23ª RAU

REUNIÃO ANUAL DE USUÁRIOS DO LNLS/CNPEM

26 E 27 FEVEREIRO 2013

RESUMOS

DE TRABALHOS CIENTÍFICOS

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LNLS sirius
CNPEM
Ministério da Ciência, Tecnologia e Inovação
GOVERNO FEDERAL
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REUNIÃO ANUAL DE USUÁRIOS DO LNLS/CNPEM

26 E 27 FEVEREIRO 2013

23ª Reunião Anual de Usuários do LNLS/CNPEM
Laboratório Nacional de Luz Síncrotron
Campinas, 26 e 27 Fevereiro de 2013

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Prefácio

O Comitê de Usuários do LNLS saúda a todos os participantes da 23ª Reunião Anual dos Usuários do Laboratório Nacional de Luz Síncrotron (LNLS).

Este encontro ocorre ao mesmo tempo em que o LNLS dá um importante passo para o desenvolvimento da ciência brasileira: o início da construção de Sirius, a nova fonte de luz Síncrotron, agendada para maio próximo. Sirius vai operar com energia de 3 GeV e emitância de 0.28 nm.rad, das mais baixas em todo o mundo. Está programada, inicialmente, a construção de 13 linhas experimentais, abrangendo grande parte das pesquisas desenvolvidas pelos mais de 1.400 pesquisadores que já utilizam as atuais instalações do LNLS. Sirius terá área de 30.000 m2 e capacidade para abrigar até 40 estações experimentais.

É fundamental que, nesse período, os usuários estreitem contato com a direção do LNLS por meio do Comitê de Usuários, para que possam acompanhar o andamento do projeto.

Agradecemos o esforço do Comitê Científico que muito auxiliou na seleção de diversos cientistas convidados e dos resumos que serão apresentados nesta edição da RAU. Foram selecionadas um total de 50 apresentações orais e 94 apresentações em forma de pôster, além das quatro tradicionais seções plenárias. Também não podemos deixar de agradecer a Diretoria do LNLS e a todos os seus funcionários que apoiaram a organização deste evento.

Desejamos a todos uma proveitosa e frutífera Reunião dos Usuários do LNLS,
Comitê de Usuários da 23ª RAU

Orientações aos Participantes

Prezado Participante, seja bem-vindo à 23ª Reunião Anual de Usuários. O Comitê Organizador pede sua atenção para as informações abaixo.

1. Credenciamento

O credenciamento no evento (retirada de material, crachás de identificação e assinaturas dos recibos para agências de fomento - FAPESP/Capes) será no seguinte horário:
26/02, terça-feira, das 8:00 às 12:00

2. Crachá de identificação

O crachá de identificação deve ser usado durante toda a reunião.

3. Sessões

As Comunicações Orais ocorrerão em diferentes salas do hotel Premium Norte: Sala Plenária, Milão, Ibiza, Madrid e Roma do Centro de Convenções, conforme programação.

4. Sessão de Pôsteres

A sessão de pôsteres ocorrerá nos dias 26 e 27 de fevereiro. Seguem os horários para fixação e retirada dos mesmos.

Data	Horário montagem	Horário de retirada
26/fev – das18:00 às 19:10	Das 8:00 às 12:00	19:20
27/fev – das 10:10 às 11:40	Das 8:00 às 9:00	Até às13:00

O local de fixação do pôster estará sinalizado por etiqueta com a numeração correspondente à área de pesquisa do apresentador.
Os organizadores da RAU não se responsabilizam por danos ou perda do pôster, e também não se comprometem a embalar, remover ou transportar o material.

5. Hotel

O hotel oferece desktops no Lobby para uso de hóspedes e participantes da 23ª RAU.
O estacionamento está disponível para uso durante a reunião – vagas limitadas.

6. Almoço

Os almoços dos dias 26/02 e 27/02 serão servidos no restaurante do hotel, a partir do horário indicado na programação.

7. Segurança

Pedimos a todos que fiquem atentos à segurança de seus objetos pessoais de valor. O CNPEM e o Hotel Premium Norte não poderão se responsabilizar pela segurança de tais objetos.

