G81) and the chymotrypsin (PDB code 4CHA) as search models.

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

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The biosynthesis of the 21^{th} 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 $tRNA^{Sec}$ using 2D detection at SAXS2 beamline at the Laboratóro Nacional de Luz Síncrotron (LNLS), allowed the determination of the global SELA structure as homodecamer composed of five SELA dimmers with a maximum diameter of 180, a molecular mass of 550 +/- 30kDa and a radii of gyration of 66.5 +/- 0.1, while SELA-$tRNA^{Sec}$ presented a maximum diameter of 203, a molecular mass of 865 +/- 40kDa and a radii of gyration of 68.0 +/- 0.1. 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 $tRNA^{sec}$, and that SELA should interact with ten tRNA molecules not five like thought before. 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 $tRNA^{sec}$.

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TRANSPORT OF A PEPTIDE THROUGH THE DOPC BILAYER MEMBRANE BY MOLECULAR DYNAMICS SIMULATION

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Non-assisted transport of peptides across biological membranes is involved on a variety of cellular functions, including signal transduction, antagonism of transmembrane receptors, cellular traffic and drug delivery. A non-assisted peptide crossing event is ordinarily driven by the free-energy variation of partitioning the peptide between water/lipids phases. In this contribution, we estimate the free-energy cost of such process using full atomistic free-energy molecular dynamics (MD) simulations using the Adaptive Biasing Force (ABF) code. We consider the transport of the canonical loop (CTKSIPPQC) from the crystal structure of a serine protease inhibitor from *Vigna unguiculata* (BTCI) through the fully-hydrated dioleyl-phosphatidyl-choline (DOPC) lipid bilayer. The whole inhibitor is a member of the Bowman-Birk family, presenting inhibitory activity against trypsin and chymotrypsin simultaneously. The peptide used in this simulation corresponds to the canonical loop containing the reactive site (Lys) against trypsin and one disulfide bond. We found that the peptide transport is opposed by a dominant free-energy barrier of approximately 15 kcal.mol^{-1} at the position -15.10^{-10}m of the reaction coordinate, corresponding to the lipid-head-group interface region. This result suggests that the formation of a peptide-contained pore on the membrane surface as the rate-limiting step of the reaction process. Overall, our results point to molecular details participating on the mechanism of non-assisted transport and provide new insights for further rational design of compounds that could facilitate the lipid transposition by BTCI-like peptides.

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NMR studies of the H-NS C-terminal domain from Xylella fastidiosa

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The nucleoid-associated protein H-NS is a major component of the bacterial nucleoid, involved in DNA compaction and transcription regulation. Extensive studies on the biological functions demonstrated that H-NS plays a role in the regulation of many genes on the Escherichia coli chromosome, and represses the expression of a variety of proteins at the level of transcription, either by binding directly to DNA or through changes in DNA topology. In this work we chose the open reading frame 0749 of the Xylella fastidiosa, an important bacterium that causes a serious disease of oranges called citrus variegated chlorosis (CVC). The XF0749 codifies a protein of 134 amino acids (15kDa), a predicted H-NS protein. In order to gain insights into its function, we are studying the C-terminal domain (H-NSc), predicted to be involved in DNA binding, by high resolution NMR. The structure was solved and is deposited on the Protein Data Bank under code 2jr1. Experiments to test whether H-NSc binds to specific promoters of the Xylella fastidiosa DNA are in progress, as well as relaxation time measurements and calculation of dynamic properties of the structure.

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Glutaredoxin 1 and Glutaredoxin 2 from *Saccharomyces cerevisiae* have very distinct biochemical properties although they share 85 % of amino acid sequence similarity.

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Glutaredoxins (Grxs) together with thioredoxins (Trx) are important proteins involved in the control of thiol/disulfide status inside cells. In most cases, there are various Grx and Trx isoforms and in many cases they are considered redundant proteins. *Saccharomyces cerevisiae* possesses five Grx proteins, two of them dithiolic enzymes (Grx1 and Grx2). Grx1 and Grx2 share 85 % of amino acid sequence similarity and deletion of Grx2 gene indicated that this enzyme is responsible for the majority of the glutathione dependent oxido-reductase activity. This phenomenon could be due to a higher expression level of Grx2 or because this oxido-reductase is a more efficient enzyme. In spite of their high amino acid sequence similarity, Grx2 specific activity was at least ten times higher than Grx1 specific activity. In an attempt to better understand the mechanisms and differences between these yeast dithiol Grxs activities, we elucidated the crystallographic structures of yeast Grx2 in the oxidized state and of yeast Grx2-C30S mutant complexed with glutathione through a mixed disulfide. Comparisons among these structures and those of yeast Grx1 (Hakansson and Winther, 2007) indicate that the substitution of Ser23, His31, Gln52 and Asp90 in Grx1 by Ala23, Lys31, Glu52 and Ser90 in Grx2 could explain the difference in their specific activities and pKa value of their reactive cysteines. Taken together, our results indicated that the biochemical roles of Grx1 and Grx2 are not fully redundant in yeast.

Acknowledgements:

Crystallization and X-ray diffraction data collection of two crystal forms of a new basic Lys49-PLA2 from *Bothrops jararacussu*

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Phospholipases A2 (PLA2; EC 3.1.1.4) are a family of enzymes that catalyze the hydrolysis of the *sn*-2 ester bond of phospholipids to release free fatty acids, including arachidonic acid. In this work, a novel Lys49-PLA2 was purified to homogeneity from the *Bothrops jararacussu* venom through HPLC chromatography. Two crystal forms were obtained by the hanging-drop vapor diffusion method, both containing two molecules in the ASU. A first crystal form grown from a solution containing sodium citrate pH 8.5, PEG 4000 and 2-propanol belongs to the orthorhombic space group $P2_12_12_1$, with unit cell parameters $a = 49.2$, $b = 66.4$, $c = 87.0$. A second crystal form belonging to the trigonal space group $P3_121$ with cell dimensions $a = b = 55.8$, $c = 128.0$, was obtained from a solution containing MES pH 8.0, ammonium sulfate and PEG MME 5000. X-ray diffraction data were collected to 2.0 and 1.9 resolution for the orthorhombic and trigonal crystals, respectively, using synchrotron radiation at the LNLS beamline D03B-MX1. Crystal structures were solved by the molecular replacement method and structure refinement is in progress.

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Structural characterization of bZIP SCF5 transcription factor from sugarcane by Small-Angle X-ray Scattering (SAXS)

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Basic leucine zipper (bZIP) proteins form a large family of transcription regulators in plants and other eukaryotes. bZIPs are characterized by a conserved region rich in basic amino acid residues that binds to the target DNA and the leucine zipper region. These proteins are important regulators of several processes of signaling in plants, such as light response, hormone signaling or pathogen defense. Protocols for cloning, expression and purification of a sugarcane bZIP SCF5 were previously reported (Schlögl, P. S. *et al.*, 2004, *Plant Sci.* **167**:583-595). Here, we present a first structural characterization of SCF5 bounded to DNA. Data were collected in the D02A-SAXS2 beamline at LNLS and processed with the programs Fit2D, PRIMUS, GNOM and GASBOR. The low-resolution model recovered for the SCF5/DNA complex has an elongated form. Our results seems to indicate that SCF5/DNA is a homodimer in solution, as judged by structural comparisons to available bZIPs crystallographic structures.

Acknowledgements: We gratefully acknowledge the SAXS beamline staff at LNLS and FAPESP for financial support.

Determinación de la distribución multielemental por μ-SRXRF en corteza renal de ratas con hidroarsenicismo tratadas con un antioxidante

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El arsénico es un cancerígeno ampliamente distribuido en la naturaleza. El consumo crónico de agua contaminada constituye la principal fuente de exposición para humanos teniendo efectos neuro, hepato y nefro-tóxico. Aunque los mecanismos moleculares no han sido totalmente dilucidados, se acepta que el estrés oxidativo producido por As es el principal responsable de su toxicidad y carcinogenicidad. Basados en resultados propios obtenidos in vitro, y de otros laboratorios in vivo, se analizó el efecto del agregado de un antioxidante en la dieta de animales con hidroarsenicismo. Un lote de 12 ratas fue dividido en 4 grupos (Control, As, Antioxidante y As+Antioxidante). Durante 60 días los animales bebieron agua con o sin 50 ppm As (según corresponda) tras los cuales fueron sacrificados. Los riñones fueron resecados y uno fue congelado a -80 ^{o}C y el otro fijado en formol para realizar estudios histopatológicos. Un día antes de su traslado al LNLS (Campinas, SP, Brasil) el riñón congelado fue cortado en láminas de 100 μm con crióstato y adherido a Ultralene. Las muestras fueron mantenidas en hielo seco hasta su respectivo análisis espectrométrico utilizando μ-SRXRF para determinar la distribución y concentración de As y otros elementos en corteza renal. Se analizaron secciones de 2 mm x 2 mm con haz blanco, utilizando un colimador capilar de 30 μm y un motor de pasos x-y (30 μm en ambas direcciones). En correspondencia con trabajos previos, se encontró acumulación de As y Cu. En los riñones de los animales As+Antioxidante se observó una disminución del 60-65% en la retención de estos elementos sin cambios en su distribución. Solamente se observaron lesiones histológicas a nivel de los túbulos renales y la cápsula de Bowman en el grupo As. Estos resultados sugieren que el uso de antioxidantes podría ser una medida preventiva frente a la patología arsenical.

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Expression of the recombinant ModC protein and production of mutants of ModA protein from the molybdate transport system from *Xanthomonas axonopodis pv. citri*

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In recent studies we have characterized biochemical and structurally the ModA protein from the phytobacteria *X. citri* (*Xac*). This ModA is very similar to other orthologs and consists of two domains that open and close upon binding of the molybdate (K_d of 0.29 μM). The genome of *Xac* presents the high affinity molybdate ABC transport system constituted by a permease protein that forms the translocation pathway across the membrane (ModB) and an ATPase-binding protein (ModC) that interacts at the cytoplasmic surface to supply the energy for active transport, both depending on a periplasmic molybdate-binding protein (ModA) which determines the affinity of the system. In order to study the possible interactions between ModB and ModA and ModC proteins we have explored the structural characterization of the soluble proteins. The gene encoding the ATP-binding protein ModC was amplified by PCR from *Xac* 306 genomic DNA, cloned into pET28a vector (Novagen) and overexpressed in E. coli K-12, as an insoluble His-tagged fusion protein. Protein purification was performed by anion-exchange chromatography after solubilization of the inclusion bodies with 8 M guanidine-HCl. Attempts to express the ModC as a soluble protein and increase its stability have been conducted in different ways. Additionally, following the initiated structural analysis of the molybdate-binding protein (ModA), mutants have been constructed focusing the residues present in the pocket that interact with the molybdate as well as some important residues for structural preservation. These results will be useful to confirm our hypotheses about the individual residues, leading to a more detailed view of the molybdate transport system in *Xac* .

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Estudos Estruturais e Planejamento Racional de Novos Inibidores da Enzima Xylellaína de *Xylella fastidiosa*

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A *Xylella fastidiosa* é uma bactéria gram-negativa responsável por doenças economicamente importantes, entre elas a Clorose Variegada dos Citros (CVC). A acessibilidade ao seu genoma acelerou a busca de genes envolvidos em sua patogenicidade, em especial as proteínas envolvidas em importantes processos biológicos. Após a liberação do genoma desse fitopatógeno, o grupo do Prof. Flávio Henrique Silva (DGE - UFSCar), identificou e caracterizou uma cisteíno protease, denominada Xylellaína, que é diferencialmente expressa na cepa patogênica 9a5c de X. fastidiosa. Recentemente, a estrutura tridimensional dessa proteína foi elucidada em nosso laboratório através da técnica de difração de raios-X com dispersão anômala a um comprimento de onda (SAD) até a resolução de 1.6 . A estrutura apresenta enovelamento semelhante às cisteíno proteases da família da papaína, com homologia estrutural às Catepsinas. Esses resultados obtidos com a Xylellaína abrem espaço para um estudo pormenorizado da relação estrutura-atividade, visando compreensão do mecanismo de atividade e ainda para o planejamento de inibidores contra as doenças ocasionadas pela X. fastidiosa. Dentro desse âmbito, os objetivos deste projeto envolvem a busca de novas moléculas capazes de inibir seletivamente a Xylellaína bem como a caracterização cinética e estrutural dessas interações. A detalhada caracterização estrutural da Xylellaína com os inibidores encontrados, será realizada através determinação da estrutural cristalográfica desses complexos e de técnicas espectroscópicas, permitindo um conhecimento avançado sobre as interações inibidor proteína.

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Estudos por RMN de interações entre a proteína PthA de *Xanthomonas Axonopodis* pv *Citri* e proteinas de citrus

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As proteínas PthA de *Xanthomonas axonopodis* pv *citri* são fatores de patogenicidade requeridos para o desenvolvimento de sintomas de cancro cítrico. Elas pertencem à familia de proteínas AvrBs3-like de proteínas efetoras de bactérias que são transportadas pelo sistema excretor do tipo três (TTSS) de bactérias para dentro das células da planta receptora, onde agem como fatores de patogenecidade ou avirulência, dependendo de como são reconhecidas pelo sistema de defesa da planta. PthAs são compostas de uma região N-terminal necessária para a transferência pelo sistema TTSS, uma região central que consiste de um número variável de repetições de um peptídeo de 34 aminoácidos, que confere seletividade de alvos para infecção, e uma região C-terminal, com características de proteínas de ligação a DNA. O objetivo desse trabalho é verificar quantas repetições são necessárias para a formação de um domínio estável, e investigar a interação desses domínios com outras proteínas e DNA, utilizando espectroscopia por Ressonância Magnética Nuclear. Estamos trabalhando com construções de tamanhos diferentes, com diferentes quantidades de repetições do peptídeo de 34 aminoácidos, obtidos na primeira etapa do projeto.

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Identification of genes involved in leukemic blasts and bone marrow mesenchymal stem cells interaction.

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Cancer is an extremely complex, heterogeneous disease and the interactions between tumors and their microenvironment reflect the physiological complexity of cancer, which is a major focus of current cancer research. Acute Lymphoblastic Leukemia (LLA) results from defective blood cell differentiation, resulting in overproduction of immature lymphocytes that overtake the normal development of blood cells in the bone marrow. LLA is the most incident cancer in early childhood. From the clinic point of view, it is important to understand the survival signals provided by bone marrow mesenchymal cells to ALL cells because the bone marrow microenvironment represents one the primary sites where residual leukemic cells survive during treatment. Genes involved in the interaction between leukemic cells and bone marrow mesenchymal cells can be used as molecular markers both for monitoring disease progression and for establishing efficacious treatments. The experimental design involves co-cultures of leukemic blasts with mesenchymal stem cells, followed by global gene expression analysis using DNA micro-array chips. A comparison of the gene expression pattern of leukemic blasts incubated with mesenchymal stem cells with the gene expression pattern of control leukemic blasts revealed the genes that are differentially expressed, which are the potential molecular markers for leukemic cell survival. These genes include transcription factors, cytokines, cell receptors, growth factors and are involved in critical cellular process such as apoptosis, cell adhesion and differentiation, cell cycle control, cell to cell signalization, DNA repair and metabolism.

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Transport coefficients, Raman spectroscopy, and computer simulation of lithium salt solutions in an ionic liquid

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Lithium salt solutions of Li(CF_3SO_2)$_2$N, LiTFSI, in a room-temperature ionic liquid (RTIL), 1-butyl-2,3-dimethyl-imidazolium cation, BMMI, and the (CF_3SO_2)$_2N^-$, bis(trifluoromethanesulfonyl)imide anion, [BMMI][TFSI], were prepared in different concentrations. Thermal properties, density, viscosity, ionic conductivity, and self-diffusion coefficients were determined at different temperatures for pure [BMMI][TFSI] and the lithium solutions. Raman spectroscopy measurements and computer simulations were also carried out in order to understand the microscopic origin of the observed changes in transport coefficients. Slopes of Walden plots for conductivity and fluidity, and the ratio between the actual conductivity and the Nernst-Einstein estimate for conductivity, decrease with increasing LiTFSI content. All these studies indicated the formation of aggregates of different chemical nature, as it is corroborated by the Raman spectra. In addition, molecular dynamics (MD) simulations showed that the coordination of Li^+ by oxygen atoms of TFSI anions changes with Li^+ concentration producing a remarkable change of the RTIL structure with a concomitant reduction of diffusion coefficients of all species in the solutions.

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Clonagem, Expressão, Purificação e Caracterização Estrutural da UGPase de Cana-de-Açúcar

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A cana-de-açúcar é um dos produtos agrícolas brasileiros de maior relevância econômica, sendo o Brasil o maior produtor mundial de açúcar de cana (sacarose). Além de açúcar, outros produtos podem ser obtidos a partir desse vegetal, tais como álcool, biodiesel e plásticos biodegradáveis. É de grande interesse econômico e social que os diversos recursos oferecidos pela cana-de-açúcar sejam explorados e por isso faz-se necessário um melhor entendimento das vias bioquímicas dessa planta. A enzima estudada neste trabalho foi a UTP:α-D-glicose-1-fosfato uridililtransferase (UGPase, EC 2.7.7.9), que está envolvida na síntese de sacarose, catalisando a produção reversível de UDP-glicose e difosfato a partir de glicose-1-fosfato e UTP. Foram determinados os protocolos de clonagem, expressão e purificação da UGPase. Iniciamos sua caracterização estrutural através da técnica de Espalhamento de Raios-X À Baixos Ângulos (SAXS) e ensaios de cristalização.

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Study of conformation changes in biological macromolecules using SAXS: the Lysozyme denaturation process

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During the last decades, the study of conformational changes in biological macromolecules has been a great challenge for the scientists, and continues to be an important subject of biotechnological interest and protein engineering. The process of folding (unfolding) of protein molecules has been intensively studied, because this investigation can contribute to the understanding of the process of protein synthesis and misfolding or aggregation processes of certain proteins. In this context, the technique of Small Angle X-ray Scattering (SAXS) appears as a valuable technique, because it provides structural information of the molecules in solution. SAXS allows dynamical studies and makes possible the study of the protein in physiological conditions. In addition, this technique can provide dimensional parameters of unstructured molecules, which would be difficult to obtain using any other technique. In this work, the denaturation process of the protein lysozyme in solution was studied by SAXS measurements in equilibrium conditions. Conformational changes were observed during the process of denaturation by the action of two independent factors: addition of urea in the solution and high temperatures. The results obtained from experiment for two pH values proved that lysozyme is a protein with a certain resistance to unfold completely. Even in extreme conditions of high concentration of urea and high temperatures, this protein does not totally lose its compactness. Moreover, only two conformational states (folded and unfolded) were observed using thermodynamic analysis. An intermediate state was not observed, because of the high cooperativity of the lysozyme unfolding process during denaturation.

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DOES *Xanthomonas axonopodis* pv. *citri* USE TYPE FOUR SECRETION SYSTEM?

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Xanthomonas axonopodis pv. *citri* (*Xac*) is the causative agent of citrus canker, a disease of significant economic importance worldwide. Since the molecular bases of the bacterium-plant interactions required for the development of citrus canker are poorly understood, the functions of the type IV secretion system (TFSS) are of great interest. In this study, we used two hypothetic TFSS proteins encoded by *vir*B loci on 64-kb *Xac* megaplasmid: XACb0032 and XACb0033. The XACb0033 is a low molecular mass (8.42 kDa), acidic protein (pI=5.60), that specifically interacts with only one effector (XACb0032), which is encoded adjacently, and does not posses ATP-binding domains, therefore, identified as Xac TFSS chaperone. The interactions of XACb0033 with its effector protein (XACb0032) and ATP and ADP were monitored. Our interest in monitoring the interactions of these proteins with nucleotides is due to similarities between TFSS and type III secretion systems that translocate protein molecules intercellularly, *i.e.*, from one bacterium to a eukaryotic host cell, utilizing ATP to drive this transport. All interactions among these molecules were monitored by fluorescence, circular dichroism, and small angle X-ray scattering (SAXS). Our results indicated size and shape differences between free and complexed XACb0033, while ADP binding to complex of these proteins resulted in evident size changes that might indicate complex breaking upon ADP production in cell. Based on these observations, we can provide the following model for TFSS pathway concerning these proteins: 1) The chaperone (XACb0033) binds to the XACb0032 to keep it in a semiunfolded conformation; 2) This complex binds to ATP and docks onto the TFSS apparatus; 3) Powered by ATP, monitored herein by ADP addition to complex, the effector (XACb0032) protein dissociates from complex and could be able to pass through the needle into the eukaryotic cell.

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Effects of gamma radiation on Beta-Lactoglobulin: Oligomerization and aggregation

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Beta Lactoglobulin (BLG) is the major protein in milk serum and whey, and has many nutritional and functional properties. BLG also has technological and medical applications. For example, the utilization of whey proteins in protein-based biodegradable edible films has been successfully applied for packing in food systems. Also, human milk allergenicity effects have been correlated to this protein. In recent years Gamma irradiation has been applied in many fields, particularly in food systems. Many studies have shown that irradiation of food can destroy or inactivate organisms that cause spoilage and decomposition, extending its shelf-life. Particularly for BLG systems, gamma irradiation decreases the degree of milk allergenicity and improves the properties of biodegradable films. However, no structural studies for irradiated BLG were available in the literature. To investigate this problem, Small Angle X-Ray Scattering (SAXS), high performance size exclusion chromatography and (HPSEC) and SDS-PAGE where applied to study BLG protein in samples with different Gamma-irradiation doses and degrees of hydration. The results show that the irradiation promotes the formation of stable BLG oligomers and the application of modeling tools for the SAXS data indicates that linear molecules where formed. Using the known crystallographic structure for the BLG protein, possible atomic models for these oligomers are proposed. Finally, these structural results will be correlated with the different functional properties of BLG in irradiated systems.

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Analysis of breast tissues (normal and neoplastic) by Small Angle X-ray Scattering

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Recently some researches have associated some types of collagen fibrils with human breast tissue, and in particular with human breast cancer[1]. Therefore, the identification of these structures in normal and neoplastic tissues could aid in a possible diagnosis, and prognosis for the tumor development. Small angle x-ray scattering (SAXS) is a powerful tool that allow determinate supramolecular systems characteristics, for example protein and therefore, can provide structural information on the changes, in supramolecular level, in normal human breast tissues due to the presence of the disease (cancer). In this work, SAXS technique was used to analyze differences between normal and neoplastic human breast tissues. Breast tissue samples analyzed, after collected, were histopathologically classified as normal tissues, fibroadenomas (benign disease) or carcinomas (malignant disease). SAXS experiment was implemented at the synchrotron radiation source of Campinas in Brazil. A focused monochromator of Si (111) was used in order to provide an X-ray beam of wavelength 1.608 and to reduce the irradiation area on the sample. The sample to detector distance was fixed in two distances, 804mm and 2043mm, allowing to record the range $0.058\text{nm}^{-1} < Q(=4\pi\sin(\theta/2)/\lambda) < 4.020\text{nm}^{-1}$ and this space was evacuated in order to minimize air scattering and absorption losses. The detector was a two-dimensional CCD camera with effective area of 261mm^2. The preliminary results of this work show that normal breast tissue (comprising collagen and adipose component) and neoplastic tissues present similar scattering patterns (shape and peaks positions), but concerning to scattering intensity each type of tissue is different. These SAXS patterns show peaks of reflections from the 1^{st} ($Q=0.086\text{nm}^{-1}$) order to the 13^{th} ($Q=1.17\text{nm}^{-1}$), corresponding a collagen-rich regions. The SAXS pattern corresponding to pure adipose breast tissue is relatively featureless. However, an characteristic peak at $Q=1.51\text{nm}^{-1}$ is present, corresponding to packing of triacylglycerols molecules. This preliminary study shows that the SAXS technique provides a potential medical tool for characterizing human breast tissues.
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Crystal Structure of the Leptospiral Antigen LIC10793 Reveals a Two-domain Protein with Putative Protein Binding Function

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LIC10793 is a 49 kDa protein of unknown function identified by bioinformatics analysis in the genome of *Leptospira interrogans* serovar Copenhageni. Recently, it was shown that LIC10793 is an outer membrane protein recognized by antibodies present in sera from early and convalescent phases of leptospirosis patients, suggesting its utility as a good antigen for the diagnostic of the disease. LIC10793 is predicted to be a lipoprotein by LipoP web server but its function could not be inferred by sequence comparison methods. Therefore, the purpose of this work was to determine the crystal structure of LIC10793 aiming to find out evidences of its possible function. The 1.99 resolution structure of LIC10793 was solved by the Single Anomalous Diffraction method (SAD) using selenomethionine-labelled crystals. It is the first structure solved by anomalous diffraction with data collected at the recently open W01A-MX2 beamline of the LNLS. LIC10793 is composed by two domains, both belonging to the all-beta-proteins SCOP class. Its N-terminal domain has an immunoglobulin-like beta-sandwich fold. Usually, proteins presenting this fold are involved in recognition, binding, or adhesion processes of cells. The C-terminal domain presents a 7-bladed beta-propeller fold. The search for structural homologues showed that the C-terminal domain is closely similar to proteins whose function involves protein binding. The most similar structures to the LIC10793 C-terminal domain are the YVTN beta-propeller domain of an archaeal surface layer protein and members of the WD40-repeat-like superfamily. In silico analyses using the PPI-PRED algorithm predict three putative protein-protein interaction sites. These hints indicate that LIC10793 may have a protein binding function. Further analyses are in progress.

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Analysis of Cross-Linked Peptides by ESI- and MALDI-MS/MS

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There are several advantages associated with the use of MS applied to structural studies of proteins, like the unlimited mass of protein or protein complex analyzed, very low time and sample consumption, ease of manipulation and interpretation of the data obtained. With the development of techniques such as cross-linking and footprinting, mass spectrometry has been used in the study of three dimensional structures of proteins and the identification of its interacting partners. In chemical cross-linking, reagents are used to generate covalent bonds between the side chains of specific residues; the distances constraints obtained are used to model the structure of the protein and to reveal the interacting regions in the case of protein complexes. Despite the ever increasing number of studies using cross-linking coupled to MS, there are few works that report how the cross-linked peptides fragment or how the presence of the cross-linkers influences the cross-linked peptide fragmentation. The aim of this work is to study the fragmentation pattern of three different kinds of cross-linked peptides: intramolecular, when the cross-linker is linked to two residues of the same peptide; intermolecular, when the reagent connects two peptides and dead end, that occur when the cross-linker is bound to only one residue leaving the other side of its chain free. We used two cross-linkers agents: DSS and a home-made, named C7XL. Both of them has the N-hydroxysuccinimide ester as reactive group and, in accordance with the literature, both should react with primary amines. All these cross-linked peptides were studied by both ESI and MALDI, usind CID MS/MS experiments.

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Crystallization and preliminary X-ray diffraction analysis of TIPRL, a protein involved in regulation of type 2A phosphatases

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The rapamycin sensitive pathway is a major regulatory pathway controlling cell growth in response to nutrients in eukaryotes ranging from yeast to mammals. Alterations in this pathway are directly related to metabolic disturbances as diabetes and cancers. Recently, TIPRL was identified as the human ortholog of the yeast protein TIP41. TIPRL interacts *in vitro* with the catalytic subunits of the type 2A phosphatases PP2A, PP4 and PP6, forming a rapamycin-insensitive complex with alpha-4 in human cells. To better understand the regulation of this pathway, we started a project aiming at the 3D structure determination of the proteins TIPRL and alpha-4 and their complex with PP2A. Histidine-tagged TIPRL was overexpressed in the *E.coli* BL21(DE3) strain and purified by metal-chelating affinity chromatography. Extensive crystallization assays were unsuccessful indicating that the wild type protein is recalcitrant to crystallize. To overcome this problem, we explored the concept of surface-entropy reduction, which sustains that large side chains residues with high conformational entropy prevent ordering of solvent and constitute an energy barrier for the formation of intermolecular contacts. For this purpose, site-direct mutagenesis was carried out in order to generate low-entropy surface patches. Specific residues of lysine, glutamine and glutamate were replaced by alanines, the mutant proteins were produced and submitted to crystallization. One of the mutants produced crystals with approximately 50 micrometers in several conditions. Although the crystals presented a poor diffraction pattern, the space group and unit cell parameters could be determined. Currently, refinement of the crystallization conditions is in progress.

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Mapping Tif34/Tif35 Interaction Domain Using Mass Spectrometry

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Tif34 and Tif35 are essential proteins in the Initiation Factor 3 of yeast. They play a major role in translation, being responsible for the correct assembly and stabilization of the other initiation factors. Despite its importance, this complex failed thousands of crystallization trials and it is too big for NMR (60 kDa), making it not amanable for high resolution structural analysis that could help to understand its function. Molecular modeling of Tif34 demonstrates that this protein belongs to the WD-repeat family, with a structure consisting of a β-propeller, while there is no available model for Tif35. SAXS studies performed on the complex showed that Tif35 binds in one side of the propeller. In order to clearly elucidate the interaction surface between these proteins, two mass-spectrometric based methods were used: cross-linking and footprinting. Cross-linking experiments generates covalent bonds between the proteins. The size of cross-linking reagents could be thus used as spatial constraints to build interaction models. After cross-linking, samples were digested and analyzed by mass spectrometry to identify cross-linked (thus spatially close) peptides. In footprinting, synchrotron radiation is used to generate hydroxyl radicals in the protein solution; owing to its reactivity, those radicals covalently modify surface exposed residues. This experiment was performed with both Tif34 alone and its complex with Tif35. After that, samples were digested and analyzed via LC/MS to obtain the oxidation kinetics. Tif34 peptides located in the interaction surface with Tif35 presented a decrease in the oxidation kinetics, as binding protects them against oxidation. Cross-linking experiments showed that only three distinct regions of Tif34 are able to form covalent bonds with Tif35: the N and C-terminus (which are close in space) and a small region in the middle of the sequence. In footprinting experiments, it was shown that only two regions of Tif34 present changes in oxidation rate upon Tif35 binding: a central region and the C-terminus of Tif34. Those results together suggest that Tif34 presents two binding sites to Tif35. These experiments show that footprinting and cross-linking were successfully applied to the Tif34/Tif35 complex, using relatively simple experiments with very low sample consumption and reduced data analysis time.

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Cristalização e Difração de Raios X de uma Lectina de Sementes de *Dioclea virgata*

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Lectinas são proteínas ou glicoproteínas com pelo menos um sítio de ligação a carboidratos, geralmente envolvidas em reconhecimento celular. *Dioclea virgata*, conhecida como feijão-pixuma, possui sementes venenosas e folhas que são usadas no tratamento de febre e malária. De suas sementes é extraída uma lectina (Dvir). Embora a estrutura tridimensional de Dvir ainda não tenha sido resolvida, a lectina já foi cristalizada, produzindo cristais tetragonais do grupo espacial $P4_32_12$. Visando obter novos dados de difração de raios X que possibilitem à resolução da estrutura tridimensional, Dvir foi purificada e submetida a um novo *screening* de cristalização. Numa nova condição de cristalização, novos cristais foram obtidos através do método de difusão por vapor. Usando raios X de uma fonte de radiação Síncrotron (LNLS), uma completa coleção de dados foi obtida a partir de cristais ortorrômbicos do grupo espacial $P2_1$ que difrataram numa resolução máxima de 2.7 Angstrons. Ensaios de substituição molecular no intuito de resolução da estrutura tridimensional com os novos conjuntos de dados encontram-se em andamento.

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Parte III

Biologia Molecular e Química de Proteínas

Estudo dos Substratos-Alvo de DNA em Diferentes Tratamentos Quimioterápicos por Espectrometria de Massas.

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Diferentes agentes anti-tumorais (Psoralenos mais Luz Ultravioleta A, Mostardas Nitrogenadas, Mitomicina C, Cisplatina) são estudados para compreensão de sua ação sobre o material genético. Estes tratamentos podem gerar danos no DNA genômico, prejudicando processos bioquímicos e a sobrevivência celular. Um dos principais objetivos do nosso grupo é a descrição do perfil dos danos induzidos por estes quimioterápicos, podendo auxiliar na correlação dos danos com mecanismos de reparo de DNA e contribuindo para aplicações na terapêutica. A fotoquimioterapia PUVA é empregada no tratamento de doenças de pele como o linfoma cutâneo. Tem como alvo as bases pirimidínicas do DNA, podendo resultar na formação de monoadutos (ligações entre psoraleno e uma das fitas de DNA) e crosslinks (ligações envolvendo o psoraleno e as duas fitas de DNA). Está em aberto a questão sobre qual das lesões está implicada em risco de mutagênese subjacente ao tratamento, sendo os crosslinks considerados mais inativantes. Já as Mostardas Nitrogenadas emergiram como agentes alquilantes bifuncionais, precursores no tratamento de linfomas. A Mostarda bifuncional HN2 interage com o DNA através de ligações com N7 de guaninas, formando monoadutos e crosslinks. A Mitomicina C possui atividade antitumoral reagindo covalentemente com o DNA, ligando-se ao N2 de guaninas, podendo formar biadutos intra-hélice e crosslinks. Padronizamos protocolos para obtenção de amostras de DNA purificado tratadas com PUVA e de DNA genômico tratado com Mostarda Nitrogenada e Mitomicina C, preparadas para posterior análise das lesões induzidas. A técnica de espectrometria de massas foi empregada para identificar diferentes tipos de substratos-alvo dos quimioterápicos no DNA. A análise dos resultados obtidos com PUVA, HN2 e Mitomicina sugerem a presença das lesões e consolidam a espectrometria de massas como importante ferramenta a ser utilizada na detecção de lesões em DNA.

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Comparative proteomic analysis of three *Mycoplasma hyopneumoniae* strains

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Mycoplasma hyopneumoniae is an important pathogen for pigs, being the causative agent of enzootic pneumonia (EP). Recently our group reported a preliminary proteomic survey of the pathogenic *M. hyopneumoniae* strain 7448. Now, we are reporting a more extensive and comparative protein profiling of three *M. hyopneumoniae* strains, including the non-pathogenic strain (J) and two pathogenic strains (7448 and 7422). Using a modified multidimensional protein identification technology (MudPIT) approach, we were able to identify 164, 155 and 158 proteins, from strains J, 7448 and 7422, respectively. A total of 230 different proteins were identified, corresponding to 34% of the 663 *M. hyopneumoniae* coding DNA sequences (CDS), and providing experimental validation for at least 36 hypothetical CDS. From the total of identified proteins, 81 were detected in a single strain, being 25 for the 7448 strain, 26 for the 7422 strain, and 30 for the J strain. Not surprisingly, 97 proteins were shared by all strains, while 53 were shared by two of them. Proteins from many different protein families have been identified, including some related to cytoadherence and possibly involved in pathogenicity. This ongoing research work is expected to provide information on proteins differentially expressed in pathogenic and non-pathogenic strains and possibly involved with *M. hyopneumoniae* virulence.

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Proteomic analysis of *Echinococcus granulosus* and *Mesocestoides corti* larval forms

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The Cestoda class harbors several parasite species of major medical and veterinary relevance. We are studying the pathogenic larval forms (metacestodes) of two cestodes, namely *Echinococcus granulosus* and *Mesocestoides corti*, seeking identification of proteins involved in parasite development and interactions with the host. The *E. granulosus* pre-adult form (protoscolex), generated within the metacestode, was analyzed by MudPIT and two dimensional gel electrophoresis (2DE) followed by MALDI-Tof MS/MS protein identification. A total of 93 proteins were identified and classified in 20 different KOG functional categories. In 2DE/MALDI-Tof MS/MS analysis, 84 spots were identified, corresponding to 31 different proteins. Many proteins were present in multiple spots, which is suggestive of post-translational modifications. To identify differentially expressed proteins during *M. corti* development, larvae (tetrathyridia) whose strobilization had been induced or not are being analysed by 2DE/MALDI-Tof MS/MS. So far, 9 tetrathyridia proteins had been identified. This analysis will be also extended to segmented worms.

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PUVA (Psoralen plus Ultraviolet A Light) photochemotherapy and genotoxicity: DNA Targets and Repair Mechanisms.

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PUVA is used against human cutaneous T-cell lymphomas and their variants. This therapy is mediated by photosensitizing agents, psoralens, that can be taken orally prior to UVA exposure. They intercalate between adjacent base pairs in double-stranded DNA photoreacting with the adjacent pyrimidine bases, mostly thymines, upon near UVA irradiation (320-400nm). Monoadducts appear as psoralens bind to pyrimidines on a single DNA strand. Then a second photon can further bind the free psoralen side to the other strand if there is an available pyrimidine in the appropriate position, causing part of the monoadducts to become inter-strand cross-links. The two types of adducts are found in genomic DNA, monoadducts being the prevalent ones. The crosslinks are nevertheless thought to critically impair cell function and survival, but are otherwise implicated in mutagenic consequences. PUVA adducts had been described as being removed by Nucleotide Excision Repair in E. coli. When modified psoralens were employed instead of the original psoralen, e.g., the clinically used 8-mehtoxypsoralen, we unexpectedly found a high sensitivity of the uvrB-deficient E. coli strain with no significant sensitivity inflicted to the uvrA and uvrC ones. Different damage recognition processes were thus supposed to occur within the predicted UvrABC mechanism, depending on the structural deformations caused by a particular psoralen on the DNA substrate. The suggested differences in the way different psoralens could affect the DNA structure, other novel damages were induced by PUVA, as observed by mass spectrometry analysis of the different DNA samples.

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Estudo metaloproteômico qualitativo comparativo para soja transgênica e não-transgênica utilizando SR-XRF

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A metalômica é um campo de pesquisa cujo foco é a verificação da distribuição das espécies metálicas e metalóides e a elucidação dos aspectos fisiológicos e funcionais das biomoléculas que contenham íons metálicos em suas estruturas. A informação metalômica pode ser classificada, de acordo com seu objetivo específico, de 3 maneiras: (i) metalômica qualitativa, que consiste na identificação das espécies metálicas individuais; (ii) metalômica quantitativa, que consiste na determinação das concentrações destas espécies; e (iii) metalômica comparativa, que consiste no monitoramento das alterações do metaloma de um determinado organismo, sob a influência de um estímulo externo [1]. O presente trabalho consistiu na comparação metaloproteômica qualitativa entre dois tipos de soja [Glycine max (L.) Merrill]: transgênica e não-transgênica. As proteínas dos dois tipos de soja foram primeiramente extraídas de acordo com um procedimento otimizado [2] e separadas por eletroforese bidimensional em gel de poliacrilamida (2-D PAGE). A seguir, 8 proteínas foram escolhidas aleatoriamente e, então, os íons metálicos presentes nestas foram mapeados por SR-XRF. Os íons metálicos detectados no mapeamento das proteínas foram Ca, Cu, Fe, Mn, Ni e Zn. Os íons metálicos detectados são macro e micronutrientes comumente encontrados em plantas e estes se ligam às proteínas de maneira específica [3]. A partir dos resultados obtidos, notou-se que a maioria das proteínas de soja transgênica avaliada apresentou um número de íons metálicos identificados maior do que nas proteínas de soja não-transgênica. Com relação à presença dos íons metálicos identificados em comum entre as amostras, observou-se uma tendência do Ca estar mais presente na soja não-transgênica. Esta mesma tendência foi observada na soja transgênica para o Cu e para o Zn. Entretanto, para o Fe, houve um comportamento aleatório com relação à sua presença nos diferentes tipos de soja. Os íons Cu e Zn são comumente encontrados em proteínas relacionadas a processos de estresse oxidativo e a tendência destes terem sido encontrados com maior intensidade na soja transgênica pode indicar algum nível de estresse sofrido pela soja com a modificação genética.

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IDENTIFICATION AND VALIDATION OF DIFFERENTIALLY EXPRESSED PROTEINS IN HEAD AND NECK CANCER

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Squamous cell carcinomas of head and neck (HNSCC) are frequent neoplasias strongly related to tobacco and alcohol consumption. The identification of aggressive and non-aggressive subgroups remains a challenge because these tumors are clinicopathologically heterogeneous. The development of a primary cancer predicts a greater risk of second cancers occurring in the contiguous epithelium, which can be a consequence of chronic exposure of the upper aerodigestive tract epithelium to carcinogens. The literature shows the importance of stromal-epithelial interactions in cancer development. In order to investigate markers of aggressiveness in HNSCC, we analyzed tumor samples and matched normal tissues by 2DE, western blot (WB) and MALDI Q-Tof. We also examined the effect of conditioned medium from cultures of oral carcinoma-associated fibroblasts and HN tumor cell lines on gene expression of normal and neoplastic cells. Aggressive (A) and less-aggressive (LA) cases included: (A) smaller tumors but already metastatic and (LA) larger tumors but non-metastatic. Protein variations between tumor and normal cells, and between (A) and (LA) tumors were detected including upregulation of S100-A9 and Gal-7 and downregulation of MLC1 and SOD in (A) tumors, and upregulation of M-CK in normal tissues. One member of CK family also showed increased expression in normal cells as validated by WB. Beta-actin and vimentin were found to be downregulated in oral carcinoma-associated fibroblasts cultured in conditioned medium from Hep-2 cell lines. The proteins identified are involved in epithelial cell differentiation, cell signaling, inflammatory response, apoptosis, development, cell motility and adhesion, indicating their potential as cancer-related markers. The data may help to understand the mechanisms governing aggressiveness in HNSCC at the molecular level and the contributions of the tumor microenvironment to carcinogenic process, providing therapeutic targets for HNSCC.

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Role of the Shwachman-Bodian-Diamond-Syndrom associated protein, SBDS, in mesenchymal stem cell differentiation into osteoblast and bone nodule formation

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Shwachman-Diamond-syndrome (SDS) is an autosomal recessive disorder characterized by pancreatic insufficiency, bone marrow deficiencies and significant predisposition to leukemia. A skeletal dysplasia is also an integral feature of SDS. This syndrome has been associated to mutations in the *SBDS* gene, encoding a highly conserved protein that was shown to function in ribosome biogenesis. Global transcription and polysome bound mRNA profiling revealed that *SBDS* knock-down in HEK293 human cells line affects translation and transcription of critical genes involved in brain development and function, blood cell proliferation and differentiation, bone morphogenesis and cell adhesion. One critical gene strongly up-regulated in our model is the negative regulator of bone mineralization, *SPP1* (Osteopondin). SPP1 is an integrin binding protein described as a bridge between bone and blood and, in addition to bone demineralization, its overexpression is associated with haematopoietic malignancies. In a breast cancer cell line, *SPP1* overexpression increases cell adhesion to vitronectin, an extracellular matrix (ECM) protein. Mesenchymal stem cell (hMSC) adhesion to vitronectin is important for proper bone morphogenesis since adhesion to this protein is sufficient to drive hMSC into an osteogenic differentiation pathway. Currently, we are quantifying adhesion of *SBDS* knock-down cells to Vitronectin and Fibronectin. We are also producing a new cell model of *SBDS* knock-down using an immortalized mesenchymal stem cell line. These cells may help us to demonstrate that *SBDS* inhibition can modify cell capacity to enter into osteogenic differentiation and to deposit calcium (calcification). Using this model, new profiling experiments may also confirm that skeletal dysplasia in SDS occurs through *SPP1* overexpression, resulting in a modification of a dialogue between the integrins of hMSC and proteins of the ECM.

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Characterization of the interaction of the human ortholog of yeast Tip41p, (TIPRL) with the transcription factor TAF10

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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 have characterized the human ortholog of Tip41p, TIPRL, as a novel interaction partner and regulator of type 2A phosphatases. In this study, we identified an interaction between TIPRL and the transcription factor TAF10, which is part of the transcription regulatory complexes TFIID and TFTC (TBP-free TAF containing complex), using the yeast two-hybrid system. This interaction was confirmed in vitro using recombinant proteins, as well as in HEK293 cell extracts. Interestingly, endogenous PP2Ac specifically associated with recombinant GST-TAF10, suggesting a ternary association mediated by TIPRL. These results suggest that TIPRL might regulate the dephosphorylation of TAF10 by PP2Ac, possibly controlling its activation state and transcriptional activity.