8. Certificado

Os certificados serão enviados por email até o dia 30 de março de 2013. Para recebê-los, os participantes deverão assinar a lista de presença no balcão de credenciamento no dia 26 de fevereiro.

O Comitê de Organização deseja a todos os participantes uma agradável e produtiva reunião.

Guidelines to Participants

Dear Participant, welcome to 23rd LNLS Users Annual Meeting. Please, read carefully the following instructions.

1. Registration

Registration at the event (identification badge, personal kit and signature on the receipt for the participants that have financial support) will be done following the schedule below:

Tuesday, 8 a.m to 12 p.m.

2. Identification Badge

The identification badge must be used at all time during the meeting.

3. Sessions

The Oral Communication Sessions will be held in the rooms: Milão, Ibiza, Madrid, Roma at the Convention Center and also in the plenary room in the Premium Norte Hotel.

4. Posters Session

The poster session will be on February 26th and 27th, following the schedules for fixing and dismantle:

Date	Fixing	Dismantle
Feb 26th – 6 p.m to 7:10 p.m	8 a.m to 12 p.m	7:20 p.m
Feb 27th – 10:10 a.m to 11:40 a.m	8 a.m to 9 a.m	until 1 p.m

The local where the poster must be fixed will be indicated with the corresponding research area of the author.

The organizing committee and staffs are not responsible for packing, removing or shipping your poster neither responsible for any loss or damage of it.

5. Hotel

The hotel offers desktop computer at the lobby area for the guest and participants' use during the event.

The parking lot is also available during the meeting.

6. Lunch

Lunch will be served at the restaurant, following the schedule in the program.

7. Security

Please, pay attention to your personal belongings. CNPEM and Premium Norte Hotel cannot be responsible for the safety of any objects.

8. Certificate

Certificates will be sending by email until March 30th, 2013. To receive this document, the participants should sign the presence list available on the registration desk on Feb 26th.

The Organization wishes all participants a pleasant and productive meeting.

Agenda, February 26th

08:00 - 09:00	**Reception /Registrations**
09:00 - 09:15 Plenary room	**Opening** Antônio José Roque da Silva Director of LNLS
09:15 - 10:15 Plenary room	**Status do LNLS e Sirius** Yves Petroff and Harry Westfahl Scientific Director of LNLS
10:15 - 10:20	**Official Photo**
10:20 - 10:40	**Coffee Break**
10:40 - 11:40 Plenary room	**Plenary I** Lucia Zuin (Canadian Light Source - CLS)
11:40 - 12:40 Plenary room	**Plenary II** Jan Ilavsky (Advanced Photon Source, Chicago, USA)
12:40 - 14:00	**Lunch**
14:00 - 16:00 Plenary room	**Sirius Beamlines**
16:00 - 17:40	**Oral Communication I**
Plenary room	Electronic Structural Properties I
Milão room	Structural Biology
Ibiza room	Surfaces Interfaces and Nanosystems I
Madrid room	Atomic Science
Roma room	Structural Materials and Industrial Applications
17:40 - 18:00	**Coffee Break**
18:00 - 19:10	**Posters Session I**

Oral Communication I, February 26th

Electronic Structural Properties I

Room	Amadeus (Plenary room)
16:00	**Caracterização estrutural do sistema LaPr(CaSr)MnO a baixas temperaturas** Gabriel Ricardo Gomez Eslava
16:20	**Electronic structure and magnetic states in La1¡xSrxCoO3 investigated by photoemission and x-ray absorption spectroscopy** Octávio Augusto Schweicerski Sobreiro
16:40	**Estudo da Estrutura Atômica e eletrônica de Materiais ferroelétricos cerâmicos através da técnica de XAS: É possível avançar mais?** Valmor Roberto Mastelaro
17:00	**Electronic structure of SrRuO3** Eduardo Bonini Guedes
17:20	**The Effect of the Organic Precursor on the Structural and Magnetic Properties of Nanoparticles CoFe2O4 Synthesized by Co-precipitation Method** Pablo Pedreira Pedra

Structural Biology

Room	Milão
16:00	**The macromolecular complex from Escherichia coli: Selenocysteine Synthase and its interactions with specific tRNAsec** Vitor Hugo Balasco Serrão
16:20	**Inhibition studies of human PTP1B, a phosphatase involved in cancer** Valéria Scorsato
16:40	**Prospecção de Ligantes para o Receptor Ativador de Proliferação de Peroxissomos** Aline Villanova Bridi
17:00	**Structure of the Canavalia maritima lectin (ConM) complexed with a dinucleotide** Derek Barroso Holanda Asp Vieira
17:20	**Analisis de los efectos de exposicion a arsenico por medio de imagenes 3D obtenidas por XRF-microtomografia en el LNLS** Guillermina Azucena Bongiovanni

Surfaces Interfaces and Nanosystems I

Room	Ibiza
16:00	**Magnetic properties, electronic structure and morphology of PtCo and PtCo/Au dumbbell nanoparticles** Martín Daniel Mizrahi
16:20	**Caracterización mediante Fe K XANES del entorno local del Fe en catalizadores Fe-Si aptos para la producción de nantubos de carbono** Facundo Carlos Herrera

16:40	**Structure of Silver-Containing Sol-Gel Hybrid Materials and its Performance as Biocide Coatings** Raúl Procaccini
17:00	**Observation of an anomalous van der Waals gap near the surface of Bi2Te3 by scanning tunneling microscopy and X-ray crystal truncation rod scattering** Paula Mariel Coelho Neto
17:20	**Deposition and Characterization of Thin Films of Ti-Nb-Zr Deposited on Si(111) and Stainless Steel** Pedro Augusto de Paula Nascente

Atomic Science

Room	Madrid
16:00	**X-ray absorption spectroscopic and multiple scattering formalism investigation of a possible S-Cu interaction in the Cu-sulfenilcarbonilic ligands** Félix Gregorio Requejo
16:20	**Fragmentation Mechanisms of Trifluoroethanol, CF3CH2OH, following Photoexcitation with Synchrotron Radiation between 100 and 1000 eV** Yanina Belén Bava
16:40	**Chemical shifts in X-ray photoelectron spectroscopy caused by pH-induced protonation on methionine and cysteine aqueous solutions** Áderson Miranda da Silva
17:00	**Fotoionização da molécula SF6 nas proximidades da camada K do enxofre** Anderson Herbert de Abreu Gomes
17:20	**Determinação Teórica-Experimental do Potencial de Ionização de Moléculas de Interesse Biológico na Região do UVV.** Frederico Vasconcellos Prudente

Structural Materials and Industrial Applications

Room	Roma
16:00	**XAFS characterization of electrodeposited Ni-W coatings** Félix Gregorio Requejo
16:20	**Estudo preliminar de filmes de Ormosis (Silicatos organicamente modificados) por meio de GIXRF assistida por Luz Sincrotron** Orlando Armando Elguera Ysnaga
16:40	**Materiais híbridos siloxano-poliéter como eficientes adsorventes para remoção de poluentes orgânicos e metais pesados** Eduardo Ferreira Molina
17:00	**XAFS studies on Ni (II) hydroxide nanoparticles obtained by eletrochemical synthesis applied as electrode material for rechargeable batteries** Santiago José Alejandro Figueroa
17:20	**Estudo eletro-morfológico de compósitos eletroativos utilizando SAXS** Laos Alexandre Hirano

Agenda, February 27th

08:30 - 10:10	**Oral Communication I**
Plenary room	Electronic Structural Properties II
Milão room	Atomic Science II
Ibiza room	Surfaces Interfaces and Nanosystems II
Madrid room	Soft Materials
Roma room	Methods and Instrumentation
10:10 - 11:40	**Posters Session II and Coffee Break**
11:40 - 12:40	**Plenary III**
Plenary room	Kay Diederichs (Universitat Konstanz)
12:40 - 14:00	**Lunch**
14:00 - 15:00	**Plenary IV**
Plenary room	Cinthia Piamonteze (Paul Scherrer Institute – PSI)
15:00 - 15:30 Plenary room	**Articulation between the Laboratories of CNPEM** Prof. Carlos Alberto Aragão de Carvalho Filho Director General CNPEM
15:30 - 16:30 Plenary room	**Round table** Evaluations and Discussions with the Users Committee of LNLS
16:30 - 18:00	**User's round table:**
Plenary room	Improvements on the TGM UV beamline