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Novel protein interactions of the human Nip7 ortholog protein

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Ribosome biogenesis is conserved throughout eukaryotes and takes place in the nucleolus, a specialized nuclear compartment where the rRNA precursors are transcribed. *Saccharomyces cerevisiae* Nip7p is involved in ribosome biogenesis being required for proper 27S pre-rRNA processing and 60S ribosome subunit assembly. Highly conserved Nip7p orthologs are found in all eukaryotes and Archaea. In this work, we determined the proteins interacting with the human ortholog of Nip7, HsNip7. We confirmed its interaction with FtsJ3 and SUMO-2 proteins using GST-pull down assays. FtsJ3 is an uncharacterized protein, ortholog of the yeast rRNA methyltransferase Spb1p. HsNip7 and FtsJ3 co-localize in the nucleolar region of HEK293 cells, thus indicating their interaction might also occur in vivo. In *S. cerevisiae*, deficiency of Spb1p affects 60S subunit biogenesis and leads to accumulation of 27S precursors, similar to the phenotype caused by Nip7p depletion. The small ubiquitin-like modifier 2 (SUMO-2) is involved in post-translational covalent modification in a wide range of substrates, and the human and yeast orthologs should play similar function in modification of pre-ribosomal subunits and several 60S-acting factors. These two novel interactions indicate that although Nip7 is a conserved protein, the human and yeast counterparts interact with different proteins during ribosome biogenesis.

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FUNCTIONAL AND INTERACTION ANALYSES OF THE HUMAN PROTEIN ENCODED BY THE INTERFERON RESPONSIVE GENE ISG95 IN RNA METABOLISM

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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 expression is enhanced in response to INF and CpG treatment, to HCV (hepatitis C virus) and VV (vaccinia virus) infection and in leukemic cells. Primary sequence analysis of ISG95 revealed four conserved domains that include: G-patch (RNA binding), FtsJ (RNA methylation), DNA ligase/mRNA capping family domain and WW (protein-protein interaction). ISG95 was expressed in insect cells and *in vitro* experiments confirmed its triphosphatase activity and its ability to bind S-Adenosylmethionine, but the protein did not show guanylyltransferase activity, which would be expected for an mRNA capping enzyme. Complementation assays in *Saccharomyces cerevisiae* were negative for the three mRNA cap biosynthesis steps. A yeast two-hybrid screen was performed using ISG95 as bait. This screen identified a group of proteins involved in RNA transcription and processing strongly indicating that ISG95 function is related to RNA splicing. ISG95 interaction with these proteins is currently being confirmed by using pull-down experiments. Regulation of ISG95 promoter by interferon was investigated in Vero cells using SEAP as a reporter gene under control of different regions of the ISG95 promoter. Expression of SEAP was highly induced in all clones following interferon treatment, confirming the activation effect that interferon exerts over the ISG95 promoter.

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Construction of a bacterial expression system for production of the human S6K1 protein kinase

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The 70 kDa kinase of the ribosomal protein S6 (S6K1) is a phosphoprotein involved in translational control, regulating cell size and glucose homeostasis. In mammalians, S6K1 has been described as an effector of the target of rapamycin (mTOR), which is implicated in cancer and metabolic diseases. S6K1 has a complex mechanism of activation that is achieved through a step-by-step phosphorylation by different kinases. This occurs in response to signaling across the mTORC1 (mammalian target of rapamicyn complex 1) and PI3K (phosphoinositide-3 kinase) pathways, linked to growth factors, cytokines and antigen receptors. As an AGC kinase, S6K1 must be phosphorylated at two sites to reach full activation. First, mTORC1 phosphorylates it at Thr389 within the hydrophobic motif, and then its ready to be phosphorylated by PDK1 (3-phosphoinositide-dependent protein kinase 1, through the PI3K cascade) at Thr229 within the T loop. In this work, we constructed expression vectors to produce S6K1 in *E. coli* to be use in biochemical and structural studies. The expression system is based on the co-expression of GST-S6K1 and GST-PDK1 fusion proteins. For this purpose, both the S6K1 and PDK1 cDNAs have been amplified by PCR from a human cDNA library and subcloned into the expression vectors pET28-GST and pGEX-4T1. PDK1 is expected to phosphorylate S6K1 in *E. coli* cells generating an active recombinant S6K1, which will subsequently be purified and used to screen for specific inhibitors. In addition to producing active S6K1, we plan to develop an assay to test S6K1 activity using the C-terminal region of the ribosomal protein S6 (Rps6) as a substrate for S6K1 phosphorylation in vitro. For this purpose, two expression vectors derived from pBUF were constructed, which express the C-terminal region of Rps6 either with or without a cystein residue at the N-terminus. This cystein will facilitate immobilization of the polypeptide in subsequent S6K1 activity assays.

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Analysis of TIPRL interaction with the putative transcription factor C1ORF124

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A yeast two-hybrid screen revealed that the human TIPRL protein (Tip41, TOR signaling pathway regulator-like *S. cerevisiae*) interacts specifically with the catalytic subunit of type 2A phosphatases, implicating TIPRL in regulation of type 2A phosphatase activity. The same screen also revealed TIPRL interaction with the product of the open reading frame C1ORF124, which corresponds to a hypothetical protein containing SprT and ZnF motifs, which are motifs described for transcription elongation factors. The parcial cDNA of C1ORF124 isolated in the yeast two-hybrid screen was subcloned into the plasmid pGEX-5x-2 and the resulting GST-fusion protein was used to test C1ORF124 interaction with His-TIPRL in vitro. In addition, the interaction between recombinant C1ORF124 and HEK293 endogenous TIPRL was tested in a GST pull-down assay using glutathione-Sepharose-immobilized GST-C1ORF124 and a HEK293 cell extract. These pull-down assays confirmed TIPRL direct interaction with C1ORF124. The full length cDNA of C1ORF124 was amplified from a human leucocyte cDNA library and subcloned into the plasmid pCRII. This cDNA will be subcloned into *E.coli* and mammalian expression vectors for functional assays in order to determine the function of this novel protein and its functional relation to TIPRL.

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

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The citrus canker disease, caused by the bacterial pathogen *Xanthomonas axonopodis* pv. *citri* (Xac), is considered a major threat to the Brazilian citriculture because it spreads easily and affects most commercial citrus varieties. During infection, Xac is thought to deliver a number of effector proteins into the plant cell via a type III secretion (T3S) system, including members of the AvrBs3/PthA protein family. PthA proteins are known to manipulate transcription of the host cell leading to the development of hypertrophy and hyperplasia, a feature of the canker lesions. To elucidate how PthA activates transcription and to establish its molecular mode of action, a yeast two-hybrid system was used to identify citrus proteins that interact with this effector. Here, we show the initial characterization of the interaction between two variants of PthA with the citrus HIP-TRX (*Hsp70-interacting protein-thioredoxin*) and Cyclophilin proteins. The interactions between HIP-TRX and Cyclophilin with PthA2 and 4 were verified by auxotrophic markers and LacZ reporter gene assays. Interestingly, while PthA2 interacted with HIP-TRX, Cyclophilin and α-Importin (positive control), PthA4 interacted with α-Importin only, suggesting that differences in the number of internal repeats between PthA2 and 4 might be responsible for the specificity of the interactions. Soluble proteins expressed in bacteria will be used to confirm these interactions through in vitro pull-down assays. Since HIP-TRX and Cyclophilin interacted with each other, and in other organisms these proteins are known to interact with Hsp90 and Hsp70, our hypothesis is that PthA2 may require a chaperone complex for folding after it is delivered into the host cell.

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Identification of proteins interacting with human Septins 3 and 9

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Septins belong to a highly conserved family of GTPases that function in citokinesis, cell polarity, membrane transport, cell cycle regulation and synaptic transmission. A typical Septin is formed by a central GTP-binding domain flanked by a polybasic and a septin unique element domain. Coiled-coil and/or proline-rich domains may be found in the C- and N-termini, respectively. In humans, fourteen Septin genes (*SEPT1-14*) have already been identified. SEPT3 is a brain-specific protein which is found in nerve terminals and is phosphorilated by PKG-I. Expression of the *SEPT3* gene is developmentally regulated and appears to be associated to malignant brain tumors. SEPT9 is expressed in all tissues and plays an important role in citokinesis. Altered SEPT9 expression is associated to different tumors and *SEPT9* mutations are involved in hereditary neuralgic amyotrophy. This work is part of an effort being developed within the CBME/CEPID/FAPESP program to identify and characterize the proteins interacting with all human septins using the yeast two-hybrid assay. In this work, we focus on the Septins 3 (SEPT3) and 9 (SEPT9). We have already performed a screen for SEPT3-interacting proteins from a human fetal brain cDNA library. From ∼110000 transformants, we have selected 200 which showed positive interaction in selective medium containing 5 mM 3-amino-triazole (3-AT) and the cDNAs of 50 clones have been isolated and identified by DNA sequencing analysis. The clones that were able to grow on selective medium containing 5 mM 3-AT were submitted to a second round of selection on plates containing 30 mM (3-AT) and only 46 clones showed activation of the reporter genes under these conditions. DNA sequencing of these clones is in progress. The cDNA encoding SEPT9 was subcloned into a pBTM116 derivative plasmid and the construction will be used to screen a human fetal brain cDNA library.

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Construction of a regulated system for expression of the *srfA* operon of *Bacillus subtilis*

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The cyclic lipoheptapeptide surfactin is produced by different *Bacillus subtilis* strains and consists of a beta-hidroxy fatty acid chain of variable lengths (12 to 15 carbon atoms). At a concentration of 20 microM, surfactin is able to reduce the surface tension of water from 72 mJ/m2 to 27 mJ/m2. This makes surfactin the most powerful biosurfactant known so far. Microbial surfactants have gained importance in the fields of enhanced oil recovery, environmental bioremediation, food processing and pharmaceuticals owing to their unique properties, like higher biodegradability, lower toxicity, and effectiveness at extremes of temperature, pH and salinity. In addition, surfactin is able to inhibit clot formation and has been described as an antibacterial, antiviral and antitumoral agent. The surfactin biosynthetic complex consists of three large nonribosomal peptides (NRPSs): SrfA-A (402kDa), SrfA-B (401kDa) and SrfA-C (144 kDa), comprising of a total of seven modules. The corresponding NRPS genes are organized in the srfA operon. Surfactin production from *Bacillus* strains is usually low and production of such large proteins in a heterologous system such as *E. coli* is not viable. One option to improve surfactin production would be to use *Bacillus subtilis* itself as an expression system and to place the srfA operon under the control of a strong promoter that can function independently of endogenous negative feedback regulation. For this purpose, a two stage expression system was devised in which the *E. coli* phage T7 RNA polymerase was placed under the control of the inducible lac promoter and the T7 RNA polymerase expression cassette will subsequently be integrated into the *Bacillus subtilis* genome. In the second stage, the promoter of the srfA operon will be replaced by the phage T7 RNA polymerase promoter. In the resulting modified *Bacillus subtilis* strain, transcription of the srfA operon depends on T7 RNA polymerase expression, which can be induced by lactose analogs. This expression system is based on a strong promoter and is not expected to be inhibited by endogenous factors and, should provide a new tool for producing higher levels of surfactin in *Bacillus subtilis*.

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

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The Dengue virus genome is a single-stranded RNA of positive polarity. The viral 3´ untranslated region (UTR) is similar to the 5UTR of eukaryotic cellular mRNAs, with 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 the 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 of several host proteins whose function on the Dengue virus biology is unknown. In this work, we have used the yeast three-hybrid (Y3H) system to screen for novel proteins that interact with the dengue virus 3´SL. This method consists in the expression in yeast cells of three chimerical molecules, which assemble in order to activate two reporter genes. This screen identified PACT as a putative 3´SL interacting protein. PACT interacts with 3´SL but not with the control RNA used in the assay, unlike other proteins which were isolated in the screen but did not distinguish the 3´SL RNA from the IRE control RNA. PACT is the PKR cellular activator 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. PACT possesses three putative RNA-binding motifs and in vitro assays indicated that it shows higher affinity to the 3´SL RNA than to the IRE RNA. This finding led us to characterize further this interaction to determine the role of PACT in the mechanism of dengue virus infection. For this purpose, we will study DV infection in cell lines knock down for PACT using the RNA interference technology based on the pMaleficent system [Heggestad, A.D. *et al.* 2004. Biochem Biophys Res Commun, 316:643] to generate an shRNA against PACT. The DV proliferation rate in cells knock down for PACT relative to DV proliferation in cells expressing PACT should answer the question whereas PACT interaction with DV 3´SL is important for PKR activation and cell protection on DV infection.

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The human Tip41 ortholog TIPRL interacts with and regulates the bZIP transcription factor MafB

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Yeast Tip41 is an inhibitor of the TOR signaling pathway, which antagonizes Tap42p interaction with PP2A type phosphatases and controls cell growth in response to nutrients. The human Tip41 counterpart (TIP/TIPRL) interacts with the catalytic subunit of type 2A phosphatases and acts as a regulator of PP2A. In this study, we have identified the bZIP transcription factor MafB as a novel TIPRL interacting partner. Maf proteins are important transcriptional regulators of cell differentiation and morphogenesis. MafB interacts with TIPRL through its bZIP domain region as determined by pull-down assays of endogenous TIPRL with the recombinant bZIP region of MafB, containing residues 252-323 (MafB/CT), as well as by using recombinant proteins. Expression of a reporter gene under the control of a promoter containing the Maf recognition element (MARE) was significantly reduced in cells over-expressing TIPRL relative to control cells. TIPRL was found in the nucleus and in the cytoplasm, overlapping with MafB localization in the nuclear compartment of HEK293 cells. TIPRL interaction with MafB has not been described in any other species so far and may represent a new mode of MafB regulation either by competing for bZIP domain binding and inhibiting its interaction with the DNA or by serving as an adaptor for PP2A type phosphatase, regulating the MafB phosphorylation state. Since TIPRL may be directly involved in mechanisms controlling regulation of transcription and development, analysis of global gene expression profiling of HEK293 cells overexpressing TIPRL is in progress to determine whether transcription of specific genes is affected by TIPRL.

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Crystallographic studies of proteins with reactive cysteines.

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Many proteins with reactive cysteines are involved in controlling thiol/disulfide exchange reactions, a central aim in cellular redox homeostase. In *Saccharomyces cerevisiae* the mithocondrial thioredoxin system (thioredoxin (Trx3), thioredoxin reductase (Trr2) and NADPH) acts as a disulfide reductase system. We obtained crystals from preliminary screenings with Trx3 and Trr2 and refinement is in progress. Proteins with reactive cysteines are also involved in reduction of peroxide bonds. AhpE (from *Mycobacterium tuberculosis*) and of Prdx6 (from *Rattus norvegicus*) are 1-Cys Peroxiredoxins (Prx) and have been described as strictly dependent on thiols to recycle, but we have shown that Prx with 1-Cys mechanism are able to receive electrons from vitamin C (*Proc Natl Acad Sci U S A*, 2007, 104:4886-91). We have obtained crystals from AhpE with a resolution of 1.7 , and soaking them with 2.5 mM ascorbate during 1 minute before data collection. However, through molecular replacement (PDB: 1xxu) we saw clearly that ascorbate was not in the active site cavity. Interestingly, Prdx6 just crystallized with 50 mM of ascorbate in the drop (crystals with 10 mM ascorbate were obtained too). *Xylella fastidiosa* possesses many antioxidant proteins, including the bacterioferritin co-migratory protein (BCP). It presented thiol-peroxidase activity against several hydroperoxides which depended on the reducing power of a thioredoxin (TSNC from *X.fastidiosa*). Presently, we are refining the screening conditions through the Reichert method. Together, all these results can clarify our comprehension about reactive cysteine proteins.

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The interaction of Ki-1/57 with proteins involved in the metabolism of RNA.

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The human protein Ki-1/57 is phylogenetically conserved, because we can find orthologues in both vertebrates and invertebrates, including *Drosophila melanogaster, Caenorhabditis elegans*, and *Aedes aegypti*. Little is known about the function of Ki-1/57 and this family of proteins. However, all possible ortologues appear to be related to metabolism, transport or processing of RNA. Among the possible ortologues found in invertebrates is the protein VIG of Drosophila, which has a region rich in arginine and glycine called the "RG Box."It was proposed that this region is involved in the binding of RNA and it is also present in Ki-1/57. The protein VIG also interacts with several proteins of the fragile X family in Drosophila (1), and with other RISC components such as Ago-2. Both interacting proteins are involved in the mechanism of gene silencing by RNA interference (RNAi). Finally, a variety of data suggest that Ki-1/57 can be a human ortologue of Drosophila VIG protein also described to be involved in the mechanism of gene silencing by RNAi (double-strand). In our studies we observe the interaction of Ki-1/57 protein with proteins of the fragile family X and with Ago-2. We also made an alignment with the possible ortologues of Ki-1/57 of different organisms. Since the regions that are conserved are likely to have an important role in the function or structure of the protein we cloned these regions for posterior structural and functional studies of the respective protein fragments. In parallel, we are studying the functional involvement of this protein in the apparatus of RNAi gene silencing.

Reference: (1) Caudy et al., Genes e Development 16:2491-2496 (2002)

Acknowledgements: Supported by: LNLS, CNPq and FAPESP

Functional analysis of the human protein Ki-1/57 in the context of its interaction with RNA and RNA binding proteins

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The human protein Ki-1/57 was originally isolated from malignant cells of Hodgkin's lymphoma throughout cross-reaction with the antibody Ki-1. It was described as a cytoplasmatic and nuclear protein, phosphorylated at serine and treonine residues. Further studies have shown that this protein has characteristics that are often associated with onco-proteins, such as: high expression in tumor cells, phosphorylation dependent on the state of cellular activation, transition between cytoplasm and nucleus and association with protein quinase activity. A recent yeast two-hybrid system screening analysis revealed that Ki-1/57 may have a pleiotropic role in the control of gene expression. It was found that Ki-1/57 not only interacts with proteins involved in transcriptional control and cellular signaling, but also interacts with several RNA binding proteins, suggesting its involvement in RNA metabolism. Moreover, we found that Ki-1/57 is also able to interact specifically with poly-U RNA probes, strengthening the hypothesis that Ki-1/57 can also regulate RNA metabolism by binding directly to RNA. Here, by using the yeast two-hybrid assays, we mapped the regions of Ki-1/57 involved in the interaction with several related RNA biding proteins. Furthermore, we mapped the region of Ki-1/57 involved with poly-U RNA binding. These experiments allowed us to understand how Ki-1/57 interacts with its related proteins and RNA. Aiming to better comprehend the functional relevance of Ki-1/57 in RNA metabolism at the cellular level, we are performing several constructions in mammalian expression vectors. These constructions will allow studies of the interaction of Ki-1/57 with RNA and RNA binding proteins *in vivo*, as well its involvement in the regulation of pre-mRNA splicing regulation.

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PROTEIN INTERACTION PROFILE OF THE HUMAN REGULATORY PROTEIN FEZ1 SUGGESTS NEW ROLES IN THE CONTEXT OF TRANSCRIPTIONAL REGULATION

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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 and efficiently promotes the neurite elongation in the rat PC12 cells. We employed the yeast two-hybrid system and identified among others several transcription regulatory proteins as FEZ1(221-392) interactors. The others identified proteins are functionally associated to neuronal cell development, intracellular transport processes and apoptosis. Here, we focused our efforts on studies with the following proteins involved in transcriptional regulation: BAF60a (BRG Associated Factor 60a involved mainly in chromatin opening), SAP30L (Sin3A Associated Protein 30 like involved mainly in chromatin compaction) and KIBRA (Kidney and Brain involved in memory performance). 6xHis-SAP30L expressed in *E. coli*, purified and employed for in vitro phosphorylation assays. We also performed subcellular localization studies of SAP30L in human cells. 6xHis-BAF60a expressed in the soluble fraction and its purification is currently being optimized. We are also performing a KIBRA(869-1113) yeast two-hybrid assay in order to obtain a better characterization of the cellular functional context of this protein and to integrate these data with the data on FEZ1. Furthermore, the proteins will be utilized in co-crystallization trials with FEZ1 and analytical gel-filtration and spectroscopic studies for the biophysical characterization of the protein-complexes.

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Structural Features and Mechanism of Action of Glyceraldehyde-3-Phosphate Dehydrogenase from Trypanosoma cruzi in complex with iodoacetate inhibitor using X ray diffraction

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Chagas disease caused by the flagellate protozoan Trypanosoma cruzi, affects about 16-18 million people in Latin America. Benznidazole and nifurtimox are the only two drugs currently available, but their use is restricted due to their toxicity. Therefore, development of new and more selective drugs poses as an important issue in the control of this ailment. One of the most studied approaches for this goal is the selective inhibition of Glyceraldehyde-3-Phosphate Dehydrogenase (GAPDH) enzyme, which, among others, controls the glycolytic flux in the tripanosomatides. Several GAPDH inhibitors have been identified, among them, one of the most studied was iodoacetate (IAA), which is described as specific and irreversible GAPDH inhibitor. Although many studies aiming at elucidating the nature of enzyme inactivation have been carried out, up to now, no crystal structure of the complex is available. Methodology Crystallization assays were performed by hanging drop method with purified protein solution at 10 mg/mL. The crystals grew in 2-3 days at 18^oC. Data collection was carried out at the LNLS. The frames were processed with the MOSFLM, SCALA and initial phasing was obtained by molecular replacement. The refinement was carried out by iterative cycles of model building with CNS and COOT programs. Results The global structures of the enzymes have a homotetrameric quaternary structure bearing IAA inhibitor covalently bound to active-site residue Cys166. To the best of our knowledge, this is the first crystal structure describing at molecular level the binding mode of IAA inhibitor. The IAA binding mode suggests a covalent fixation at the active site cysteine, preventing the enzyme/substrate complex formation and the charge transfer between cysteine and NAD^+which occurs during the dehydrogenation of the substrate. Conclusion This complex analysis identified some key structural features relevant to biological activity and can be used to guide the development of novel inhibitors with enhanced inhibitory activity.

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Sub-cloning, expression and purification of the human FEZ1-interacting protein fragment CLASP-2(1192-1407) for functional and structural studies

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The human protein CLASP2 (*CLIP Associated Protein 2*), was identified by its interaction with CLIP, and has functions associated to the cytoskeleton and microtubular transport processes. It localizes at the microtubular plus ends where it stabilizes their bundle formation. CLASP2 also acts in the formation of microtubule organization centers (MTOCs) and is involved in cell division processes. In previous yeast two-hybrid assays our group identified the interaction of the C-terminal region of CLASP2 with FEZ1, a protein that acts in neuronal polarization and differentiation. A fragment encoding the C-terminal region of CLASP2 (amino acids 1192-1407) was sub-cloned into bacterial expression vectors for its expression and purification in the form of GST and 6xHis-fusion proteins in order to perform structural studies in complex with FEZ1. The best condition for the expression of GST-CLASP2(1192-1407) was determined. This same fragment was also sub-cloned into the vector pET28-Tev-6xHis. Moreover, this fragment was sub-cloned in fusion with Red (RFP) and Green-fluorescent proteins (GFP) in mammalian expression vectors that allows its super-expression and the microscopic visualization of its localization in human cells. The sub-cellular localization of RED-CLASP2(1192-1407) was analyzed, as well as its functional relation with GFP-FEZ1(1-392), by their co-expression in HEK293 cells. Our results show that CLASP2(1192-1407) is predominantly cytoplasmic and localizes to the centrossome.

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Cloning and expression of human NEK 1, 6 and 8 for functional and structural studies

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The vertebrate NIMA-related kinases (Neks) represent an evolutionarily conserved family of serine/threonine kinases (designated Nek1 to Nek11), containing 40-45% identity to the Aspergillus nidulans mitotic regulator NIMA within their N-terminal catalytic domain. Both Nek1 and Nek8 were implicated in cilia function and associated with polycystic kidney disease (PKD) in mouse models. Nek8 is over-expressed in multiple breast tumors and human Nek6 was also recently associated with hepatic cell carcinomas. In previous two-hybrid studies our group identified hNek1 interacting proteins involved in the G2/M DNA damage checkpoint, neural cell development and PKD. In this work, we present new expression constructs for human Nek 1, 6 and 8 for structural and functional studies. We PCR amplified cDNAs encoding full length proteins, kinase and regulatory domains of hNek1, 6 and 8. The PCR products were sub-cloned into pET28a-TEV vectors for expression in E. coli and/or into pFastBacHT vector for the expression in the baculo virus system. Several mutations were introduced by PCR-based mutagenesis of the mentioned plasmid constructs in order to reduce toxicity of the kinase domains and obtain higher protein yields. Purification assays of recombinant 6xHis-Nek6 and the mutant version 6xHis-Nek6(S206A) are currently being optimized. Although some of the tested Nek kinase domains and mutant kinase domains show significant expression in the bacterial systems, our results suggest that for the expression of the full length proteins Nek1 and Nek8 we need to employ the baculo virus expression system.

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Expression of FNDC4 for structural studies and the analysis of its interaction with STC1, a putative marker protein of the acute lymphoid leukemia microenvironment

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Fibronectin type III domain containing protein 4 (FNDC4) is located at the cell membrane and strongly expressed in the brain, suggesting a role in its development and neuronal functions during the embryonic stages. We found that FNDC4 interacted with the protein bait Stanniocalcin-1 (STC1) in a yeast two-hybrid screen of a human fetal brain cDNA library. Previous studies and ongoing experiments from our group suggested that STC1 may be a marker protein of the tumoral microenvironment in childhood acute lymphoid leukemia (ALL). This project has the objective to test the possible interaction between STC1 and FNDC4 *in vitro* by pull down assays and mass spectrometry analysis of the recombinant proteins incubated with lysates of co-cultured leukemic and stromal cells. To this end we sub-cloned and expressed the cDNA fragment encoding the extra-cellular fibronectin type 3 domain (FN3D) of FNDC4 using bacterial expression vectors. Currently the expression and purification of FN3D in fusion with GST and a 6xHis-tag are being optimized. Purified proteins will be utilized for *in vitro* pull down assays and a spectroscopic characterization of the interaction. It should be possible to confirm the interaction, new light may be shed on the molecular details of the interactions between stromal cells and the leukemic blasts, whose survival depends critically on this cellular interaction. Also new ways of intervention which are targeted to block this interaction may be envisaged.

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THE HUMAN REGULATORY PROTEIN Ki-1/57 HAS CHARACTERISTICS OF A NATIVELY UNFOLDED PROTEIN

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The human protein Ki-1/57 was first identified through the cross reactivity of the anti-CD30 monoclonal antibody Ki-1, in Hodgkin lymphoma cells. The expression of Ki-1/57 in diverse cancer cells and its phosphorylation in peripheral blood leukocytes after mitogenic activation suggested its possible role in cell signaling. Ki-1/57 interacts with several other regulatory proteins involved in cellular signaling, transcriptional regulation and RNA metabolism, suggesting it may have pleiotropic functions. In a previous spectroscopic analysis, we observed a low content of secondary structure for Ki-1/57 constructs. Circular dichroism experiments, *in vitro* RNA binding analysis and limited proteolysis assays of recombinant Ki-1/57(122-413) and proteolysis assays of endogenous full length protein from human HEK293 cells suggested that Ki-1/57 has characteristics of a natively unfolded protein. Small-angle X-ray scattering (SAXS) experiments were performed with the stable C-terminal fragment Ki-1/57(122-413). These results indicated an elongated shape and a partially unstructured conformation of the molecule in solution, confirming the characteristics of a natively unfolded protein. Experimental curves together with *ab initio* modeling approaches revealed an extended and mobile molecule in solution. A large hydrodynamic radius was also observed by analytical gel filtration. Furthermore, sedimentation velocity analysis suggested that Ki-1/57 is a highly asymmetric protein. These findings may explain the functional plasticity of Ki-1/57, as suggested by the wide array of proteins with which it is capable to interact in yeast two-hybrid interaction assays.

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Identification and characterization of proteins that interact with the human septins 6 and 8

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Septin proteins are members of a highly conserved GTPase family found in fungi and animals. In mammals, 13 septins have been identified to date. They are implicated in a variety of cellular functions including cytokinesis, vesicle trafficking and exocytosis. Furthermore, they are related to certain human pathologies, including Alzheimers disease, Parkinsons disease and cancer. Some studies suggest that septins may have additional functions in cellular signaling, related to those functions widely documented for the functionally and structurally related Ras family proteins. Recently, it has been shown that septins participate in homo-and hetero-specific interactions, forming larger complexes that regularly seem to consist of three different septins. These complexed septins may also act as scaffolds to recruit other signaling proteins. This work intends to identify the proteins that interact with the septins 6 and 8 as well as to study the function of these interactions. We set out to clone human septins 6 and 8 in the yeast bait vector pBTM116 in order to identify septin interacting proteins. Human fetal brain and leukocyte cDNA libraries were screened with both baits. The results of two hybrid system screen revealed several interesting new interacting proteins related to diverse signaling processes, tumor necrosis factor pathways, protein degradation and septin biology, including already known and novel interacting septins. The detailed functional and structural analysis of the individual interactions between septins 6 and 8 with selected proteins is ongoing.

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Human FEZ1 has characteristics of a natively unfolded protein and dimerizes in solution

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The Fasciculation and Elongation protein Zeta 1 (FEZ1) is the mammalian orthologue of the *Caenorhabditis elegans* protein UNC-76, necessary for axon growth. Human FEZ1 interacts with Protein Kinase C (PKC) and several regulatory proteins involved in functions ranging from microtubule associated transport to transcriptional regulation. Theoretical prediction, circular dichroism, fluorescence spectroscopy and limited proteolysis of recombinant FEZ1 suggest that it contains disordered regions, especially in its N-terminal region, and that it may belong to the group of natively unfolded proteins. Small angle X ray scattering experiments indicated a mainly disordered conformation, proved that FEZ1 is a dimer of elongated shape and provided overall dimensional parameters for the protein. In vitro pull down experiments confirmed these results and demonstrated that dimerization involves the N-terminus. *Ab-initio* 3D low resolution models of the average full-length conformation of FEZ1(1-392) and of the also dimeric N terminal fragment FEZ1(1-227) fused to a 6xHis-tag were obtained. Furthermore, we performed *in vitro* phosphorylation assays of FEZ1 with PKC. The phosphorylation occurred mainly in its C-terminal region, and does not cause any significant conformational changes, but nonetheless inhibited its interaction with the FEZ1 interacting domain of the protein CLASP2 *in vitro*. The C terminus of FEZ1 has been reported to bind to several interacting proteins. This suggests that FEZ1 binding and transport function of interacting proteins may be subject to regulation by phosphorylation.

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Desenvolvimento de Ferramentas de Bioinformática para a Análise de experimentos de ligação cruzada acopladas com Espectrometria de Massas

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A análise de estruturas superiores (terciárias e quaternárias) de proteínas por espectrometria de massas (MS) pode ser feita através de algumas metodologias. Dentre essas metodologias, o uso de ligação cruzada (cross-linking) vem recebendo uma grande atenção devido às suas características atrativas. As ligações cruzadas são realizadas através de reagentes bifuncionais que formam ligações covalentes entre regiões espacialmente próximas de uma proteína ou um complexo proteína-proteína. Uma vez que essas ligações cruzadas fixam covalentemente as regiões espacialmente próximas de uma proteína, a identificação dos peptídeos contendo as ligações cruzadas revelam informações estruturais que podem ser usadas para modelar estruturas e identificar sítios de interação das proteínas dentro de um complexo. O grande atrativo desta metodologia é que ela traz consigo todas as vantagens de MS, tais como sensibilidade, rapidez e facilidade de uso. No entanto, a análise dos dados de MS de um experimento de ligação cruzada não é trivial e a quantidade de dados gerados torna a análise manual muito difícil. Ao mesmo tempo, não há programas que realizem a interpretação automática de ligação cruzada. O objetivo desse trabalho é criar um programa que seja capaz de analisar os dados dos espectrômetro de massas e compará-los às sequências das proteínas estudadas a fim de se encontrar dados relacionados à identificação de peptídeos contendo a ligação cruzada. O programa MassXL foi desenvolvido em PERL, com interface Web (CGI), de forma que os arquivos nos formatos PKL e MGF são lidos e comparados com as massas de todos os possíveis peptídeos contendo ligação cruzada. Os peptídeos com massa igual (dentro de uma valor de erro fornecido) são relatados, facilitando assim a identificação dos peptídeos.

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Study of spatial constrains

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The great interest to obtain data about the three-dimensional structure of proteins and protein complexes, along with the difficulties in obtaining such information, prompted for the development of methodologies employing the mass spectrometry (MS).[1] Mass spectrometry is, currently, one of the main tools for structural characterization, and its attractiveness is based on its intrinsic advantages, mainly its high sensitivity.[2] Chemical cross-linking is a form of chemical modification which involve the union of two chemical groups through a covalently bound through compounds known as cross-linkers (XL).[3] By using these cross-linkers, only the chemical groups that presents the correct reactivity and are within a well-defined range of distance can be linked. Thus the formation of cross-linked peptides reveals distance constrains in proteins and can be used to obtain structural information about proteins and protein complexes. The cross-linking technique is a new and promising approach, in which the peptides from a proteic complexes linked by cross-linkers are detected by MS.[3] However, the accuracy of the distance constrains obtained by this method depends on the dynamics of the cross-linker / protein system. Therefore, a good characterization of the real distances of the amino acid residues in the protein, i.e. the protein dynamics, and the actual cross-linker distance is of great importance. In this work were developed performed strucutral studies for cross-linkers using ab initio calculations and evaluate the actual residues distance of Tif34 protein that are capable of forming cross-linked products using molecular dynamics. The data were compared to the preliminary results of experiments of XL + MS employing these cross-linkers and Tif34.

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Parte IV

Ciência Atômica e Molecular

Quantitative Evaluation of Osteoporosis and Osteopenia by TXRF Analysis of Oral Fluids

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Osteoporosis, osteopenia and periodontal disease have in common several risk factors. There is scarce information in the literature about the association between periodontal disease and osteoporosis and/or osteopenia. Osteoporotic women are propend to a higher loss of periodontal insertion, alveolar bones, and teeth. Since osteoporosis and osteopenia produce similar alterations to bone density and metabolism than periodontal disease, elemental analysis of the mineral content of oral fluids could establish a correlation with the severity of those pathologies.

Thirty adult women coming from a gynecologic service were studied. All he patients were coursing post-menopause; some of them were healthy (control group) and the others were undergoing some stage of osteoporosis or osteopenia. They were systemic healthy, non smoker, with no dental implants, and suffering certain degree of periodontal disease (CPI>1). Samples of saliva and gingival crevice fluid were extracted with micro-capillaries and deposited on plate reflectors. Known amounts of Ga were added to the samples in order to act as internal standard.

The samples were analyzed by TXRF using two systems: beam guides mounted in a conventional spectrometer and standard TXRF using synchrotron radiation at the XRF beamline of the LNLS. The conventional spectrometer consists of a 3 kW x-ray tube with a Mo target, an angular sample stage to align the beam guides, an 8K multichannel analyzer. The TXRF station and the XRF beamline have been described in detail previously. The spectra were analyzed with standard programs for spectrum analysis and correlations were employed for the quantification.

Elemental concentrations of several elements, from P to Zn, were determined. The concentration of some elements in saliva showed different behavior as compared to gingival crevice fluid. Some critical elements for bones, such as calcium and zinc, present very distinguishable behaviors. Improvements in the statistics are required for a better assessment of a routine method and to establish some correlation with periodontal disease. TXRF seems to be a promising method to evaluate the evolution of osteoporosis.

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Fragmentação iônica na região de valência da molécula do isopreno

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O isopreno (C_5H_8) é um composto de origem natural e de fundamental importância na química atmosférica [1]. Também é empregado em alguns setores industriais sendo, por exemplo, utilizado como matéria-prima para a produção de elastômeros [2]. É também a unidade fundamental de uma família imensa de compostos: a dos terpenos. Para compreender melhor os processos de fragmentação dessa molécula na presença de radiação ionizante, submetemos o isopreno à luz síncrotron, na faixa de 12 a 21 eV, correspondente à região de valência. Os experimentos foram realizados na linha TGM, utilizando um filtro de Neônio para a eliminação de harmônicos [3]. Os fragmentos foram caracterizados por um espectrômetro de massas de tempo-de-vôo de alta resolução [4], obtendo-se espectros de coincidência fotoelétron-fotoíon (PEPICO). A partir desses espectros, foram calculados os rendimentos iônicos parciais e dos fragmentos (PIY). Verificamos que na faixa de 12 eV o maior rendimento parcial corresponde ao íon molecular $[M]^+$. Em torno de 14 eV, o maior rendimento passa a ser do íon m/z 67 $[M-1]^+$, enquanto que em energias acima de 16 eV o íon m/z 53 $[M-15]^+$ é o mais abundante.

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Interação de produtos naturais com o ultravioleta de vácuo: ionização da molécula do limoneno na faixa de 12 a 21 eV

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O limoneno ($C_{10}H_{16}$) é um importante monoterpeno, constituindo-se no principal componente do óleo obtido a partir das cascas da laranja e do limão. É produzido em vastas quantidades na indústria de frutas cítricas, setor onde o Brasil ocupa um papel preponderante. Recentemente, analisamos a fotoionização do limoneno em torno da borda 1s do Carbono [1]. De forma geral os espectros obtidos com fótons de alta energia assemelhavam-se ao espectro obtido com elétrons de 70 eV e disponibilizado na base NIST. Em particular, o pico mais intenso correspondia a m/z = 68 ($C_5H_8{}^+$). No presente trabalho, estudamos com mais detalhes a fragmentação iônica desta molécula na região de valência. Espectros de massa foram obtidos na linha TGM e na faixa de energia de 12 a 21 eV. A metodologia experimental, essencialmente baseada no emprego da técnica de tempo-de-vôo, já foi descrita em detalhes anteriormente [2]. Um novo sistema de filtragem de harmônicos, recentemente implantado na linha TGM, mostrou-se extremamente eficiente [3]. O rendimento iônico parcial dos principais íons foi obtido na faixa de estudo. Observa-se que, a 12 eV, o pico molecular é o mais intenso do espectro. A partir de 14 eV, entretanto, os espectros passam a ser dominados pelo pico correspondendo a m/z = 68. Nossos dados corroboram, desta forma, a grande estabilidade do íon $C_5H_8{}^+$ cujo mecanismo de formação envolve uma reação retro-Diels-Alder [4].

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Fragmentação iônica na região de valência da molécula do isopreno

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O isopreno (C_5H_8) é um composto de origem natural e de fundamental importância na química atmosférica [1]. Também é empregado em alguns setores industriais sendo, por exemplo, utilizado como matéria-prima para a produção de elastômeros [2]. É também a unidade fundamental de uma família imensa de compostos: a dos terpenos. Para compreender melhor os processos de fragmentação dessa molécula na presença de radiação ionizante, submetemos o isopreno à luz síncrotron, na faixa de 12 a 21 eV, correspondente à região de valência. Os experimentos foram realizados na linha TGM, utilizando um filtro de Neônio para a eliminação de harmônicos [3]. Os fragmentos foram caracterizados por um espectrômetro de massas de tempo-de-vôo de alta resolução [4], obtendo-se espectros de coincidência fotoelétron-fotoíon (PEPICO). A partir desses espectros, foram calculados os rendimentos iônicos parciais e dos fragmentos (PIY). Verificamos que na faixa de 12 eV o maior rendimento parcial corresponde ao íon molecular $[M]^+$. Em torno de 14 eV, o maior rendimento passa a ser do íon m/z 67 $[M-1]^+$, enquanto que em energias acima de 16 eV o íon m/z 53 $[M-15]^+$ é o mais abundante.

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Ionic Fragmentation of Small Organic Species Induced by Synchrotron Radiation

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Inner-shell excitation, and associated spectroscopies of the ionic fragmentation of inner shell states, are site specific probes of electronic and geometrical structure and photoionization dynamics [1]. Here we present recent results of coincidence studies in the C 1s and O 1s regions of gaseous formic acid, acetic acid, dimethyl sulfoxide (DMSO) and acetone. The ionic fragmentation has been measured with tuned synchrotron light and time-of-flight mass spectrometry apparatus [2].

One of the reasons to study these small organic species is to observe their photofragmentation pattern at the K edge. Formic acid and acetic acid are the simplest carboxylic acids and may be used as a model system for other organic acids with more complicated chemical structures. The fragmentation of both acids has been extensively studied at the C 1s region [3]. This present work analyses more carefully the O 1s region. Comparing the DMSO and acetone samples it is possible to observe site specific behaviour on both C 1s and O 1s regions due to the exchange of the carbon atom by the sulphur one.

The experiments have been performed using the Spherical Grating Monochromator (SGM) beamline at the Laboratório Nacional de Luz Síncrotron (LNLS), Campinas - SP. High purity samples were obtained commercially and used without any further purification. They were introduced into the apparatus from the vapours of the room temperature liquids after removing air and volatile impurities by a series of freeze-pump-thaw cycles. The work pressure was maintained at 1.0×10^{-6} mbar during data acquisition. The base pressure was 1×10^{-8} mbar. The mass spectra have been measured using different photon energies, such as 280 eV, $C1s \rightarrow \pi*$, $C1s \rightarrow \sigma*$, 305eV, 530eV, $O1s \rightarrow \pi*$, $O1s \rightarrow \sigma*$ and 550 eV.

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Photon stimulated ion desorption from condensed methanol near the O 1s-edge: relevance to cometary and planetary surface

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The simplest amino acid, glycine (NH_2CH_2COOH), was detected in the molecular clouds SgrB2, Orion KL, and W51. In these objects, the precursor molecules like ammonia, methanol, formic acid and acetic acid have already been observed. Some of these precursor molecules have also been found in comets and planet surfaces. In order to simulate the effects of high energy particles (e.g. cosmic rays) and soft X-rays photons from solar wind on the cometary methanol icy surface, we have employed two different experimental techniques (Plasma Desorption Mass Spectrometry (PDMS) and Photon Stimulated Ion Desorption (PSID)) at the Brazilian Synchrotron Light Laboratory (LNLS), Campinas, Brazil. We have results of positive and negative ion fragmentation patterns of the CH_3OH ice using the PDMS techniques in the mass/charge (m/q) range up to 400 u/e and using the PSID techniques recorded with photons with energy around the O 1s resonance. The Partial Ion Yield (PIY) curves are also presented.

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X RAY RESONANT INELASTIC SCATTERING ON PURE SAMPLES AND OXIDES

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By means of X ray spectroscopy it is possible to characterize materials since when X rays interact with atoms different processes take place such as the photoelectric absorption, the Rayleigh scattering and the Compton scattering, leading to spectra with characteristic lines that allow to identify the components of the target and it is also possible to perform a quantification. But there are other processes that can alter the spectra obtained with X ray fluorescence, producing peaks that interfere with the fluorescent one causing a problem that has not been studied in detail so far. These processes are inelastic scattering processes, such as the resonant Raman effect with an enhancement of the resonant behavior as the incident energy approaches the absorption edge. In this work we present a comparison of the inelastic resonant scattering (Raman effect) on pure samples and oxides in order to study if the oxidation state of the sample can interfere with the scattering process. The measurements were carried out in XRF station of the D09B-XRF beamline at Brazilian synchrotron facility (LNLS, Campinas). Seven samples were analyzed: Mn, Mn_2O_3, Fe, Fe_2O_3, Cu, CuO, Cu_2O using monochromatic synchrotron radiation to determine experimentally the cross sections of the resonant Raman effect as a function of the incident energy; energy scannings were carried out in different ranges of energies near the absorption edge of the target element. According to our results, the cross sections for pure samples are similar to those for oxides, showing that the Raman scattering takes place in the same way in both kinds of samples.

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Ozônio – Revisão da Banda de Valência

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A grande importância da molécula de ozônio na atmosfera terrestre tem despertado um grande interesse de pesquisadores e muitos estudos experimentais e teóricos têm sido realizados para determinar a sua estrutura eletrônica [1-3]. As últimas publicações concordam quanto ao ordenamento dos estados, mas não quanto à determinação das energias de ionização, principalmente do primeiro estado eletrônico. Isto porque estes estados apresentam várias progressões vibracionais que somente com o aumento na resolução dos equipamentos de medidas e com o uso da radiação síncrotron começaram a ser detectadas. Nós já medimos a região de valência do ozônio e publicamos um artigo [1] com estes dados. Refizemos este trabalho, pois com a melhora tanto do espectrômetro TOF quanto da linha de luz, foi possível obter espectros muito mais resolvidos revelando estruturas não medidas anteriormente. A linha de luz TGM está agora com um filtro de gás que filtra altos harmônicos da luz [4]. Para o ozônio em especial isto á crucial, pois podemos determinar com precisão os limites de ionização da molécula e o limite de produção dos fragmentos. Neste trabalho apresentaremos os espectros de produção parcial de íons do ozônio medidos na linha TGM do Laboratório Nacional de Luz Síncrotron-LNLS. Como resultado, determinamos definitivamente as energias adiabáticas de produção de íons e as energias verticais dos primeiros estados ionizados da molécula de ozônio. [1] A. Mocellin, et al., J. Chem. Phys. 115, 5041 (2001). [2] H. Couto, A. Mocellin, et al., J. Chem. Phys. 124, 204311 (2006). [3] A. J. McKellar, D. Heryadi, D. L. Yeager, J. A. Nichols, Chem. Phys. 238, 1 (1998). [4]R. L. Cavasso-Filho, A. Naves de Brito, et al., J. Elect. Spect. Rel. Phen., 144-147, 1125 (2005).

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Partial Ion Yield of core excited ozone

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The Partial Ion Yield (PIY) has been studied with photoelectron−photoion coincidence technique, using synchrotron radiation from the SGM beamline at Brazilian National Synchrotron Laboratory (LNLS). The central and terminal oxygen atoms in ozone provide two chemically shifted core orbitals. Another interesting characteristic of ozone is to present nuclear motion in a timescale of a few femtoseconds to core excited states [1, 2]. The resonant core excited spectra of ozone is composed by the first sharp peak assigned as (1) O_T $1s^{-1}2b_1{}^1$ (π^*) (529.4 eV), the second peak that is a mixture of states (2) O_C $1s^{-1}2b_1{}^1$ (π^*) (534.4 eV) and (3) O_T $1s^{-1}7a_1{}^1$ (σ^*) (535.9 eV), and the large band above 537.0 eV that is a mix-ture of several states. The most abundant fragment is the O^+ followed by the ${O_2}^+$, O^{++}, and a very small contribution of ${O_3}^+$. A remarkable feature is an increase in ${O_2}^+$ fragment at resonance (3). At the large band above 537.0 eV interesting changes in PIY of the different ions were observed, mainly in O^{++}. The mixture of states (2) and (3) related to each fragment ion has been estimated. [1] L. Rosenqvist, et al., J. Chem. Phys. 115, 3614 (2001). [2] A. Naves de Brito, Chem. Phys. Lett. 328, 177 (2000).

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Observation of strong correlation effects in photoionization of water

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Dynamical electron correlation effects involves mutual interaction between two electrons whose description requires, as a rule, an extension of the independent particle approximation or of first-order claculations, involving for example , secondo-order time-dependent perturbation theories. The study of the interaction of photons and charged particles with the water molecule plays a crucial role in atmospheric and interstellar sciences. Besides it importance in these applications, photoionization of molecules, such as water, have a particularly rich dynamics, presenting a large number of structures in the cross section, involving the photoelectrons, and associated with both bond breaking and intra nuclear scattering. In this work, partial ion yields (PIY) for the photoionization and fragmentation of water vapour molecules are presented for 100-1000 eV photon impact. This energy range encompasses the O 1s edge, where the fragmentation pattern of the water molecule is expected to show an abrupt change due to the inner shell effects. However, an unexpected, appreciable and broad resonance-like structure was also observed around 230 eV. The PIY were obtained by means of coincidence techniques between the ejected electrons and the masses of the recoil ions, the latter measured by time-of-flight spectrometry (PEPICO). The experiment was performed at the Laboratório Nacional de Luz Sincrotron (LNLS), Campinas, Brazil. The photon beam intersected an effusive water vapor sample inside a high vacuum chamber, with base pressure in the 10-8 Torr range. The emergent photon beam was recorded by a light sensitive diode. The ionized fragments produced by the interaction of the vapor sample with the light beam, were accelerated by a two-stage electric field and detected by a pair of micro-channel plate detectors mounted in a chevron configuration. The ions produced stop signals to a time-to-digital converter (TDC). Our present results show that photoionization and the resulting photofragmentation of molecules can lead to complex resonant-like structures in the energy region where the de Boglie wavelength of the photoelectron is of the same order of the molecular size. The kinetic energy release of the some fragments indicates that the internuclei interference effects only affects the fragmentation associated to some selected molecular levels.

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Photoionization and Photofragmentation after inner shell excitation in $FC(O)SCH_3$ and $CH_3C(O)SCH_3$

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As part of a general project aimed to the understanding of the processes occurring after photoexcitation of molecules belonging to the carbonylsulfenyl family of compounds,[1−5] we present here photoionization and photofragmentation studies of $FC(O)SCH_3$ and $CH_3C(O)SCH_3$ in vapour phase after C 1s, O 1s, F 1s and S 1s excitations.

The Total Ion Yield (TIY) spectra of $FC(O)SCH_3$ following C 1s excitations are dominated by an intense resonance near 289 eV, accompanied by a series of less intense resonances both at lower and higher energies, while the most intense signal in the spectra of $CH_3C(O)SCH_3$ appears close to 287 eV, followed by a series of less intense resonances at higher energies. In the O 1s region, resonances near 531 and 530 eV are the most prominent features of the TIY spectra of $FC(O)SCH_3$ and $CH_3C(O)SCH_3$, respectively. The TIY spectra of $FC(O)SCH_3$ in the F 1s region exhibit two signals of similar intensities near 687 and 693 eV. Finally, only one resonance band is observable in the TIY spectra of these two molecules at about 2473 eV when an excitation energy in the S 1s region is used.

PEPICO and PEPIPICO spectra for $FC(O)SCH_3$ and $CH_3C(O)SCH_3$ were recorded on each resonance, and also below and above the resonance bands. The spectra are observed to depend on the excitation energy. Possible fragmentation mechanisms are deduced from the interpretation of the PEPIPICO spectra.

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Chemical effects in high-resolution $K\beta$ spectrum in Mn compounds

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$K\beta$ spectrum ($K\beta'$, $K\beta_{1,3}$, $K\beta''$ and $K\beta_{2,5}$ lines) in Mn metal and various Mn compounds was measured at the D12A-XRD1 beamline using an X-ray high resolution spectrometer [1]. The instrumental resolution at the Mn–$K\beta_{1,3}$ energy was calculated to be 1.9 eV. This improved energy resolution allowed chemical effect–induced enhancement and shift of emission lines to be examined with high accuracy. Relative intensity, linewidth and line shift were investigated in Mn compounds exhibiting different oxidation state (Mn^0, $\mathrm{Mn}^{\mathrm{II}}$, $\mathrm{Mn}^{\mathrm{III}}$, $\mathrm{Mn}^{\mathrm{IV}}$, $\mathrm{Mn}^{\mathrm{VI}}$, $\mathrm{Mn}^{\mathrm{VII}}$) and different type of ligand atom (oxygen, fluorine, sulfur).

It was found that the $K\beta_{2,5}$ and $K\beta'$ energy related to the $K\beta_{1,3}$ is very sensitive to oxidation state. These parameters could be used to determine oxidation states with an accuracy higher than using the $K\beta_{1,3}$ energy, as suggested by other authors [2, 3]. The observed energy shift of the $K\beta'$ line is in agreement with a previous work [4]. In addition, some influence of the oxidation state on the $K\beta'$ relative intensity and linewidth has been observed. $K\beta''$ satellite line was measured to be shifted about several eV from the $K\beta_{2,5}$ line, depending on the type of ligand atom in the investigated Mn compounds, as previously found by Bergmann *et al* [5].

The results found in this work prove that high resolution $K\beta$ fluorescence can be considered as a good technique to characterize chemical environment.

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INTERSTELLAR MOLECULES STUDY: METHYLAMINE

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The protostars are extremely efficient sources of X-ray photons that are capable of traversing large column densities of gas of the proto-planetary disk before being absorbed. In these regions the radiation field can promote several photophysical and photochemical process onto molecules, including photoionization and photodissociation. The products of organic molecules dissociation can also provide the formation of complex molecules like carbon chain molecules and amino acids. We present experimental results obtained from photoionization and photodissociation processes of the abundant interstellar methylamine (CH_3NH_2), which recently we proposed as an alternative route for the production of H_3^+ in interstellar and star forming environments (Pilling et al. 2007). The measurements were taken at the TGM beamline employing soft X-ray photons with energies between 200 and 310 eV and time of flight mass spectrometry. Mass spectra were obtained using the photoelectron photoion coincidence technique. The methylamine is destroyed by soft X-rays photons producing several ionic fragments, double and triple ionizations. We have determined the dissociative and non-dissociative photoionization cross sections as a function of the photon energy. The laboratory data were extrapolated to different interstellar environments and we found that CH_3NH_2 could survive in dense cloud environments longer than the average lifetime of the cloud.

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Interação de produtos naturais com o ultravioleta de vácuo e raios X: fotofragmentação seletiva da molécula de carvona induzida pela radiação síncrotron

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A carvona é um composto estereoisomérico de odor mentolado, que é utilizado industrialmente na manufatura de várias preparações farmacêuticas e alimentícias. Faz parte da classe dos monoterpenos, substâncias ubíquas em plantas e que apresentam funções de grande importância [1]. A fotofragmentação da molécula de carvona foi estudada a partir da técnica de tempo de vôo (TOF/MS), utilizando-se luz síncrotron como agente ionizante. Vários estudos semelhantes com compostos de interesse biológico têm sido desenvolvidos por nosso grupo, com foco na estabilidade das espécies iônicas simples e multiplamente carregadas [2]. Buscamos caracterizar as principais vias de relaxação das moléculas ionizadas em diferentes níveis (valência e camada interna) pelo uso de diferentes formas de radiação (elétrons luz, etc.). Os resultados de um estudo sistemático de fotoionização da molécula de carvona ao redor das bordas C 1s e O 1s, conduzido ao longo dos últimos 3 anos no LNLS, utilizando-se radiação síncrotron monocromatizada das linhas TGM e SGM, revelaram que o padrão de fragmentação iônica depende da energia, embora a maioria dos estados iônicos finais a altas energias se assemelhe às formas de decaimento em baixas energias. A formação de íons atômicos como o C^+ (m/z = 12) passa a ocorrer após a borda do C 1s (310 eV); ao passo que só a partir da borda do O 1s é que se observa a formação de oxigênio atômico mono e duplamente carregado: O^+ (m/z = 16) e $O_2{}^+$ (m/z = 8). Relata-se portanto a primeira evidência de fragmentação sítio-seletiva ao redor das bodas de ionização dos elementos C 1s e O 1s envolvendo a molécula de carvona.

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Sulfur K shell photo-fragmentation of CH3C(O)SH and CH3OC(O)SCl species

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There are reported scarce data related with absorption of x-ray photons for medium size molecules. Continuing our studies on -SCO- species, CH3OC(O)SCl and CH3C(O)SH molecules have been selected because complementary studies have been already conducted at the LNLS for these molecules [3], [4]. The aim of this work is to investigate the electronic properties of sulfur 1s core electrons and the dynamic of fragmentation followed by the photon absorption. Tunable synchrotron radiation at the soft X-Ray SXS beamline has been used to excite and ionized the sulfur 1s electrons. Total Ion Yield spectra and multi coincidence PEPICO and PEPIPICO spectra were acquired. Below the ionization threshold, the Total Ion Yield (TIY) spectra of thioacetic acid are dominated by an intense resonance near 2473 eV, with a less intense feature at 2476 eV. Comparing with previous spectra for related molecules, the former excitation could be associated to an electronic transitions to the vacant pi* orbital in the C(O)S group. This absorption is observed at 2472 eV for CH3OC(O)SCl. Fragmentation patterns from the PEPICO spectra denote the presence of simple, double and even triple ionized atomic fragments, which should be originated in fragmentation processes arising from multiply charged ion. Highly repulsive states should be populated in the absorption process. These states could dissociate by Coulombic explosion mechanism causing atomization processes as the leading fragmentation channels [5], [6]. PEPIPICO spectra are being analyzed in order to better understand these mechanisms.

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Experimental simulations of Titan's tholin using synchrotron light as a photochemistry trigger

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Titan, the largest satellite of Saturn, has an atmosphere chiefly made up of N_2 and CH_4, and including many organics. This atmosphere also partly consists of hazes and aerosols particles which shroud the surface of this satellite, giving it a reddish appearance. As a consequence of its high surface atmospheric pressure (∼1.5 bar) the incoming solar UV and soft X-ray photons are mostly absorbed. As a consequence only low amounts of energetic photons reach the surface. However, during the last 4.5 gigayears, the photolysed atmospheric molecules and aerosol particles have been deposited over the Titan surface composed by water-rich ice (80-90 K) delivered by comets. This process produced in some regions a ten meter size, or even higher, layers of organic polymer (Griffith et al., 2003, Science, 300, 628.).

In an attempt to simulate the photochemistry process on the water-rich icy surface inside a Titan atmosphere (0.95 N_2; 0.05 CH_4), we performed irradiation experiments on a 65 K cryostat finger mounted inside a high vacuum chamber. The experiments have been carried out at the Brazilian Synchrotron Light Laboratory (LNLS) located in Campinas/Brazil employing mainly UV and soft X-rays photons from the Soft X-ray Spectroscopy (SXS) beamline. During the irradiation the pressure was kept around 10^{-6} mbar which represents about one atomic monolayer deposition per second. At this pressure, most of the incoming photons reach the water-rich icy surface with N2 and CH_4 adsorbed molecules, and surface photochemistry occurs. About 1-2 mg of reddish-brown colored complex organic heteropolymer (tholin) was produced over the half-mm square sized aluminum substrate kept at 65 K. After 20 hours of continuous irradiation, the sample presents a green fluorescence which seems to be associated with the presence of aromatic species (Hodyss et al., 2004, Icarus, 171, 525). Infrared (IR) spectra of the simulated Titans tholin indicate the presence of several organic functional groups including, alkanes, amines, aldehydes, ketones and acids. The IR spectra also suggest the presence of aromatics with single and double bonds. The functional groups detected may help to elucidate the mass spectrum features obtained by the Huygens probe at Titan surface (Niemann et al., 2005, Nature, 438, 779).

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Aqueous Glycine pH Dependence Study Using Core Level Photoelectron Spectroscopy

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During the last few decades synchrotron radiation (SR) based experiments in the range of soft x-ray have been very successful in studies of the electronic structure in the fields of molecular, surface and solid state physics. The atomic level knowledge obtained from such experiments is of fundamental importance to understand the physical and chemical properties of materials. However, for liquid samples, only a few SR based experiments in the soft x-ray energy range have been performed, due to experimental problems such as the high vacuum demand in the analysis chambers, and the inelastic scattering problem of the emitted electrons in the vapor around the liquid. By developing a novel source, based on a differentially pumped liquid micro-jet, we have overcome this problem, and have been able to perform a core level photoelectron spectroscopy study of the pH dependence of aqueous glycine at the C1s and N1s edges. The measurements were performed at the beam line I411 of the Swedish synchrotron laboratory MAX-lab, using a Scienta R4000 electron spectrometer.

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Recent experiments carried out at the single bunch period revealed exotic fellows in the ionization process, the negative ions. What can we learn from them?

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Photo excitation and ionization of deep core electrons lead to the creation of multiply charged ions due to the well known process called Auger decay. Indeed when a photoelectron is ejected from a core level such as the Sulfur 1*s* electron in a molecule like SO_2 the most likely decay pathway is the filling of the core level by a 2*p* electron and a ejection of a second 2*p* electron. This leaves the molecule in a doubly charged state. This ion is still highly excited and a second decay process takes place: Two electrons from the valence shell fill the 2*p* vacancies while two other electrons are ejected from the valence. This explains why the quadruply charged positive ions are the most abundant species produced in this case. The detection of singly charged negative ions resulting from deep core excitation must be regarded as surprising in this context. Using the timing window provided by the single bunch operation of LNLS we were able to detect negative ions and follow their production as a function of the excitation photon energy. The most likely mechanism for the production of the negative ions observed in our experiments is the ions pair formation from the dissociation of this highly excited molecules. Our preliminary results suggest that the atomic negative ions S^- and O^- are the only species observed in the negative ions spectra at this energy range. It was observed a surprising behavior of one of these ions when their production is monitored at different photon energies across the Sulfur 1*s* edge. In the talk the results and what we can learn from them will be discussed.

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Parte V

Geociência, Meio-ambiente e Aplicações em Materiais Biológicos

MINERAL CONTENTS IN FETAL AND MATERNAL PLACENT FROM TEENEGARES MOTHERS USING TOTAL REFLECTION X-RAY FLUORESCENCE SPECTROMETREY

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Maternal nutritional requirements are increased during pregnancy (embryo, placenta, amniotic liquid, breasts, uterus and reserves for final phase of the gestation and lactation). It is well also known that adequate maternal nutrional state during pregnancy is important for normal fetal growth. During pregnancy, trace elements are indispensable for life maintenance not only for the mother but also for the fetus, therefore, the pregancy in the teenegare period is a serious problems of health public, and it can be considered as a group of nutritional risk, due to the teenagers alimentary habits. Although, there are some studies reported in the cientific literature about the mineral concentrations in placenta of adults mothers, it is still unkown the mineral concentrations in the placenta tissues of teenagers mothers. In this way, the purpose of this study was to examine the mineral concentrations (K, Ca, Fe, Cu and Zn) in maternal and fetal placenta tissue from teenegares mothers. using Total Reflection X-Ray Fluorescence. All measurements were carried out at the XRF beam line at Brazilian Synchrotron Laboratory (Campinas, São Paulo). About the results, we can observe that Ca levels were higher in the maternal placenta than in the fetal one, on the other hand, Fe and Cu were less in the maternal placenta than in the fetal one, and K and Zn concentrations did not present changes between the maternal and fetal placentas tissue. Comparing our results from mothers' teenegares with , both maternal and with the results from mothers' adults, it was possible to observe that all the minerals studied were higher in maternal and fetal placenta of adults mothers than in the teenagers ones. These resulte reinforce the idea that the alimentary habits of teenagers mothers can affect the fetal growth trought the deficiency in the minerals intake.

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Ethanol intake during lactation. Evaluation of the mineral concentrations on pups brain using total reflection X-ray fluorescence spectrometry

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It is known that during lactation, the ingestion of a diet that obtained approximately one third of its calories from ethanol reduced milk production, altered milk composition and retarded offsprings body and central nervous system growth. In this way, the aim of this work was to study the elemental concentrations changes in the hippocampus, frontal cortex and entorhinal cortex of pups Wistar rats related to dams ethanol intake during lactation. On day 20 (n = 6) of life the pups of ethanol and control (n = 6) groups were sacrificed. The analysis of the elemental concentration was performed by total reflection X-ray fluorescence spectrometry with synchrotron radiation (SR-TXRF). These measurements were carried out at XRF beam line at Light Synchrotron Brazilian laboratory, Campinas, Brazil. The alcohol administration increased the Zn levels in the entorhinal cortex of the pups. On the other hand, these administration lead to a decreased in the Fe and Cu levels in the entorhinal cortex of the same animals. Moreover, P, S, K and Ca concentrations were higher in the entorhinal cortex of the pups of the alcohol group, 20 days old, than to the control group, 20 days old. In the hippocampus of the alcohol group with 20 days old it was observed a decrease in the K, Ca, Fe, Cu and Zn levels in relation to the control group with 20 days old. The alcoholic diet lead an increase in the Cu and K levels and a decrease in the S and P levels in the frontal cortex. However, Fe and Zn levels did not presented statistical differences significative between the alcohol and control groups in these structures. Therefore, the ethanol intake for the dams during lactation period, leads to several changes in the mineral concentrations in the brain of their pups.

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Arsenic speciation by a modified thiol resin: sulfate influences evidenced by XAS analyses

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The study of the arsenic speciation in natural waters and effluents is increasingly important for the assessment of toxicity and bioavailability of arsenic species in aqueous environment. Nowadays, the most applied techniques for the evaluation of the arsenic speciation are based on the use of anion exchange resins, which are able to immobilize only the pentavalent arsenic species (Parker and Ciminelli, 2005). An option for the arsenic speciation based on the As(III) immobilization was investigated by our research group (Duarte *et al.* 2006), where the strong affinity of the As(III) by a modified thiol chelating resin at a wide pH range was proved using XAS analyses. A potential practical advantage of using these resins for As(III) immobilization is the possibility of their assemblage into solid phase extraction cartridges, thus providing an option to the anion exchange resins that have been currently used for As(V) retention. It was also observed by Duarte *et al.* (2006) that the resin specificity was altered in the presence of sulfate ions at concentration higher than 100 mg.L^{-1} since a significant fraction of the As(V) species (around 30 %) became immobilized by the resin. However, it was not clear if the resin became able to retain the As(V) or it was reduced to As(III) in the presence of high concentrations of sulfate ions. In order to explain this behavior, the thiol resin loaded with As(V) in the presence of sulfate at 250 mg.L^{-1} was submitted to XAS analyses. XANES analyses show that the arsenic loaded in the thiol resin is in its trivalent form, indicating that occurs a reduction of the As(V) to As(III) in the evaluated conditions. The E_0 values obtained with the Athena software were found as 11865.4 eV for the arsenic loaded onto the thiol chelating resin; 11867.2 eV for the As(III) standard, and 11870.7 eV for the As(V) standard. The EXAFS analyses were performed using the Artemis program, and the phase and amplitude parameters were calculated with the FEFF 6.0 software. The results showed that each arsenic atom is bound to three sulphur atoms, with an As-S interatomic distance, R = 2.26 and a coordination number, CN = 2.3. These results indicate that the sorption mechanism is similar to that found when the As(III) species was loaded on the thiol resin at pH 5.0.

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LOW Z TOTAL REFLECTION X-RAY FLUORESCENCE ANALYSIS IN SERUM IN PATIENTS WITH CHRONIC MYELOGENOUS LEUKEMIA (CML)

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Leukemia is a disease that occurs all over the world. The Chronic Myelogenous Leukemia (CML) is one type of leukemia. The CML can occur in adults, usually middle-aged, and children and it affects 1 to 2 people in 100,000 people. However, there are few studies that correlate the elemental concentrations in blood with the diagnostic, evolution and prognostic of the CML. On the other hand, the low Z elements are very essential to every cell in the body to function normally. A number of enzymes, hormones and cell-signaling molecules depend on these elements for their activation. In this work, low Z elements were determined in serum of patients with CML using Total Reflection X-Ray Fluorescence induced by Synchrotron Radiation. SRTXRF analyses were performed at the X-Ray Fluorescence Beamline D09B at Brazilian National Synchrotron Light Laboratory (LNLS) using a polychromatic beam with maximum energy of 20 keV for the excitation and an Ultra-LEGe detector with resolution of 148 eV at 5.9 keV. The detector was equipped with an ultrathin entrance window of Polymer (0.4 μm) required to measure low-energy X-ray fluorescence radiation of low Z elements. All samples were excited for 100 s and the experiments were performed in a high vacuum chamber (2.5 x 10^{-5} mbar) to avoid air absorption. It was possible to determine the elemental concentrations of the following elements: Na, P, S, Cl, K and Ca. Using analysis of Student‘s t-tests it was observed that contents of the elements Na, Cl and K differed significantly ($\alpha = 0.05$) between groups of healthy subjects and CML patients. Prior to this conclusion cannot be considered as a closed one. However, these results can be associated to a new hypothesis: Na, Cl and K elemental concentrations can be very important in the biochemical processes of CML.

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Evaluation of elementar content changes in blood and blood componentes after irradiation

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Currently the major application of blood and blood component irradiation is for the prevention of graft-versus-host disease in immunodeficient patients and also in studies about the investigation of radioinduced biological effects in order to correlate them with the radiation dose. Radiation effects on cells have been studied in vitro using variable techniques to determinate trace elements concentration. The quantification of trace elements in biological samples with X-ray total reflection fluorescence with synchrotron radiation (SR-TXRF) is recognized as powerful analytical technique. The aim of this study was to investigate the suitability of measuring essential trace elements using SR-TXRF as a monitoring tool for the diagnosis of alterations caused by irradiation. Fresh blood specimens were obtained from volunteers by vein puncture at the Dr. Eliel Figueiredo Laboratory, Rio de Janeiro. The whole blood samples were irradiated in INCA (National Cancer Hospital), Rio de Janeiro, with low doses from 2 to 100 cGy and with high doses from 15 to 30 Gy using of gamma radiation (60Co). Whole blood samples were left to rest in glass test tubes for a period of 1 hour at ambient temperature. Plasma was separated from formed elements by aspirating the clear supernatant solution. The sediment was considered formed elements. Prior to analysis, blood samples were lyophilised for 48 h.The time was optimised for total removal of water. Following this procedure, a powder was obtained of each sample in a porcelain mortar, and the samples were stored under controlled humidity conditions. Then the samples were submitted to standard chemical digestion by adding nitric acid. In this study Ga was used as an internal standard because it is not usually found in matrices of interest. In order to evaluate repetitiveness, the sampling and analytical procedures were carried out in triplicate. The mixture were transferred to a Perspex support and dried with infrared light. SR-TXRF measurements will be performed at the XRF Beamline under the project XRF-6634 in september, 2007.

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Preliminary estimate of bone mineral loss associated with cancer using Scattering Computed Tomography

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Bone is a connective tissue largely composed of an organic protein, collagen and the inorganic mineral hydroxyapatite. Since bone mineral has a crystal-like structure, Braggs law will describe the conditions under which the constructive interference of x-ray photons occurs. X-ray computed tomography and x-ray diffraction are very attractive for noninvasive quantification and provide complementary information. This study is part of a larger series of studies examining the biological effects of bone exposure to radiation using different techniques, i.e. X-ray diffraction, X-ray fluorescence and PhC micro-CT. First XRD measurements in bone were carried out at the X-Ray Diffraction beamline (XRD1) at the LNLS under proposals XRD1-4765 and XRD1-5368 and at the SYRMEP beamline at ELETTRA synchrotron radiation facility, Italy, under proposals 2004625 and 2004747. The preliminary results suggest that the measurement of bone mineral content within trabecular bone can be performed by using quantitative coherent scattering information [1-2]. First SR-TXRF measurements were performed at the XRF Beamline at the LNLS under proposal XRF-5369. First PhC micro-CT images were obtained in the SYRMEP beamline under proposal 2006832. The histomorphometric analysis, connectivity and anisotropy evaluations will be used to relate values obtained from the PhC micro-CT images with the 3D structure of human bone samples. The main goal of this work is to obtain bone-sensitive images in terms of their mineral and non-mineral components. We propose a different approach to coherent X-ray imaging by fixing the detector at a given scatter angle, which produces an interference peak and then, carried out a tomography in the standard way. The detector will be fixed in the position of the characteristic peak for mineral component then carrying out a onedimensional scanning producing a projection where the presence of mineral component would be enhanced, distinguishing by marrow bone tissue. [1] J.C. Lima, R.C. Barroso et al, 2007. Nucl. Instrum. Meth. A, 580: 469-472. [2] R.C. Barroso, L.F. Oliveira et al, 2007, Nucl. Instrum. Meth. A, 579: 318-321.

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Fragmentação iônica da molécula da zerumbona na região do Ultravioleta de Vácuo

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A zerumbona ($C_{15}H_{22}O$) é um sesquiterpeno isolado de uma planta conhecida com gengibre selvagem ou amargo, cultivado extensamente em área tropical e subtropical, inclusive na região amazônica. Estudos científicos mostram que a zerumbona possui atividades antioxidante, citotóxica, antimicrobiana e antiviral [1]. Se a atividade biológica é relativamente bem documentada, poucas informações existem em relação a processos de absorção de radiação e conseqüentes processos de fragmentação. Assim, uma amostra de zerumbona, isolada de uma espécie de gengibre da Amazônia, foi irradiada com luz síncrotron nas energias de 12, 16, 21 e 160 eV, na linha TGM do LNLS. Um pequeno forno foi utilizado para a volatilização da amostra [2] e um espectrômetro de massas do tipo tempo-de-vôo permitiu a análise dos fragmentos [3]. Nas energias de valência, usou-se um filtro de harmônicos de neônio [4]. Foram obtidos espectros de dupla coincidência fotoelétron-fotoíon (PEPICO), a partir dos quais foram calculados os rendimentos iônicos parciais (PIY). Conforme esperado, há uma maior o grau de fragmentação quanto maior a energia. Os resultados mostram que na região de valência o íon molecular (m/z 218) apresenta maior rendimento, sendo este muito maior a 12 eV do que em 16 e 21 eV. Em 160 eV predominam íons mais leves como o m/z 27, 39, 41 e 53. Referências 1 Pinheiro, C. C. de S; Dissertação de Mestrado UEA 2005; Huang, G. C., et al. Planta Medica 71(3): 219-224, 2005; Matthes, H. W. D., et al. (1980). Phytochemistry 19(12): 2643-2650, 1980; Nakamura, Y., et al. FEBS Letters 572(1-3): 245-250, 2004. 2 Lago, A.F. et al Chemical Physics 307, 9-14, 2004. 3 Santos, A.C.F. et al Chemical Physics 282, 315-326, 2002. 4 Cavasso Filho, R.L., et al, Journal of Spectroscopy and Related Phenomena 144-147, 1125-1127, 2005 .

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Quantificação de metais em águas e sedimentos do reservatório Billings por SR-TXRF

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A Represa Billings é o maior reservatório de água da região metropolitana de São Paulo, com aproximadamente 100 km^2 de espelho dágua. Sua bacia hidrográfica ocupa mais de 500 km^2 em seis municípios da região. Ao seu redor concentra-se o maior parque industrial da América do Sul e somente suas margens são ocupadas por quase um milhão de habitantes. A qualidade de suas águas é, portanto, motivo constante de preocupação de toda a sociedade. Neste trabalho foi empregada a SR-TXRF, para a identificação e quantificação de metais em águas e sedimentos da Represa Billings. Foram quantificados os metais Cr, Ni, Cu, Zn e Pb, freqüentemente investigados em trabalhos na área ambiental, já que são largamente usados em processos industriais e estão presentes em vários produtos de consumo doméstico. Para o trabalho de campo, foram coletadas amostras em dezoito pontos, incluídas as margens e a porção central da represa, localizados em regiões com ocupação residencial e industrial, como também em regiões preservadas, próximos de pontos de monitoramento adotados pela CETESB. Foi estabelecida uma comparação entre as concentrações de metais obtidas e os valores de referência para águas e para sedimentos, recomendados pela legislação em vigor. Os resultados obtidos indicam concentrações acima dos valores permitidos para o cobre, generalizada para todos os locais de amostragem, como também para o chumbo na grande maioria desses locais. Os demais metais estudados também apresentaram concentrações acima do permitido para alguns dos pontos de amostragem. A finalidade de contexto social é contribuir para a preservação dos mananciais locais e o aproveitamento racional de suas águas.

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Avaliação da água e do sedimento das microbacias dos ribeirões Graminha e Águas da Serra na cidade de Limeira (SP) empregando a SR-TXRF

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A cidade de Limeira está localizada no Estado de São Paulo e possui economia expressiva, com indústrias em vários setores produtivos, entre elas, galvanoplastias voltadas para a produção de jóias, semijóias e bijuterias. Visando elucidar se há influência antropogênica nos mananciais da cidade, avaliou-se a qualidade das águas e as concentrações de metais presentes na água e nos sedimentos dos ribeirões Graminha e Águas da Serra, cujas nascentes estão na zona urbana de Limeira. As determinações de metais foram realizadas pela técnica de SR-TXRF. Os limites de detecção para amostras de água estão na faixa de 0,50 a 0,05 μg.L^{-1} para Ca e Zn, respectivamente, enquanto que para as amostras de sedimento os limites de detecção obtidos foram iguais a 0,22 e 0,02 μg.g^{-1} para os mesmos elementos. Nas amostras de água dos dois mananciais e para ambos os períodos amostrados (seco e húmido) as concetrações de Al e Fe foram superiores aos limites máximos permissíveis estabelecidos pela legislação vigente. Os elementos Zn e Cu apresentaram o mesmo comportamento. Para o Cr e Ni apenas alguns pontos de amostragem apresentaram valores acima dos limites permitidos. No ribeirão Águas da Serra os valores foram superiors ao permitido para todos os pontos exceto os pontos 2 e 6 no período seco, enquanto que para o ribeirão Graminha os resultados foram superiores para os pontos 2, 3, 4 e 6 no período húmido. Nas amostras de sedimento o elemento Cu ultrapassou o valor estabelecido pela legislação em ambos os mananciais. Os valores para Pb nas amostras de sedimento também foram ultrapassados para todas as amostras do ribeirão Águas da Serra e em alguns pontos do Graminha. Os resultados obtidos para Cr foram excedidos em três pontos (1, 3 e 4) no período húmido e em dois pontos (1 e 4) no período seco para o ribeirão Águas da Serra, e no Graminha apenas no período seco (pontos 2 e 6) os valores foram excedidos. Para Ni e Zn em apenas alguns pontos foram observados valores acima do permitido. As concentrações de metais foram superiores aos valores máximos permissíveis estabelecidos pela legislação vigente para vários elementos tanto nas amostras de água quanto nas amostras de sedimento.

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Monitoramento e avaliação da emissão de dutos e fontes estacionárias de indústrias cerâmicas empregando a SR-TXRF

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Neste trabalho foi realizado um estudo dos gases emitidos de dutos e fontes estacionárias, de empresas cerâmicas da região do Pólo Cerâmico de Santa Gertrudes (SP). As investigações mostram que nos últimos anos houve um crescimento das empresas neste setor, causando reflexos ambientais na região, que há alguns anos era predominantemente agrícola. O principal objetivo foi realizar um levantamento das emissões atmosféricas pelo setor industrial cerâmico entre 2004 e 2007, através de amostragens isocinéticas de dutos e fontes estacionárias de 8 empresas da região. Empregando a SR-TXRF foi possível determinar as concentrações de Al, S, Cl, K, Ca, Fe, Mn, Ni, Cu, Zn e Pb. A resolução CONAMA 264/99 estabelece que o valor máximo permitido de emissão (LME) para o elemento Pb é de 0,35 mg/Nm^3. Neste trabalho a concentração de Pb variou de 0,03 a 1,42 mg/Nm^3, e em duas empresas foi superior ao limite máximo de emissão estabelecido. Ainda segundo a mesma resolução a somatória das concentrações dos elementos (As+Be+Co+Cr+Cu+Mn+Ni+Pb+Sb+Se+Sn+Te+Zn) não deve exceder o valor de 7,0 mg/Nm^3, como limite máximo de emissão. A somatória dos elementos metálicos determinados por SR-TXRF (Cr+Cu+Mn+Ni+Pb+Zn) nas oito empresas amostradas foi comparada à legislação CONAMA, e observou-se que a maior parte das empresas cerâmicas lançam metais para a atmosfera em concentrações superiores ao LME. Os limites de detecção obtidos estão na faixa de 0,1 μg/Nm^3 para a maioria dos metais de interesse. Pelos resultados obtidos podemos concluir que é necessário implantar medidas e programas de minimização para o controle das emissões atmosféricas na região do Pólo Cerâmico de Santa Gertrudes.

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Análise quantitativa do material particulado (PM_{10}) por SR-TXRF

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Nos últimos anos a poluição ambiental tornou-se foco de preocupação nos grandes centros urbanos, devido à associação com patologias humanas. A cidade de Campinas é uma das maiores regiões urbanizadas do interior do Estado de São Paulo e um importante centro industrial. Devido a sua localização e importância foram instalados 3 postos de monitoramento para coleta do material particulado (PM_{10}). Um dos postos está localizado na Avenida Anchieta, região central da cidade e uma via com grande fluxo veicular. Outro posto foi instalado no distrito de Barão Geraldo (no campus da UNICAMP) e o terceiro em Paulínia (próxima ao pólo petroquímico). Em todos os postos foi coletado o material particulado, correspondente a duas frações, a grossa e a fina, amostradas por 24 hs durante 6 meses (Outubro/05 a Março/06) totalizando 21 semanas. No posto de amostragem no Centro de Campinas foram observados valores acima do considerado como regular para a qualidade do ar, estabelecido pela CETESB (150 μg.m^{-3}). De forma geral os valores de PM_{10} para Paulínia e para o Centro de Campinas, foram superiores aos de Barão Geraldo. Utilizando a SR-TXRF foram identificados e quantificados 19 elementos os quais após a análise das componentes principais (ACP) e a análise de cluster permitiu agrupá-los em função da fonte emissora. Dos resultados obtidos verificou-se que a poeira do solo contribui com 62%, 51% e 46% do total da fração grossa no posto de Barão Geraldo, Paulínia e Centro de Campinas, respectivamente. Para o posto localizado no Centro da Cidade de Campinas a emissão veicular foi responsável por 16% do total na fração grossa do material particulado e 11% na fração fina. Valor esperado uma vez que o posto foi instalado na Avenida Anchieta, um local com alto fluxo veicular. No posto de Paulínia, a emissão veicular contribui com 20% (fração grossa) e 13% (fina) enquanto que a contribuição industrial corresponde a 25% e 29% para as frações grossa e fina, respectivamente. A contribuição da emissão industrial no Posto de Barão Geraldo foi de 27% e 31% para as frações grossa e fina, valores acima do esperado para uma região urbana, mas aceitáveis quando verificamos que a predominância dos ventos na região favorece a dispersão dos poluentes do Pólo Petroquímico na região de Barão Geraldo.

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Avaliação de metais pesados em emissões atmosféricas de indústria automotiva por SR-TXRF

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A qualidade do ar está diretamente à qualidade de vida da sociedade. Nos últimos anos vários episódios de poluição nos grandes centros urbanos, bem como as doenças causadas pela baixa qualidade do ar têm feito com que os órgãos governamentais apresentem padrões para qualidade do ar e também para as emissões atmosféricas que geralmente são as responsáveis pela alteração da qualidade do ar. Neste estudo foram determinado vários elementos tais como: Ba, Br, Ca, Pb, Cl, Cu, Cr, Sr, Fe, Mn, Ni, K, Si, Ti e Zn, nos poluentes atmosféricos gerados em uma indústria automotiva localizada em Engenheiro Coelho no interior do estado de São Paulo. O procedimento adotado para a amostragem e o preparo das amostras foi baseado na norma CETESB L9.234 (Determinação de chumbo inorgânico em Dutos e chaminés de fontes estacionárias) e também no método EPA29 (Detemination of metals emissions from stationary sources). As amostras foram coletadas nas diferentes etapas do processo produtivo. A concentração de Zn variou de 30 a 80 mg/Nm^3. Os menores valores foram observados na fonte de Despoeiramento Seco e na Exaustão dos Fornos. Para o elemento Cr a menor concentração (0,040 mg/Nm^3) foi observada na fonte de Central de Areia, enquanto que na fonte de Transporte de Macharia foram encontrados os valores mais elevados de concentração (0,3350 mg/Nm^3). Para o elemento Ni a menor concentração (0,040 mg/Nm^3) foi observada no processo de Exaustão dos Fornos. No caso do Pb os padrões de emissão (0,35 mg/Nm^3), são observados em todos os processos, exceto na chaminé da Exaustão dos Fornos. Comparando-se os valores obtidos, com o limite máximo de emissão (LME) estabelecido pela resolução CONAMA 264/99 para a soma das concentrações dos metais As, Be, Co, Cr, Cu, Mn, Ni, Pb, Sb, Se, Sn, Te e Zn, que é de 7,0 mg/Nm^3, todas as fontes estão acima do LME devido principalmente as altas concentrações de Zn encontradas nas amostras analisadas. Os limites de detecção do método estão na faixa de 0,02 (Zn) a 2,58 μg/Nm^3 (Si), muito abaixo dos padrões de emissão referenciados neste estudo. Os metais encontrados provavelmente são provenientes das sucatas metálicas empregadas no processo de produção da indústria em estudo.

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Análise quantitativa de partículas individuais do material particulado grosso por micro-SRXRF

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As partículas em suspensão na atmosfera são de extrema importância entre os contaminantes do ar, devido a sua complexidade em termos de composição química e propriedades físicas. As pesquisas sobre material particulado têm progredido de determinações relativamente simples como a determinação de massa total para classificação do tamanho das partículas e determinação da composição química. 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. Entretanto há grandes deficiências nas informações sobre o gerenciamento efetivo da qualidade do ar no que se refere às partículas individuais. Empregando a micro-SRXRF foram analisadas partículas do material particulado grosso coletado em postos localizados em Barão Geraldo, Paulínia e no Centro da cidade de Campinas. A correção do efeito da absorção pela matriz foi realizada pelo método dos parâmetros fundamentais. Foram detectados Al, Si, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Ba e Pb na maioria das amostras. O S apresentou concentrações mais elevadas no posto de Barão Geraldo quando comparado aos outros postos, indicando que as queimadas, contribuem fortemente neste local de amostragem. O elemento Pb foi detectado em todos os postos e apresentou altos valores no posto de Campinas. Os elementos característicos da resuspensão do solo, como Al, Si, Fe e Ti foram verificados em maior concentração no Posto de Barão Geraldo como esperado. Quanto ao elemento Zn as concentrações mais elevadas foram observadas nos postos de Paulínia e no Centro da cidade indicando uma contribuição de fontes de origem industrial nestes locais. Quanto ao Cr concentrações de 45 ppm foram observadas no posto de Barão Geraldo, seguido pelo posto de Campinas (40 ppm) e de Paulínia (19 ppm), indicando que nestes locais pode haver uma contribuição de fontes emissoras de origem industrial. Pelos resultados obtidos podemos concluir que no posto de Barão Geraldo a resuspensão do solo tem grande contribuição na fração grossa do material particulado enquanto que no Posto de Paulínia e do Centro da cidade de Campinas, os elementos associados a emissão industrial estão presentes em maior concentração.

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BIOACCUMULATION OF LEAD BY PISTIA STRATIOTES FROM A HYDROPONIC SOLUTION

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In the present work the uptake of the lead ions onto a living free floating aquatic macrophytes *Pistia stratiotes* was investigated. The bioaccumulation mechanism were applied to understand the metal uptake by the autochthonous free floating Pistia, common in ponds and shallow lakes from southern Brazilian states from a Clarks hydroponics solution. The experiment was performed using several healthy acclimatized plants *Pistia stratiotes*. For the metal uptake, aquatic plants were grown in plastic containers containing $5\,L$ test liquids into a greenhouse for 35 days. Twenty one replicates were used for each metal treatment. Only healthy acclimatized plants of a uniform size and weight were selected for experimental purposes. Approximately $30\,g$ wet weights of Pistia stratiotes were put into aqueous solution. The room temperature and pH were daily measured and deionized water was adding to compensate for water losses. Seven collections were carried out during five weeks which both plants and test liquids were collected from three replicate containers of each metal treatment. The plant wet weight was measured before the experiment and after the each collection. Plants were oven-dried at $80\,^{\circ}C$ for 72 hours and weighted reducing their mass around 90%, and then they were grinded and digested in acid attack. A Gallium internal standard was added to an aliquot of water or digested plant. An aliquot of $5\,\mu L$ was deposited on a pre-cleaned acrylic disk ($\phi\,30$ mm, 3mm thick) and dried at room temperature. Blank control samples containing de-ionized water and all reagents used in the experiment were prepared by the same procedure. Metal concentrations on dried weight plants and cultivation water were measured using the SR-TXRF technique. The chromium bioaccumulation mechanism was represented by a mathematical model which the uptake rate of chromium was described by the kinetic of the Langmuir irreversible model. The constant of the kinetics adsorption process and the maximum chromium uptake for *Pistia stratiotes* were the parameters adjustable from the model.

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REMOVAL OF INORGANIC AND ORGANIC COMPOUNDS FROM TANNERY EFFLUENTS USING THE ELECTRO-FLOCCULATION AND SR-TXRF TECHNIQUES

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In this work the efficiency of the electro-flocculation technique for removal of organic substance (Oxygen Chemical Demand), solids (total, fixed and volatile), turbidity and metals mainly chromium in treatment tannery effluent, was investigated. A 5-liter electro-chemical reactor containing two iron or aluminum plate electrodes was used. Before the experiment, the untreated effluent was characterized with five chemical-physical parameters (pH, COD, Turbidity, fixed and volatile solids) and at least six elementary concentrations (Cr, Ca, Cl, Zn, Br, Fe). Elementary concentrations before and after electro-flocculation process in each sample were measured using the SR-TXRF technique. For SR-TXRF analysis, a 2 mL aliquot of each sample was taken and 20 μL standard solution of Ga (1000 mgL^{-1} gallium) was added as an internal standard. Aliquots of 5 μL were deposited on pre-cleaned 3 mm thick acrylic disks and dried at room temperature, obtaining samples with thin layers of dry residues. For iron electrodes, chromium concentrations have shown a good correlation with pH, time, and electric current, while calcium ones were correlated with time and pH. Moreover, for Aluminum electrodes, calcium concentrations were correlated with pH, time, distance between electrodes. Experiments for iron and aluminum electrodes were also carried out varying pH values from 6 to 9 at 5.5 Amp., 4 cm and 30 min. Due to have a good reduction on the most of physical chemical parameters, it was chosen a pH of 7.5, which is more near to one natural effluent. Using iron and aluminum electrodes, the results have showed that the Oxygen Chemical Demand (COD) values were reduced up to 50 and 80%, respectively; while total solid values were reduced up to 55 and 45%, total fixed solids were reduced up to 20 and 45% and volatile total solids were reduced up to 85 and 79%, respectively. Calcium, Zinc and Bromine concentrations were reduced around 80, 90, and 55%, respectively. This technique has also shown a high removal of inorganic substance, mainly the chromium presents in tannery effluent.