Oral Communication II, February 27th

Electronic Structural Properties II

Room	Amadeus (Plenarry room)
08:30	**Electronic Properties of the coordination compounds of the ligands trithiocarbonate, perthiocarbonate and xanthate in the S 1s region** Glaucio Braga Ferreira
08:50	**Effect of metallic composition of Ni and Co based catalysts towards steam reforming of etanol** Adriano Henrique Braga
09:10	**Speciation of Ti and Co in nanostructured titanates of composition (La,Sr)Ti1-yCoyO3-d used as electrodes in symmetric SOFCs** Analía Leticia Soldati
09:30	**Exchange spring coupling in NiFe/IrMn/Co heterostructures** Valberto Pedruzzi Nacimento
09:50	**Si local order at Ca2Al2SiO7 and XEOL studies in doped systems** Verônica de Carvalho Teixeira

Atomic Science II

Room	Milão
08:30	**Photoionization and photofragmentation study of ClC(O)OSO2CF3 in the valence-, inner-, and core-electrons energy regions** Rosana Mariel Romano
08:50	**Dissociation mechanisms of SO2- containing molecules after photoexcitation with synchrotron radiation in the energy range between 100 and 1000 eV** Angelica Moreno Betancourt
09:10	**Determinaciones experimentales de Secciones Eficaces de Produccion de Fluorescencia** Edgardo Bonzi
09:30	**X-Ray Resonant Raman Scattering Extended Fine Structure** Juan José Leani
09:50	**Fragmentation Mechanisms of Perfluorinated compounds using Synchrotron Radiation: Study of CF3CF2CF2C(O)Cl** Yanina Berrueta Martinez

Surfaces Interfaces and Nanosystems II

Room	Ibiza
08:30	**Alkanethiols Adsorbed on Platinum, Palladium and Bimetallic Pd/Au Surfaces** Mariano Hernán Fonticelli
08:50	**The influence of chondroitin sulfate and chitosan on structural and superficial properties of composite multilamellar liposomes** Maria Ismenia Zulian Lionzo

09:10	**Use of operando XAS-Raman-Mass Spectroscopies to evaluate catalytic behavior of Cu/Al2O3 catalysts on ethanol dehydrogenation reaction** Wellington Henrique Cassinelli
09:30	**Photon and electron stimulated ion desorption on thiophene-based polymers** Bruno Gabriel Alves Leite Borges
09:50	**Understanding the stability of Ni/CeO2/Al2O3 catalysts for reforming of ethanol as addressed by temperature-resolved XANES analysis** Carla Eponina Hori

Soft Materials

Room	Madrid
08:30	**The study of structural and elastic properties of lipid lamellar phases** Barbara Bianca Gerbelli
08:50	**Estudio sobre micelas unimoleculares derivadas de la polietilienimina hiperramificada: SAXS, XRR, LB** Agustin Silvio Picco
09:10	**On the action of surfactants in the protein denaturation: a study by SAXS and ITC** Pedro Leonidas Oseliero Filho
09:30	**Silica gels and xerogels prepared by sol gel process: acid catalysts and microstructure** Roberto Jorge Candal
09:50	**Report on the design and test of liquid sample holder for SAXS measurements under static magnetic field** Diego Coral

Methods and Instrumentation

Room	Roma
08:30	**Setup for inelastic x-ray scattering at the XDS beamline** Sergio Andrés Ceppi
08:50	**A plug flow microreactor for operando X-ray studies** Santiago José Alejandro Figueroa
09:10	**Reactive sputter magnetron reactor for preparation of thin films and simultaneous in-situ structural study by X-ray diffraction** Jorge Nestor Feugeas
09:30	**Development of a Two-Dimensional Detector for X-Ray Experiments** Eraldo de Sales
09:50	**X-ray imaging of biomolecules: different resolutions achieved with crystallography, SAXS and coherent diffraction imaging** Julio Cesar da Silva