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LEAD IONS UPTAKE BY AQUATIC MACROPHYTES SALVINIA AURICULATA FROM AN AQUEOUS SOLUTION

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The uptake study by the aquatics macrophytes *Salvinia aurculata* were carried out using a Clarks hydroponics solution containing macro- and micro-nutrients. For the experiment, aquatic plants were grown in 42 plastic containers containing $5\,L$ test liquids containing $2\,\mu g L^{-1}$ of lead into a greenhouse for 35 days. Only healthy acclimatized plants of a uniform size and weight were selected for experimental purposes. Approximately $5\,g$ wet weights of *Salvinia aurculata* were put into aqueous solution. The room temperature and pH were daily measured and deionized water was adding to compensate for water losses. Seven collections were carried out during five weeks. At each collection both plants and test liquids were collected and stored from three replicate containers of each metal treatment. Plants were oven-dried at $80\,^{\circ}C$ for 72 hours and weighed reducing their mass around 90%, and then they were grinded and digested in acid attack. A $2\,mL$ aliquot of each 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-cleaned 3 mm thick acrylic disks and dried at room temperature, obtaining samples with thin layers of dry residues for metal analysis. Blank control samples containing deionized water and all reagents used in the experiment were prepared by the same procedure. Metal concentrations on dried weight plants and cultivation water were measured using the SR-TXRF technique. Lead uptake mechanism was simulated by a Langmuir irreversible kinetic model. The constant of the kinetics adsorption process and the maximum lead uptake for *Salvinia auriculata* were the parameters adjustable from the model.

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Parte VI

Matéria Mole e Fluídos Complexos

New insight about the starch structure

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Starch is the main source of carbohydrates in the human diet and is supplied by traditional foods such as cereals, roots and tubers. A wide range of starchy products have been used as additive in the food industry. Some of them have been developed to take up water and produce viscous fluids, pastes and gels with desired textural quality [1]. Moreover, a synthetic enzymatic pathway consisting of 13 enzymes used to produce hydrogen at 30C from starch and water was recently reported [2]. Thus, hydrogen can be produced from an inexpensive abundant renewable biomass, reducing the reliance on fossil fuels and allowing to achieve virtually zero net greenhouse gas emission. However, despite the several advances in the experimental methods for starch characterization during the last decades, the relation between the microscopic structural characteristics of the granules and the macroscopic properties, desired in several applications, remains still unsolved.
Starch can be found in the form of partially crystalline microscopic granules whose size (from 1 to 100 microns) and shape significantly vary depending on the botanical origin. Starch granules are composed by two chemically identical but structurally different homopolymers of glucose : linear amylose and highly branched amylopectin [1] The granules have an onion-like structure composed of concentric semicrystalline and soft amorphous growth rings ranging from 120 to 400 nm in thickness. Independently of botanical source, size or shape, the semicrystalline growth rings of the granules are constituted by alternating crystalline and amorphous lamellae with a 9-10 nm repeat distance [4]. The crystalline lamellae of native starch are attributed to the clustered organization of amylopectin branches arranged as double helices and packed in small crystallites. The double helices can be organized in a monoclinic or hexagonal unit cell, yielding so-called A- or B-type diffraction patterns, respectively [3].
In this work will be presented a new insight about the starch structure by means of scanning electron microscopy, atomic force microscopy and wide and small angle X- ray scattering techniques. The main goal of this work is the association between experimental data and modeling procedures allowing a mathematical description of the lamellar structure of starch.
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Estruturação de micelas gigantes em soluções aquosas.

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Moléculas de surfatantes em solução aquosa ou não-aquosa são capazes de se auto-organizar em uma gama de estruturas supramoleculares: micelas esféricas, cilíndricas, estruturas lamelares, entre outras. A força motriz para essa auto-estruturação reside na natureza anfifílica dos surfatantes. Em solução aquosa, as cadeias hidrofóbicas tendem a se agrupar e se isolar do meio aquoso, minimizando a razão área/volume, enquanto a repulsão entre as cabeças hidrofílicas tende a aumentar essa razão. Logo a curvatura da interface surfatante/solvente, e portanto a forma da estrutura supramolecular, é definida pelas características da cadeia hidrofóbica e da cabeça hidrofílica e pela interação dessas com o meio[1]. A estrutura supramolecular mais comum é a micela esférica, contudo, com a adição de co-solutos é possível modificar os parâmetros de empacotamento do surfatante de forma a induzir a formação de micelas gigantes cilíndricas (com dimensões da ordem de centenas de nanômetros)[2]. No caso do surfatante utilizado neste estudo, brometo de cetiltrimetilamônio (CTAB), a adição de salicilato de sódio (NaSa) diminui a repulsão entre as cabeças catiônicas, levando a uma diminuição da curvatura da micela. Nosso principal interesse em sistemas com micelas gigantes cilíndricas reside nos efeitos causados pela interação destas estruturas com vórtices gerados em regime de fluxo turbulento[3]. O resultado desta interação é a atenuação da turbulência e possivelmente modificações na estrutura micelar. Os estudos de SAXS com micelas gigantes foram usados para correlacionar informações sobre as estruturas das micelas gigantes com dados reológicos relativos à atenuação da turbulência. Observou-se que para a proporção CTAB/NaSa onde o efeito de atenuação de turbulência se inicia, o decaimento na região de Porod é $\approx$ -2, que é compatível com cadeias Gaussianas. Ao aumentar a proporção CTAB/NaSa, o efeito de atenuação de turbulência se intensifica, mas o ajuste do padrão de espalhamento obtido não foi bom, provavelmente devido a um grande entrelaçamento das micelas gigantes. Observou-se também, que a estrutura das micelas gigantes é recuperada espontaneamente se as mesmas são previamente destruídas termicamente e posteriormente deixadas por alguns minutos à temperatura ambiente.

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XAFS Temperature Investigations of Intercalation Processes in Synthetic Nanosilicates.

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Ni-Fluorohectorite has the chemical formula per half unit cell Ni_x-$(Mg_{3-x}Li_x)Si_4O_{10}F_2$. Hectorite is a 2:1 phyllosilicate and it is classified as a trioctahedral smectite since Li^{+1} substitutes for Mg^{+2} in the octahedral sheet sites, which are fully occupied. Fluorohectorites differs from natural hectorites in that the OH groups have been replaced by F. The proportion x of the Li^{+1} ions determines the surface charge of the platelets, which are held together in the stacked structure by an interlayer cation: in our case, $x = 0.3$ Ni^{+2} ions per half unit cell. Water can be intercalated in between each platelet causing the clay to swell. For Ni-Fluorohectorite this intercalation process, which can be controlled by temperature and relative humidity, yields stable hydration states. The structures, referred to as having either 0, 1, and 3 intercalated water layers (0WL, 1WL and 3WL), are quite well ordered along the stacking direction [1]. Previous result [2] shows that the Ni-Fluorohectorite presented a meta-stable two-water layer regime, but in this work we show that this behavior is completely dependent of the way the temperature is changing by doing temperature smaller and bigger steps in the region of this 2WL regime. The EXAFS measurements were done as a function of the temperature in an interval between 0 and 160 Celsius degrees. A special cell was designed for this purpose. The temperature control was done by water circulating bath with the sample mounted on the top of a Peltier element to have finer temperature control. The open face of the cell was sealed with a capton foil and the humidity was generated by a circulating humid air connected to a pump and measured by small sensor inserted close to the sample. [1] Y. Meheust, B. Sandnes, G. Lovol, K. J. Maloy, J. O. Fossum, D. M. Fonseca, G. J. da Silva, M. S. P. Mundim and R. Droppa Jr., *Clay Science* **12**, 66(2006). References therein. [2] S.B. Lutns, *Diploma thesis*, Faculty of Physics, Informatics and Mathematics, Norwegian University of Science and Technology, Trondheim, Norway, 1999.

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Parte VII

Materiais Estruturais e Aplicações na Indústria

EFFECT OF FOOD ADDITIVES ON THE MICROSTRUCTURE OF POLYURETHANE FILMS FOR PACKAGING APPLICATIONS

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The incorporation of an active compound to a polymeric matrix can provide distinctive functionalities as controlled release system of the active compound. The effect of additives on the morphological structure of a polymeric film is an important aspect in film characterization from a practical point of view, due to changes in permeability and mechanical properties. The objective of this study is to investigate the effects of common antioxidant molecules like butylated hydroxytoluene (BHT) and α-tocopherol (Toc) and antimicrobial compounds as the sodium salt of the ethylenediamine tetra acetic acid (EDTA-Na) and potassium sorbate (PS) on the morphological structure of polyurethane (PU) films based on IPDI/PPG1000. The influence of additives on polymer structure was evaluated by SAXS. Measurements of films samples were performed at the SAXS2 beam line at the LNLS (Campinas, Brazil) using a monochromatic beam of wavelength 1.608 and exposure time of 300 sec, and a sample-detector distance of 728.32 mm for values of scattering vector $0.02<q<0.355$ $^{-1}$. Pure PU shows in the SAXS curve the typical shoulder at about 0.1 $^{-1}$ due to the hard segments/soft segments segregation and the interdomain spacing. Samples with BHT display a decrease on the intensity of this shoulder probably due to the BHT molecules break the segments interaction, leading therefore to a good incorporation of additive. The remaining SAXS curve does not show any change. In the other hand SAXS spectra of films with α-tocopherol do not show important differences respect to pure PU, probably because of the bigger size of the α-tocopherol molecule compared with BHT. In this case, the microrange of heterogeneity in the PU matrix is not affected and phase segregation is expected. On the contrary, SAXS spectra of films doped with EDTA or PS show an important change at a q value around 0.08 $^{-1}$, increasing scattering intensity with increasing the additive content in the film. Unlike BHT, EDTA and SA are ionic compounds and specific ionic interactions, preferentially with the urethane groups, are expected changing the size of aggregates.

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Estudio comparativo de la cristalinidad y composición química de la hidroxiapatita de huesos humanos, en pacientes con osteoporosis en todos los estadíos de la enfermedad, respecto al hueso sano

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Este trabajo consistió en el análisis de huesos humanos extraídos de pacientes con osteoporosis y osteoartritis y que debido a la fragilidad de sus huesos, por las mismas enfermedades, han sufrido fracturas en cadera, muñeca, espina u otra parte del esqueleto. Casi no existen estudios cristalográficos de las hidroxiapatitas (HA) de huesos humanos de pacientes con estas enfermedades. No se sabe que tipo de variaciones presentan los tejidos a nivel cristalográfico y como se produce esa fragilidad. Millones de personas sufren fracturas de hueso debido a esta enfermedad, por año en todo el mundo, lo que representa sumas ingentes de recursos médicos. Este proceso tiene un crecimiento alarmante y ha motivado a gobiernos y organizaciones como IBMS o NOS a promover su investigación. Los análisis de rayos X (línea XRD1 del LNLS) mostraron diferencias en el tamaño de las cristalitas y en las proporciones de los elementos (Ca y P. Relación Ca/P) y compuestos minerales (HA: $Ca_{10-x}(HPO_4)_x$ $(PO_4)_{6-x}$ $(OH)_{2-x}$; $0 \leq x \geq 2$, β-TCP: β-$Ca_3(PO4)_2$, TTCP: $Ca_4(PO_4)_2$ y CO^{2-}) presentes en los tejidos óseos estudiados. También se observaron variaciones en las formas y tamaños de las celdas. Para estas determinaciones se analizaron las distancias interplanares correspondientes a las familias de planos (002), (300) en HA y (0210) del β-TCP, principales componentes minerales de los huesos. Las caracterizaciones y las proporciones de cada componente mineral de los huesos se obtuvieron por refinamiento con el método de Rietveld en base a los datos de difracción de rayos X realizados en la línea del LNLS.

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Síntese e caracterização de óxidos com baixa expansão térmica

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Óxidos cerâmicos representados pela fórmula $A_2M_3O_{12}$, (A = metal de transição trivalente, M = Mo^{+6} ou W^{+6}) apresentam expansão térmica baixa ou negativa após a transição de fase da estrutura monoclínica à ortorrômbica. Estes materiais possuem grandes usos potenciais, por este motivo, no presente trabalho foram avaliadas a expansão térmica em três sistemas da família $A_2M_3O_{12}$ com o objetivo de produzir materiais de expansão térmica controlada, onde A são os cátions Al^{3+}, Cr^{3+} e Fe^{3+}. Os sistemas produzidos foram: $Cr_{2x}Fe_{2-2x}Mo_3O_{12}$, $Al_{2x}Cr_{2-2x}Mo_3O_{12}$ e $Al_{2x}Fe_{2-2x}Mo_3O_{12}$, sendo os valores de x = 0; 0,3; 0,5; 0,7 e 1. Além destes, o composto $HfMgMo_3O_{12}$ foi também sintetizado, onde A é o cátion divalente (Mg^{2+}) e o tetravalente (Hf^{4+}). Os coeficientes de expansão térmica intrínsecos foram determinados por difração de raios-X utilizando luz síncrotron, encontrando-se valores bem reduzidos para todos os sistemas estudados, a saber: para o $Al_2Mo_3O_{12}$, α_l = 2,32 x $10^{-6}/^oC$, para o $Cr_2Mo_3O_{12}$, α_l = 0,65 x $10^{-6}/^oC$, para o $Fe_2Mo_3O_{12}$, α_l = 1,72 x $10^{-6}/^oC$ e para $HfMgMo_3O_{12}$, α_l = 1,0x$10^{-6}/^oC$.

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Structural analysis of Co-doped lanthanum chromite by anomalous X-ray scattering

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Lanthanum chromite ($LaCrO_3$) is the most adequate material for use as interconnector in solid oxide fuel cell (SOFC) applications, due to its intrinsic properties, namely, its good electrical conductivity and resistance to environment conditions in fuel cell operations. $LaCrO_3$ presents a perovskite-type structure. At a temperature of approximately 260°C it undergoes a crystallographic transformation, from orthorhombic (Pnma) to rhombohedral (R-3c) structure. In the present contribution we report the results of the refinaments of the crystalline structures of cobalt-doped lanthanum chromite ($LaCr_{1-x}Co_xO_3$, $x = 0.10; 0.15; 0.20; 0.25; 0.30$), performed by means of the Rietveld method. The powders of cobalt-doped lanthanum chromite were obtained by combustion synthesis, using urea as fuel. The X-ray diffraction patterns were obtained using synchrotron radiation of energy equal to 5.85 keV, near the chromium K edge and at room temperature. For the Co-doped samples, except for $x = 0.25$ and 0.30, one observed a structure similar to the non doped $LaCrO_3$, namely, Pnma symmetry, with variations in the lattice parameters (a, b, c) and diminishing unit cell volumes. The samples with $x = 0.25$ and 0.30 presented both orthorhombic and rhombohedral structures, showing that cobalt additions over 25% produces the stabilization of rhombohedral lanthanum chromite at room temperature.

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Morfología de bordes de granos y microtextura cristalográfica de la aleación ERNiCrFe-7 modificada con adiciones de Ti, Nb y V.

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Se estudia la morfología de bordes de granos y la microtextura cristalográfica de la aleación ERNiCrFe-7 modificada con adiciones de Ti, Nb y V. Las muestras fueron caracterizadas mediante Microscopía Electrónica de Barrido y Difracción de Electrones Retrodifundidos. La distribución de misorientaciones entre granos resultó similar a una distribución aleatoria, si bien se observaron algunas desviaciones cerca de los valores de mínima y máxima misorientación. Los granos se orientaron con la dirección 100 cercana al gradiente de temperaturas establecido durante la solidificación. Las adiciones de Ti, Nb y V a la alreación ERNiCrFe-7 indujeron, por un lado, un incremento en la tortuosidad de los bordes de granos y en la misorientación local en el interior de los granos, y por otro lado, una pequeña variación en la distribución de misorientación entre granos, incrementando la fracción de bordes de bajo ángulo; pero no produjeron ninguna variación apreciable en la textura.

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Uso de XAS no estudo catalítico de cobaltato de lantânio substituído por cálcio

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O estudo de estruturas perovsquitas tem despertado o interesse da comunidade científica, porque tais sistemas apresentam propriedades elétricas, magnéticas, espectroscópicas e catalíticas que podem ser exploradas tecnologicamente para o desenvolvimento de vários dispositivos, entre os quais células a combustível, semicondutores, pigmentos e catalisadores. Um catalisador com estrutura perovsquita, que contém La no sítio A e Co no sítio B, fornece excelente atividade catalítica para oxidação. Tal atividade é posteriormente melhorada pela substituição de La no sítio A com íons que tem um estado de valência diferente. Neste trabalho foram sintetizadas cobaltitas de lantânio com estrutura perovsquita, onde o cálcio e bário substituíram parcialmente os sítios do La^{3+}. Os óxidos foram sintetizados via método combustão com uréia, e caracterizados por DRX, FTIR, TG, BET e espectroscopia XANES na borda do cobalto. Os espectros das amostras dopadas com bário apresentam muita similaridade com a amostra não dopada. No entanto, diferenças importantes são observadas nas amostras dopadas com Cálcio, nas quais se observa um salto da borda na região de maior densidade dos estados 2p. Esta observação pode ser atribuída a maior ocupação destes estados. Os espectros obtidos a várias temperaturas indicam que para a amostra dopada com Cálcio, existe uma sutil diminuição na amplitude do pico A quando a temperatura diminui abaixo da Tc, sem energia de deslocamento observada. A posição e a intensidade do pico B não foram sensíveis as variações de temperatura dentro da relação sinal:ruído. Argumentos de simetria e estrutura da banda sugerem que A e B parecem emergir do acoplamento entre estado 4p e 3d do Cobalto, especificamente A corresponderia ás transições dentro de estados eg de spin maiores e B está relacionado com estados eg e t2g menores. Por outro lado, pode ser observado que a magnitude da transferência massa espectral é menor para o composto dopado com Bário, quando comparados com composto dopado com Cálcio. Pode-se associar esta transferência reduzida com a menor quantidade de distorções locais induzidas pelo dopante Bário.

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Mapeamento de tensões residuais em discos de freios automotivos por difração de raios X

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Os freios estão entre os dispositivos mais importantes na segurança de veículos automotivos. O disco de freio que é uma das peças mais solicitadas em termos de resistência mecânica e ciclagem térmica, é normalmente confeccionado em ferro fundido cinzento classe FC-200 em razão do custo, usinabilidade e condutividade térmica. A indústria vem desenvolvendo novas materiais visando aumentar a segurança do componente, reduzir ruído e peso e melhorar o seu desempenho. Adições de elementos de liga podem conferir propriedades específicas a estes ferros fundidos, como com adições de Nb e Ti para o aumento da resistência ao desgaste e adições de Mo para o aumento da resistência a quente e resistência à fadiga térmica. Atualmente estão sendo estudados os seguintes tipos de ferro fundidos cinzentos e sua aplicação em discos de freio: FC 250, FC 250 ligado com Ti, FC 250 ligado com Mo, FC 150 HC e FC 150 HC ligado com Mo e ferro fundido vermicular. Para a sua produção a peça passa por processos como fundição, forjamento, soldagem, flexão, laminação, torção, trefilação, usinagem, retífica etc. Como resultado são desenvolvidas tensões residuais que, combinadas às tensões aplicadas, podem dar inicio a trincas que levam à fratura do componente. Em outros casos as tensões residuais podem melhorar as propriedades. Por exemplo, tensões residuais de compressão podem tornar um material menos susceptível ao trincamento por fadiga. Entretanto, gradientes de tensões podem degradar as propriedades mecânicas, causar corrosão sob tensão, diminuir a vida útil, e mesmo causar uma falha severa. Para o mapeamento de gradientes de tensão numa superfície é necessária uma boa resolução espacial, que nem sempre é possível num equipamento convencional. Assim, a utilização da técnica de difração de radiação síncrotron permite aliar a alta intensidade do feixe à característica de feixe paralelo e de pequenas dimensões, o que possibilita o mapeamento de gradientes de tensões na superfície. O mapeamento de gradientes de tensão nestes discos de freio permite analisar a sua influência na fadiga da peça para, eventualmente, alterar parâmetros de sua fabricação visando maior segurança. Neste trabalho são apresentados resultados de mapeamento de tensões residuais em discos de freios desenvolvidos pela General Motors do Brasil, realizados na estação D10B XPD do LNLS.

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Estudo do tratamento térmico utilizado em supercondutores de Nb_3Sn com CAA de Cu(Sn) em escala nanométrica

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Grande parte das aplicações de fios supercondutores de Nb_3Sn são utilizados em magnetos supercondutores para gerar altos campos magnéticos, acima de 10 Tesla. Isso demanda a necessidade de se projetar supercondutores capazes de suportar altas densidades de corrente com resistividade nula, característica do estado supercondutor. Uma técnica que vêm se mostrando altamente eficiente na melhoria das propriedades de transporte é a introdução de centros de aprisionamento artificial (CAA) de fluxo magnético na matriz supercondutora, numa tentativa de unir, ou misturar, os tipos de aprisionamento já encontrados nesses materiais. Contudo, foi projetado e fabricado um supercondutor de Nb_3Sn com CAA de Cu(Sn), em escala nanométrica, produzido pelo método da difusão-sólido líquido que consiste de um fio multifilamentar, com 1,0 mm de diâmetro, contendo 1.451.610 filamentos de Nb com diâmetro médio de 410 nm, 36 elementos de Sn, Cu estabilizador interno e uma barreira de difusão de Ta, e CAA com diâmetro médio 20 nm. O tratamento térmico usado comercialmente já não pode mais ser aplicado, devido às dimensões nanométricas, e novos perfis de tratamentos devem ser analisados de tal maneira que permitam a difusão, reação e formação da fase supercondutora de Nb_3Sn. O objetivo desse trabalho é analisar os diferentes perfis de tratamentos térmicos, de modo que se obtenha os melhores parâmetros supercondutores possíveis. Para isso foi feito um estudo dos diferentes perfis de tratamentos térmicos utilizando-se microscopia eletrônica de varredura convencional com detector de sinais retro-espalhados com auxilio de um espectroscópio de energia dispersiva, para determinação das fases formadas e suas respectivas composições. Ainda, devido as pequenas dimensões, foi utilizado o microscópio eletrônico de varredura com canhão de elétrons de Field Emission Gun do Laboratório de Microscopia Eletrônica do LNLS, para poder caracterizar os filamentos de Nb e os centros de aprisionamento artificial de Cu(Sn). E para complementar o estudo foi feita análises supercondutoras para determinação dos parâmetros supercondutores críticos e das características de transporte das amostras em todas as etapa de tratamento térmico.

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STUDY OF ANNEALED TiO$_x$ FILMS FOR MOS CAPACITORS

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Dielectric layers (SiO_2 and SiO_xN_y), in CMOS applications, is presently reaching its limiting value, so nowadays much research is directed to the substitution of these films by high k materials making possible the use of thicker films. Among the materials HfO_2 is one of the more promising, mainly because it is more stable, thermodynamically, on Si than other high-k materials and its dielectric constant is reasonably high (25). However this film presents a high oxygen diffusion rate, which results in a low-k interfacial layer growth, a low crystallization temperature (500oC), which generates grain boundaries which acts as oxygen diffusion and leakage current path, resulting in high leakage current. Other problem is that this films present a poor interface quality with Si, in this way a high k/SiO_2 stack is need, resulting in a much better interface but also in the reduction of the dielectric constant. Several works report nitrogen incorporation in HfO_2 (HfO_xN_y), physical and electrical results show that it leads to better interface properties, suppressing impurity penetration and improving reliability, since it is a thermodynamically stable material, however k is reduced to values close to 13. In this way, the study of other metal oxides, with dielectric constant higher than 25, is very interesting, however, up to this moment, the Internacional Technology Rodmap Semiconductor does not have an adequate material for MOS gate dielectric. TiO_2 presents two important phases, Anatase and Rutile. The last one is the thermally stable phase that presents the higher dielectric constant (higher than 80). With this, in this work these films obtained with different deposition conditions and annealed were studied. With this in this work a study of titanium dioxide (TiO_x) is presented. Titanium oxide films (TiO_x) deposited with different O_2 parcial pressure (30,35 and 40 %) and annealed at 550, 750 and 1000oC were deposited and characterized. RBS, FTIR and O-K and Ti-K Edge XANES and Elipsometry measurements were performed to characterize these films. The films dielectric constant were obtained by C-V measurements. The FTIR and O-K and Ti-K Xanes measurements shown that films deposited with 35 and 40 % are crystallizing in anatase phase while obtained with 30 % apparently in Ti_2O_3 + rutile phase. The film dielectric constant obtained is varying of 40 to 170.

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HRTEM Characterization of Phase Separation in Ti-35Nb-7Zr-5Ta Alloy.

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The class of β titanium alloys is highly attractive metallic material for biomedical applications due to their high specific strength, high corrosion resistance and excellent biocompatibility, including low elastic modulus. The mechanical properties of Ti alloys can be tailored adjusted through compositional variations, thermomechanical processing, and microstructural control. This work aims to clarify the hardening mechanism on these β-Ti alloys through phase separation. Ingots weighting 50 g of Ti-35Nb-7Zr-5Ta (wt%) alloy were arc-furnace melted in argon atmosphere as presented elsewhere. TEM samples were prepared using ion milling PIPS equipment and the analyses were performed at 300 kV using a Jeol JEM3010-URP. TEM bright field (BF) micrographs of Ti-35Nb-7Zr-5Ta alloy water quenched and annealed at 400°C for 4 h, reveals contrast between β and β phases. β-Ti and Nb phases have both bcc structure with very similar lattice parameters leading to practically identical XRD and TEM-SAD patterns. It can be seen a heterogeneous microstructure alternating dark and bright regions 10 nm size. HRTEM image and respective Fourier space map of this regions at the [111] β zone axis reveals the splitting of (110) reflections, which suggests the coexistence of two phases (β and β) with orientation relationship, the same bcc crystal structure and slightly different lattice parameters. XEDS nanoanalysis with 5 nm probe revealed Nb enrichment (β phase) of the dark regions and Ta-Zr enrichment (β phase) of the bright regions, indicating the occurrence of phase separation phenomenon. It is reasonable that composition fluctuations of heavy elements as Ta and Zr induce lattice parameter distortions and, consequently, the splitting of peaks in the Fourier space. The small difference in lattice parameter and HRTEM image evidences the presence of a coherent interface between both phases and explains the hardening mechanism of Ti35Nb7Zr5Ta alloy. Thus, during suitable annealing conditions, Ti35Nb7Zr5Ta alloy undergoes coherent spinodal decomposition of β phase into two solid solution phases with different compositions and elastic strain associated to the domains of Nb-rich β and Ta-Zr-rich β phases.

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Microstructural Evolution Characterization During Friction Stir Welding of High Strength API5L GRADE X65 Steel

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The goal of this work was to investigate the microstructural evolution in FSW API5L grade X65 steel, commonly used for pipe line in oil and gas industry. The microstructural characterization was carried out in optical and scanning electron microscopy and micro-hardness profiles were used for this chacaterization. The macroscopically distinct regions that include the base metal BM, the stir zone SZ, and the heat affect zone HAZ with their corresponding low magnification optical image microstructure. The base metal refined microstructure is composed of poligonal ferrite and a small fraction of perlite colonies. Thermo- mechanically affected zone usually observed on aluminum, is not evident at all in this steel because the SZ, the TMAZ, and part of the HAZ were heated to above the ferrite-to- austenite (A1) transformation temperature. But banded structure was observed on the lower part of the joint, with a microstructure composed of recristalized ferrite grains with rich nucleus carbides due temperature reach in this zone and the perlite deformation respectively. The stir zone exhibited microstructure consisting of ferrites products (polygonal, acicular and widmanstatten).In order to examine the property variation across the weld micro-hardness, measurements with a 300-gram load were taken across the width of the upper , central and lower zone of the joint and can be seen that the weld metals properties are matching the base metals. In addition, there could be evidenced a planar defect in SZ , which is evidence of the recent development of the process for this kinds of materials .There is no doubt that this kind of defect is harmful for the joint, but it can be eliminated by proper choice of tool design and process parameters .

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Influence of process parameters on Hydro-pillar friction welding of C-Mn steels.

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Friction Hydro-pillar welding (FHPP) is a promising solid state welding process developed by TWI in the nineties, which is becoming successfully applied in underwater repair operations in petrochemical and oil industries. Recent works about this process on C-Mn steels has showed the ability to produce undamaged and sound joints. This work evaluated the influence of preheat temperature (PT) and axial force (AF) on size and mechanical properties of the thermomechanically affected zone (TMAZ) of C-Mn steel FHHP welding joints. The characterization of TMAZ was made through light and electron microscopy, microhardness, and a simulation of equilibrium conditions and CCT diagrams using the CALPHAD method and Ac3 software, respectively. The results showed that TMAZ size is larger insofar as axial force is smaller, but these last kinds of joints are more susceptible of defects. As AF values rise, the cooling rates also raises in the TMAZ because of smaller process time evolved; consequently the microhardness obtained in this condition is bigger. The cooling rate severity expects in the different conditions was reduces due to application of preheat; consequently the microhardness of the TMAZ in these specimens were lower.

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Effect of process parameters in SiO_2-GeO_2 glasses structure, synthesized by flame aerosol technique

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Silica-germania glasses are very important components for photonics devices, being widely used in optical fibers and applications related to non-linearity effects. However, the process condiction to obtain the samples can induce structure defects, where these defects are associated to the second-order optical non-linearity in SiO_2-GeO_2 glasses. The silica-germania glass structure is a very important parameter to control the glass properties, such as viscosity, crystallization, stress, density and refractive index. The vapor-phase axial deposition method (VAD) is a flame aerosol technique largely used to produce silica-germania glass preforms in which it is possible to control the processing conditions through the gases flows, carrier gases and burner position. Fine particles of silica-germania glasses were synthesized by hydrolysis and oxidation of $SiCl_4$ and $GeCl_4$ in H_2/O_2 flame, to form the porous perform. After thermal-treatment (consolidation process), consolidated and transparent performs can be obtained. In the present research we have used the X-ray Absorption Fine Structure analysis (XAFS) near the Ge K absorption edge to study local parameters of the material structure. Silica-germania porous preforms were prepared with H_2/O_2 ratio in the range 0.65 to 1.0. Afterwards, they were consolidated in an electric furnace with He atmosphere at 1400 °C for 2 h, producing consolidated preforms. These preforms were sliced and powdered for characterizations. The GeO_2 concentrations were determined by X-ray Fluorescence Spectroscopy, RIX2100, Rigaku Co. The spectra were recorded at Ge K-edge in transmission mode at room temperature using synchrotron radiation from XAS D04B beamline equipped with a Si (111) monochromator. The data analysis was performed with the Athena and Artemis software. The estimated values of coordination numbers (CN) were in the range 4.71 to 4.85 ± 0.30 and the Ge-O bond distance were 1.72 to 1.73 ± 0.02 . In the samples deposited at same H_2/O_2 ratio, the DW factor increased when incleasing the GeO_2 concentration (6.9 to 15.7 wt. %). For samples with same concentrations, it was observed a decrease in the DW factor when increasing the H_2/O_2 ratio. The EXAFS results showed that the GeO distances and coordination numbers are kept constant, indicating that the GeO_2 polymorph has a quartz-like structure.

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The Influence of process parameters on thermomecanically affected zone microstructure in Hydro-pillar friction welding of C-Mn steels

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Friction Hydro-pillar welding (FHPP) is a promising solid state joining process developed by TWI in the nineties, which is becoming successfully applied in underwater repair operations in the petrochemical and oil industries. Recent work on C-Mn steels FHPP has proven the capability to produce sound joints. This work evaluated the influence of preheat temperature (PT) and axial force (AF) in the size and mechanical properties of the thermomechanically affected zone (TMAZ) of C-Mn steel FHHP welding joints. The TMAZ characterization of was performed through light and electron microscopy, microhardness, and thermodynamics and kinetics modeling. Simulation of equilibrium conditions and CCT diagrams was done using the CALPHAD method and Ac3 software, respectively. The results showed that TMAZ size gets smaller with the increase of axial force. However, joints produced with high axial forces are more susceptible to defect formation. The TMAZ cooling rate increases with axial force due to the consequent shorter process time. Therefore, the microhardness obtained with larger AF is higher. The cooling rate was reduced for all the conditions when preheat was applied; consequently under these conditions the TMAZ microhardness was reduced.

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Effect of freezing-thawing and chemical crosslinking on the structure of poly (vinyl alcohol) films

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Poly (vinyl alcohol) (PVA) is a hydrophilic, hemo and biocompatible polymer which has been used in many biological and pharmaceutical applications due to its non-toxic properties. A useful method for preparing PVA consists of cooling the films to -20 ^{o}C and thawing them back to room temperature several times in a process described as freezing-thawing (F/T) cycles. This process leads to the formation of thermoreversible (physical) gels stabilized by weak bonds. Physical hydrogels can be used as vehicles to drug delivery, with the advantage of preventing the elution of impurities associated with traditional chemical cross-linking processes. Moreover, it can be used as an interpenetrated network (IPN) to improve the mechanical properties of fragile crosslinked hydrogels as PNIPAAm/PAAc (Poly (N-Isopropylacrylamide)/ Poly (Acrylic Acid)). Despite of the wide use of freezing/thawing of PVA in biomedical and technological application, studies on the effect of F/T cycles on its structure are still lacking. In this work, SAXS was used in order to improve the understanding of the microstructural modifications obtained in these treatments. The SAXS profiles showed that the scattering profile of the PVA film not submitted to F/T cycles is quite different from those of PVA films submitted to 1, 3 and 5 F/T cycles. The broad peak observed in the former at maximum q = 0.025 $^{-1}$, corresponds to an average distance between the scattering crystallites of 25.1 nm. This value is in accordance with previous works. However, for the films submitted to 1, 3 and 5 cycles the correlation peak was lost. This result is in accordance with the model of gelation of PVA already described in other works, where the growing ice crystals formed during cooling expel the amorphous polymer segments to the concentrated surrounding solution, allowing the formation of more extensive intra and inter-molecular hydrogen bonds and leading to an increase in the distance between crystallites. Micrographies obtained by SEM (Scanning Electron Microscopy) also support this interpretation, as the films tend to have interconnected porous, becoming less dense with the increase in the number of F/T cycles. In the IPN PVA/PNIPAAm/PAAc hydrogel, the correlation peak in the SAXS patterns was not observed. It indicates that the presence of chemical crosslinking decreases the formation of physical crossliking. However, TMA (Thermal Mechanical Analysis) measurements showed better mechanical properties for matrix with PVA not submitted to cycles and submitted to 1 F/T cycle.

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Parte VIII

Métodos e Instrumentação

Focusing synchrotron radiation with home-made polycapillary x-ray optics

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Polycapillary optics has emerged in the last twenty years as a powerful tool for collimating and focusing x-rays[1]. It can provide small, high intensity, focused x-ray spots. The possibilities of performing non-destructive elemental microanalysis with synchrotron radiation by means of home-made polycapillary optics are described. We manufactured three monolithic polycapillary half-lenses using fiber glass technology, which consists of drawing of package of glass capillaries at high temperature in a heating furnace. The polycapillaries were constructed using borosilicate glass. The section of each channel was circular for the three lenses with a input diameter in the range of 0.04 0.12 mm. The hollow volume of the lenses was in the order of 20%. The performance of polycapillary half-lenses with different geometries was evaluated at the D09B-XRF fluorescence beamline of the Brazilian Synchrotron Light National Laboratory (LNLS)[2]. A gold knife edge scanned at the output of the lenses was used to determine the spot size at different distances. Measurements of photon flux impinging on the entrance end of the lenses and photon flux leaving the lenses were used to obtain the transmission efficiency. The lens with the best performance had a focal distance of 76μm and a transmission efficiency of 5%, which represented a gain factor of 22.

Using the manufactured polycapillary half-lens with the best performance, we carried out a micro-XRF experiment. The overall efficiency of the system was studied by means of the determination of the detection limits for several elements in an organic sample. For Fe, Cu, Zn and As, detection limits in the order of ppm were obtained.

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Diffusion Studies by X-Ray Microfluorescence Induced by Synchrotron Radiation

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The theoretical and experimental investigation of the transport of molecules and ions in solution through dispersed systems of different nature has recently acquired special meanings. This is to the fact that this knowledge is used in a great variety of technologies applied to different areas of engineering: emulsion preparation, gel permeation chromatography, operations of separation and filtration, enhanced oil recovery, medicinal and cosmetic products, etc. Models of diffusion in soft polymeric systems include considerations as much for solutions as also for porous media, since these systems include from cuasi-homogenous dispersions, in which the number, the position and the size of pores are fluctuating, to porous heterogeneous rigid structures. For a much smaller solute that the polymer macromolecules that spreads in a dispersion of this type, the solute-solvent system can be treated like a continuous one in which the macromolecules are suspended. Besides the hydrodynamic interactions, specific other ones between particles of the solute, solvent and polymer exist. The classic techniques of detection for these systems are complex and laborious with very high detection limits, low sensitivity and, in addition, a considerable amount of analyzed sample is required. This has been an impediment to realize fast and precise experiences of diffusion in both, static and dynamic conditions. X-Ray Microfluorescence is a spectrometric technique with high resolution properties that allows studying dynamic systems that could made adaptable for these systems. In this work, results obtained from measurements realised in the National Laboratory of Light Synchrotron, Campinas, Brazil, are shown. This work was done in order to optimize instrumental and practical parameters to make possible subsequent transport properties studies in these systems for varied applications.

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The new soft x-ray scattering and dichroism chamber for magnetic studies at LNLS

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We report on the design and construction of a new diffractometer for soft x-ray resonant scattering and magnetic circular dichroism at LNLS. A high vacuum-compatible diffractometer (1x10-8 Torr) comprises a pseudo 4-circle goniometer which works in vertical scattering geometry connected to a home-made magnet. Rotation of the detector and sample is realized by a 2-circle HUBER diffractometer with two +/- 15 degrees arcs for Chi and Phi movements. The sample environment consists of a closed-cycle He cryostat that allows cooling down to 80 K (so far) and applying a magnetic field of 0.5 kOe.

All functions of the experimental setup have been extensively tested at beamline SGM of LNLS. Initial mesurements on a film of Fe/MnAs/GaAs will be presented. The experimental results demonstrate the performance of the instrument. The instrument will now be available for external users.

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DEVELOPMENT OF A GREAT AREA X-RAY DETECTOR BASED ON SET OF SMALL PROPORTIONAL COUNTER WITH NEEDLE ANODES AND THEIR POTENTIAL APPLICATIONS IN SYNCHROTRON RADIATION

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The high intensity of a beam synchrotron and the increase of this one, bring with himself the necessity to count on fast and more and more able detectors to respond to high rates count maintaining certain degree of energy resolution. The gas proportional counter with needle anode offer interesting applications in the ray-x detection its potential applications mainly due to its geometric versatility, easy operation and low cost, all characteristics very convenient for applied in X-ray detection. High rates of count are obtained with this unit with a resolution in energy near 20 %, for 5.9 keV which makes analysis XRFSR in dedicated applications feasible that they do not require of great resolution, in which it is tried to know one or more specific elements at level of trace elements. Its high answer in count would allow to applications with light synchrotron or intense beams being avoided the saturations that happen with the detectors of solid state. This work presents a robust and compact X-ray detector with spherical geometry formed by a set of small cylindrical proportional counter unit with needles anodes. Theses units are located in the surface of a hemispherical support, the sample has to analyze is put in center of the hemisphere base; the radiation can enter by one of its flanks or the top of the hemisphere. Each proportional counter is a small aluminum cylinder that has a central anode formed by a steel needle to sew, this one is selected microscopically and whose end has hemispheric form with a diameter of approximately 80 μm. The set of detectors can measure to practically all the radiation emitted by the sample in 2π solid angle where each one of them is to the same distance of this one, improving well-known the geometric efficiency without lost of resolution in energy. The units can work in independent or parallel mode, when doing it in parallel integrate the rates of count by an factor equal to the number of units, which implies a remarkable increase of the count rate. Preliminary results that are in this work they report great versatility and capacity of this detector, it makes recommendable for applications with synchrotron light.

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Caracterização de um monocromador 4-Cristais de Si 551 na linha XRD2 do LNLS

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Aqui é reportado os resultados da instalação de um monocromador a quatro cristais (4C) utilizando a reflexão 551 do silício, na estação XRD2 do LNLS, operando em 13,7 keV. O feixe branco foi pré-condicionado através de um espelho (ajustado com o foco no infinito) e um monocromador duplo cristal (DC) Si 111, sendo o segundo cristal com focalização sagital, cujo o foco foi ajustado para a posição da amostra no centro do difratômetro 6-círculos. Após o monocromador DC a linha conta ainda com uma câmara de ionização que monitora a intensidade do feixe após o DC. Dois conjuntos de atenuadores e um conjunto de fendas limitam o tamanho do feixe, que incide no primeiro cristal do 4C. O 4C foi montado em um difratômetro duplo eixo adaptado na linha. O 4C é composto por um par de cristais monoliticos do tipo "channel cut"e cada um montado em um dos eixos do difratômetro. Estes cristais foram projetados para operar em energias entre 8,9 keV e 15 keV. Na saída do 4C foi instalado uma fenda para limitar a dimensão vertical do feixe e, em seguida, um espalhador de kapton e um detector cintilador a 90 graus para monitorar a intensidade do feixe fornecido pelo 4C. Foi obtido um tamanho máximo de feixe na vertical de 0,7 mm, tamanho este que foi limitado pela divergência passante permitida pelo 4C. Ajustando a fenda horizontal para 2,0 mm (dimensão horizontal do feixe incidente no primeiro sulcado), obteve-se intensidade de saída do 4C na ordem de 300.000 contagens por segundo. Analisando-se o feixe de saída do 4C através de um cristal de Si 333, obteve-se uma largura a meia altura (FWHM) da ordem de 2 segundos de arco, resultado semelhante obtido utilizando-se um analisador de Si 400. Também observou-se que o 4C limita a divergência horizontal, logo a focalização sagital torna-se irrelevante para esse tipo de montagem. Observou-se que o feixe que sai do 4C é não homogêneo na horizontal. Isto foi atribuído ao cristal sagital, que por construção, opera tensionado. Durante as medidas foi possível observar pequenas variações de intensidade na saída do 4C (picos na ordem de 10 por cento) que foi atribuído a correções da órbita do feixe de elétrons.

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Comparison between XRFCT images with and without absorption corrections

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The transmission microtomography (CT) and X-ray fluorescence microtomography (XRFCT) is complementary and noninvasive techniques used for sample characterization. The CT provide information on the attenuation coefficients, while the XRFCT can provide the distribution of all elements into a sample. XRFCT is a noninvasive technique, based on the detection of X-ray fluorescence emitted by the elements in the sample, and it is used to complement other techniques for sample characterization. The main of this work is to determine the elemental distribution map in reference samples and breast and prostate tissue samples in order to verify the concentration of some elements correlated with characteristics and pathology of each tissue observed by the transmission CT. The experiments were performed at the X-Ray Fluorescence beamline (D09B-XRF) of the Brazilian Synchrotron Light Source (LNLS), Campinas, Brazil. A quasi-monochromatic beam produced by a multilayer monochromator was used as an incident beam. 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. The CT images were reconstructed using a filtered-back projection algorithm and the XRFCT were reconstructed using a filtered-back projection algorithm with and without absorption corrections.

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A new design for the LNLS soft X-ray spectroscopy beamline (SXS)

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The soft X-ray spectroscopy beamline - SXS is operational for users since 1997 and have been used by a broad scientific community such as material science, surface science, atomic physics, chemistry and astrophysics among others. Due an increasing demand from the users, this beamline will have a new X-ray optics in order to provide photons in the energy range from 1000 eV up to 6000 eV. The beamline optics will change to incorporate a new toroidal focusing mirror and a new UHV double crystal monochromator (DCM) with crystal cooling. The project is being supported by a Multi-user FINEP grant and the beamline refurbishing should occur during the second semester of 2008. The new mirror (1010 x 100 x 100 mm) will be installed at 7.0m from the source, half-way between the source and the sample position, the incidence angle was fixed at 0.6^o, and the toroidal shape was chosen in order to focus in both horizontal and vertical directions. Simulations using Shadow program give a spot size of about 3 x 1 mm^2 at the sample position when slits are fully opened. Nickel coating will permit to increase the operational energy range from currently 1.8 up to 3 KeV to 1 up to 6 KeV with a transmission superior than 80 % and free of absorption edges. The new UHV DCM will have four pairs of crystals: Si (111), InSb (111), YB66 (400) and beryl (10-10), which can be selected by an internal translation movement. The first crystals will be water-cooled considering the ring current and thus the thermal load, which should significantly improve the stability and repeatability during measurements. Together those main changes, other improvements will be installed such as new photon beam positioning monitors (PBPMs), differential pumping to reach UHV (10^{-10} mbar) regime at the experimental workstations, etc. In this presentation we show a detailed description of the new design for the SXS beamline as well as some aspects of the technical challenges and scientific opportunities in X-ray spectroscopy expected with the new beamline and their associated experimental workstations.

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Micro-Sistema de Análise Multi-Canal com Eletrodo Único para Detecção Eletroquímica Integrada

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A disciplina da Microfluídica se propõe a substituir dispositivos hidro-pneumáticos convencionais por seus homólogos em miniatura, que proporcionam vantagens como as reduções do tempo de análise, dos gastos com reagentes e das quantidades de resíduos. Além disso, a portabilidade dos micro-dispositivos implica na possibilidade de utilização de técnicas analíticas em campo, o que aumenta ainda mais a sua abrangência e importância. Com efeito, existe na literatura um bom número de trabalhos demonstrando que a eficiência de dispositivos microfluídicos, aplicados a problemas de cunho tanto industrial quanto acadêmico, podem superar aquelas atingidas por seus correlatos macroscópicos, além de viabilizar tarefas impossíveis para os sistemas convencionais. Dentre os campos de aplicação promissores, destacam-se as áreas de pesquisa genética, processos farmacêuticos e em química analítica, onde a utilização de dispositivos microfluídicos acabou por criar o conceito de Micro- Sistemas de Análise Química Total (m-TAS, da sigla em inglês).

Esse trabalho reporta nossos avanços no processo de fabricação de um dispositivo microfluídico multi-canal com eletrodos integrados para detecção eletroquímica. Técnicas de litografia suave, lift off e selagem por ativação superficial via plasma de O2 foram empregadas para prototipagem rápida de microchips Poli(dimetilsiloxano)-vidro de baixo custo e descartáveis. As geometrias dos dispositivos foram projetadas para permitir procedimentos rápidos de calibração e resultados de confiança pra aplicações em campo. Exercendo uma influência grande sobre o rendimento do dispositivo, o processo de selagem foi otimizado com a deposição de filmes-finos auxiliares de TiSiO2. O desempenho do sistema foi verificado por análises amperométricas em soluções padrão de N-acetil-p-aminofenol, através das quais avaliou-se a influência exercida pelos métodos de fabricação na reprodutibilidade e confiabilidade do dispositivo.

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Desenvolvimento de um sistema para medidas de XMCD e SMOKE com altos campos magnéticos e em ambiente de ultra-alto vácuo (UHV)

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Dicroísmo circular magnético com absorção de raio-X (XMCD) e efeito Kerr magneto-ótico de superfície (SMOKE) são técnicas poderosas para investigar as propriedades magnéticas dos materiais. XMCD destaca-se por ser elemento específico e permitir separar as contribuições ao sinal magnético de cada elemento presente na amostra, bem como determinar o momento de spin e orbital em materiais ferromagnéticos e antiferromagnéticos. Esta técnica é particularmente indicada no estudo de filmes ultrafinos e sistemas nano-estruturados. A obtenção destas informações em alguns sistemas, exigem condições experimentais muito específicas como UHV, baixas temperaturas e altos campos magnéticos. A detecção do sinal XMCD pode ser feita de duas maneiras: transmissão ou rendimento total de elétrons (Total Electron Yield - TEY). Medidas de magnetização podem ser feitas in-situ através do sinal de XMCD ou utilizando SMOKE polar (campo magnético é perpendicular a amostra). Em XMCD o feixe de luz incidente na amostra possui polarizaçã circular e sua direção de propagação é paralela ao campo magnético aplicado. Desenvolvemos no LNLS uma câmara de ultra-alto vácuo onde é possível expor as amostras a campos magnéticos que podem ser variados (no momento até 1.5 T). Este sistema é composto de um eletroimã com bobinas refrigeradas e peças polares cônicas que produzem um campo uniforme numa região de 40 mm de diâmetro com distância interpolar de 26 mm. As peças polares são furadas para permitir a entrada da radiação síncrotron na câmara de UHV que fica alojada entre as mesmas.O sistema permite transferência de amostras para um manipulador que acomoda múltiplas amostras e tem possibilidade de refrigeração até 120K com LN2 ou 20K com um criostato de circuito fechado de He. Neste trabalho descreveremos esta nova facilidade instalada no LNLS, bem como apresentaremos alguns resultados obtidos nas linhas SXS e SGM com amostras padrões (Co, Fe e Ni) e nanopartículas de CoPd e NiPd encapsuladas com nanotubos. Telling et al. Rev. Sci. Instrum. Vol. 77, 073903 (2006). C.T. Chen et al, Phys. Rev. Lett,Vol. 75, 152 (1995).

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Residual stress analyses using synchrotron radiation

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It is well know that residual stress in crystalline solid materials can be measured non-destructively using x-ray diffraction [1]. The application of such a technique to the characterization of deformations of the atomic structure of metals and of the residual stress was done for the first time in 1925 in the United States. Since then, the analysis of the mechanical behavior of metals using the x-ray diffraction technique was limited due to the utilization of conventional x-ray sources. There, the measurement process requires a lot of time and the limited resolution of such sources does not allow a very detailed analysis. With the advent of synchrotron light sources this technique became more powerful and many interesting metallurgical problems could be solved with the use of an extremely intense and highly collimated monochromatic x-ray beam. The XRD1 beamline of the LNLS has some favorable conditions for the development of the residual stress measurement technique, namely, high photon flux, a 3-circle diffractometer and a relatively broad working range of energies going from 5 keV to 15 keV. In this work it is shown the results obtained in measuring the residual stress of metallic pieces in this beamline [2]. Two experiments are reported here: the mapping of the residual stress of the surface of a metallic part utilizing both a single channel detector and a position sensitive detector (PSD), and the stress analysis of materials submitted to a special treatment. In the first one, the focus is on the capabilities of the instrumentation and the evaluation of time performance by comparing measurements using different detectors. The second case shows a real application of the method to the analysis of the effects on the stress state of a nitrided steel sample that was submitted to noble gas bombardment a special technique that has been developed at Unicamp [3]. Such an analysis will provide extra information that will help understanding this novel steel treatment process.

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Present status of the X-ray powder diffraction (D10B-XPD) beamline

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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 low temperatures, a recently acquired cryostat allows measurement to be performed in temperatures down to 1.7 K. A new specially-built furnace, which has been operating since June 2007, was purchased to overcome problems with respect to the old home-made furnace. This furnace operates up to 1273 K and has a spinning system and a computer-controlled vertical positioning system. The thermocouple is in contact with the sample-holder, which guarantees a more reliable control of the temperature gradient. It operates both in air and vacuum and it is possible to pass a gas flow through it in order to perform catalyses experiments.

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Parte IX

Não se aplica

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

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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 inorgánicos presentes en muestras de pinturas rupestres procedentes del Abrigo El Trébol en San Carlos de Bariloche, Río Negro, Argentina. El conocimiento químico composicional de la fracción inorgánica 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.

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Metastable phase diagram of nanostructured ZrO_2-Sc_2O_3 solid solutions: influence of the crystallite size

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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 $P4_2/nmc$ 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. A metastable phase diagram for compositionally homogeneous ZrO_2-Sc_2O_3 solid solutions has been proposed by Yashima et al. (Solid State Ionics 86-88 (1996) 1131).

In this work, we have investigated the influence of the crystallite size on the metastable phase diagram of the ZrO_2-Sc_2O_3 system by high-temperature X-ray powder diffraction. These experiments were carried out at the D10B - XPD beamline of the LNLS, operated in the high-intensity (low-resolution) mode. The materials analyzed in this work were synthesized by a novel nitrate-lysine gel-combustion route and the crystallite size was controlled by changing the calcination temperature. The retention of the tetragonal forms and the cubic phase for materials and the transformation to the monoclinic and β phases for increasing crystallite size will be discussed.

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SIMULAÇÕES RIETVELD DE MEDIDAS DE DIFRAÇÃO ANÔMALA DE RAIOS X DE UMA LIGA NANOCRISTALINA $Ni_{25}Se_{75}$

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Este trabalho visa apresentar estudos de difração anômala de raios-x da liga binária de $Ni_{25}Se_{75}$ produzida por mechanical alloying. Para tal, a linha XRD1 do LNLS foi utilizada com energias de radiação incidente próxima e distante da borda K do Ni. A Difração anômala de raios-x ocorre quando a energia da radiação incidente no átomo é próxima à energia de uma de suas bordas de absorção, ocasionando mudança abrupta no poder dispersivo do mesmo. Tendo em vista que os aparelhos de difração de raios-x existentes nos laboratórios convencionais utilizam tubos de radiação com comprimentos de onda fixos, o Laboratório Nacional de Luz Síncroton torna-se extremamente importante por possibilitar medidas de difração de raios-x com diferentes comprimentos de onda, inclusive naqueles próximos à borda de absorção dos átomos de Ni, permitindo potencializar o estudo da liga $Ni_{25}Se_{75}$. Os padrões de difração de raios-x da liga $Ni_{25}Se_{75}$ obtidos na linha D12A do LNLS, dentro da Proposta de Pesquisa XRD1/4144, foram ajustados pelo método de Rietveld através do sistema de análise estrutural GSAS. Os resultados obtidos do ajuste pelo Método de Rietveld e as respectivas estratégias de refinamento usada no GSAS para os padrões de difração de raios-x da liga de $Ni_{25}Se_{75}$ serão apresentados com o intuito de levantar discussões com especialistas da área sobre estratégias de refinamento, tipos de funções utilizadas (funções perfis e funções background), combinações de várias medidas de difração de raios-x em um único ajuste, etc.

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Local order of the precursor gel for the synthesis of ZrO_2 based materials by gel-combustion routes.

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The aim of this work is to study the structure of the precursor gels for the synthesis of ZrO_2-based nanopowders by gel-combustion processes. In particular, we focus on precursors for the synthesis of ZrO_2-based materials exhibiting the metastable tetragonal phase, which is very important for several applications. In the proposed gel-combustion routes, these gels are the final step previous to the combustion reaction. The final powders obtained from the gel-combustion synthesis were previously characterized by XRD, and some samples, specially in lightly doped zirconias, show the presence of a small concentration of the stable monoclinic phase, which is not desirable for technological applications. Besides, the BET specific surface areas were determined, and important differences were found (ranging from 20 to 69 m^2/gr), depending mainly on the fuel used. For this study, different precursor gels varying selected parameters, such as final pH, fuel, ratio of Metal/fuel and composition were prepared. We studied the gels to evaluate the correlation between the gel structure and the final phase composition, carbon content, BET surface area and crystallite size of the samples. We used EXAFS to follow the local coordination of our samples around Zr and Y or Ce atoms and monitor if the local order presents a proto-tetragonal or monoclinic structure It was necessary to use Raman and/or IR spectroscopies, to determine if the Zr is coordinated by carboxy and/or nitro groups.

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Desenvolvimento de eletrólitos polimérico gel para aplicação em células solares de TiO_2/corante

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As células solares de TiO_2 sensibilizadas por corante, são constituídas por um filme nanoporoso de TiO_2 modificado por uma monocamada de corante fotosensibilizador, um eletrólito líquido no qual esta presente o par redox $I^-/I_3{}^-$, e um contra-eletrodo de platina. Células solares de TiO_2 /corante montadas com eletrólito líquido necessitam de uma vedação perfeita para impedir problemas de vazamento e evaporação do solvente, que afetam o tempo de vida do dispositivo. Visando eliminar estas limitações, uma abordagem promissora tem sido a substituição dos atuais eletrólitos líquidos, por eletrólitos polimérico gel. Neste trabalho, foi investigado um novo eletrólito polimérico gel baseado em poli (óxido de etileno-*co*-2-(2-metoxietoxi)etil glicidil éter), P(EO/EM), NaI, γ-butirolactona como plastificante e I_2, visando obter células solares com maior eficiência. A microscopia eletrônica de varredura realizada no filme de TiO_2 mostrou uma morfologia com estrutura similar a uma "esponja". Esta estrutura permite um aumento no espalhamento da radiação e uma maior penetração do eletrólito na estrutura do óxido. A maior eficiência do dispositivo (3,7%) foi obtida com a maior quantidade de γ-butirolactona no eletrólito (70% em massa) a 100 mW cm^2. Este resultado é decorrente do aumento da condutividade iônica do sistema (2 x 10^{-3} S cm^{-1}). Utilizando baixa intensidade de iluminação, 10 mW cm^2, a eficiência da célula solar alcançou valores de 5,5 % com a adição de 30% em massa de γ-butirolactona no eletrólito polimérico. Este fato é conseqüência de um favorecimento no transporte de massa entre os eletrodos do dispositivo, ocasionado pela diminuição da densidade de corrente gerada. A utilização dos eletrólitos poliméricos gel mostrou-se promissor para a aplicação em células solares de TiO_2/corante. Dependendo da intensidade de iluminação do ambiente, pode-se empregar mais ou menos plastificante no eletrólito, visando obter o máximo de rendimento do dispositivo.

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TcNEK: structural and functional studies of a new *Trypanosoma cruzi* protein kinase family.

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Trypanosoma cruzi is the causative agent of Chaga´s disease, an incapacitating illness that affects ∼18 million people from South and Central American countries. *T. cruzi* possesses a complex life cycle alternating from vertebrate to invertebrate hosts and presenting at least three morphologically distinct developmental forms where the trypomastigote is the infective form and, amastigote and epimastigote are proliferative forms found in mammalians and insects hosts, respectively. The knowledge of stage specific processes may be useful to develop strategies to block the progress of its life cycle. In this context, we have focused our study on the metacyclogenesis, a process in which the epimastigotes differentiate into metacyclic trypomastigotes in the posterior end of insect´s gut. A preliminary microarray analysis of mRNA levels differentially associated to polysomes during metacyclogenesis identified an mRNA encoding an uncharacterized protein with similarity to human NEK kinases, which belongs to a family of dual-specificity kinases structurally related to the mitosis regulatory protein NIMA from *Aspergillus nidulans*. A search for NIMA or NEK in the *T. cruzi* genome database (www.genedb.org) retrieved 30 genes encoding for proteins with molecular masses ranging from 47 to 163 kDa and pIs between 5.03 and 9.95. Although all of them contain a conserved Ser/Thr kinase catalytic domain (S/TK), no direct assignment of a specific NEK ortholog was possible due the high sequence similarity between the S/TK domains of these kinases. An analysis taking into account the different domains and motifs found in each TcNEK is in progress and the preliminary results revealed two domain combinations not seen in other organisms, S/TK plus CASH (carbohydrate binding) or PH (plekstrin homology) domains. Structure prediction analyses indicated a high content of intrinsically disordered regions in TcNEK kinases, therefore, only structurally defined domains were selected for cloning and expression. A total of 22 expression vectors from sixteen selected genes are being constructed using conventional and “gateway” cloning technologies. At present, three expression vectors were tested and the recombinant TcNEKs showed soluble expression in *E. coli* BL21(DE3) Arctic Express. Purification of these kinases is currently in progress.

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Eletrocatalisadores de Pt-Sn/C preparados por redução química de metais em solução para ânodos de células a combustível de etanol direto

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Célula a combustível de membrana trocadora de prótons (PEMFC) é um sistema alternativo promissor de conversão de energia e se destaca pela compatibilidade com o meio ambiente e eficiência em baixas temperaturas. Para este sistema o etanol é considerado um combustível atrativo devido a facilidade de produção e baixa toxicidade. Entretanto, para a oxidação total deste álcool a CO_2 é necessário desenvolver catalisadores capazes de romper a ligação C-C e oxidar os intermediários que ficam adsorvidos no catalisador. Neste sentido o material Pt-Sn tem mostrado resultados interessantes na eletrocatálise de etanol. Neste trabalho foram preparados eletrocatalisadores de Pt-Sn/C através da redução química de sais metálicos precursores (H_2PtCl_6 e $SnCl_2$) adicionados a uma solução de ácido fórmico contendo carbono Vulcan XC 72R. Uma porção do catalisador foi submetida ao tratamento térmico a 200^oC em atmosfera redutora de H_2. A caracterização física destes catalisadores foi feita por EDX, DRX, XAS e HRTEM. Os experimentos eletroquímicos, foram realizados em uma célula a combustível unitária alimenta com 3 atm de O_2 no cátodo e com 1 mL min^{-2} de solução 1 mol L^{-2} de etanol no ânodo, e foram levantadas curvas de densidade de corrente em função do potencial. A análise de EDX dos materiais Pt-Sn mostrou que as razões atômicas de Pt e Sn obtidas estão próximas às nominais. Os difratogramas de raios-X apresentam picos característicos da estrutura fcc da Pt e observou-se um deslocamento, para menores valores, destes picos com a adição de Sn, o que sugere uma substituição de Pt por Sn na rede cristalina da Pt. Com o tratamento térmico observou-se um maior deslocamento dos picos de difração indicando uma maior formação de uma solução sólida. O tamanho médio de cristalito foi calculado usando-se a equação de Scherrer. HRTEM mostrou que as partículas possuem um formato cuboctaedrico e estão distribuídas homogeneamente sobre o suporte de carbono. Desta forma pode-se concluir que o método de preparação empregado é eficiente para obter a composição desejada do material e produzir uma distribuição homogênea das partículas metálicas sobre o substrato de carbono. Os difratogramas de raios-X evidenciam a formação de uma liga Pt-Sn. Os experimentos eletroquímicos na célula a combustível indicaram que o catalisador Pt-Sn/C com um maior grau de liga apresenta um melhor desempenho para a oxidação de etanol.

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Deposição por camadas automontadas de filmes finos de nanopartículas de MnO_2 e sua caracterização eletroquímica em um líquido iônico

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Os óxidos de manganês apresentam-se como bons candidatos ao uso em cátodos de baterias de lítio devido ao seu baixo custo e ausência de impacto ambiental; no entanto, este material apresenta problemas relacionados à queda de capacidade ao longo dos ciclos de carga e descarga, devido a mudanças na sua estrutura causadas pelos sucessivos ciclos de inserção e deinserção de íons Li^+. O tamanho e a morfologia do material influenciam no seu desempenho eletroquímico; o uso de nanomateriais como material ativo nos eletrodos faz com que essas variações estruturais sejam minimizadas, uma vez que o caminho difusional do Li^+ é menor; além disso, a maior área superficial por massa de material confere ao dispositivo uma maior capacidade, uma vez que mais sítios estão disponíveis para intercalação. Nesse trabalho nanopartículas de MnO_2 foram preparadas e caracterizadas por HRTEM e DRX. Os resultados mostram que foram obtidas nanopartículas esféricas e relativamente amorfas de diâmetro entre 10 e 20nm. No entanto, não basta a obtenção de nanopartículas; é necessária a obtenção de um eletrodo nanoestruturado. Para isso foi utilizado o método de automontagem camada por camada. A deposição foi monitorada por MECQ, AFM e UV-vis, mostrando que o crescimento das camadas é linear, sendo possível determinar a massa e a espessura de cada bicamada (MnO_2/PDDA). O eletrodo obtido foi caracterizado por MEV, mostrando que este é nanoestruturado, ocorrendo pouca aglomeração das nanopartículas durante a deposição. Os resultados eletroquímicos mostram que a conectividade eletrônica entre as nanopartículas é mantida até a 12^a bicamada e que a compensação de carga pelos cátions (Li^+ e $BMMI^+$ - do líquido iônico) se dá em tempos mais longos; em tempos curtos a compensação se dá pelo ânion ($TFSI^-$ - do líquido iônico). O fato de o cátion do líquido iônico participar da compensação de carga prejudica o desempenho do dispositivo, uma vez que este é mais volumoso, participando apenas superficialmente, agindo como uma barreira à intercalação de Li^+.

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Progressive Non-linear Digital Image Correlation for Micro- and Nano-Strain Mapping

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Deformation maps at the micro and nano scale are very important for the comprehension of several phenomena related with materials fracture mechanics, chemical composition and even functional properties. In the specific case of mechanical properties, the failure phenomenon known as ductility dip cracking (DDC), which occurs at high temperatures in materials like Ni-base alloys and stainless steels, is being studied using deformation mapping at the micro-scale. This project aims to use quantitative deformation mapping with space resolution of 100nm to 10μm by processing images recorded at different stages of the fracture during an in-situ experiment performed in a scanning electron microscope (SEM) coupled with a high temperature tensile stage.

The most important algorithm for this image processing task is DIC (digital image correlation), which is an optimization method based on Newton-Rapson algorithm. In this project, several improvements have been done to the DIC algorithm. The optimization process is very dependent on the initial model, which can be obtained using cross-correlation or here proposed zero-order DIC and predictive methods. The images are divided in sub regions to facilitate the optimization. These sub-regions can have rectangular or polygonal shapes, as chosen by the user. A dilation morphological operation was implemented on each sub-region in order to assure the continuity of models. Finally, the most important improvement was the non-linear DIC, which allows the user to build n-order polynomial models. However, terms powered to negative and decimal numbers are also allowed, which may be helpful to obtain high performance deformation models for non-linear deformation processes.

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Parte X

Propriedades Estruturais, Eletrônicas e Magnéticas de Sólidos

Reordering phase transition in Co: The quantitative analysis of planar faulting avalanche

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The phase reordering transition with varying temperature from HCP to FCC in Cobalt is studied . By analyzing the peak profiles of the diffractiion pattern the pair correlation function (PCF) between the close packed layer is extracted. From the PCF the correlation length of the stacking sequence is obtained in the whole range of studied temperature, allowing to follow the disorder behavior during the phase transition. An avalanche type of disorder pileup is observed where disorder climbes slowly up to near the transition temperature region and then an abrupt fall on the correlation length occurs. The described behavior occurs for both the HCP and the FCC phase. In both high temperature and low temperature region none of the two phase disappear. The nature of the diosrder during phase transition is also followed by studying the "form factor"of the decaying term in the PCF. Again the nature of the disorder changes abruptly at the phase transition region. Initial disorder far way from the phase transition is random in nature, characterized by uncorrelated individual events. Correlation among the planar faulting starts to happen near the transition region but they do not lead to any intermediate polytype: disorder correlation length frustrates any polytype with longer periodicity than FCC and HCP. An arrested state results in both the HCP and FCC structure where an intrisinc amount of disorder density can not me annealed out.

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The influence of external pressure on the intrinsic term in Hg,Re-1223 superconductor

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XANES study of Hg,Re-1223 ceramic superconductor was developed using a DAC cell pressure in the DXAS beam line - LNLS. The investigation was focosed in the L_{III} edge from the ReO_6 octahedron. The influence of the external pressure on XANES region is associated with the intrinsic term, which appear on the equation that have been used to described the behavior of the Tc as a function of the external pressure. We have identified changes in the overlap between two gaussians that it is used to fit the XANES region. These gaussians are related with the T_{2g} and E_g energy split from the ReO_6 distorted octahedron present in the Hg,Re-1223 superconductor.

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High-temperature XRD study of the tetragonal-cubic phase transition in nanostructured ZrO_2-CeO_2 solid solutions synthesized by citrate complexation and gel-combustion methods.

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Since ZrO_2-CeO_2 materials have been proposed as anodes in intermediate-temperature solid oxide fuel cells (IT-SOFC), it is really important to know what is happening with the structural properties of the material at SOFC working temperatures (500-800C). One of the most notable characteristics of some zirconia-based solid solutions is the existence of three tetragonal forms, all belonging to the $P4_2/nmc$ space group. The stable tetragonal form is called the t-form. 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).

The aim of this work is to study the tetragonal-cubic phase transition as function of temperature on nanocrystalline powders of ZrO_2-50 and 65%mol CeO_2 by high-temperature X-ray diffraction (HT-XRD) employing synchrotron radiation (XPD 10B beamline of LNLS). Both compositions were synthesized by different chemical routes: citrate complexation and gel-combustion (glycine as fuel). ZrO_2-50%mol CeO_2 solid solution exhibits the metastable t-form while the t-form is observed in ZrO_2-65%mol CeO_2. The evolution of the (112) peak with temperature was studied in all systems. The (112) peak is a characteristic reflection of t''-form (pseudo-fluorite), while it is a forbbiden reflection in a fluorite-like structure of the cubic phase. This reflection is related to the displacement of the oxigen anions. By monitoring of this peak it was possible to discriminate between tetragonal and cubic phases. The fractional z-coordinate of the oxygen atom in the asymmetric unit, z(O), can be determined from the measured integrated intensities, I(112) and I(111). The data were collected at temperatures ranging from room temperature to 900^oC.

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S 1S STUDIES OF ORGANIC DERIVATE OF DMIT, DMIO AND DMT COMPOUNDS

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The sulphur heterocyclic systems are important coordination ligands because their electrical conduction, ferromagnetism and non-linear optic (NLO) [1] properties. The variety redox and polarizability of the sulphur atoms in the compounds are the main factors that contribute to those properties. Photoabsorption and Photoelectron spectra in the S 1s region of some organic derivates DMIT, DMIO and DMT ligands have been acquired for $(PhCO)_2$dmit, $(PhCO)_2$dmio, $(PhCO)_2$dmt, $(Me)_2$dmit and $(Cs)_2$dmit compounds. All compounds were synthesized following the literature [1−3]. TEY and XPS spectra have been acquired at Soft X-ray Spectroscopy (SXS) beamline, LNLS-Campinas. The samples were introduced into the main chamber as a solid using a carbon sticky tape. The work pressure was kept at 2 x 10^{-8}mBar. The ionization potentials (IP) of these compounds have been determined and the electronic transitions have been studied. Ab initio calculations associated with improved virtual orbital (IVO) method, carried out from the GSCF3 program, were used to help us in the assignments. The geometric parameters were optimized with the GAMESS program.

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Crystal structure of nanostructured ZrO_2-CeO_2 solid solutions synthesized by different chemical routes

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ZrO_2-CeO_2 substitutional solid solutions are extensively used as redox or oxygen storage promoters in three-way catalysts, which are applied in controlling the emissions of NOx, CO and hydrocarbons from automotive exhausts. The properties of zirconia-ceria mixed oxides are strongly related to their crystal structure and local order. In particular, the metastable forms of the tetragonal phase have been widely investigated since they are the most suitable for applications. One of the most notable characteristics of some zirconia-based solid solutions is the existence of three tetragonal forms, all belonging to the $P4_2/nmc$ space group. The stable tetragonal form is called the t-form. 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).

In this work, a detailed crystallographic study performed by X-ray diffraction (XPD 10B beamline of LNLS) was carried out on nanostructured ZrO_2-50 and 65%mol CeO_2 solid solutions. Both compositions were synthesized by different chemical routes: citrate complexation and gel-combustion (employing lysine and glycine as fuel). The lattice parameters, a and c and the fractional z-coordinate of the O^{2-} anion in the tetragonal asymmetric unit, z(O), were refined by Rietveld method. ZrO_2-50%mol CeO_2 solid solution exhibits the metastable t-form while the t-form is observed in ZrO_2-65%mol CeO_2. The crystallite size was determined by Scherrers formula. The influence of the synthesis method on the crystal structure of these solid solutions were evaluated.

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Short-range order study of $Bi_{4-x}La_xTi_3O_{12}$ ferroelectric system

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In the last years, it was shown that La-substituted $Bi_4Ti_3O_{12}$ compound exhibited excellent ferroelectric properties and fatigue-free behavior. Although the electrical properties of this system have been extensively studied, few works have been published concerning the short-range order structure, mainly the effect caused by the substitution of bismuth by lanthanum ions. The purpose of this work is study the short-range order structure around titanium, bismuth and lanthanum atoms on the La-substituted $Bi_4Ti_3O_{12}$ compound, hereafter denoted as BLT system. The BLT samples were prepared by a solid-state reaction method. Sintered ceramic samples were obtained after a heat-treatment at temperatures ranging from 1373 to 1523 K. X-ray absorption near edge structure (XANES) spectra at the titanium K edge and lanthanum and bismuth L_3 edges, were collected at room temperature on the D04B-XAFS1 beam line at the LNLS storage ring using a transmission mode. XANES spectra collect at the Ti K-edge and Bi and La L_3 edges shows that the local structure around these atoms are not significantly affected by the substitution of Bi by La atoms and only few changes are observed at the medium range-order. Ab-initio calculations of the XANES spectra using the FEFF software was used in order to interpret the variations observed on the XANES spectra obtained at the Ti K-edge.

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Dielectric and X-ray diffraction study of phase transition in relaxor ferroelectric ceramics

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Relaxor materials are characterized mainly by frequency dispersion and broad peaks in the dielectric susceptibility versus temperature variation. A large number of perovskite materials exhibit relaxor ferroelectric behavior which are of great interest for applications and fundamental physics. In spite of the quantity of published works, several ferroelectric phenomena must be still investigated. Among some controversial questions founded in the literature, the correlation between the local disorder and the relaxor character observed in several ceramics systems is not well understood. Moreover, another important subject yet in discussion relates the existence or not of a spontaneous structural phase transition process at low temperatures from a relaxor ferroelectric phase to a classical ferroelectric phase. The $Ba_{0,9}La_{0,2/3}Zr_{0,3}T\ddot{\imath}_{0,7}O_3$ (BLZT) and $BaZr_xTi_{1-x}O_3$ (x=0,25, 0,30) (BZT) ceramics were prepared by solid state reaction. The samples have been studied by dielectric permittivity measurements whereas the long-range order structure was characterized by using the high-resolution x-ray diffraction (HRXRD) technique, at the D10B- XPD LNLS beam line. The dielectric and the HRXRD experiments were undertaken in a temperature ranging from 15 to 350 K. Dielectric measurements demonstrate a typical relaxor behaviour with the magnitude of the dielectric constant decreasing with the frequency increasing. Moreover, a shifting of the maximum of the permittivity curve to higher temperatures was observed. The temperature dependence of dielectric permittivity and the degree of diffuseness of the relaxor ferroelectrics ceramics became more pronounced for higher zirconium concentration and for a heterovalent substitution on barium site. The HRXRD experiments show that the all samples exhibit a cubic structure in all range of the temperature and any spontaneous phase transition above or below the maximum of the dielectric permittivity was observed.

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Linear vs. Tilted / Bent Nitrosyl Paradox: an EXAFS and XANES study to determine the nature of Spin Isomers

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A linear vs. tilted/bent metal-nitrosyl isomerism is observed for pentachloronitrosyliridate(III) ($[IrCl_5(NO)]^-$) by EXAFS. While its Na^+ and K^+ salts comprise octahedral anions with linear IrNO moieties, the crystal structure of $PPh_4[IrCl_5(NO)]$ shows a nitrosyl with an off-axis tilting. A multiple scattering EXAFS fitting was used to determine the alignment of the Ir-N-O atoms. The pentachloronitrosyliridate(III) anions are spatially distributed in a curious arrangement in which one is over the other forming an infinite cable, with a short distance between the N-O moiety of one anion and the trans-chloride of the nearby upper one. In addition XANES data shows that the oxidation state for $PPh_4[IrCl_5(NO)]$ is notably higher than that for $K[Ir(III)Cl_5(NO)]$. This results as well as DFT calculations suggest an unprecedented spin isomerism for this third row transition metal complex, $Ir^{III}NO^+ \leftrightarrow Ir^{IV}NO^{\bullet}$, in contrast to the Na^+ and K^+ salts. The spin isomerism could be seen as an electron promotion from a metal-chloride orbital to a metal-NO one due to the small HOMO-LUMO gap in $PPh_4[IrCl_5(NO)]$. This is probably induced by electrostatic interactions acting as a result of the closeness and cable-like spatial arrangement of the Ir metal centers, imposed by lattice forces due to π-π stacking interactions among the phenyl rings.

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Correlation between photoluminescence emission and local order-disorder

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Relative attention has been done on visible photoluminescence (PL) at room temperature observed in ABO_3 perovskite-type disordered materials. The existence of a local structural disorder has been mainly attributed to the presence of different local coordination of A and B atoms. X-ray absorption near-edge structure (XANES) spectroscopy has been used to provide information about coordination number and site symmetry of A and/ or B atoms in perovskite materials since the XANES spectrum is highly sensitive to the disorder at the short and medium range order. In particular, the results obtained at the pre-edge XANES spectra of Ti and Ca K-edge confirm the presence of different coordination numbers of Ti and Ca atoms in the disordered structure of $CaTiO_3$ compound. In a general way, XANES results shows that the order-disorder on the ABO_3 compounds varies even in amorphous samples when heat-treated at different temperatures. A relationship between photoluminescence intensity, local order-disorder and the presence of structural defects is proposed based on ab-initio calculations.

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Long-Range Order Structure in the $\mathbf{Pb_{1-x}La_xTiO_c}$ (x = 0.30) Ferroelectric Ceramics

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Lanthanum-doped lead titanate ceramics ($Pb_{1-x}La_xTiO_3$ or PLT) is a family of ferroelectric compound which have been studied in detail due to their interesting physical and technological properties. The isomorphic substitution of lead in $PbTiO_3$ by lanthanum atoms induces significant changes in its electrical properties. We have studied the long and short-range order structure of the PLT and its dependence with the normal and relaxor behaviour presented on PLT ceramics with x=0.20 (normal ferroelectric) and x=0.30 (relaxor ferroelectric) by in-situ XRD and XAS techniques above and below T_C and T_m respectively. Part of this work, concerning the long order structure of the PLT ceramics with x=0.30, was performed at LNLS. The XRD patterns were collected on a Huber diffractometer with geometry θ-2θ, $\lambda = 1.37741$. The instrument was calibrated using silicon (SRM-640c). To study the behaviour of the phases as a function of the temperature, some peaks of x=0.30 sample were selected and measured varying the temperature with a step of 10 K around the transition temperature. The separation between the 2θ angles from (200) and (002) tetragonal reflections diminishes with increasing temperature collapsing into the (200) cubic reflection at 180 K. In order to determine precisely the structure at high and low temperatures, a Rietveld refinement of a complete 2θ range was performed on the patterns collected at 20 and 298 K. According to the data obtained from the refinement, the pattern collect at 298 K correspond to a cubic symmetry, space group number 221 ($Pm\bar{3}m$) whereas that one collected at 20 K presents a tetragonal symmetry, space group number 99 (P4mm). Thus, XRD results shows that although the x=0.30 sample is characterized from dielectric measurements as presenting a relaxor character, a structural phase transition from a cubic to a tetragonal symmetry was observed at around 180 K when the temperature decrease. This behavior has been interpreted as a spontaneous phase transition effect where material that is a relaxor undergoes a spontaneous phase transition into a normal ferroelectric material upon cooling.

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FABRICATION OF AAO FILMS WITH REGULAR NANOMETER-SIZE PORES

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Anodic aluminum oxide (AAO) films exhibiting a homogeneous morphology of parallel pores perpendicular to the surface are widely used as protective films of aluminum surfaces. We studied the effect of growth parameters to find the optimum condictions for the formation of an AAO film with perfect nanometric-hexagonal pore arrangement. An high-purity aluminum foil was anodized in an 0.3 M oxalic acid solutions and 40 V in a two-step anodization process. The temperature of electrolyte and the time of the final chemical treatment were studied. The field emission scanning electron microscopy (FE-SEM) images show the honeycomb structures with uniform pores size distribution for films with pore diameters between 40 - 100 nm and lengths of 0.7 - 90 μm. The ideal temperature condiction found was 15 ^{o}C. The time of final chemical treatment control de pore diameter. For time intervals 5 and 20 minutes the widening of pores reaches up to 30 nm at room temperature. The FE-SEM results show perfectly ordered hexagonal pores with parallel channels and their botton of pores with connical morphology.

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Estudo in situ por espectroscopia de absorção de raios-X da formação de nanopartículas do espinélio $NiAl_2O_4$

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Ultimamente as nanopartículas têm despertado a atenção de diversos pesquisadores devido a várias aplicações em diferentes dispositivos eletrônicos de meios de gravação magnética, catálise de CO e H_2S, produção de medicamentos, entre outros. As nanopartículas podem ser produzidos por vários métodos, entre eles o método sol-gel protéico usado nesse trabalho. O método sol-gel tradicional apresenta algumas dificuldades como, por exemplo, o alto custo na produção dos precursores. O método sol-gel protéico consiste na preparação de uma solução gelatinosa a partir da mistura de dois componentes relativamente baratos, um sal do metal e a gelatina que é comercializada em supermercados. O metal liberado em solução aquosa é ancorado pelos radicais negativos presentes nos aminoácidos (hydroxy-Prolina), constituintes da cadeia protéica da gelatina. Durante a calcinação, a gelatina (proteína) é quebrada e o metal que se encontra ligado ao oxigênio da proteína dará a formação aos óxidos. O resultado final da síntese é a produção de partículas de óxidos do metal com dimensões da ordem de centenas até dezenas de angstrons. O objetivo global deste projeto consiste em acompanhar a evolução, como função do tempo e da temperatura de calcinação, da formação dos óxidos nano-particulados produzidos a partir de soluções de diversos sais metálicos, obter informações estruturais complementando resultados de difração de raios-X e obter informações sobre a estrutura local de cada metal. Nessa contribuição, apresentaremos resultados de espectroscopia de absorção de raios-x na borda K do Ni realizados recentemente no LNLS em um conjunto de amostras pertencentes à série de produção de nanopartículas de $NiAl_2O_4$ calcinadas a várias temperaturas. Observamos a formação de NiO nano-estruturado em uma fase intermediária seguida pela formação do $NiAl_2O_4$ desejado. A análise dos dados nos permitiu observar a cinética de transformação e elucidar a estrutura local dos sítios de Ni.

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STRUCTURAL AND MORPHOLOGICAL CHARACTERIZATION OF ALUMINA NANOTUBES

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In this work, we show some problems related with the structural and morphological characterization of nanoparticulate materials. Alumina nanotubes (monolith and powder) were synthesized by sol-gel process, dried under hypercritical condition and calcined at several temperatures. The structural and morphological properties of the material were evaluated by powder X-ray diffraction, electron diffraction, scanning and transmission electronic microscopy and atomic force microscopy. The as-prepared powder (300C) was formed by boehmite crystallites, which changed to gama, tetha and alpha alumina nanophases at higher temperatures. Some alumina shapes were found in the used microscopic techniques, among them, alumina nanotubes, and the observed structures were not destroyed by calcination.

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X-ray Diffraction in KDP-Mn System as a function of dopant concentration

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X-ray diffraction was applied in the study of manganese-doped potassium dihydrogen phosphate single crystal (KDP:Mn) as a function of dopant concentration. The high-resolution Renninger Scans of KDP crystals were carried out in the Brazilian synchrotron radiation facility (LNLS) at Campinas, with the wavelength of 1.65382 . This value was determined through the use of silicon standard [111] crystal. The samples for X-ray multiple diffraction measurements (in this work) no presented habit modification and were prepared from one crystals grown from solutions at PH 3.8 doped with 1, 3 and 5 weight percent of manganeses ions. Elemental composition analyses of the samples were made using Rutherford backscattering spectroscopy (RBS). Our results suggest that Mn ions take the position of K ions or of P in the PO4 molecule group by a substitutional incorporation mechanism for crystals grown from the solution containing 1 and 3 weight percent of manganeses ions. Nevertheless for crystals grown from that containing 5 weight percent of manganeses ions the analysis of the Rennenger scans is consistent with the presence of the impurity atoms occupying interstitial crystalographic sites in the lattice. A careful investigation of the x-ray powder diffraction patterns taken at room temperature by Rietveld refinement was also performed. These results show that all doped samples of KDP-Mn have the same tetragonal structure of the pure KDP crystal.

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Characterization of impregnated NaY Zeolites by X-Ray Absorption Spectroscopy

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The chemical reactions for carbocations by nucleophilic substitution have been studied using halogenated NaY zeolites as a solid solvent [1,2]. A better comprehension of the rearrangements and nucleophilic substitutions and halogens exchanges in the inner zeolites structures leads to the development of more powerful manufacturing catalysts [3]. Our goal in the present work is to characterize various impregnated halogens NaY zeolites and to study the ionization potential (IP) and the electronic transitions of these samples by X-ray absorption spectroscopy. We intend to associate the experimental results with theoretical simulations based on calculations of the zeolitic site fragments, with improved virtual orbital (IVO) methods, to get better assignments. The samples have been prepared by impregnation over commercial NaY zeolite using aqueous solutions of NaF, NaCl, NaBr and NaI and dehydrated at 400^{o}C. Just before the experiments the zeolites were kept at 150^{o}C for 24h to eliminate any humidity. The experiments were performed using the Soft X-ray Spectroscopy (SXS) beamline at the Laboratório Nacional de Luz Síncrotron (LNLS), Campinas - SP. The samples were introduced into the main chamber as a solid using a carbon sticky tape. The work pressure was kept at 2×10^{-8} mBar. The X-ray absorption near edge spectra (XANES) of the zeolites have been measured at Si 1s and Cl 1s edges. The X-ray photoelectron spectra (XPS) have been measured for O 1s, Na 1s, Al 1s, Si 1s, F 1s, Cl 1s, Cl 2p, Br $2p_{1/2}$ and I $3d_{5/2}$ edges. Long scan spectra have been acquired to help the samples characterization.

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Spectral weight evolution of the Mott-Hubbard series: $SrVO_3$, $CaVO_3$, $LaVO_3$, YVO_3

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Transition metal compounds present a rich variety of physical properties. Particularly, some perovskite series show a metal-insulator transition (MIT), which is often achieved by a *band-width* or a *band-filling* control. We present here a high energy photoemission spectroscopy study of the valence band of $SrVO_3$, $CaVO_3$, $LaVO_3$, and YVO_3. The samples were single crystals grown by the floating zone method, and the high energy photoemission spectra were measured at the SXS beamline in the LNLS. The experimental results were compared to cluster model calculations, which allowed us to interpret the different features in the spectra. The VO_6 cluster was solved within the configuration interaction method, which includes charge-transfer fluctuations from the oxygen. For the metallic systems ($SrVO_3$ and $CaVO_3$), the model also included a fluctuation from a coherent state at the Fermi level. For the insulating materials ($LaVO_3$ and YVO_3), the model also added a Mott-Hubbard channel from the neighboring V ions. In the metallic phase, the V $3d$ band is formed by the *coherent* peak, which is related to the *well-screened* $3d^1\underline{C}$ configuration, giving the metallic character to both compounds, and the *incoherent* part is mostly due to the *well-screened* $3d^1\underline{L}$ configuration. Further, the *poorly-screened* $3d^0$ state is at higher energies, hidden in the much intense O $2p$ band. In the insulating phase, the coherent fluctuations ($3d^n\underline{C}$) are suppressed and replaced by the Mott-Hubbard channel ($3d^n\underline{D}$). The result is the shift of the $3d^n\underline{D}$ configuration to higher energies. Thus, the V $3d$ band is now formed only by the *incoherent* feature ($3d^2\underline{L}$), whereas the Mott-Hubbard $3d^2\underline{D}$ and the poorly-screened $3d^1$ configurations are in the O $2p$ band region. Finally, we found distinct trends across these materials: (i) throughout the metallic $Ca_{1-x}Sr_xVO_3$ series, the band-width control is responsible for the transfer of spectral weight from the coherent to incoherent feature; (ii) from $CaVO_3$ to $LaVO_3$, the band-filling inhibits metallic fluctuations, which are replaced by the Mott-Hubbard fluctuation, producing an insulating character; (iii) the $Y_{1-x}La_xVO_3$ series, in the insulating phase, presents a bandwidth control, which reduces the V $3d$ bandwidth.

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Dopant local structure and magnetic behavior of Fe-doped TiO_2 anatase nanoparticles

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We present an investigation of the local structure of dopant sites and magnetic behavior of Fe-doped TiO_2 anatase nanoparticles (2.8 and 5.4 at.% Fe) through x-ray absorption experiments, ^{57}Fe Mössbauer spectroscopy, ab initio calculations and magnetometry. The iron K-edge near-edge and extended x-ray absorption fine structure results indicate that Fe(III) replaces Ti(IV) and causes an enlargement of metal-anion bonds length. Mössbauer spectra recorded at room temperature show asymmetric Fe^{3+} broad doublets. Structural, hyperfine and magnetic properties were investigated from first-principles calculations using the density-functional approach assuming that iron substitutionally replaces Ti in the anatase lattice. A good agreement between theory and experiment is achieved when anionic vacancies at the iron-oxygen octahedron are taken into account. Mössbauer and magnetic measurements indicate that a fraction of Fe^{3+} diluted in TiO_2 remains paramagnetic down to low temperatures. Further, the emergence of magnetically isolated clusters is favored as the amount of dopant increases. We also show that there is no evidence of a ferromagnetic order induced by the dopant.

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Estudio de los efectos de campo cristalino en films mesoporosos ordenados de óxidos mixtos de ZrO_2-SiO_2 mediante espectroscopía XANES.

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La estructura de los óxidos mixtos ZrO_2-SiO_2 reviste interés por su potencial aplicación en nanotecnología por sus propiedades catalíticas, sensoras, mecánicas, eléctricas, etc. Para la formación de una fase cristalina de un compuesto zirconia-silica ($ZrSiO_4$) se necesitan temperaturas superiores a los 1400 ^oC. De aquí que la obtención de óxidos mixtos ZrO_2-SiO_2 requiera de síntesis complejas y de múltiples caracterizaciones de estos materiales. En particular, para estos sistemas, el Zr^{+4} no puede sustituir isomórficamente al Si^{+4}, debido al tamaño de ligadura Zr-O (coordinación 6-8) y a la alta carga del Zr frente al Si, lo que constituye un factor relevante estrictamente vinculado a las propiedades de este nuevo material. En este trabajo se reportan los efectos de campo cristalino sobre los orbitales Zr 4d debido a la dilución porcentual de ZrO_2 en films de óxidos mesoporosos mixtos.

Mediante espectroscopía XANES (X-ray absorption near edge spectroscopy) se caracterizaron estructural y electrónicamente seis films delgados de óxidos mesoporosos de ZrO_2-SiO_2, altamente ordenados y soportados sobre FTO (x% ZrO_2-y% SiO_2, x+y=100, x= 10, 20, 30, 70, 80, y 90). Los experimentos XANES en los bordes de absorción L2 y L3 del Zr, y K del Si fueron realizados en el Laboratorio Nacional de Luz Síncrotron (LNLS, Campinas, SP, Brasil).

Se observó que el desdoblamiento t_{2g}-e_g es mayor para los films con x menores a 30, lo que indica que para una distribución homogénea de iones Zr, el porcentaje x altera el entorno local y electrónico del Zr respecto del ZrO_2 en sus distintas fases. Esto es compatible con la relación lineal obtenida entre la transición 1s → 3s-3p (borde K del Si) y la concentración de SiO_2 presente en los films. Estos resultados permiten analizar cuantitativamente la interacción electrónica entre el Zr y el Si, y la modificación en el entorno local del Zr respecto a la que presenta en el ZrO_2, en función de la relación porcentual de los óxidos presentes en el film.

Acknowledgements:

High-temperature EXAFS study of the tetragonal-to-cubic phase transition in compositionally homogeneous ZrO_2-CeO_2 nanopowders

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ZrO_2-CeO_2 solid solutions have been proposed as anodes in intermediate-temperature solid oxide fuel cells (IT-SOFCs) due to their excellent catalytical properties for direct oxidation of hydrocarbons. The investigation of the crystal and local structure of these materials is very useful for the understanding of their catalytical properties. In previous XPD and EXAFS studies at LNLS, we found a tetragonal/cubic transition as a function of composition, which is associated to a tetragonal-to-cubic symmetry change of the Zr-O bonding, while the Ce-O one has a cubic symmetry for all compositions (Lamas et al., Journal of Applied Crystallography 38 (2005) 867; Fábregas et al., Journal of Physics: Condensed Matter 18 (2006) 7863). Considering that IT-SOFCs usually operates at temperatures in the range of 500-800^{o}C, it is also important to study the phase transitions and changes in the local order as a function of temperature. In recent high-temperature XPD studies at LNLS, we found a tetragonal-to-cubic phase transition in ZrO_2-50, 60 and 65 mol% CeO_2 nanopowders and we proposed a metastable phase diagram for nanostructured solid solutions (Acuña et al., Latin American Workshop on Applications of Powder Diffraction, 2007).

In this work, we studied the features of the cation-oxygen bonding in compositionally homogeneous ZrO_2-50 and 65 mol% CeO_2 nanopowders as a function of temperature, including the range at which the tetragonal-to-cubic transition occurs (700-850^{o}C). To our knowledge, this transition has not been investigated by high-temperature EXAFS before. This investigation was carried out at the D04B-XAFS1 beamline of the LNLS. As in the case of our EXAFS study as a function of composition, we found that the high-temperature tetragonal-to-cubic phase transition is related to a change in the local order around Zr cations.

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XANES study of pure and Fe-doped TiO_2 and SnO_2 films

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TiO_2 and SnO_2 semiconductor films, pure and doped with magnetic impurities, have been the subject of numerous studies due to their potential applications in spintronics and optoelectronic devices. In this work we present an electronic and structural study of pure and Fe doped TiO_2 and SnO_2 thin films deposited on $LaAlO_3$ by pulsed laser deposition (PLD). XANES were recorded at the O K-edge, Sn M- edge, Fe L-edge and/or Ti L-edge. TiO_2 and SnO_2 in powder and a palette of metallic Fe were also measured for comparison. These spectra were recorded on the SGM beamline (LNLS) in total electron yield detection mode. We explore the influence of the impurity and the material nature (film or powder) in the electronic and structural properties of the samples. The films were also characterized by X-ray diffraction, and SQUID magnetometry measurements.

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The structural dynamics of SBA-15 ordered mesoporous silica calcination process

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Ordered mesoporous silica is a new alternative material for many technologies, ranging from microelectronics to medical applications [1]. In this work, in-situ analysis of the calcination process, that removes the tri-block copolymer template, was carried out by means of Small Angle X-ray Scattering (SAXS) at the SAXS2 beamline of LNLS. The analyzed system was the bi-dimensional hexagonal mesoporous silica, known as SBA-15. This as-synthesized powder was submitted to a heat treatment procedure in vacuum ($\sim 1 \cdot 10^{-3} torr$), from room temperature up to $\sim 540°C$, at a constant temperature increase of around $2°C.min^{-1}$. The sample was kept at this temperature for 6 hours. The cooling process was also monitored. At every 15 (or 30 minutes) a SAXS diagram was collected. The as-synthesized sample presents five diffraction peaks, which were followed in position and area for each temperature. Up to $300°C$ the lattice does not present any structural modification, but the decrease of the SAXS background indicate densification of the walls. At around $300°C$ the polymer starts to decompose and the lattice parameter decreases from $a = 12.8nm$ to $a = 12.4nm$, until the temperature reaches $\sim 540°C$, when the polymer decomposes, as demonstrated from thermogravimetric analysis. This shrinkage and densification effect continues for the isothermal treatment at $\sim 540°C$ during 6 hours and, the lattice parameter reaches a final value of $12.3nm$, remaining at this constant figure until the final cooling process. The peak areas do not change up to $300°C$, when experience a strong increase due to the enhancement of the electronic contrast density of the silica walls and less dense pores. The decrease of the peak areas during the isothermal calcination process is under investigation. The cooling process does not affect the structure. Comparison with a sample previously calcined in nitrogen and air atmospheres, revealed a larger shrinkage effect, resulting in $a = 11.8nm$. Also, a large background was observed when compared to the data after the final heat treatment in vacuum. This result could be attributed either to the presence of disordered pores, with maximum gyration radius of $7nm$, and also to inter-grain scattering, characteristics of a less dense material. The final structure dynamics is more clearly seen by the simulation of the electronic density evolution.

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IMAGEAMENTO DA BARREIRA DE POTENCIAL EM CERÂMICAS VARISTORAS DOPADAS

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Os varistores ou supressores de surtos são dispositivos eletrônicos e, devido às suas características elétricas de corrente-voltagem (I-V) altamente não-lineares, são utilizados para limitar surtos de voltagem transiente desde linhas de tensão até circuitos eletrônicos. Estas características são fortemente dependentes da composição química e das variáveis de processamento, responsáveis pela formação da microestrutura característica dos varistores, tais como: tratamento térmico inicial, preparação, tamanho médio das partículas, técnica de compactação, tempo e temperatura de sinterização. O que diferencia os varistores de outras cerâmicas é a formação de um material policristalino multifásico, por exemplo, com fases nos contornos de grãos de varistores de ZnO que dão origem à formação de barreiras Schottky, as quais são responsáveis pelo comportamento não-linear. O objetivo deste trabalho foi imagear as barreiras Schottky em cerâmicas varistoras do tipo ZnO+(0,5%-molCu)+x%-peso G (G é uma frita de vidro moído; x=0; 0,1; 1 e 5%) sinterizadas às temperaturas de 950^{o}C e 1050^{o}C utilizando a microscopia de força elétrica (EFM). As imagens foram obtidas em um microscópio de força atômica (AFM) Nanoscope IIIa da Digital Instruments operando no modo de microscopia de força elétrica (EFM). A partir das imagens EFM foi possível determinar a largura e intensidade das barreiras de potencial nas amostras em estudo.

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Effect of preparation conditions on structure and thermal properties of siloxane-PMMA obtained by sol gel process

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Organic-inorganic hybrid monoliths of cross-linked polymethylmethacrylate (PMMA) and siloxane groups were prepared by sol-gel process, from copolymerization of methylmethacrylate (MMA) and organically modified silicon alkoxide, 3- (methacryloxy) propyltrimethoxysilane (MPTS). Many types of monoliths were prepared, using different pH of the initial sol (1 or 3) and molar ratio compositions [MMA]/[MPTS]. Depending on the molar ratio, opaque, translucent or transparent monoliths were obtained after gelation. The structure of the hybrid monoliths were studied by Small-Angle X-Ray Scattering (SAXS), ^{13}C and ^{29}Si Nuclear Magnetic Resonance (NMR) and nitrogen adsorption (BET).Thermal properties of the samples were investigated by Differential Scanning Calorimetry (DSC) and Thermogravimetry (TG). The structural ordering, the BET specific surface area, pore volume and pore size decreased for monoliths with increasing amount of MMA. Glass transition temperature (T_g) and thermal stability increased with increasing Siloxane content. These results are a consequence of the fulfilling of the pores promoted by MMA and the reinforcement produced by the silicon species in the organic-inorganic hybrid matrix.

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IMAGEAMENTO DA BARREIRA DE POTENCIAL EM CERÂMICAS VARISTORAS DOPADAS

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Os varistores ou supressores de surtos são dispositivos eletrônicos e, devido às suas características elétricas de corrente-voltagem (I-V) altamente não-lineares, são utilizados para limitar surtos de voltagem transiente desde linhas de tensão até circuitos eletrônicos. Estas características são fortemente dependentes da composição química e das variáveis de processamento, responsáveis pela formação da microestrutura característica dos varistores, tais como: tratamento térmico inicial, preparação, tamanho médio das partículas, técnica de compactação, tempo e temperatura de sinterização. O que diferencia os varistores de outras cerâmicas é a formação de um material policristalino multifásico, por exemplo, com fases nos contornos de grãos de varistores de ZnO que dão origem à formação de barreiras Schottky, as quais são responsáveis pelo comportamento não-linear. O objetivo deste trabalho foi imagear as barreiras Schottky em cerâmicas varistoras do tipo ZnO+(0,5%-molCu)+x%-peso G (G é uma frita de vidro moído; x=0; 0,1; 1 e 5%) sinterizadas às temperaturas de 950^{o}C e 1050^{o}C utilizando a microscopia de força elétrica (EFM). As imagens foram obtidas em um microscópio de força atômica (AFM) Nanoscope IIIa da Digital Instruments operando no modo de microscopia de força elétrica (EFM). A partir das imagens EFM foi possível determinar a largura e intensidade das barreiras de potencial nas amostras em estudo.

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Structural and Redox Study of Molybdate Phosphate Glasses

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Molybdate phosphate glasses are well-known because of their high glass forming ability and interesting thermal properties and were intensively investigated for their ionic conducting properties. It is also suggested that phosphate glasses containing high amounts of MoO3 should exhibit specific optical properties such as non linear optical behavior or photochromism in the visible. However, large absorption bands in the visible are characteristic of these glasses and hinder applications in optics. These absorptions are generally attributed to reduction of molybdenum Mo6+ species because of the tendency of this element to form non-stochiometric oxides. In this work, it is shown for the first time that control of the conditions of preparation can result in the obtention of more transparent glasses in the visible. The oxidation state and coordination shell of molybdenum atoms were estimated by X-ray absorption near edge structure (XANES) at the Mo L2 and L3 edges. Based on the results, it is suggested that molybdenum atoms are present in octahedral coordination MoO6. In addition, the better transparency in the visible obtained by controlling synthesis parameters was not accompanied by a shift of the absorption edge as expected for oxidation state changes. This behavior can be due to the fact that even transparent samples contain a small quantity of reduced species. In conclusion, XANES at the Mo L2 and L3 absorption edges was used for the first time in glasses to access structural and redox informations of molybdenum species.

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INVESTIGATION OF SILICA PARTICLE STRUCTURE CONTAINING METALLOCENE IMMOBILIZED BY A SOL-GEL METHOD

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Different metallocenes (Cp_2ZrCl_2, $n\mathrm{Bu}Cp_2ZrCl_2$, $i\mathrm{Bu}Cp_2ZrCl_2$, $t\mathrm{Bu}Cp_2ZrCl_2$, Cp_2TiCl_2, Cp_2HfCl_2, $EtInd_2ZrCl_2$ and $Et(IndH_4)_2ZrCl_2$) were immobilized within a silica matrix concomitantly with its preparation by a non-hydrolytic sol-gel method. Supported metallocenes were characterized by Small Angle X-ray Scattering (SAXS) in order to study the influences of different metallocene complexs on the oxide structure. The results showed that the fractal dimensions in the metallocene-located environments for complexes such as Cp_2MCl_2 (M= Zr, Ti or Hf) lie between 1.6-1.7, which are related to a random polymer coil shape. More huge complexes, such as indenyl and the alkyl-substituted cyclopendienyl series, show a fractal dimension around 2.15, which is somewhat higher than the values found for the cyclopentadienyl metallocenes. Besides, a relation is identified between the metallocene steric hindrance (measured by the angle formed between ligand-metal-ligand) and the oxide fractal dimension. Despite the differences on the fractal dimension, the silica primary structures showed a broad size dispersion with the mean diameter about 160 nm for all synthesized silicas. According the aforementioned results, it is possible to infer that the metallocene structure affects the environmental in which is entrapped. In addition, the results suggest that the metallocene complex is surrounded by primary particles having a deeper location in the oxide matrix. Some metallocenes, which usually are less active, showed a neglected catalytic activity for ethylene polymerization when entrapped within the oxide matrix by the proposed method. This result could be related to problems of catalyst fragmentation leading to monomer mass transfer limitation along the partially fragmented particle.

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Inversão magnética em filmes finos de Fe crescidos sobre MnAs/GaAs(001) estudados por espalhamento ressonante magnético

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Neste trabalho, estudamos uma bicamada magnética composta de um filme de aproximadamente 130nm de MnAs crescido epitaxialmente sobre um substrato de GaAs(001), template sobre o qual depositamos 5nm de Fe. Filmes finos de MnAs crescidos sobre GaAs exibem coexistência de fases próximo à temperatura ambiente (15 a 40^{o}C) devido a tensões decorrentes do crescimento. A fase de baixa temperatura (α-MnAs) é ferromagnética (estrutura hexagonal), enquanto a fase de mais alta temperatura (β-MnAs) é paramagnética (ortorrômbica). Devido a diferente densidade de cada fase, formam-se terraços periódicos no filme que alternam a fase α (menos densa) e a fase β (mais densa). Durante o crescimento de Fe sobre o MnAs, a 180^{o}C, o MnAs encontra-se na fase γ (paramagnética), sem terraços. Ao baixar a temperatura, as fases α e β surgem e a estrutura alternada entre fase para e ferromagnética influenciam diretamente o comportamento do filme de Fe. Para estudarmos o comportamento magnético das duas camadas foram feitas medidas de refletividade nas bordas ressonantes magnéticas (L3) do Fe(706eV) e do Mn(640eV) para diferentes temperaturas. Em temperaturas abaixo da coexistência de fases do MnAs, os momentos magnéticos do Fe e do Mn estão alinhados e seguem o campo magnético aplicado, independentemente. A T=15^{o}C, quando surge a fase β-MnAs, o sinal magnético do Fe começa a diminuir e alinhar-se antiparalelo ao campo magnético e também ao momento do Mn. Essa reversão magnética é completa em T=22^{o}C e manifesta-se também na mudança drástica da forma da curva de histerese e do campo coercivo para medidas feitas na borda do Fe. A medida que a temperatura é elevada, a fase ferromagnética do MnAs dá lugar a fase paramagnética e o ferro realinha-se com o campo externo. Em temperaturas mais altas, a partir de T=24-25^{o}C, o MnAs realinha seu eixo de fácil magnetização perpendicular ao plano do filme. Neste caso, o ferro se acopla mais fracamente ao campo do manganês e se alinha novamente ao campo externo aplicado. Este estudo detalhado de cada camada magnética da amostra é possível apenas com a seletividade química que o espalhamento ressonante magnético permite, onde cada camada magnética é estudada separadamente escolhendo-se a energia do fóton na borda do elemento químico.

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XAS study of SiO_2-TiO_2 glasses synthesized by flame aerosol technique

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Silica glasses doped with TiO_2 have a particular interest for presenting a very high refractive index and unique properties such as ultra low coefficient of thermal expansion (CTE). The structural studies of the SiO_2-TiO_2 glass system have a particular interest in the influence of Ti on the glass properties due to its structural role in the silicate glasses. In the present research we have used the X-ray Absorption Fine Structure analysis (XAFS) near the Ti K absorption edge to study local parameters of the material structure in the XANES (X-ray Absorption Near Edge Structure) region. High purity SiO_2-TiO_2 glasses with concentrations varying from 6.4 to 8.2 wt. % TiO_2 were produced by a process known as VAD (Vapor-phase Axial Deposition), a cost-effective and versatile flame aerosol synthesis technology. At first, soot preforms (boules) composed by SiO_2 and TiO_2 nanoparticles were synthesized by a hydrolysis and oxidation reaction, provided by a high temperature oxihydrogen flame. $SiCl_4$ and $TiCl_4$ were used as precursors and O_2 was used as carrier gas, as well as to control the TiO_2 concentration. Afterwards, a consolidation process in an electric furnace with Helium atmosphere was carried out at 1400 ^oC, resulting in a sintered and bubble-free preform. At last, these samples were annealed at 1500 ^oC for 5h. The spectra were recorded at Ti K-edge in transmission mode at room temperature using synchrotron radiation from XAS D04B beamline equipped with a Si (111) monochromator. The consolidated samples were pulverized and deposited onto membranes. The XANES spectra of the standard sample (rutile TiO_2) showed three low intensity pre-edge peaks, characteristic of a typical octahedral Ti sites. The intensity of the pre-edge increases when the TiO_2 concentration decreases, although the energy position of peak at 4968.6 eV did not change. These pre-edge features suggest the Ti^{4+} valence for all samples. After the annealing, the highest TiO_2 concentration sample presented some change in the structure. The pre-peak increased after the heat treatment indicating that the ratio of octahedral to tetrahedral Ti sites is increasing. X-ray diffraction analysis before annealing to the sample with 8.2 wt. % TiO_2 revealed the silica amorphous halo and weak diffraction peaks attributed to the TiO_2 anatase phase; however after annealing the sample became completely amorphous.

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Structural properties of pure and Fe-doped L-Arginine.HCl. H_2O crystal using n-beams X-ray diffraction

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We use Renninger scans (RS) of the X-ray multiple diffraction (XRMD) to determine the piezoelectric coefficients of the Fe-doped L-arginine.HCl. H_2O (L-AHCl. H_2O:Fe) trough of the distortions produced in the unit cell under the influence of an applied electric field. The advantage of this technique is the possibility to obtain more than one piezoelectric coefficient from a single Renninger scan measurement. It was verified a decreasing in the coefficients of Fe-doped crystal (d_{22}=6.2(7)x10^{-10}CN^{-1}) when compared to the coefficients of the non doped crystal (d_{22}=2.2(3)x10^{-9}CN^{-1}), due change in the ferroelectrics domains, caused by the presence of the Fe^{3+} ions in the structure that difficult the alignment with the electric field. Another contribution of this work, it was the study of secondary peaks with greater sensibility to the displacement of the peak (1-74) as function applied electric field evidenced by the presence of the angle $\beta^{‘} =35.3^{o}$, noted in the RS with primary (500) for non doped crystal.

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MAGNETIC IRON OXIDES FROM A SOIL DEVELOPING ON TUFFITE OF THE ALTO PARANAÍBA, STATE OF MINAS GERAIS, BRAZIL

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Magnetic soils developing on tuffite, a pyroclastic rock found in the Alto Paranaíba region, state of Minas Gerais, Brazil, have variable mineralogy but usually contain iron-rich spinels, more specifically, (Mg,Ti)-rich magnetite and (Mg,Ti)-maghemite. In this work, magnetic portions (saturation magnetization, 34.4 J T^{-1} kg^{-1}) were separated from sand fractions of pedomaterials of a Brunizém (Chernossolo) (according to the Brazilian Soil Classification System; the sample labeled AP31CR) developing on tuffite was collected near the city of Patos de Minas. Maghemite (ideal formula, γ=Fe_2O_3), hematite (αFe_2O_3) and a newly characterized magnesioferrite ($MgFe_2O_4$) were identified in these magnetic extracts, with synchrotron X-ray (wavelength, (λ=0,1760268 nm) diffractometry and 298 K and 110 K ^{57}Fe Mossbauer spectroscopy. The room-temperature Mössbauer spectrum for this magnetic sample shows two overlapping six-line patterns. The hyperfine parameters indicate the occurrence of a well crystallized magnesioferrite along with maghemite, in this soil. The crystallographic structure as deduced from the Rietveld refinement of these X-ray diffraction data shows, for magnesioferrite, a = 0.837563 nm (the corresponding value for pure magnesioferrite is a = 0.83873(6) nm, according to JCPDS card 36-0398), and, for maghemite, a = 8.35758 nm. The proposed overall model for the main pedogenetic transformation pathways, related only to iron oxides, in this pedosystem, implies that a magnesioferrite is the precursor for maghemite, which is further transformed to hematite: $MgFe_2O_4$ to γFe_2O_3 to αFe_2O_3).

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Resonant x-ray diffraction study of EuTe films and EuTe based superlattices

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Resonant x-ray diffraction is an useful technique in the characterization of magnetic materials [1,2]. In this work we studied the resonant x-ray diffraction of a 1.5 μm EuTe film and EuTe/SnTe(PbTe) superlattices grown on BaF_2(111) substrates by molecular beam epitaxy. The measurements were made in the XRD2 beamline at the Laboratório Nacional de Luz Síncrotron, Campinas, Brazil. EuTe is a wide gap semiconductor, with AFM ordering below the Nèel temperature at 9.6K. As a consequence of the AFM ordering, half order peaks are expected to appear below T_N. The resonant behavior of both europium LII and LIII absorption edges was investigated, and an enhancement of the diffraction signal of more than two orders of magnitude was observed, with maximum counting rates around 37000 cps. The magnetic origin of the peak was checked through a polarization study with a graphite analyzer, that indicated a pure $\sigma \rightarrow \pi$ scattering. The phase transition of EuTe was investigated by measuring the magnetic peak intensity as a function of temperature. The peak width and center position remain approximately constant between 1.7 and 8 K. From 8 K to T_N the width increases and the center position decreases monotonously. Magnetic diffraction peaks were also recorded for EuTe/SnTe and EuTe/PbTe superlattices. The satellite structure observed for the EuTe/PbTe superlattice indicated the presence of magnetic correlations among EuTe layers across PbTe spacer. For the EuTe/SnTe superlattices only wide peaks were observed, discarding the presence of interlayer correlations.

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X-ray Absorption near Edge Structure Study of Titanate Oxide Nanotubes

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Materials with different structures at the nanometer scale, such as grains, dots, ribbons, tubes and wires may have a conspicuous impact on future advanced technology. So one of stand out is the alkaline titanates, that have attracted increasing attention for the applications, based on their high photocatalytic activity [1]. The first report of titanium oxide nanotubes using titanium alcoxi was done by T. Kasuga [1] using the sol-gel method, and hydrothermal treatment (HT). Since them, there are been reported several methods of titanium oxide production with different phases, structure, and formula. This work will present the XANES measurements of the Ti edge performed in beamline Db04-XAFS1 in the LNLS at Campinas in sodium titanates oxide nanotubes samples with a formula NaxH2-xTi3O7, synthesized in the Nanomaterials Laboratory. Some of the preliminary results show that the pre-edge curves measured in the energy region of 4964-4974 eV show a change in the forbidden transitions from the core 1s level to unoccupied 3d states of a Ti4+, as a result a degree of distortion in the TiO6 octahedron is show it that can be related with the phase, and formula of the nanotubes [2]. Acknowledgements: This work was supported by Rede Nacional de Pesquisa em Nanotubos de Carbono (CNPQ Brazil) and at the Brazilian Light Synchrotron Laboratory (LNLS).

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Effect of TM doping on strcutural properties TM-doped CuO (TM=Fe, Ni)

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Stoichiometric CuO is a Mott-Hubbard insulator with a gap of the charge-transfer type [1]. On the other hand, it has been reported [2] that oxygen vacancies can cause a narrowing of its band gap. From the point of view of high$_{TC}$ superconducting cuprates, the CuO can offer an easier scenario to understand the role of the copper in the appearing of the superconductivity in cuprates. Recently, Zheng et al. [2] observed the T$_N$ suppression of CuO doped with a non-magnetic Li^{1+} ion. It is well known that this kind of doping create one hole in the valence band because the charge difference between Cu^{2+} and Li^{1+} ions. Magnetic order was shifted to around 100 K at concentrations larger than 16%. This suppression is believed to be due the different electronic structure of the Li^{1+} ion related Cu^{1+}. To test the role of the electronic structure in the magnetic ordering of CuO we have used the co-precipitation method to synthesize polycrystalline TM-doped CuO samples (TM = Ni^{2+} and Fe^{3+}). The magnetic and structural properties of $Cu_{1-x}TM_xO$ samples have been investigated as function of doping concentrations(x). Magnetization measurement as function of temperature show that T$_{N2}$ is suppressed from 213 K (CuO) to 70 K in the Fe-doped sample with concentration around x = 0.06. Surprisingly, for Ni-doped samples, T$_N$ seem to be unaffected by the TM substitution. X-ray absorption analysis be presented for the systems in regions of the magnetic transitions T$_N$.

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Towards the Metallic State in $LaMnO_3$: Structural Insights by High Pressure X-ray Absorption Spectroscopy

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$LaMnO_3$ doped alloys are puzzle materials whose magnetic and transport properties can be drastically changed by subtle modifications in their chemical composition and experimental conditions. These changes are related to modifications in the local order (octahedral distortions and tilting angle among adjacent octahedra) through a delicate balance between charge trapping and hybridization. High pressure is a unique tool to tune the interplay between lattice and electronic degrees of freedom and to investigate the actual path from a given magnetic and transport state towards another one. Here we report on the local environment of manganese atoms in $LaMnO_3$ under pressure up to 15.3 GPa studied by x-ray absorption spectroscopy. For pressures below 8 GPa, no change is detected within the MnO_6 octahedra. Above this pressure a continuous reduction of the long Mn-O distance takes place, however, the octahedral distortion persists over the whole pressure range. At 15.3 GPa the average Jahn-Teller splitting of the distances is reduced by about one-third, indicating that a total removal of the local Jahn-Teller distortion would occur only for pressures around 30 GPa, where metallization is reported to take place. A hysteresis in the long distance reduction is observed down to ambient pressure, suggesting the coexistence of MnO_6 distorted and undistorted units.

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Optical Properties of GaN(x)As(1-x) Thin Films Grown on Si Substrates by r. f. Sputtering

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Visible light emission devices have been developed and are commercially available, based on InGaN and AlGaN ternary semiconductor alloys, producing green-to-violet visible emission. GaN(x)As(1-x) ternary alloys in the GaN-rich side, are expected theoretically to have band-gap energies in the full range of the visible spectrum for just a small change in the nitrogen concentration in the range of about 70-85 percent. Using the r. f. sputtering and the laser ablation film deposition techniques, we have reported the growth of ternary GaNAs layers with band-gap energies in the range between 1.4 to 2.6 eV [1,2]. In this work we report the growth of GaNAs thin films on Si substrates using the r. f. sputtering technique at high substrate temperatures; the r. f. power used in the sputtering process was varied in order to control the nitrogen incorporation in the film. The low temperature photoluminescence (PL) and the photoacoustic (PA) spectroscopies were used to characterize the optical properties of the series of GaN(x)As(1-x) films grown with different stoichiometries. The PL and PA spectra show that the films present the presence of three phases: a cubic GaAs phase; the ternary GaNAs phase; and the GaN cubic and hexagonal phases. We discuss the origin of the transitions observed in the PL spectra and the shoulders around 2.5 eV observed in the PA spectra.

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Characterization of p-InGaAsSb/n-GaSb and p-GaAs/n-GaAs Structures for the Fabrication of Fusion-Stacked Solar Cells

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Higher-efficiency photovoltaic devices can be realized through an improved use of the solar spectrum using a two solar cell configuration; one for the visible part and the other for the infrared one. We are developing a two-stacked solar cell, using for the infrared portion a p-InGaAsSb/n-GaSb heterostructure, and a p-GaAs/n-GaAs for the visible part. Both structures were grown using the liquid phase epitaxy growth technique, and doping at different levels the p-type layers in order to obtain p-n junctions with different electrical characteristics and depletion layer depths. For the quaternary layers, p-type doping was achieved using Zn as the impurity; and for the GaAs layer, Ge was used as the p-type dopant. We present results on the characterization of both structures using the photoluminescence spectroscopy to characterize the layer crystalline quality [1], and the photoacoustic effect to characterize the layer-substrate interface [2] for both structures. Also, we present the results on the I-V characterization and spectral response of both p-n structures for the different doping levels in the p-type layers used. Finally, details on the fusion process to stack the two solar cells are discussed.

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ESTUDO DA MICROESTRUTURA POR XAS DO SISTEMA RuO_2/Ta_2O_5 PREPARADO VIA METODOLOGIA DE PRECURSORES POLIMÉRICOS

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Neste trabalho foi estudado o sistema RuO_2-Ta_2O_5 por absorção de raios X. Inicialmente a contribuição do background do espectro de EXAFS foi removida usando um algoritmo (AUTOBK) presente no programa Athena e baseando se no dado teórico obtido pelo programa Artemis. Desta forma, minimizaram-se os valores de R-espaço no baixo k-espaço. Após a subtração do background e da normalização, os espectros de XANES foram comparados com o espectro dos padrões. Para todos os materiais investigados os dados de EXAFS do Ru e Ta foram analisado no intervalo de 2 a 14 $^{-1}$. Os dados de XANES do Rutênio do puro RuO_2 e do RuO_2-Ta_2O_5 (Ru:Ta = 80:20 % atômico) mostraram que a característica do Ru em ambos as amostras se assemelha ao Ru(IV)O_2 padrão, sugerindo que as amostras apresentam ambiente semelhante em torno do átomo de Ru. Análise preliminar do sinal de EXAFS da borda L_3 do Tântalo no puro Ta_2O_5 sugere que a primeira camada de coordenação em torno do átomo de Ta é composta de seis átomos de oxigênio localizados a R(Ta-O) = 2,01 . A contribuição em alta frequência no sinal de EXAFS na borda L_3 do Ta, a qual é responsável em sua transformada de Fourier para o pico longo na primeira camada de coordenação é devido ao efeito de múltiplos caminhos dentro do octaedro distorcido (TaO_6).

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Caracterização de magnetitas dopadas com estanho ou cobre

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A dopagem de compostos inorgânicos é um método empregado na preparação de materiais que promove alterações substanciais de suas propriedades através da incorporação de pequenas quantidades de outros elementos químicos. A magnetita, $[Fe^{3+}]Fe^{3+}$, $Fe^{2+}O_4$, é um exemplo clássico de um espinélio invertido e, devido à relativa flexibilidade da sua rede cristalina e a grande afinidade do ferro por outros elementos metálicos (p. e., Ti, Mg, Ni, Zn e Co), é comum a ocorrência de substituição isomórfica nesse óxido. Essas substituições exercem grande influência e, às vezes, até determinam importantes propriedades físicas e químicas desses materiais. Amostras de magnetita dopadas com diferentes percentagens de estanho ou cobre ($Fe_{3-x}M_xO_4$, M = Sn ou Cu, e x = 0.2, 0.6 e 1.0) foram sintetizadas via co-precipitação e caracterizadas através de análises de espectroscopia Mössbauer de ^{119}Sn e ^{57}Fe, e difração de raios X de policristais na linha de luz Síncrotron do LNLS (Campinas, SP). Análises preliminares dos difratogramas utilizando o método de refinamento Rietveld indicaram que, para as ferritas dopadas com estanho, houve a formação de magnetita e hematita, para x = 0.2 e, para x = 0.6 e 1.0, houve a formação de magnetita e cassiterita. Para as ferritas dopadas com cobre (x = 0.2, 0.6 e 1.0), observou-se apenas a formação de magnetita. Os espectros Mössbauer de ^{57}Fe para as ferritas dopadas com estanho confirmam a presença de magnetita com baixa quantidade de ferro no sítio octaédrico. No entanto, o espectro Mössbauer de ^{119}Sn para x = 1.0 sugere que o estanho esteja em duas coordenações distintas.

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Possíveis transições eletrônicas em $\mathbf{Sr_2MUO_6}$ (M=Co, Ni) investigadas por difração de raios-X e espalhamento Raman

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Perovskitas duplas com fórmula geral $A_2MM^{'}O_6$ (A=terra-rara ou alcalino terroso, M, $M^{'}$=metal de transição ou actinídeo) constituem uma ampla família de materiais com propriedades físicas diversas. Particularmente, o acoplamento magneto-estrutural entre os íons M e $M^{'}$ é freqüentemente objeto de interesse. Neste trabalho, medidas de difração de pó de raios-x de alta resolução em função da temperatura, realizadas na linha de luz XPD do Laboratório Nacional de Luz Síncrotron (LNLS), foram feitas em dois compostos desta família (Sr_2CoUO_6 e Sr_2NiUO_6), complementando resultados anteriores de Espalhamento Raman. Anomalias estruturais , mas sem mudanças de grupo espacial, foram observadas em temperaturas similares àquelas em que mudanças significativas no espectro Raman haviam sido detectadas. Fenômenos de natureza eletrônica, como ordenamento orbital ou troca de estado eletrônico do urânio podem estar relacionados às anomalias encontradas.

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Análise por TEM e EXAFS/XANES *in situ* da influência do CeO_2 na atividade e estabilidade dos catalisadores de Pt/Al_2O_3 nas reações de reforma do CH_4

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O interesse estratégico no estudo de catalisadores para produção de H_2 e gás de síntese (CO e H_2) para a síntese de combustíveis sintéticos a partir do CH_4 baseia-se no fato da energia ser um fator determinante do desenvolvimento econômico. Neste trabalho, os catalisadores Pt/Al_2O_3 (A) e Pt/CeO_2-Al_2O_3 (B) (contendo 12 % de CeO_2) foram caracterizados através das técnicas de TEM e XAS *in situ* da borda L_3 da Pt. Os catalisadores frescos foram reduzidos e testados em reações de reforma usando-se uma mistura de H_2 O:CH_4:O_2 (x:2:1, onde x = 0 ou 0,64) a 1073 K. Resultados de TEM mostram pequenas partículas de Pt bem dispersas em ambos os catalisadores frescos. Contudo, medidas da velocidade de desidrogenação do cicloexano revelam uma maior densidade de sítios de Pt em A. O catalisador B apresenta alta atividade (ou velocidade de reação - TOF_{CH4}) e maior estabilidade por 24 h em relação à A, que apresenta forte sinterização da Pt e cristalização da Al_2O_3. Esses resultados sugerem uma menor acessibilidade dos sítios de Pt quando suportados em A possivelmente devido ao acúmulo de carbono na superfície do catalisador. Os resultados de EXAFS *in situ* das amostras sob H_2 a 773 e 293K, revelam, respectivamente, NC_{Pt-Pt} 5,4 e 8,3 para A e 5,1 e 7,2 para B. Ambos os catalisadores apresentam contração das ligações Pt-Pt em relação à folha de Pt metálica e uma leve contribuição do espalhamento Pt-O a 773 K, o que indica que o ancoramento das partículas ocorre em sítios de vacâncias de oxigênio do suporte. Logo, a morfologia das partículas é alterada com a temperatura promovendo uma maior interface metal-suporte. Entretanto, pouco se pode concluir sobre modificações eletrônicas da Pt promovidas pelo suporte do catalisador B, apesar de certa resistência à contração e ao aumento do *cluster* metálico a 293 K. Assim, o menor tamanho de partícula e a menor densidade dos sítios de Pt no catalisador de B sugerem um recobrimento parcial das partículas de Pt por espécies CeO_x que pode favorecer a oxidação do carbono na superfície do catalisador, melhorando sua performance. A ocupação da Pt nas vacâncias de oxigênio do suporte CeO_2-Al_2O_3 possivelmente facilita esse mecanismo de oxi-redução.

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Mecanismos de recombinação de portadores em cintiladores cerâmicos Y_2O_3 dopados com íons lantanídeos: XEOL e EXAFS

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A ítria (Y_2O_3) dopada com terras raras é um cintilador com aplicação em tomografias e em física de altas energias. Neste trabalho combinamos as formas usuais de detecção de EXAFS, (fluorescência de raios-X ou total electron yield - TEY) com a técnica de XEOL (X-Ray Excited Optical Luminescence). Na XEOL a luz na região do UV-Vis-Ir é monitorada em função da energia do fóton do raios X incidente. A combinação do EXAFS usual com a XEOL permite o estudo das etapas de geração, transferência e recombinação de cargas no material. Amostras de Y_2O_3 dopado com íons terras raras, na forma de nanopós pela rota de sol-gel ou na forma de corpos cerâmicos, apresentaram fase cristalina única, confirmada por medidas de DRX, com tamanho de partícula em torno de 50 nm. As medidas de XEOL foram realizadas nas linhas SXS, XAFS-1 e XAFS-2 do LNLS, nas bordas LII e LIII do Y e das terras raras. A luz emitida pela amostra era coletada por uma fibra óptica acoplada a um espectrômetro (Ocean Optics, HR2000). Para cada energia do raios-X, um espectro de luminescência completo de 200 e 1100nm era obtido. A intensidade da XEOL é obtida da área sob o espectro completo de luminescência ou a área de uma dada linha de emissão como função da energia dos raios-X. Os resultados podem ser resumidos da seguinte forma: i) O espectro óptico de luminescência obtido é característico das transições 4f-4f, indicando que o processo final de produção da luz de cintilação está relacionado com a formação do íon terra rara num estado excitado. Este comportamento foi observado tanto nas bordas de absorção do Y quanto nas bordas de absorção dos íons terras raras; ii) Quando as amostras são excitadas na região das bordas de absorção do Y, a intensidade da XEOL apresenta um comportamento inverso a absorção. Este resultado indica que o aumento da absorção pelo ítrio gera rotas alternativas de recombinação dos pares elétron- buraco, sem excitar o centro luminescente, principalmente através da XRF; iii) A excitação nas bordas de absorção das terras raras produz um pequeno aumento na XEOL, devido a recombinação elétron-buraco produzindo na etapa final o íon luminescente num estado 4f excitado.

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Caracterização do supercondutor $Hg_{0,82}Re_{0,18}Ba_2Ca_2Cu_3O_{8+\delta}$ por difração de raios X com aplicação do método de Rietveld

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O composto $Hg_{0,82}Re_{0,18}Ba_2Ca_2Cu_3O_{8+\delta}$ é uma cerâmica supercondutora pertencente à família dos mercurocupratos, onde parte dos sítios cristalográficos do Hg são ocupados pelo elemento Re. A composição de estequiometria 1223 é a que apresenta a maior temperatura crítica já obtida à pressão ambiente (Tc = 135 K) e também sob pressão hidrostática externa (Tc = 165 K). A substituição parcial do Hg por cátions de maior valência, como o Re, facilita o processo de síntese, que é muito complexo, e também aumenta a estabilidade do supercondutor, diminuindo sua degradação em atmosfera ambiente. Isto se deve ao fato de que o Re ao ocupar o sítio cristalográfico do Hg leva consigo átomos extras de oxigênio ao plano Hg-O. O cátion Re se encontra no composto com valência +7 e tem uma coordenação octaédrica distorcida similar à do Re no óxido ReO_3 quando submetido a altas pressões hidrostáticas e/ou altas temperaturas. Devido à difícil reprodutibilidade da síntese há grande discordância nos resultados apresentados na literatura por diferentes autores com relação ao teor de rênio incorporado e ao grau de oxigenação das amostras e, consequentemente, quanto à sua estrutura cristalina. Neste trabalho são estudadas amostras com um mesmo teor nominal de Re (18%) e diferentes teores de oxigênio. As amostras foram analisadas por difração de raios X com radiação síncrotron em duas energias: E = 10535 eV e E = 6930 eV que correspondem, respectivamente, a energias próxima e afastada da borda de absorção L_{III} do rênio, com aplicação do método de Rietveld.

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STM and TEM investigations of STM and TEM investigations of reactive epitaxy: $HfSi_x$.

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New material has attracted the scientific and technology communities attention due to the improvement of the electronic properties of nano-devices. At the nanoscale regime the stability of these structures can be affected their structural and electronic characteristics, which strongly depends on the material growth conditions. Recently, Hf compounds have been explored of its direct impact in the semiconductor industry. A home made molecular beam epitaxy, with a base pressure of 4.2 x 10^{-11} torr, coupled to a VT-UHV Omicron Scanning Tunneling Microscope (STM) was used to the growth and the subsequent *in-situ* structural characterization of $HfSi_x$. Metallic Hf was deposited on a Si(001) substrate at room temperature and annealed at 720^oC for 10 seconds. STM atomic resolution images showed Volmer-Weber growth mode ensembles of uniform four-fold symmetry islands with 60 in lateral size and 5 height grown along the [001] direction. Electron diffraction Transmission Electron Microscopy (TEM) was performed in order determines the material crystalline structure using the HRTEM JEM URP 300kV equipment available at the LNLS.

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Análise Estrutural das Cerâmicas Ferroelétricas/Relaxoras $Sr_{0,73}Pb_{0,27}TiO_3$ e $PbNb_2O_6$ por meio da Técnica de Difração de Raios X

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Entender a origem das propriedades físicas dos relaxores ferroelétricos é com certeza um dos grandes desafios no campo da ferroeletricidade atualmente [1]. Investigações anteriores realizadas nos sistemas cerâmicos $Pb_{1-x}La_xTiO_3$ (PLT) e $Pb_{1-x}Ba_xZr_{0,65}Ti_{0,35}O_3$ (PBZT) combinando difração e absorção de raios X, ou seja, sondas de ordem local e longo alcance mostraram que a ordem local e as suas transições de fase afetam o comportamento dielétrico destas amostras [2]. Os compostos cerâmicos $Sr_{0,73}Pb_{0,27}TiO_3$ (SPT) e $PbNb_2O_6$ (PN), também apresentam características dielétricas similares aos sistemas citados acima. Neste trabalho foram realizadas medidas de difração de raios X por pó em função da temperatura em amostras do SPT e PN, com o objetivo de investigar o comportamento da estrutura cristalina e contribuir para a compreensão física das propriedades peculiares dos relaxores ferroelétricos. A amostra do SPT apresentou transição de fase estrutural cúbica para tetragonal em temperatura próxima do máximo da permissividade dielétrica relativa. Transição típica de um material ferroelétrico ordinário. No entanto, as amostras apresentam características ferroelétricas não convencionais. A composição PN possui uma estrutura cristalográfica bem mais complexa que a estrutura perovskita dos outros sistemas estudos. Os difratogramas de difração de raios X coletados a temperatura ambiente e a 30 K não apresentaram diferenças, indicando que a estrutura permanece com a mesma simetria em todo o intervalo de temperatura, não apresentando transição de fase estrutural.

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EXAFS e XEOL de Nanopós de $SrAl_2O_4$ Dopados com Terras Raras

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O desenvolvimento de uma nova rota de produção de materiais através da técnica sol-gel possibilita a produção de nanopós usando temperaturas de calcinação mais baixas e tempos menores quando comparada com outras rotas cerâmicas como, por exemplo, a reação de estado sólido. Este trabalho tem como objetivo estudar o espectro de XEOL (X-ray Excited Optical Luminescence) do $SrAl_2O_4$ dopado com terras raras produzido através do método sol-gel protéico, bem como seu espectro de absorção de raios X. Neste trabalho foram produzidas amostras de $SrAl_2O_4$: Eu^{3+}, $SrAl_2O_4$: Eu^{2+} e $SrAl_2O_4$: Eu^{2+}, Dy^{3+} todas na forma de pó, através do método sol-gel protéico, utilizando-se da água de coco processada como solvente de partida para preparação do sol. Todas as amostras produzidas foram analisadas através das técnicas de Difração de Raios X (DRX), Microscopia de Força Atômica (AFM) e Espectroscopia de Fluorescência. A emissão luminescente (XEOL) do $SrAl_2O_4$ foi verificada quando exposto aos raios X. O espectro de absorção de raios X foi realizado utilizando as linhas XAS (X-ray Absorption Spectroscopy) e XAFS-2 (X-ray Absorption Fine Structure) no Laboratório Nacional de Luz Síncrotron, Campinas, Brasil (LNLS). Os materiais produzidos apresentaram fase cristalina única, confirmada por medidas de difração de raios X de pó, e tamanho de partícula em torno de 53nm, observado por microscopia de força atômica. As emissões características do Eu^{3+} e Eu^{2+} foram observadas através dos espectros de fluorescência, indicando a presença do Eu na matriz do $SrAl_2O_4$ tanto na forma reduzida quanto na forma Eu^{3+}. Resultados de espectroscopia de absorção de raios X mostram a absorção das bordas L_1 L_2 do Sr e a borda L_3 do Eu. A emissão luminescente das amostras de $SrAl_2O_4 : Eu^{3+}$ também foi registrada e mostra um pico de emissão em torno de 520nm e outro menos intenso em 612nm, associados, respectivamente, às emissões do Eu^{2+} e do Eu^{3+}. Esses resultados indicam que a irradiação com raios X induz a redução de parte do Eu^{3+} para Eu^{2+} no estado excitado levando às emissões em 520nm e em 612nm. Os resultados de XAS e XEOL revelam uma possível transferência de energia, via fluorescência de raios X, do Sr para o Al para valores de energias próximos das bordas L_1 e L_2 do Sr.

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Parte XI

Superfícies, Interfaces e Nanossistemas

Degradation of the N,N'-bis-(1-naphthyl)-N,N'-diphenyl-1,1'-biphenyl-4,4'-diamine (NPB) by photon irradiation

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The increase of operational lifetime for OLEDs has stimulated many studies focused on the mechanisms responsible for their degradation. The study of degradation in N,N-difenil-1,1-bifenil-4,4-diamina (NPB) have been performed using synchrotron radiation on Brazilian Synchrotron Light Source (LNLS), for a nonmonochromatized beam light in core level photoabsorption at N 1s-edge and Valence level photoemission to elucidate the structure of organic electroluminiscent material. The results suggest a bigger structural stability and a minor loss in the hole transport propriety. The degradation leads to the decrease of the injection and mobility charge, associated to the loss of nitrogen and benzene rings, which causes an increase of the impedance in the electroluminescent device.

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SAXS STUDIES OF NANOSILICA/POLYURETHANE COMPOSITES

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Polymer nanocomposites materials prepared using nanosilica fillers have unusual properties and in these materials the polymer chains are confined to nanoscale dimensions (1-10 *nm*). Film-forming, silica-based materials are useful as tough, abrasion-resistant coatings with increasing friction coefficient and reduced tackiness, with no change in gloss. In this work, films of polyurethane (IPDI/PPG1000) with different content (5, 10 and 15 *wt*%) of colloidal nanosilica (Bindzil$^{\circledR}$ CC40, 12 nm) were studied by SAXS. Samples were prepared by using two different synthetic methods starting from a PU prepolymer containing vinyl end groups. In one case the PU prepolymer was dispersed in water containing the colloidal nanosilica particles and then dispersion polymerized; in the other, the PU prepolymer was dispersed in water, then colloidal nanosilica was added to the dispersion and polymerized. A mixture from the PU prepolymer dispersed in water and polymerized, was prepared with the colloidal nanosilica for comparative purpose. Films were prepared by casting the dispersion at room temperature. A monochromatic beam of wavelength 1.608 was used and the scattering intensity was registered using a sample-detector distance of 2043.72 *mm*. SAXS curves show oscillations with maximums at q around 0.030 and 0.055 $^{-1}$. They are the common features found in dilute systems of nanoparticles in a homogeneous matrix. Scattering intensity increases as silica content of sample increases. Porod$'$s plots have an asymptotic linear regime for all the samples indicating that the structure can be described by a two-electron density model. SAXS curves for q $>$ 0.035 $^{-1}$ do not show appreciable differences for the two first strategies. This indicates that the structure is globally similar. However for the blend a noticeable smaller scattering intensity for the entire wave vector range is observed, which is more evident for the low silica content samples. For q $<$ 0.035 $^{-1}$ some differences appear in all cases. Samples from first and second strategies show a scattering contribution at q around 0.02-0.03 , which is not observable in blends. This behavior is related partly to particle interaction and partly to the formation of a different structure depending on the preparation method. This observation is consistent with TEM results.

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Photon stimulated ion desorption studies from polypyrrole film doped with $[\mathrm{Ni(dmit)_2}]^{2-}$ anion following S K-edge excitation

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The synthesis and characterization of polypyrrole (PPy) doped with metal complexes based on dmit (1,3-dithiole-2-thione-4,5-dithiolate) has been reported very recently. Although the conducting polymers based on PPy can offer a combination of the properties that make them attractive alternatives for certain technological application, the physical and chemical effects of the soft x-ray irradiation of theirs have been evaluated for photon energies just above C and N 1s binding energies. Thus, it is important to perform other studies about the interaction of high energy photons with these materials, which are not fully understood. In this work, we have performed NEXAFS and photon stimulated ion desorption (PSID) studies on polypyrrole (PPy) films doped with $Ni(dmit)_2]^{2-}$ complex anion. The experiments were taken at 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. 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 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. The Auger process seems to play an important role in the desorption of S^+ and S^{2+} species at the S K-edge. Although no enhancement in the S^+ ion yield was observed at the first resonance, the spectator Auger process was used to interpret the results, since no desorption of S^+ was observed below the sulphur K-edge. Furthermore, for the S^{2+} ion an enhancement at higher photon energies suggests that the normal Auger process dominate. On the other hand, the production of H^+ and molecular fragments seem to be induced by both XESD and ASID mechanisms.

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Atomic reorganization in PtPd nanoparticles induced by thermal annealing

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The nanoscience provides numerous and interesting applications of metallic nanoparticles in areas such as catalysis, information storage and optoelectronic. It is possible to tailor the physical and chemical properties of the nanoparticles by varying their morphology and the crystalline structure. In special for catalysis, it is possible to obtain improved performance and chemical stability of a catalyst with the introduction of a second metal (bimetallic systems). Moreover, the range of possible catalytic properties is even larger if one varies the atomic distribution of the different metals within the nanoparticles. In this work, we have studied Pt_xPd_{1-x} (x = 1, 0.7 or 0.5) nanoparticles subjected to H_2 reduction and sulfidation under H_2S atmosphere, both at 300 ^oC. The system was studied by *in-situ* x-ray absorption spectroscopy (*in-situ* XAS) and x-ray photoelectron spectroscopy (XPS) techniques before and after the thermal annealings. The results show an evidence of atomic rearrangement after reduction and sulfidation steps. The Pt_xPd_{1-x} nanoparticles structure evolves from a random atomic distribution to a core-shell type with Pt atoms in the core and Pd atoms in the shell. We also observed that the amount of S adsorbed during sulfidation of the system is higher for lower x values (higher quantity of Pd atoms).

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Antimicrobial activity of bacterial cellulose-silver nanoparticles membranes

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In this work, hydrated bacterial cellulose (BC) membranes obtained from cultures of Acetobacter xylinum were used in the preparation of silver nanoparticles containing cellulose membranes. In situ preparation of Ag nanoparticles was achieved from the hydrolytic decomposition of silver nitrate solution and triethanolamine (TEA) complexes. Scanning electron microscopy (SEM), Transmission electron microscopy (TEM) images and X-ray diffraction (XRD) patterns both lead to the observation of spherical metallic silver nanoparticles attached onto the BC fibrils. Antimicrobial tests for the BC-silver nanoparticles membranes show strong antimicrobial activity against Gram-positive (Staphylococcus aureus) and Gram-negative (Pseudomonas aeruginosa).

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Funcionalização superficial seletiva de poliuretana e poliestireno por irradiação síncrotron e UV. Efeito na exposição a oxigênio e ácido acrílico

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As superfícies dos materiais poliméricos mais comumente usados são hidrofóbicas, constituindo-se isso num obstáculo para muitas das aplicações desejadas. A metodologia principal utilizada para modificar suas superfícies é o tratamento com plasma. Estudos recentes [1] mostraram que em tratamentos de plasmas de baixa potência as espécies radicalarias superficiais são geradas pela radiação VUV-UV e não pelos íons. Esses resultados abrem novas possibilidades no uso de radiação UV-VUV no tratamento superficial de materiais. Neste trabalho, serão apresentados os resultados obtidos no estudo de dois polímeros de amplo uso na indústria e na biomédicina: poliuretana (PU) e poliestireno (PS). PU e PS foram preparados pela técnica de spin-casting a partir de soluções 10-4 M. As medidas foram realizadas na linha SGM, LNLS (bordas 1s do C, N e O) utilizando uma câmara de UHV com um analisador hemisférico (XPS) e um manipulador X-Y-Z. Espectros NEXAFS foram obtidos monitorando a corrente total de elétrons na amostra. Os filmes foram irradiados com radiação não-monocromática e monocromática. Espectros NEXAFS e XPS foram obtidos antes e após irradiação em diferentes tempos. Uma degradação geral dos filmes foi observada com irradiação não-monocromática. Os filmes expostos posteriormente à atmosfera de O2 mostraram diminuição no contido de O superficial e aumento de C. Excitação correspondente às bordas 1s do N e O no PU não produziram importantes modificações. Pelo contrario, excitação da borda 1s do C, e posterior exposição a O2, causou um importante aumento na concentração do O superficial junto com uma correspondente diminuição de C. Esses resultados mostraram que uma funcionalização seletiva é possível. Funcionalização dos mesmos filmes de PU assistidos por irradiação UV (lâmpada de 250 W de Hg) na presença de oxigênio e ácido acrílico na UFRGS, exibiram resultados comparáveis aos obtidos por tratamento convencional de plasma. Foto-funcionalição de filmes finos de PS com O2 e ácido acrílico estão em andamento.

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Phase transitions in ferritin-encapsulated copper nanoparticles

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Ferritin is an iron storage protein responsible for the sequestering of potentially dangerous excess of iron. The internal cavity of ferritin is able to harvest up to 4500 iron atoms within forming, mostly, the iron hydroxide ferrihydrite. 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 size and shape. Recently a reductive route for the synthesis of metal nanoparticles within the AF cavity was presented [1-3]. Here we present the results obtained from XAS experiments on ferritin-encapsulated copper-nanoparticles produced following the route outlined in [1-3]. 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. The temperature behaviour of the EXAFS spectrum indicates that the ferritin encapsulated copper NPs suffer a temperature-extended phase transition in the range 100-140 K from a FCC high temperature phase to a low temperature phase compatible with a BCC structure. 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.

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CHARACTERIZATION OF ULTRA-THIN FILMS OF Pd DEPOSITED ON Au(111)

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Ultra-thin films of transition metals deposited on single crystal metal substrates have attracted considerable scientific interest due to their catalytic, electronic and magnetic properties. There are controversial results in the literature regarding the composition and structure of Pd-Au system. In this work, we report preliminarily the surface composition and structure of palladium ultra-thin films deposited on Au(111). The films were evaporated in ultra-high vacuum; the surface composition and structure were characterized by X-ray photoelectron spectroscopy (XPS), low-energy electron diffraction (LEED), and X-ray photoelectron diffraction (XPD).

The experiments were performed at LNLS using the soft X-ray spectroscopy (SXS) beam line. It was used a InSb(111) monochromator and the photon energy was 1840 eV. The measurements were done with a surface analysis system equipped with LEED optics, a high-resolution electron analyzer (Omicron HA 125HR) mounted in the plane of the storage ring, a differentially pumped argon ion sputter gun and a two axis sample manipulator. The Au(111) surface was cleaned by cycles of argon ion sputtering and annealing, and the cleanliness was verified by XPS and the surface ordering, by LEED. We used the Pd 3d (KE = 1500 eV) and Au 4p (KE = 1293 eV) peaks for the XPD measurements, and the MSCD code for simulating the XPD patterns, including an average T-matrix approximation (ATA) subroutine that makes the program able to simulate ordered and random alloy systems.

Two Pd films having one monolayer and three monolayers were deposited at room temperature. The following models have been considered: (1) Pd overlayers on Au(111), (2) Pd islands covering the Au(111) surface, and (3) a random AuPd alloy. For the 1 ML film annealead at 450 C, Pd diffuses into the Au bulk, causing alloy formation. For the 3 ML film, the preliminary results indicate that Pd stays over the Au(111) surface. A full analysis is under development.

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Correlation between Phase Transition and Morphological changes in Tin Oxide Nanobelts

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Nanostructured materials are interesting due to the new properties presented by them and the capacity of increase devices properties. Among them, tin oxide is an interesting material from technological point of view, and SnO_2 nanostructures have been successfully synthesized using several approaches. Recently we have showed that it is also possible synthesize SnO nanobelts, through a control of synthesis atmosphere, using carbothermal reduction process [1]. In this work we present a study about the thermal stability and morphological changes of tin oxide nanobelts grown in the orthorhombic SnO phase. The samples were heat treated at 800 ^oC for 1 hour, at heating and cooling rate of 5 ^oC $min^{-1}C$, in argon or oxygen or synthetic air atmospheres, with gas flux of 50 sccm. The samples were characterized by differential scanning calorimetry (DSC), X-ray diffraction (XRD), high resolution transmission electron microscopy (TEM) and high resolution field emission scanning electron microscopy (FE-SEM). The results confirmed that orthorhombic SnO phase is a thermodynamically non stable phase, so the belts stabilize in SnO_2 phase when heat treated. During the phase transition, if oxygen is available in the furnace atmosphere, dendritic growth occurs at the edge of nanobelts at about 50^o of belts growth direction by a self catalytic VLS process. By other hand, in oxygen absence in the furnace atmosphere, particles grow on the belt surface. A chemical model was proposed to explain these differences based on the decomposition reaction of SnO. Although the decomposition process reduces the nanobelt cell volume in about 22%, most of belts maintain single crystalline after the heat treatment.

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Caracterization of Calcium Phosphate Coatings Using Synchrotron Light

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Synchrotron light is an efficient way of phase characterization, specially when high resolution is required. This mode is appropriate for solution and/or refinement of crystalline structures, where minimum superposition between the Braggs peaks is desirable. In this study, the authors investigate the presence of an intermediate phase, ocatacalcium phosphate, during the conversion of monetite to hydroxyapatite. 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. XRD analysis with synchrotron light showed to be efficient in the elucidation whether intermediate phases were present or not. These phases are seldom detected by conventional X-ray diffraction, using Cu K-alpha radiation. This finding shows that the conversion time of 12 hours is enough for the full conversion of monetite to hydroxyapatite in the conditions of the present study. XRD analyses in intermediate time points showed that no intermediate phases were present.

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Filmes finos de dióxido de titânio nanoestruturado e nanoparticulado confeccionados pelo método Sol-Gel

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A deposição de filmes finos em substratos como vidro, cerâmicas e metais é uma das mais importantes aplicações do processo sol-gel. A solução coloidal precursora utilizada deve apresentar propriedades físico-químicas de modo a produzir filmes transparentes, aderentes e homogêneos com larga variabilidade de propriedades. Pela adição de tetraisopropóxido de titânio a isopropanol e ácido clorídrico formou-se a solução precursora, na qual substratos de vidro foram imersos (processo dip-coating) e retirados na velocidade de 1mm/s, ocorrendo simultaneamente reações de hidrólise e condensação. Os filmes foram tratados termicamente nas temperaturas de 100 a 400 C por 10 min. A evolução da estrutura cristalina foi observada por difratometria de raios X de baixo ângulo (feixe D12A-XRD1) no Laboratório Nacional de Luz Síncrotron (LNLS) usando radiação de 1,5424 . O tamanho médio de partícula e a morfologia dos filmes foram analisados por microscopia de força atômica (Nanoscope II e um Dimension 3000, Digital Instruments-LNLS). Os filmes finos foram preparados a partir de soluções com pH entre 2 e 4, viscosidade entre 2.0 e 5.0 cp e tensão superficial de 20,1 0,1 mN.m-1. As linhas apresentadas nos difratogramas de raios X caracterizam a presença da fase cristalina anatásio, além destes mostrarem um aumento de cristalinidade juntamente à um aumento de temperatura. As análises por AFM revelaram que os filmes finos tratados a 100C são mais porosos do que aqueles tratados a 400C, além de apresentarem uma distribuição homogênea de poros. O tamanho médio de partículas foi estimado em $\sim$ 20 nm para ambas as temperaturas. Como conclusão, temos que os filmes finos obtidos se mostraram puros, cristalinos, aderentes, transparentes, homogêneos e livres de trincas. Filmes tratados termicamente nas temperaturas de 100 a 400C apresentaram baixa cristalinidade quando comparados com nanopartículas de dióxido de titânio também preparadas pelo método sol-gel. A cristalinidade aumentou e a porosidade diminuiu com o aumento da temperatura de tratamento térmico.

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Determinación de distancias interatómicas y número de coordinación en ZnO dopado con Yb, Er y Nd

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Los materiales nanométricos dopados con tierras raras mostraron un gran potencial en los últimos años para su utilización en fósforos, displays de monitores y comunicaciones ópticas entre otros. Dentro de los fósforos se pueden diferenciar aquellos que emiten fotones de baja energía cuando son excitados con fotones de alta energía, o sea, que intervienen procesos de *downconversion* (DCP),de aquellos que emiten fotones de mayor energía que la que fue utilizada para excitarlos, estos responden a procesos llamados de *upconversion* (UCP). Estos últimos son útiles a la hora de diseñar fósforos y láseres de estado sólido bombeados por IR. El ZnO es un material fácilmente sintetizable en dimensiones nanométricas por vías hidrotérmicas y que no presenta complicaciones al incorporar dopantes como Yb, Er y Nd, los cuales pueden ser involucrados en UCP al ser estimulados por radiación IR. En este trabajo se mostrarán los resultados en la técnica de EXAFS a fin de obtener información sobre la ubicación de los dopantes (Yb, Er y Nd) dentro de la red de ZnO, su entorno químico y la correspondiente coordinación.

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Estudo do empacotamento molecular na formação de nanofibras preparadas a partir de agentes gelificantes de baixo peso molecular

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Nos últimos anos o estudo sobre agentes gelificantes orgânicos de baixo peso molecular tem despertado interesse graças a suas possíveis aplicações, como transporte de fármacos, moldes para nanotubos e nanoestruturas, entre outras. A versatilidade de aplicações destes compostos se deve à termorreversibilidade em algumas de suas propriedades. Essas moléculas têm a capacidade de formar géis em determinados solventes, aprisionando os componentes do meio através de redes fibrilares formadas durante a transição sol-gel. Neste trabalho foi feita a síntese de agentes gelificantes baseados em glicosídeo com diferentes grupamentos doadores de elétrons (n-alcoxi) com $n = 1, 2, 3, 4$ e 8 átomos de carbono na posição *para* do anel aromático do gelificante 4,6-O-benzilideno-alfa-glicopiranosídeo de metila. Foram realizados testes de gelificação para classificar estes compostos modificados quanto a capacidade de formar géis em vários solventes orgânicos e, com ajuda das técnicas de SAXS, MEV e IVTF fez-se um estudo morfológico das fibras formadas. A partir das intensidades de SAXS, usando a aproximação de Guinier para formas cilíndricas foi possível determinar os raios mínimos e máximos das fibras e avaliar a influência de fatores como a concentração e o tipo de solvente nos raios fibrilares. Os resultados mostraram que para o agente gelificante com 3 átomos de carbono em propanol o raio máximo da fibra é maior em concentrações baixas. Já com 8 átomos de carbono, os raios máximos e mínimos não apresentaram dependência com a concentração em propanol. Em tolueno, no entanto, observamos nanofibras com uma distribuição de raios indo desde 3,3 nm até 12,5 nm, e ainda um aumento no raio máximo com o aumento da concentração. Verificou-se que para o solvente propanol não há uma relação direta entre o raio das fibras e o número de carbonos no agente gelificante. Em suma, a técnica de SAXS evidenciou a formação de nanofibras para todos os gelificantes estudados e forneceu informações valiosas na escala de $2 - 70$ nm, complementando aquelas obtidas com o MEV, na faixa acima de 100 nm.

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Ga interdiffusion in InAs free-standing nanowires

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Semiconductor nanowires (NWs) have considerable potential for applications in various devices of microelectronics, optoelectronics, and analytical instrumentation. At the present time, NWs are grown mainly by chemical beam epitaxy [1], metal organic chemical vapor deposition [2] and molecular beam epitaxy [3] on surfaces activated by droplets of the catalyst. Despite of all progress in thesynthesis, the influence of the growth parameters on the structural properties of the NWs have not been thoroughly explored. In this work we present results of gracing incidence x-ray diffraction (GID) experiments that indicates that InAs free-standing NWs grown in GaAs (111)B are actually InGaAs nanowires. We propose that the InGaAs nanowires are formed by the diffusion of surface Ga adatoms from the substrate surface towards the sidewalls of the InAs NWs. This assumption is supported by recent theoretical models and similar effects have been observed in self-assembled quantum dots.

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Size distribution of Pt nanoparticles supported on alumina and silica substrates. A differential resonant SAXS study

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Supported metal clusters are widely applied to catalyze many chemical reactions, such as methanation, reforming, and partial oxidation. The size of the metallic clusters strongly influences the turnover rates and selectivity for structure-sensitive catalytic reactions. For CO_2-CH_4 and H_2O-CH_4 reforming and CH_4 decomposition reactions. CH_4 activation turnover rates increase for decreasing size of noble metal nanoclusters [1], which is consistent with experimental and theoretical evidences that demonstrate the higher reactivity of unsaturated coordination of surface atoms on single crystals [2]. Pt surfaces exhibit a reactivity for activation of C-H bonds in CH_4 higher than other noble metals (Rh, Ru, Ir) for an equivalent cluster size [1]. We have studied two samples containing 2% wt of Pt nanoparticles, one of them being supported on SiO_2 and the other on Al_2O_3 porous and amorphous substrates. Differential resonant (or anomalous) small angle X-ray scattering (ASAXS) measurements performed at the XRD2 LNLS synchrotron beam line, employing several photon energies, allowed us to quantitatively determine the size distribution of Pt nanoparticles for both samples. The use of the differential ASAXS technique enabled us to identify the SAXS intensity produced by metallic clusters, which in the studied type of materials is usually much weaker than the strong contribution from the nanoporous substrate. By assuming a modeled structure consisting of a dilute set of spherical and homogeneous metal clusters embedded in a two-electron density nanoporous substrate, differences in the volume weighted radius distributions determined for each sample were clearly established. Details of the rather complex ASAXS technique when applied to dilute systems and special care that was required along our experiments is described and discussed. [1] J. Wei, E. Iglesia, J. Phys. Chem. 108 (2004) 4094. [2] D. Bazin, Topics Catal. 18, 79 (2002).

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A XAFS Study of the Spontaneous Adsorption of Thiol-Capped Gold Nanoparticles on Carbon

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X-ray absorption fine structure spectroscopy has been used to characterize gold nanoparticle-(AuNP)-modified carbon surfaces which have been prepared by simple immersion of highly oriented pyrolytic graphite (HOPG) in hexane solutions containing 3 nm diameter thiol-capped nanoparticles. XANES and EXAFS results show that the AuNP adsorb on the HOPG surface free of unbounded thiols, remaining unchanged with time. The amount of adsorbed thiol-protected AuNP depends on concentration and time. The reductive desorption of thiols from the AuNP produces an efficient release of more than 90% of the AuNP from the carbon surface to the aqueous solution. The remaining thiol-free Au nanoparticles do not sinter on the HOPG, forming stable and electrochemically active islands. These results could open interesting possibilities for easy transfer of thiol-capped metallic NP from one environment to another, for controlled release of biomolecules from metallic NP, and for the preparation of catalytic or decontamination systems on large area C surfaces.

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TEM and SAXS structural characterization of magnetic fluids composed by organic-covered magnetite nanoparticles

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Nanoparticles produced by chemical methods join several desirable characteristics for both basic science and technology, like controlled size, small size distribution, regular shapes, and organic capping. This last one prevents from direct contact between NP, making them interesting as a bench test for models of magnetic interactions and magnetotransport, like giant magnetoresistance and giant Hall effect. To understand these properties, knowledge of nanoparticles structure 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 = 7.5 0.1 nm (σ = 0.2 0.1 nm) for tartaric-acid-covered NP; d = 9.1 0.1 nm (σ = 0.3 0.1 nm) for polyaspartic-acid-covered NP; and d= 8.4 0.2 (σ = 0.25 0.02 nm) for carboxyldextran-covered NP. We carried out Small Angle X-ray Scattering measurements on these samples, in diluted and concentrated samples, where we found features compatible with a distribution of nanosized particles. We also measured magnetoresistance at room temperature and at 77K, and resistance vs. temperature. It was found a huge increase in the magnetoresistance at RT, and features indicating a high degree of electron polarization at 77K. Resistance vs. temperature shows that electron conduction is done through thermally activated tunneling. We will show relationships between the structure of our systems and the observed magnetotransport properties, and how the organic capping can affect those features.

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Fabricação de biossensores oscilométricos integrados em sistemas microfluídicos

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O presente trabalho descreve a construção de um biossensor oscilométrico integrado em um sistema microfluídico para monitorar interações biomoleculares. O dispositivo é composto basicamente de três componentes: (i) eletrodos microfabricados para detecção oscliométrica; (ii) camada isolante de SiO_2 contendo monocamadas biomoleculares adsorvidas à superfície e; (iii) microcanal fluídico fabricado em poli(dimetilsiloxano) (PDMS). Os eletrodos foram fabricados em substrato de vidro através de uma etapa fotolitográfica, para definir a geometria dos eletrodos, seguida por uma etapa de deposição metálica de Cu (100 nm) usando um sistema de electron beam. Três eletrodos para detecção oscilométrica foram microfabricados numa orientação antiparalela, com largura e espaçamento de 0,75 mm. Em seguida, estes eletrodos foram isolados eletricamente com uma camada de SiO_2 (500 nm) depositada através da técnica de deposição química em fase de vapor assistida por plasma (PECVD). A camada isolante foi funcionalizada com grupos amino-silanos e a extremidade de um dos eletrodos foi modificada bioquimicamente com moléculas de fotobiotina. A fotobiotina contém um grupo fotossensível, que conseqüentemente permite que esta molécula seja ancorada à superfície dielétrica quando exposto à radiação ultra-violeta (UV). A fotobiotina foi exposta à radiação UV por 15 min. Após as etapas de modificação química, os canais foram fabricados em PDMS, através de litografia suave, e integrados aos eletrodos microfabricados, isolados e modificados. A selagem reversível dos microcanais foi realizada através do simples contato dos canais com a placa contendo os eletrodos. As diferentes modificações químicas realizadas e a morfologia das superfícies foram caracterixadas por espectroscopia de fotoelétrons por raios-X (XPS) e por microscopia de força atômica, respectivamente. Os protótipos contendo biomoléculas ancoradas à superfície foram utilizados para monitorar interações entre proteína-ligante usando o princípio de detecção oscilométrica. A interação entre avidina e biotina foi monitorada com sucesso nos primeiros protótipos desenvolvidos. As próximas etapas estão direcionadas para o estudo cinético e analítico do microssistema proposto. A utilização da infra-estrutura do LNLS durante os próximos 12 meses será de fundamental importância para a conclusão do presente projeto.

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Characterization of New Polyaniline / Polycardanol Conductive Blends by X-Ray Photoelectron Spectroscopy

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The demand for natural resources impels to the development of new chemicals pathways able to produce Green Materials. Pointing that, new composites based on polyaniline-H_2SO_4 (PANI. H_2SO_4) / polycardanol (PCard) were prepared by a mechanical mixing method. The influence of the blending process on oxidative state of different kinds of nitrogen inside polyaniline was evaluated by XPS (Al Kα with resolution equal to 0.8eV).

Usually, XPS spectra of PANI can be deconvoluted into three distinct curves, related to the quinoid imine, the benzenoid amine and the positively charged nitrogen. XPS N 1s spectrum of the studied polyaniline does not present quinoid imine species, suggesting high doping level. On the other hand, the blend of Pani.H_2SO_4 and PCard shows a different behavior. The blended material possesses lower amounts of positively charged nitrogen and presents a considerable amount of imine, which is a strong indication of the relatively smaller degree of protonation. This way, amount of H_2SO_4 used as acidic catalyst (10phr) is not enough to avoid Pani.H_2SO_4 deprotonation by PCard in the blend. Deprotonation may be caused by a competitive mechanism between Pani and PCard, as both are nucleofilic species that can interact with H_2SO_4 molecules.

In spite deprotonation, the surface resistivity behavior of the blends (Sr) and the percolation threshold calculations showed that addition of small amounts of Pani.H_2SO_4 to the PCard can produce effective electrical pathways inside the insulating matrix, allowing for the production of bio-conductive devices, which may be useful in several applications, such as the production of pressure and displacement sensing materials, due to its inherent electrical properties and easiness of fabrication and molding.

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SnO_2 Nanoparticles Functionalized in Amorphous Silica and Glass

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Here we describe a single chemical route to obtain highly dispersed nanometric SnO_2, by way of functionalization in amorphous SiO_2 and in other materials including glass (consisting mainly of SiO_2). The synthesis of these SnO_2 nanoparticles, undoped and doped with rare earth metals (Eu and Pr), was based on the sol-gel method. The materials were characterized by N_2 physisorption, XRD, EDS and TEM analyses. We also present the results of catalytic experiments involving nanocrystalline composites based on SnO_2-SiO_2 as nanocatalysts in ethanol steam reforming. The doped compounds may lead to the obtainment of catalytic properties which differ from their non-doped analogs. Keywords: Nanomaterials, Sol-gel preparation, Amorphous material.

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Carbon-coated SnO_2 Nano-belts and Nano-particles

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Several types of carbon nano-structures (amorphous, fullerenes and spheres), for the coating of SnO_2 nano-belts and nano-particles were obtained by a single catalytic process, during methane, natural gas and methanol decomposition using a surface-modified SnO_2 nano-structure as a nano-template. The nano-structured catalyst templates were based on transition metal nano-particles supported on SnO_2 nano-belts previously prepared by a carbothermal reduction process. Carbon-coated La-doped SnO_2 nano-powders were also successfully synthesized for the fabrication of carbon spheres. The carbon coating process and yield, along with the nature of the nano-structured carbon, are strongly influenced by the chemically modified surface of the SnO_2 nano-structure template and the chemical reaction gas composition during the catalytic decomposition.

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Caracterizaciòn XAFS y TEM de aleaciones nanoestructuradas binarias obtenidas por aleamiento mecànico: Fe-Cu, Fe-Au

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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, han sido objetos de investigación desde los años 90. Aleaciones binarias nanoestructuradas metaestables han sido sintetizadas con gran eficacia mediante tècnicas de aleamiento mecánico. Nanopartìculas de hierro incorporado en matrices no magnéticas (Cu o Au) presentan interesantes propiedades magnéticas y de magnetotransporte [1,2], entre ellas el efecto de magnetoresistencia gigante (GMR). Para comprender los procesos involucrados en tal efecto, es de vital importancia una caracterizaciòn estructural precisa. La tècnica XAFS presenta importantes ventajas frente a otras tècnicas de caracterizaciòn, permitiendo determinar el tipo y número de vecinos pròximos, distancias interatòmicas, estructura electrònica, etc. Junto con la microscopìa electrònica de transmisiòn (TEM) es posible obtener una caracterizaciòn muy precisa. Ajustando un modelo teòrico con los resultados experimentales XAFS, es posible determinar directamente diferentes parámetros adecuados para estudiar el comportamiento nanotermodinàmico local de los sistemas antes mencionados. En el presente trabajo se investigaron empleando XAFS y TEM, dos sistemas que incluyen nanopartículas de hierro en matrices no magnèticas: Fe-Cu y Fe-Au. Se realizaron experimentos XAFS y TEM en el LNLS, y los resultados obtenidos del anàlisis de los datos sobre un conjunto de muestras de Fe$_x$Cu $_{100-x}$ y Fe$_x$Au$_{100-x}$ (15 % at. $\sim$ x $\sim$ 45 % at.), mostraron excelente compatibilidad: A travès de un anàlisis de componentes principales (PCA) realizado con las medidas XAS fue encontrado que existem dos fases, diferentes de los materiales de origen. Este resultado està de acuerdo con las medidas de composición quìmica EDS, realizadas con el microscopio TEM. En el caso del Fe-Cu, este resultado es compatible con càlculos de primeros principios que fueron realizados usando datos de espectroscopia Mössbauer (MS) y difracción de rayos X obtenidos en las mismas muestras. [1] L. M. Socolovsky, F. H. Sánchez and P. H. Shingu; Hyp. Interact. 133 (2001) 47-52 [2] L. M. Socolovsky, F.H Sánchez and P.H.Shingu; J. Magn. Magn. Mat. 226-230 (2001) 736

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$Au - Fe_xO_y$ core-shell nanoparticles investigated by SAXS and XAFS techniques

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Core-shell nanoparticles are heteronanostructures that comprise a core of one material and a coating shell of another material. The composition of the core and shell can be varied to give a wide range of different properties. Since the size and material properties of both the core and the shell can be manipulated at will, a vast range of particles can be made with myriad properties, useful in areas like, nano-sensors for cellular imaging, gap controlled semiconductor, etc.

The samples under study in this work were synthesized in a two-step procedure. Nanoparticles used as seed (core) are then incubated with a second emulsion containing the monomers and initiators that will synthesize the shell. In our case the nanoparticles under study have Au core and the shell is made of iron oxide (Fe_xO_y). To investigate the shape and size of the nanoparticles we perform Transmission electron microscopy (TEM) and Small angle X-ray scattering (SAXS) experiments on the core-shell system and seed nanoparticles. Modeling the SAXS curves we determine an average core radius and the thick of the shell. XAFS techniques were used to determine the average oxidation state of Fe atoms in the shell. In addition, we present a combined study of Au $L_{2,3}$ and Fe $K, L_{2,3}$ edges to investigate the charge transfer between Au and Fe_xO_y.

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Morfologia e Magnetorresistência em Filmes Finos de Fe_3O_4 Eletrodepositados

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Neste trabalho filmes finos de Fe_3O_4 (magnetita) foram eletrodepositados em substratos condutores de Cu, utilizando uma célula eletroquímica convencional com três eletrodos e eletrólito contendo $Fe_2(SO_4)_3$, NaOH e Trietalonamina. Os filmes foram eletrodepositados aplicando potencial constante ou pulsado e em temperatura de 65 ^oC. O potencial constante para deposição da magnetita foi de -1,1 V, em relação ao eletrodo de referência (SCE). Nas deposições pulsadas foi aplicado um potencial de -1,1 V, com duração entre 1 e 10 s, e intervalos de potencial de -0,6 V, com duração de 0,5, 1, 5 e 10 s, com repetição de até 2400 pulsos. A devida caracterização da micromorfologia desses filmes é de fundamental importância para a descrição dos fenômenos de transporte eletrônico, tais como, o efeito da magnetorresistência, observado na magnetita. Esta caracterização foi realizada através de imagens obtidas por Microscopia Eletrônica de Varredura (MEV) com elétrons secundários. Os resultados revelaram uma morfologia granular altamente dependente do método de deposição, sendo que, os filmes depositados com potencial pulsado apresentaram uma distribuição uniforme dos grãos, enquanto que nos filmes depositados com potencial constante os grãos estão em forma de aglomerados. Medidas de magnetorresistência mostraram um efeito de 7 % com campo magnético de até 6 kOe aplicado paralelo ao plano da amostra. As imagens de MEV foram obtidas no microscópio eletrônico de varredura JSM-5900 LV, do Laboratório de Microscopia Eletrônica (LME) do LNLS.

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HfO/Si$_3$N$_4$ films grown on Si(100) and Si(111): thermal stability, and electronic and structural information

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The development of alternative high-k gate dielectrics for future complementary metal-oxide-semiconductor (CMOS) devices is indispensable for achieving both low leakage current and small equivalent oxide thickness. HfO$_2$ is a possible candidate because of its high dielectric constant (which can be as high as 25 for HfO$_2$ on Si(100) [1]), but HfO$_2$ films grown on Si are not thermally stable for temperatures above 700 C, a temperature easily exceeded during standard device fabrication ($>$ 900 C). Silicon nitride (Si$_3$N$_4$) deposited on a silicon substrate is of interest for many applications, in particular as a barrier to dopant diffusion that for nitrides is much improved relative to oxides [2,3]. The interface between Si$_3$N$_4$ and Si(100) is significantly more stable and impenetrable than for other high-k dielectrics [4]. The growth of high quality thin silicon nitride films has been studied by many groups. Highly ordered Si$_3$N$_4$ films are not easily formed on a Si(100) substrate because of the large lattice mismatch, but for the (111) direction, an epitaxial beta-Si$_3$N$_4$(0001) film is formed with a (8×8) surface structure [5]. In this study, we report the results of a systematic study on the thermal stability of the HfO$_2$ ultra thin films grown on Si$_3$N$_4$/Si(100) and Si$_3$N$_4$/Si(111) for different silicon nitride films thicknesses. We created Si$_3$N$_4$ ultra-thin films on Si(100) and Si(111) by using a low energy ion gun (300eV) that implanted N$_2$ ions into the surface obtaining different film thicknesses from 2 to 18 . The electronic and crystallographic structure determination of these surfaces was performed using XPS, LEED and XPD measurements. After these characterizations, high-k dielectric HfO$_2$ films were grown onto the Si$_3$N$_4$/Si(100) and Si$_3$N$_4$/Si(111) surfaces. We then performed a systematic study of the thermal stability of this system from room temperature up to 1000 C. From these studies it was possible to determine the minimum thickness to stabilize the HfO$_2$ film up to 1000 C on top of the silicon surfaces.

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Acknowledgements:

Caracterização Elétrica e Análise Morfológica de Eletrólitos da PaCOS de ZEI 8 % em mol Produzidos pela Técnica de Spray Pirólise

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A pilha a combustível é um dispositivo eletroquímico, que realiza a conversão de energia gerada por uma reação eletroquímica em energia elétrica, sendo uma tecnologia eficiente e de concepção ambiental, pois emite concentrações desprezíveis de NO_x; entretanto, devido ao seu elevado custo de fabricação e operação, as pilhas ainda não têm a sua comercialização em larga escala viabilizada. A redução dos custos para o desenvolvimento das pilhas a combustível de óxido sólido (PaCOS) em geral, ocorre na preparação dos componentes utilizados, dentre estes, os método de deposição de filmes pela técnica de spray-pirólise se destacam, principalmente devido a sua simplicidade, eficiência e baixo custo. Visando conciliar o custo as propriedades das PaCOS, foram produzidos filmes com 8 % em mol de zircônia estabilizada com itria (ZEI) por spray-pirólise, que podem ser utilizados como eletrólitos para pilhas, depositados em substrato de quartzo e tratados térmicamente. Estes filmes devem possuir como características principais: elevada densificação (livres de poros, trincas e fissuras), baixa rugosidade e elevada condutividade iônica na temperatura de operação. Para a análise destas propriedades, foram realizadas as caracterizações elétricas através da variação da condutividade elétrica com a temperatura, utilizando a técnica de quatro pontas colineares, cujos resultados aplicados a equação de Arrhenius possibilitou a determinação da energia de ativação dos filmes e forneceu a estimativa de sua condutividade iônica. A estrutura e morfologia dos filmes foram analisadas através da técnica de difração de raios X, microscopia ótica com aumento de até 500 vezes e de força atômica, respectivamente, para os filmes após o tratamento térmico. Através do DRX e a indexação com o padrão JCPDS foi possível comprovar o alcance da fase cúbica dos filmes, onde o material apresenta os maiores valores de condutividade iônica. Após as análise das microscopias ótica e de AFM para aumento de 5 μm a 250nm, verificou-se que os filmes apresentaram-se livres de poros abertos, com boa distribuição dos grãos e que o mesmo não apresentou trincas aparentes.

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Nanodiamond grown on porous silicon substrate

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Nanocrystalline diamond (NCD) films were grown on porous silicon (PS) substrate by Chemical Vapor Deposition/Infiltration (CVD/CVI) process using a hot filament reactor. NCD formation on PS structures could be an innovative procedure for obtaining porous diamond electrode with large surface area associated with its high active sites. For PS substrate, diamond nucleation occurs preferentially on it active nucleation sites such as surface defects, apices and atom ledges promoting high nucleation rates that improve the adhesion between the film and the substrate. But, when the porosity increase over a certain extent it results in the problem of infiltration pores due to the decrease of atomic hydrogen and carbon growth species into the pore. This problem may be solved from CVI process with an additional carbon source by forming reacting species close to the substrate. In this sense, we present NCD films grown on PS substrate by the combination of CVD/CVI processes using a hot filament reactor. This procedure showed to be determinant to grow diamond grains uniformly into the pores, covering the different growth planes forming a NCD/PS porous compound. In this CVI process, pieces of reticulated vitreous carbon, produced at different temperature (RVC-2000 and RVC 1500), were used, just below the PS substrate, as an additional solid source of carbon that ensures the production of pertinent carbon growth species directly on PS sample and in its pores. PS substrates were obtained by anodization etching process of n-type silicon wafer in a hydrofluoric acid solution containing acetonitrile. Depositions of diamond films were performed using a Ar-H_2-CH_4 where the methane concentration varied from 0 up to 1.0 vol. %, to analyze the influence of RVC use as an additional carbon source on growth mechanism. Scanning Electron Microscopy (SEM) and Field Emission Gun (FEG) images of PS and NCD film morphology showed a strong influence of RVC presence in NCD nucleation. XRD diffractograms presented the characteristic diamond diffraction peaks while micro-Raman spectra also confirmed the features of NCD coating.

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EPOXY RESIN CONTAINING POLYHEDRAL OLIGOMERIC SILSESQUIOXANE (POSS): EFFECT OF COMPOSITION ON NANOSTRUCTURE

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The present work aims to determine the nanostructural features of epoxy networks containing different amounts of polyhedral oligomeric silsesquioxane (POSS) and to correlate the nanostructure by small angle X-ray scattering (SAXS). The POSS was obtained from sol-gel method trough the hydrolysis and polycondensation of the silicon species of hybrid precursor MPTS (methacryloxypropyltrimethoxysilane) and the polymerization of the methacrylate (MMA) groups covalently bonded to its silicon atoms. The desired amounts of MMA were determined in order to prepare hybrid samples containing weight fractions of siloxane phase corresponding to 44%, 21%, 14% and 8%. A second family of hybrid was synthesized using the same methodology, except by addition of 3 (%mol) of acrylic acid (AA). The POSSs (3 wt %) were incorporated into the epoxy resin with intensive mixing to form a homogeneous blend. Since the density of the siloxane phase is much higher than of both polymer phases (PMMA and epoxy) we attribute the X-ray scattering to the electronic density contrast between the siloxane and polymeric phases. A first analysis of our SAXS results lead us to the conclusion that the primary siloxane particles concentrate in relatively large domains embedded in a particles-depleted matrix. This effect of phase separation is assumed to be responsible for the formation of the two-level hierarchical structure. The structure parameters G1, Rg1, k1, d1, G2, Rg2 and P2 determined. For the composite prepared using 44% of siloxane in the hybrid a tendency to Guinier plateau is observed, allowing the determination of the average gyration radius (Rg2 = 100 angstron) of the secondary domains dispersed in the polymer matrix. In absence of acrylic acid the chemical affinity between siloxane nanoparticles and epoxy resin is low, leading to a segregation effect of siloxane particles forming siloxane-rich hybrid large domains embedded in the epoxy resin without spatial correlation between them. By increasing MMA content in the POSS a decrease of the compacity factor k1 simultaneously with a shift towards lower q-range of the linear regime associated to the secondary large domains with a disappearance of the Guinier plateau are observed for the Epoxy-POSS composites. This shift of Guinier regime to a region of q-values lower reveals the progressive increase in size of the large aggregates by increasing MMA content in the POSS.

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Fabricação e Otimização de Micromotores Eletrostáticos

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Com o advento da tecnologia de microfabricação de MEMS (*Micro-Electro-Mechanical Systems*), a partir de 1980, a construção de micromotores eletrostáticos atraiu o interesse do meio científico internacional. Atualmente, os micromotores vêm sendo pesquisados em diversos campos da Engenharia devido ao seu grande potencial no desenvolvimento de novas tecnologias, que vão desde o chaveamento óptico de dados na área de telecomunicações até à construção de dispositivos destinados à realização de microcirurgias. Este trabalho tem como objetivo a fabricação de micromotores eletrostáticos otimizados. A metodologia utilizada consistiu no projeto de máscaras para fotolitografia UV (com base em modelos desenvolvidos por simulação computacional e otimização topológica), desenvolvimento e otimização de processos para fabricação de moldes de rotores e estatores e a posterior eletroformação dos mesmos. Paralelamente, foi desenvolvido um *driver* eletrônico composto por componentes discretos destinado a operar eletricamente o micromotor. Resultados preliminares indicaram problemas relativos ao atrito entre as partes móveis e à definição das estruturas de elevada razão de aspecto do dispositivo, dificultando o funcionamento do micromotor. A análise destes dados irá nos permitir projetar e fabricar um novo dispositivo.

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EVALUATION OF THE CO TOLERANCE IN ANODES FORMED BY BIMETALLIC CATALYSTS

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Fuel cell is a promising alternative to environmentally damaging devices powered by fossil fuels. In the polymer electrolyte membrane fuel cell (PEMFC) the main fuel is hydrogen, produced from natural gas or methanol/ethanol by reformer systems. CO is a byproduct of this process and this contaminant poisons the Pt catalyst of the PEMFC anode, blocking the sites for adsorption and oxidation of hydrogen. So, a good electrocatalyst for the PEMFC anode must present CO tolerance and this has been partially achieved by using several kinds of Pt bimetallic materials. In this work, the CO tolerance was evaluated on PtFe/C, PtRu/C, PtMo/C, and PtW/C anode electrocatalysts. For a better understanding of the CO tolerance mechanism, X-ray absorption spectroscopy (XAS) analyses were performed to characterize the Pt electronic properties in the several electrocatalysts and DEMS (Differential Electrochemical Mass Spectrometry) measurements were made to analyze the CO_2 content in the PEMFC anode outlet. For all bimetallic materials, which presented higher CO tolerance as compared to Pt/C, XAS analyses in the XANES region indicated that the Pt 5d-band is more vacant in the Pt alloys, this leading to a weakening of the Pt-CO bond, helping to improve the CO tolerance (the so-called electronic effect). On the other hand, DEMS results indicated that the CO_2 production starts at lower potentials in the bimetallic catalysts in agreement with the occurrence of the so-called bifunctional mechanism, which also helps improving the CO tolerance.

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Erbium environment in ZnO:Er polycrystalline fibers produced by electrospinning

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Abstract - ZnO:Er fibers were prepared by electrospinning from organo-metallic precursors. After annealing at 500^{o}C in air they present up to 25-fold increase of the Er^{3+} photoluminescence intensity. This increase is associated with a modification of the Er environment in the fibers detected by EXAFS measurements. After annealing the Er neighborhood becomes an octahedron with oxygen atoms in each corner, very similar to that of Er_2O_3 but significantly more disordered. This contributes to the enhanced luminescence efficiency. Electrospinning allows for the synthesis of ZnO fibers with efficient Er^{3+} luminescence.

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Erbium doped silicon nanoparticles from SiO_x:Er prepared by reactive sputtering

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Abstract Erbium-doped silicon nanocrystals (nc-Si) were obtained by annealing SiO_x:Er prepared by reactive sputtering of a pure silicon target covered with pieces of metallic erbium. Erbium enhances the onset of nc-Si formation. The annealed samples present room temperature photoluminescence in the nc-Si and in the Er^{3+} ranges. HRTEM shows that often nc-Si is in contact with a small Er_2O_3 nanocrystal. The formation of nc-Si is detrimental for the Er^{3+} photoluminescence, probably because the excitation energy transfer from the amorphous matrix is more efficient than the nc-Si exciton-Er^{3+} coupling.

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Surface Structure Determination of Cr_2O_3 on Pd(111) studied by Angular Photoelectron Diffraction

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The increasing technological importance of metal oxides has fomented numerous surface science investigations of these materials. The ability to produce ordered metal oxide surfaces with well defined structure and chemical composition is critical to the success of these investigations. Chromium oxide surfaces, in particular, are interesting for a variety of reasons: for example, ultra thin and monolayer films of chromium oxide are predicted to show strong magnetic moment enhancement and may exhibit ferromagnetic behavior [1]. Such oxides are also important in catalysis. A variety of different strategies, mostly based on structure-reactivity relationships, have been put forward. It is recognized that the thickness of the oxide films, as they grow on metal substrates, constitutes a design parameter for creating materials of potential importance in catalysis[2]. The most stable phase of chromium oxide is the corundum structured a-Cr_2O_3, which is an important industrial catalyst, often used in polymerization reactions [3]. We grew thin films of chromium oxides on Pd(111) by chromium metal deposition in an oxygen atmosphere (1,0.10-6 mBar) on to a hot substrate to try and obtain crystalline order and good stoichiometry of the oxide film. Deposition for 5 (15) minutes produced 3.5 (12.0) thick chromium oxide films, which were subsequent annealed at approximately 823K. The electronic structure and the surface composition were determined by XPS. For the 3.5 film a well-ordered p(2x2) structure was observed. The thicker film showed a (R3xR3)R30^o structure, due to the formation of a stable a-Cr_2O_3 phase. To determine the atomic structure of the surface alloys, we used a combination of Low Energy Electron Diffraction (LEED) and Photoelectron Diffraction (PED) [4], exploring the forward and multiple scattering regimes, with photon energies corresponding to 700 eV synchrotron radiation and to a conventional x-ray source (Mg Ka radiation). The experimental spectra were collected using a hemispherical electron analyzer and synchrotron radiation from the SGM beam line of the Brazilian Synchrotron Laboratory.

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CHANGES ON IRON ELECTRODE SURFACE DURING HYDROGEN PERMEATION IN BORATE BUFFER SOLUTION

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Hydrogen interaction with iron oxide films at open-circuit potential (Eoc) and in the passive region (+0.30 VECS) was studied by using chronopotentiometry, chronoamerometry and electrochemical impedance spectroscopy techniques. The results were obtained in deaerated borate solution (BB, pH 8.4) solution before, during and after hydrogen permeation. The iron oxide film modification was also studied using in situ X-ray absorption near edge spectroscopy (XANES) and scanning electrochemical microscopy before and during hydrogen permeation. It was shown that hydrogen permeating the iron membrane reacts with the passive film existing on the electrode surface. It was seen that an almost identical active surface is obtained by cathodic reduction and by hydrogen permeation, in which an increase of the geometric area was observed after that. The increase of the surface area was confirmed by electrochemical impedance spectroscopy and optical microscope. The changes on passive iron oxide caused by hydrogen were detected by in situ X-ray absorption near edge spectroscopy (XANES) and in situ scanning electrochemical microscopy (SECM). The formation of hydrogen bubbles on a previously passivated iron electrode after certain time of hydrogen permeation was explaining as a consequence of the action of atomic hydrogen on the iron oxide which can lead iron surface to stabilize at a potential near or a little lower of water stability line where the only process is the hydrogen evolution due to the hydrogen recombination.

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Study of the luminescent emission in silicon based systems grown by PECVD technique

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In order to study the influence of quantum confinement effects and interface phenomena in the luminescent properties of silicon rich silicon oxynitride films, produced by PECVD technique, exhibiting luminescent emission in the visible region of the spectrum [1, 2], two types of silicon multilayer stacks were produced: a-Si/SiO2 stack and a-Si/SiNX stack. These configurations are based on the sequential arrangement of quantum wells with interfacial potential barriers. It is observed that the peak emission is tunable by the amorphous silicon layer thickness. These systems are utilized to explain our results on the luminescence observed in silicon rich where it is believed the exceeding silicon segregates as silicon nanocrystals or nanoclusters embedded in the oxynitride matrix, responsible for the confinement effects producing intense visible luminescence at room temperature. Both, the multilayers and the silicon rich silicon oxynitride films were characterized by: Raman scattering, Fourier Transform Infrared spectroscopy (FTIR), X-ray absorption near edge spectroscopy (XANES), photoluminescence (PL) and transmission electron microscopy (TEM). The results show that in both multilayers as deposited the silicon layer is amorphous and after heat treatment at temperature of 1000oC crystallization of the silicon layer occurs as indicated by Raman, TEM and XANES experiments. For the silicon rich silicon oxynitride films after heat treatment is observed a decrease in luminescence intensity and a shift of the band towards lower energies. This last result is compatible with the segregation of larger silicon nanocrystals. Even more a stage is attained where no luminescent emission at all was observed, indicating the absence of confinement effects due to the large crystal size.

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Studies of the water intercalation and difusion in Ni-Fluorohectorite nanostructures

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The system studied here is based on Hectorite, which is a 2:1 phyllosilicate with platelets formed by two inverted silicate tetrahedral sheets, sharing their apical oxygens with one octahedral sheet sandwiched in between. The fluorohectorites differ from natural hectorites in that the OH groups have been replaced by F. Ni-Fluorohectorite has the chemical formula per half unit cell Nix-(Mg32xLix)Si4O10F2. The proportion of the Li[+1] ions determines the surface charge of the platelets, which are held together in the stacked structure by an interlayer cation: in our case, x = 0.3 Ni[+2] ions per half unit cell. The Fluorohectorite has one of the largest values for particle diameter, up to 1 mm and water can be intercalated in between each platelet causing the clay to swell. For Ni-Fluorohectorite this intercalation process, which can be controlled by temperature and relative humidity, yields stable hydration states. The structures, referred to as having either 0, 1, and 3 intercalated water layers (0WL, 1WL and 2WL), are quite well ordered along the stacking direction. But, differently from the case where the intercalated ion was the Na, we show that the Ni-Fluorohectorite presents a meta-stable two-water layer regime completely dependent of the way the temperature is changing. Thus, in this experiment we vary the temperature in smaller and bigger steps in the region of this 2WL regime, to see how it is the dependence of the water intercalation behavior to the gradient of the temperature. In this way, x-ray diffraction patterns of a Ni-Fluorohectorite sample, mounted on a special cell, is registered as a function of temperature and time. The temperature of cell is controlled with a circulating water bath and, additionally, the sample is mounted on the top of a Peltier element to have finer temperature control. The open face of the cell is sealed with a Capton foil. The humidity is generated by a circulating humid air connected to a pump and measured by small sensor inserted close to the sample.

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A SAXS Study of the copolymer formed of sodium styrenesulfonate and methyl methacrylate in aqueous solution

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The irradiation of concentrated solutions of styrene sulfonate (StyS) in the presence of Safranine led to polymerization of the monomer [1]. There is no need of a co-initiator, as the relation between the oxidation and reduction potentials of the dyes and the monomer are sufficient as to assure an efficient electron transfer to form the semi-reduced dye and an initianting radical based on the monomer. In a sufficiently high StyS concentration, hydrophobic domains will be formed in which other monomers, like a methyl methacrylate (MMA), might dissolve. In view of this feature, the photo-initiated copolymerization of StyS and MMA (1:0,5) was attempted using the dye Safranine, which incorporaters readily in the StyS aggregates. The presence of MMA in the copolymer were deduced from the ^{1}HNMR spectra. SAXS data were collected at the small-angle scattering beamline on the LNLS (National Synchrotron Light Laboratory, Campinas, Brazil) using a two-dimensional detector (MarCCD), the experiment was carried out at a wavelength (λ) of 0.148 nm and a distance between sample-detector of 1094.4 mm covering the momentum transfer range of 0.13 nm^{-1} ¡ q ¡ 3 nm^{-1} (q = 4 π sin θ/ λ where 2θ is the scattering angle) at the concentration range between 1 and 5 mg/mL. In higher concentrations occurred a conformation change showing a higher order degree. Guinier analysis [2] at lower concentration show a polidisperse system with Rg around 8 and 5 nm.

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DXAS Studies of Water Intercalation in Nanosilicates

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Previous works of the of water diffusion process in the synthetic clay fluorohectorite has been studied at synchrotron mainly by utilizing the x-ray scattering technique. The controlling physical parameters are the temperature and humidity. For example, in these studies was observed the appearing of hysteresis behavior, Hendrix-Teller states [1], and the spatial width of the intercalation front was measured as its velocity decreases with time in a typical diffusion process [2, 3]. In summary, all these studies were done by observing the platelets moving wall behavior.

However, in this work we did a similar study observing the process of water intercalation in the same clay by using the LNLS Dispersive X-ray Absorption Technique (DXAS). For this work the probe utilized was the cation Ni^{2+} intercalated between the platelets and because of that the sample is called Ni-Fluorohectorite $(Ni_{0,3} - (Mg_{2,4}Li_{0,6})Si_4O_{10}F_2)$. The measurements were done by increasing the temperature from $5°C$ until $125°C$ and down, with and without humidity.

Fourier transform of the data shows that the position of the first peak corresponds to the average distance between nickel and the oxygen of the first coordination sphere [4]. The second sphere coordination is characteristic of Ni-Ni and Ni-Si interaction. Quantitative analyses made by using EXAFS longer energy range data are also discussed.

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Stability of Li insertion during the growth process of carbon nanotubes

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Lithium stable insertion during the arc discharge growth process is investigated by using resonance Raman spectroscopy as probe. The measurements were performed in two series of single–wall carbon nanotubes. A member of the series was prepared employing a lithium–contained catalyst and another the lacking lithium catalyst. A third sample was prepared by washing the Li–contained SWNTs. For the Li–catalyst prepared sample the spectrum is seen to be completely distinct from the spectrum of its Li–lacking counterpart. The differences are enhanced resonances for all modes currently attributed to metallic tubes. The results show that this effect can be tracked to the charge transfer occurring from lithium atoms intercalated interstitially into the bundles and inserted into the tubes. One Li–SWNT was found to keep intercalation under ultrasound washing, evidencing Li–insertion stability, probably due to those atoms localizing inside the tubes in the growth chamber prior to capping.

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QUANTITATIVE CHARACTERIZATION OF INGAP/GAAS INTERFACES FROM ATOMIC RESOLUTION HRTEM IMAGES

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A demand for characterization techniques with subnanometer spatial resolution has been created by the current level of material and device engineering. On this scale, spatial variations on chemical composition have important roles in devices functionality. HRTEM offers image resolution at this scale. Intensity contrast in HRTEM images contains chemical information. In 1990, Ourmazd proposed a method to derive quantitative chemical changes from HRTEM images (Chemical Mapping). Based on this method, we implemented a pattern recognition software that analyzes contrast variations in HRTEM image. Our software separates an image in small regions that occur periodically. From the analysis of the intensity distribution in these cells a chemical map is constructed. Because of image acquisition and sample preparation limitations our data sampling is limited to cells of 34 pixels (0.28 nm). This procedure is validated by HRTEM image simulation using JEMS software. The influence of experimental parameters (noise, thickness, defocus) on chemical sensitivity was carefully characterized by means of simulated images. This method was implemented for III-V semiconductors. Our objetive was to quantify interface parameters, such as abruptness and roughness. To do this, error functions (erf(x)) are fitted to profiles of the interface's chemical map. Using the derivatives of the fitted functions we determine the positions and widths of interfaces. To illustrate the applicability of the method we have characterized roughness in InGaP/GaAs quantum wells (QW). Between samples, interface growth schemes were altered by the addition of thin GaP or InP layers. We have chosen three parameters to classify a QW: its width, average depth and average lateral size of valleys on the interface. From this analysis, we show the influence of interfacial layer on interfaces structural characteristics. We concluded that a GaP layer on InGaP/GaAs interface and none on the inverted one minimized roughness. Structural data, such as presented, can aid optimization of interfaces in materials and the advancement of materials modeling.

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Structural Effects on the Conductance Quantization of Atomic-Size Contacts at Low Temperatures

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In this work, we have studied how thermal effects influence the atomistic aspects of the NW deformation and how these influence the quantum conductance behavior. The structure of NWs (Au, Ag) has been studied by means of time-resolved high resolution transmission electron microscopy (HRTEM); the NWs transport measurements were based on a mechanically controlled break junction operated in ultra-high-vacuum (UHV-MCBJ). The experiments were performed at 150 and 300 K. Our results have shown that at room temperature the atomic-size metal NWs are always crystalline and free of defects. Low temperature observations revealed that: i) Au NWs show extended defects, mainly stacking faults and twinning generated by partials Schockley dislocations; ii) Au NWs elongated along the [110] axis evolve to suspended atomic chains, while at room temperature they break abruptly; iii) the formation of smallest tubular Ag structure along the [001] axis; and iii) the enhancement of generation of suspended atomic chains (Au, Ag). In order to make measurements of conductance at low temperatures, some important modifications of the UHV-MCBJ were realized to cool the sample and obtain a high performance of the instrument. The global histograms of conductance of Au NWs showed that: i) a increase of the 1 Go peak intensity; ii) slight reduction of the NWs conductance due to scattering at defects and; iii) the peak at 2 Go shows a sub-structure, what is due to the occurrence of two different atomic arrangements with similar conductance. Finally, global histograms of Ag NWs indicated an increase of the 1 Go peak intensity, due to the formation of suspended atomic chains at low temperature is enhanced.

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Nanopartículas de Co suportadas em SiO_2: Síntese, Caracterização e Propriedades Catalíticas para a Reforma a Vapor do Etanol

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Nanopartículas coloidais de Co (Co-NPs) foram utilizadas na preparação de catalisadores de Co suportados. As Co-NPs foram obtidas por decomposição térmica do precursor octacarbonil dicobalto ($Co_2(CO)_8$), na presença dos surfactantes ícido oléico e óxido de trioctilfosfina (TOPO), sob atmosfera inerte (Ar). Os catalisadores Co-NPs/SiO_2 foram obtidos por impregnação de uma suspensão coloidal de Co-NPs sobre a SiO_2(9%). O efeito do solvente utilizado na etapa de precipitação das partículas e a variação da razão ácido oléico/precursor nas propriedades catalíticas para a reforma a vapor do etanol foram investigados. As Co-NPs e os catalisadores foram caracterizados por meio de Microscopia Eletrônica de Transmissão (TEM), Difração de Raios X (XRD), Área Superficial Específica (SBET) e Espectroscopia na Região do Infravermelho com Transformada de Fourier do CO adsorvido (FTIR-CO). Variando-se a razão ácido oléico/precursor (0,2 0,4 e 0,8) foi possível obter partículas ϵ-Co com uma faixa de tamanho entre 2 e 17nm. Os resultados de quimissorção de H_2 e CO sugerem que a fração de sítios de Co acessíveis, tanto ao H_2 como ao CO, dependem do tamanho das partículas e do ácido oléico residual. Os catalisadores preparados a partir de Co-NPs apresentaram-se ativos para a reações de reforma a vapor do etanol e a seletividade dos catalisadores depende tanto do tamanho de partícula como das condições de sínteses dos catalisadores (agente precipitante das partículas). O aumento do tamanho das partículas leva a uma diminuição da atividade catalítica para as reações de reforma devido a uma menor Área superficial e um menor número de sítios de Co acessíveis. Para um mesmo tamanho de partícula a precipitação com metanol apresentou um efeito positivo em relação ao etanol, visto que o metanol remove o ácido oléico residual tornando a superfície deste catalisador mais reativa para as reações de reforma.

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Atomic scale composition and strain mapping of self-assembled $\mathbf{Si_{1-x}Ge_x}$/Si(001) islands by quantitative high resolution transmission electron microscopy

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Self assembled islands in heteroepitaxial semiconductor systems have been intensively studied, because of their optoelectronic and electronic properties. In these semiconductor quantum dots the chemical composition is the most important factor that determines their size, stability and electronic properties. Strain and interdiffusion are key parameters that influence island growth and therefore essential in discerning their properties. The study of these issues is thus a fundamental step for the understanding of island formation and evolution. The $Si_{1-x}Ge_x$ islands grown on Si (001) have emerged as prototypical model systems for the study of self assembled semiconductors nanocrystals. There are presented atomic scale bi-dimensional maps of chemical composition (Ge%) and elastic strain in $Si_{1-x}Ge_x$/Si(001) islands growth by CVD method [1]. The elastic strain and chemical information was obtained, using a method of geometric phase analysis (GPA) [2] applied to high-resolution transmission electron microscopy images. The GPA method is a powerful technique that allows to quantify small geometrical changes in the periodicity of phase contrast TEM images, which allows to calculate the displacements fields, strain maps and composition (from Vegards Law). To improve the accuracy of quantitative maps the images used for GPA processing were obtained from an exit-plane wave-function reconstruction process using a focal series method [3]. The focal series reconstruction is a useful method for restoration of a aberration-free exit surface wave function from a series of images, obtaining a high quality image free of aberrations and improving the point to point resolution, from 0.17 nm to 0.13 nm in the HRTEM Jeol JEM 3010 URP (300 KV) at the LME/LNLS. The bi-dimensional composition and strain maps show a Si-rich edge and a Ge-rich alloying at the center, with high concentration of Ge on the surface (100%) and a high concentration of Si near to the substrate. The composition profiles are slightly related to islands size and shape, which are studied in groups with 8, 10 and 12 nm height.

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Síntese de nanocatalisadores Pt-NPs/CeO_2-Al_2O_3: síntese, caracterização e propriedades catalíticas em reações de reforma do metano

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No presente trabalho é descrito um novo método para preparação de nanocatalisadores, com nanopartículas de Pt (Pt-NPs) suportadas em CeO_2-Al_2O_3. Para clarear o efeito do suporte na atividade e estabilidade desses catalisadores, as amostras foram testadas em reforma a vapor do metano (RVM) e OPM. Pt-NPs de ∼3 nm foram obtidas por um método coloidal, para garantir uma alta homogeneidade na distribuição dos tamanhos. A solução de Pt-NPs foi adicionada durante a síntese sol-gel dos suportes, para a obtenção dos nanocatalisadores Pt-NPs/Al_2O_3 e Pt-NPs/CeO_2-Al_2O_3. As amostras foram caracterizadas por fisissorção N2, DRX, TEM, FTIR-CO e medida de dispersão a partir da velocidade de reação de desidrogenação do ciclohexano. Os resultados de TEM das Pt-NPs coloidal, Pt-NPs/Al_2O_3 e Pt-NPs/CeO_2-Al_2O_3, depois de calcinação a 773K em ar e depois de reação de OPM a 1073K por 24h mostraram que as Pt-NPs estão bem dispersas no suporte e não se observa modificações pronunciadas no tamanhos das NPs ou aglomeração pela calcinação e reação de OPM. O FTIR-CO adsorvido reflete a estreita distribuição de tamanho de Pt-NPs e similaridade de densidade eletrônica da Pt nas 2 amostras. No entanto, a amostra contendo Ce apresentou supressão da banda de CO adsorvida na forma de ponte, sugerindo que a superfície das partículas de Pt é modificada por um efeito geométrica do CeO_x, que recobre a superfície da partícula. Os resultados de Eaap, obtidos para a RVM, apresentaram-se bastante similares, porém os valores de TOF_{CH4} para Pt-NPs/CeO_2-Al_2O_3 apresentou-se de 2 vezes maior que para o Pt-NPs/Al_2O_3, apesar do mesmo tamanho de NPs. Este resultado aponta para uma influência do suporte da atividade desses catalisadores em RVM, o que está de acordo com resultados obtidos para catalisadores de Pd/xCeO_2-Al_2O_3 obtidos por impregnaçãox[3]. A alta atividade do catalisador contendo Ce possivelmente está associada a maior acessibilidade do CH_4 aos sítios de Pt, devido a maior remoção de espécies C*, adsorvido na superfície, pelo mecanismo de transferência de oxigênio pela céria do suporte. O uso das NPs coloidais levou a catalisadores com maior controle no tamanho das partículas e a caracterização revelou importante papel das espécies de Ce na atividade desses catalisadores.

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Radioluminescence Properties of Rare Earths Doped $SrAl_2O_4$ and $Ca_{12}Al_{14}O_{33}$ Nanopowders

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The scintillators are luminescent materials that absorb ionizing radiation and converts it into light within the region of the visible/IR. This property is named radioluminescence. A long lasting phosphor (LLP) is a material that shows bright light emission after the exposure to ionizing or UV radiation. The LLP elements, which emit photons for a long period after stopping the irradiation without any external excitation, are a promising candidate as simple and easy-to-use radiation detection elements, especially for digital radiography. The aim of this work is the study the radioluminescent (RL) emission of rare earths doped $SrAl_2O_4$ and $Ca_{12}Al_{14}O_{33}$ nanopowders prepared via new proteic sol-gel method. Nanopowder of $SrAl_2O_4$ and $Ca_{12}Al_{14}O_{33}$ pure a doped with rare earths was prepared via a sol-gel proteic methodology, using coconut water as the initial solvent. The crystalline structure, particle size and morphology of samples were determined using XRD and AFM. The RL emission was obtained when the sample was exposed to the X-ray beam of Cu Kα radiation. XEOL measurements were done in the XAFS-2 beamline at the LNLS in the region of the RE absorption edges. The prepared materials presented single crystalline phase, confirmed by XRD measurements. AFM results indicate that the average particle size is about 53nm. The RL measurements of $SrAl_2O_4$:Eu^{2+}, Dy^{3+} exhibit an intense peak around 520nm followed by a emission peaking at 570nm attributed to emissions of Eu^{2+} and Dy^{3+}, respectively. It was observed that the intensity of RL emission during irradiation with X-rays decreased as a function of the irradiation time, indicating the build up of radiation damage in the nanopowders. These initial results reveal that new proteic sol-gel method showed useful in production of nanopowders of SrA_l2O_4 and $Ca_{12}Al_{12}O_{33}$ pure a doped with rare earths. The analysis of the RL results point out to a possible application of the produced materials as scintillators.

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Estudos de sistemas altamente diluídos

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Neste trabalho estudamos soluções homeopáticas, adequadamente preparadas em uma farmácia de manipulação, por meio de uma língua eletrônica. Filmes ultrafinos de quitosana, lignina, polipirrol, perileno butil (BuPTCD) e um ionômero de poli(estireno-co-metil metacrilato) foram depositados sobre eletrodos interdigitados de ouro possuindo 50 pares de dígitos com 10μm de largura e 10μm de separação entre eles, fabricados no Laboratório Nacional de Luz Síncroton (LNLS). Os filmes foram depositados através das técnicas Langmuir-Blodgett e de automontagem. A aquisição de dados foi realizada com o protótipo feito na Faculdade de Ciências e Tecnologia de Presidente Prudente (UNESP). Por envolver medidas estáticas, esperamos 30 minutos após a imersão das unidades sensoriais no líquido analisado para estabilização do sistema. Entre uma medida e outra os eletrodos foram cuidadosamente lavados em água destilada, obtida em um sistema Milli-Q (Direct-Q System). Todos os frascos utilizados foram adequadamente limpos antes do uso. Longe da polêmica envolvendo homeopatia, com a língua eletrônica diferenciamos amostras distintas (aurum, lachesis e lycopodium) em diferentes graus de diluição (5CH e 30CH).

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Methylene Blue interaction with phosphatidylcholine and Cardiolipin in liposome bilayer environments: small angle X-ray scattering and raman studies.

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In the last decade a photoactive phenotiazine Methylene Blue has been recognized as a potential candidate for application as an non-toxic photosensitizer drug in photodynamic therapy (PDT) [1]. MB binds to the cell mitochondrion membrane, which is made up for 20-30 % in mass of Cardiolipin, and 45 % of saturated and unsaturated phosphatidylcholine/ethanolamine phospholipids. In this work, the binding properties of MB affecting phospholipid bilayer structure and shape in unilamellar liposomes of anionic Cardiolipin and zwitterionic DOPC and DPPC, were accessed by SAXS (LNLS, Campinas, Brazil). Structural features of drug bound to phospholipid liposomes were monitored by Raman spectroscopy in a Raman Renishaw Microscope RM2000 with 785 nm laser excitation. SAXS profile of 50 mM liposomes were broadned with scattering vector q values of 0.12 $^{-1}$ for Cardiolipin, and 0.10 with smaller shoulder at 0.19 $^{-1}$ for DOPC or DPPC, providing repeated distances values of bilayers around 53 and 62 , respectively. Sharp Bragg peaks emerged at $q = 0.12$ $^{-1}$ and 0.23 $^{-1}$ in Cardiolipin SAXS curve, indicating strong changes of liposome structure up to 400 mol% of MB. Raman data showed that the energy and amplitude in monomeric MB vibration modes were unchanged upon interaction with liposomes solutions and casting-like films. SAXS data suggest a strong presence of Cardiolipin-MB multilamellar complexes with tighly packed bilayers separated 57 among them, instead mostly unilamellar liposomes observed to zwitterionic DOPC and DPPC, whereas raman results evidenced that any drug moiety are affected in specific interaction with all phospholipids. Therefore, a preferential drug location nearby the polar headgroup-bulk interface of both phospholipids is ascribed, while electrostatic forces should be more relevant in the interaction of cationic MB with negatively double charged Cardiolipin.

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Estudos em solução de ligninas submetidas a diferentes processos de deslignificação e oxidação

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O bagaço e a palha de cana-de-açúcar são constituídos basicamente de celulose, hemicelulose e lignina. cerca de 25 % do peso seco do bagaço é constituído de lignina. Individualmente cada componente possui uma infinidade de aplicações como fabricação de papel, açúcares redutores, álcool e síntese de novos produtos químicos, porém para isso é necessária uma etapa de separação para aproveitamento destes componentes. Existem diversos processos para promover a separação dentre eles: o processo soda, soda/antraquinona, kraft entre outros. Após a separação cada componente poderá sofrer modificações para obtenção do produto final desejado. Essas modificações podem ser químicas, como reações de oxidação, físicas, por extrusão ou microbiológica, por fermentação. As reações de oxidação em ligninas são utilizadas para obtenção de produtos com características quelantes e dispersantes que podem ser utilizadas desde estações de tratamento de efluentes até produtos auxiliares para indú stria têxtil. Dados de SAXS de ligninas submetidas a diferentes tipos de oxidação foram coletados na linha de espalhamento de raios-X a baixo ângulo do LNLS utilizando detector bidimensional, $\lambda = 0.148$ nm e distância amostra-detector de 485.6 mm. Foram estudadas ligninas submetidas a oxidações químicas, tanto em meio alcalino como em meio ácido, e oxidações enzimáticas, utilizando tanto a enzima lacase comercial como a obtida a partir da batata. Comparando-se os resultados obtidos para ligninas obtidas por processos de deslignificação diferentes, pode-se afirmar que as ligninas de processo antraquinona possuem maior globularidade do que ligninas obtidas por processo soda. Além disso, o processo antraquinona gera fragmentos de ligninas menores do que o processo soda. Como neste último foram detectados fragmentos grandes, as amostras foram submetidas a filtragem. Pode-se verificar também que as ligninas oxidadas em meio alcalino possuem mudança conformacional com o aumento de pH e a quantidade de agente oxidante utilizada. Estas mudanças são verificadas até um limite de pH de 13.30 e 40 volumes de agente oxidante, concentrações maiores do que as citadas não possuem influência significativa.

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Caracterização estrutural do sistema InP(QD)/InGaP/GaAs(001) usando difração múltipla de raios-X com radiação síncrotron

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Neste trabalho, as reflexões híbridas coerentes (CHR)[Morelhão e outros, Appl. Phys. Lett., 73(15), 2194 (1998)], da estrutura semicondutora InGAP/GaAs(001) que aparecem nas varreduras Renninger com radiação síncrotron, são utilizadas na caracterização estrutural desses materiais. As varreduras Renninger para estruturas epitaxiais semicondutoras mostram, pelo menos, duas interessantes regiões para estudo: i) a região em torno do espelho de simetria para $\phi = 0^o$, onde aparecem as reflexões BSD (Bragg-superfície) e que permitem a investigação da distribuição de tensão ao longo da superfície do substrato das estruturas, i.e., a interface camada/substrato, pois o feixe secundário se propaga ao longo dessa superfície; ii) a região em torno do espelho de $\phi = 45^o$, onde aparecem as reflexões híbridas coerentes que são seqüências diferentes de reflexões dentro das estruturas camada/substrato, onde as reflexões secundária e de acoplamento estão em diferentes redes (camada e substrato), e que podem dar informação sobre o comprimento de coerência na mencionada interface. Camadas de InGaP foram crescidas sobre substratos de GaAs(001) por epitaxia de feixe químico (CBE), no LPD,IFGW,UNICAMP, e em algumas das amostras foram depositados pontos quânticos de InP sobre a camada de InGaP. Varreduras Renninger usando a reflexão primária (002) do GaAs e InGaP foram realizadas na estação XRD1 do LNLS. Através de figuras de pólo na direção [001] obtidas com curvas de rocking (varredura ω) espaçadas de 15^o foi possível constatar a presença da reflexão híbrida (1 -1 3)(1 -1 -1), em posições específicas de ϕ, ou seja, próximas da posição angular para a reflexão correspondente ao caso de 4-feixes simultâneos. Pode-se observar em cada figura de pólo as contribuições do substrato, da camada e das híbridas, obedecendo a simetria para o eixo 4 (vetor primário). Foram também realizados os mapeamentos ω:ϕ para as CHR, de onde pode-se obter a melhor condição para a observação dessas reflexões híbridas. A tensão ao longo das direções [1 1 0] e [-1 1 0] para as estruturas analisadas (com e sem pontos quânticos) será determinada a partir das medidas das posições angulares correspondentes à entrada e à saída dos picos BSD (1 -1 1), (1 1 1), (-1 -1 1) e (-1 1 1) da esfera de Ewald.

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Caracterização Eletroquímica e Morfológica de Compósitos NTC/PDMcT/PAni

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Três diferentes tipos de supercapacitores são comumente descritos na literatura, dependendo da natureza do material ativo utilizado. Supercapacitores baseados em carbono ativado, usando eletrólito orgânico, são os sistemas mais promissores, apresentando melhor desempenho e custo acessível. Um desses materiais a base de carbono que vem sendo bastante estudado e utilizado para esta aplicação são os nanotubos de carbono (NTC). Cabe ressaltar que quando estes materiais são associados a polímeros condutores formando compósitos, apresentam excelentes propriedades eletrônicas e mecânicas, melhorando o seu desempenho como eletrodos em supercapacitores. Tendo isso em vista, este trabalho teve como objetivos a caracterização eletroquímica e morfológica de compósitos de NTC/PDMcT/PAni, visando a aplicação como eletrodos em supercapacitores. Primeiramente, os nanotubos foram funcionalizados em solução ácida (H_2SO_4/HNO_3 3:1) e em seguida, dispersos em ultrassom. A polianilina foi sintetizada via química em solução ácida contendo pós de NTC/PDMcT já sintetizados e dispersos previamente. Os voltamogramas cíclicos do compósito NTC/PDMcT/PAni apresentaram um aspecto retangular caixa, indicando a predominância de processos capacitivos. Os valores de carga determinados foram superiores aos dos compósitos de NTC/PAni e de seus materiais constituintes. A morfologia do compósito NTC/PDMcT/PAni manteve as características da PAni, indicando que esta revestiu de maneira homogênea os NTC. A ausência dos cristais característicos do PDMcT foi um indício de que este atuou como agente ligante entre a PAni e o NTC. A condutividade eletrônica do compósito NTC/PDMcT/PAni (96 S cm^{-1}) foi superior àquelas obtidas para a PAni (3,2 S cm^{-1}), NTC (59 S cm^{-1}) e PDMcT (10^{-5} S cm^{-1}). A capacitância específica para o compósito foi de 284 F g^{-1} enquanto para seus materiais constituintes: NTC, PAni e PDMcT foram 44 F g^{-1}, 68 F g^{-1} e 4 F g^{-1}, respectivamente. Os altos valores de capacitância específica e condutividade eletrônica obtidos para o compósito indicaram uma intensificação de suas propriedades, resultante da provável interação entre seus materiais constituintes.

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On the nucleation of GaP/GaAs and the effect of buried stress fields

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In this work we study the growth by chemical beam epitaxy (CBE) of GaP islands on a GaAs buffer layer and under the influence of the InP dots growth on the InGaP layer with periodic compositional modulation. The topographical analysis of this samples, was mede with atomic force microscopy (AFM). High resolotion trasmission electron microscopy (HRTEM) images was made for structural analysis of the GaP islands in the first case and for study the relation between GaP dots and the InP dosts in the template InP/InGaP. The relaxation process, in the two cases, was studied with grazing incidence x-ray diffraction (GIXD) measurements.

The characteristics of GaP films grown on unstressed GaAs were evaluated by means of surface roughness and size distribution for GaP nucleation islands, as well as from the RHEED patterns formed during deposition and cool down. Even though GaP/GaAs growth is assumed to occur in theWolmer-Weber mode, a two-dimensional (2D) RHEED pattern was observed. HRTEM images for this sample, shown a wetting layer presence ab1nm thickness and smal islands (height and radius in the range of 1-2nm and 10-20nm respectively). This characterizes the Stranski-Krastanov growth mode as being predominat mode, em agreement with the results suggested by the RHEED pattern.

The relation between the ordering of the GaP dot layer and the buried InP template was investigated by cross-section HRTEM measurements. Our results show that dots are vertically anti-correlated, with GaP dots nucleating in the position between two InP dots. In this latter case, GIXD measurements have shown that the strain relaxation rate is not significantly altered with regard to the GaP dots grown on unstressed GaAs, although the strain at the base of the dots is lowered when the template is used.

Acknowledgements:

Phase Equilibria and Structures of CTAPAn complex salts with water and n-alcohols

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This work reports studies on phase behavior of mixtures of a complex salt formed by a cationic surfactant and an oppositely charged polyelectrolyte, hexadecyltrimethylammonium polyacrylate, in ternary mixtures containing water and different alcohols: decanol, octanol, hexanol and butanol. The liquid crystalline structures formed were identified by small angle X-ray scattering measurements, which also provided information about changes in the size of the aggregates as a function of the system composition. For these ternary systems a large alcoholic isotropic phase region (L2 phase) was observed. This region increases with the decrease of the alcohol chain length, which is interpreted as consequence of the entropy of mixture, which is higher for small molecules. L2 phase samples were analyzed by NMR self diffusion, rheology and SAXS measurements, aiming to elucidate the type of aggregates that compose this isotropic phase. NMR self diffusion measurements showed that the surfactant diffusion coefficient increases with the increase in the water content. A possible explanation for this fact is that a dissociation process of the complex salt takes place, and it is favored by the increase of the dielectric constant of the medium. SAXS measurements revealed spectra with sharp correlation peaks, which probably are related to the distance between elongated inverted micelles. It was also observed that the correlation peak became sharper with the increase in the water content. If a dissociation process really occurs, as pointed out by NMR results, the repulsive force between these aggregates would also increase, leading to a shaper peaks. Finally, to characterize the viscoelasticity of the alcoholic isotropic phase dynamic rheology measurements were performed. The results showed typical behavior for elongated micelles with entanglements: the viscous modulus is large in lower frequencies and the elastic modulus is larger in higher frequencies.

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Feasibility study of diffusion effects at interfaces in layered thin films by depth profiling using X-ray microbeam under grazing-exit conditions

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Characterization techniques sensitive to the chemical and physical properties of the material surface are of key importance in modern science and technology. We have been explored in this opportunity the capabilities of surface analysis and spatial resolution of the micro x-ray fluorescence spectrometry technique under grazing-exit conditions to inspect the feasibility of performing a nondestructive study of surfaces and interfaces in patterns of layered thin films samples. For this purpose, layered materials of Au ($20nm$) and Cr ($40nm$) thin films were deposited by sputtering on a polished silicon substrate. The measurements were performed on samples as they were deposited and after a thermal treatment to 200^oC and 400^oC in order to induce diffusion at the Cr/Au interfaces. A combined angular and spatial scanning across a perpendicular line between different patterns of layer thin films was performed to follow possible changes of the chemical depth profiling. Some results will be presented consisting of a comparison between the experimental data and theoretical calculation based on a multi-layered model in which a matrix approach is used for the evaluation of the electromagnetic field in the stratified medium.

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Caracterização do equilíbrio de fases e determinação de estruturas em sistemas contendo óleos e surfatantes siliconados utilizando SAXS

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Óleos e surfatantes siliconados apresentam grande potencial industrial devido a algumas características específicas, podendo ser empregados em uma grande variedade de produtos, tais como, cosméticos e produtos farmacêuticos. Seu comportamento é diferenciado daquele apresentado por solventes hidrocarbonetos, devido à baixa energia coesiva, fato que dificulta a incorporação de água neste solvente, mas que pode ser obtida com o uso de surfatantes siliconados. Apesar de sua importância, a literatura contém muito poucos relatos caracterizando estes sistemas ternários. A aplicação de técnicas como espalhamento de raios-X em baixo ângulo (SAXS) pode ser utilizada para uma melhor compreensão destes sistemas. Neste trabalho utilizou-se SAXS para caracterização de equilíbrios de fases e determinação de estruturas formadas por um surfatante siliconado em sistemas binários e ternários. O diagrama de fases apresentou uma predominante região de microemulsão (monofásica, transparente, isotrópica) de água-em-óleo (L_2). Estas amostras apresentam viscosidade variando de baixa viscosidade a géis. Uma outra observação do sistema é referente à formação de estruturas líquido-cristalinas na forma de lamelas (L_α) e estruturas hexagonais (H_i). Uma característica diferente comparada a um outro sistema estudado foi a ausência da região de microemulsão óleo em água e a diminuição da quantidade de água incorporada no sistema, que neste caso é de aproximadamente 10%.

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CARACTERIZAÇÃO E AVALIAÇÃO DE FILMES METÁLICOS PARA USO EM ULTRA-ALTO VÁCUO

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A construção de câmaras de ultra-alto vácuo para aceleradores de partículas exige a obtenção de pressões de operação na faixa de 10^{-8} Pa, particularmente mais difícil para as câmaras de vácuo, com uma relação entre o comprimento e a seção transversal de aproximadamente 150:1. Dentre os vários procedimentos usados para obter esta condição, destaca-se o recobrimento interno com um filme de metais capazes de absorver gases, chamados de NEG (do inglês "Non-Evaporable Getter"). Estes metais, para poderem ser usados em aceleradores síncrotron, não podem conter gás em sua superfície e devem ser depositados por toda a superfície interna da câmara, tornando-a numa bomba de vácuo. Usualmente estes materiais são constituídos por elementos de grande reatividade e solubilidade (no caso, Ti, Zr e V) a temperatura ambiente para o oxigênio e outros gases tipicamente encontrados em UAV (H_2, CO e CO_2), além de ter difusibilidade para desfazer a camada superficial oxidada em baixa temperatura (<700 K), a chamada temperatura de ativação. O objetivo deste trabalho é caracterizar e avaliar filmes metálicos produzidos por pulverização magnética catódica da liga TiZrV e de Au para uso em ultra-alto vácuo quanto a suas estruturas cristalinas, morfológicas e envelhecimento revelando quanto da propriedade de absorção de gás a abaixa temperatura pode ser atribuídas à estrutura formada devido ao processo de posição ou a reatividade química dos elementos. Foram feitas análises de microscopia de força atômica, microscopia de varredura de alta resolução, microscopia de transmissão de alta resolução, espectroscopia de fotoelétrons excitados por raios x, difração de raios x, espectroscopia de retroespalhamento de Rutherford e dessorção estimulada por fótons. Os materiais produzidos foram comparados com amostras de TiZrV produzidas por uma empresa, deixando claro que as características desejadas estão vinculadas à estrutura nanométrica do material e que esta é sensível a tratamentos térmicos de forma acentuada.

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Índice Remissivo