Sumário

Parte I Biologia Estrutural

Parte II Biologia Molecular e Química de Proteínas

Parte III Ciência Atômica e Molecular

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

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Parte V Matéria Mole e Fluídos Complexos

Parte VI Materiais Estruturais e Aplicações na Indústria

Parte VII Métodos e Instrumentação

Parte VIII Propriedades Estruturais, Eletrônicas e Magnéticas de Sólidos

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Parte IX Superfícies, Interfaces e Nanossistemas

Parte I

Biologia Estrutural

Análisis de los efectos de exposición a arsénico por medio de imágenes 3D obtenidas por XRF-microtomografía en el LNLS

Bongiovanni, G.A.[1], Jorge P. Grossi[2], and Pérez, C. A.[3]

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[2] Universidad Nacional de Cordoba - Cordoba Argentina
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El arsénico (As) es uno de los metales tóxicos más abundantes de nuestro medioambiente. El consumo crónico de agua con As o de alimentos contaminados, está asociado al desarrollo de patologías cancerosas y no cancerosas como el HACRE (hidroarsenicismo crónico regional endémico). Sin embargo, no son claros aún los mecanismos patogénicos de este contaminante y esto está relacionado, en gran medida, a la falta de modelos experimentales. Este equipo interdisciplinario de investigación científica ha desarrollado modelos in vivo e in vitro para estudiar su bioacumulación y sus mecanismos de acción, a fin de determinar la relación dosis-efecto en órganos blanco. En este trabajo se muestran imágenes 3D de la distribución de elementos en tejidos sanos y tumorales de organismos expuestos crónicamente a As.

Acknowledgements: Agradecemos al LNLS por el apoyo a la propuesta D09B-XRF-13421/2012. én los aportes de ANPCyT, CONICET y a la Clínica Regional de Villa del Rosario

Structure of the *Canavalia maritima* lectin (ConM) complexed with a dinucleotide

ASP VIEIRA D.B.H.[1], SILVA-FILHO, J. C.[1], Nóbrega,R.B.[2], Santi-Gadelha, T.[1], GADELHA, C. A. A.[1], and Delatorre, P.[1]

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[2] Universidade Federal do Ceará - Fortaleza CE Brazil

The DNA molecule is capable of interacting with several different proteins, non-specifically or in a sequence-specific manner, with a key role in all cellular regulation, being capable of forming lectin-DNA complexes. Lectins belong to a group of proteins of non-immune origin which have at least one non-catalytic sugar binding site reversible and can be found in vertebrates, invertebrates, microorganisms and plant kingdom. The aim of this work was to crystallize and solve the three-dimensional structure of the lectin from *Canavalia maritima* (ConM) complexed with DNA fragments of *Bauhinia variegata* by the vapor diffusion method. The purified DNA was incubated in a water bath at 37 C with ConM, lyophilized and the homogeneously sample was diluted in Tris-HCL 1mM pH 7,0 containing 5mM $CaCl_2$ and 5 mM $MnCl_2$ at a concentration of 40mg/ml, and used to prepare crystallization plates. It was obtained a crystal in a reagent consisting of 0.2 M magnesium format and the crystal belongs to the orthorhombic space group I222 with cell parameters $a = 140.6$, $b = 140.6$, $c = 199.0$. In the central cavity of ConM was found an electron density of a dinucleotide between residues HIS 127 of the tetramers chains in which the dinucleotide interacts with three of the four amino acids in this region, through hydrogen bonds and Van der Waals interactions. HIS 127 residues are conserved in the tribe of Dioclea lectins, corroborating to the idea that legume lectins are able to form complexes with DNA.

Acknowledgements: This Work was supported by CNPq and DBM-UFPB

The macromolecular complex from Escherichia coli: Selenocysteine Synthase and its interactions with specific tRNAsec

Serrão, V.H.B.[1], Manzine, L.R.[1], Bettini J.[2], Portugal, R. V.[3], van Heel, M.[4], and Thiemann, O. H.[1]

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Selenocysteine (Sec U) is co-translationally incorporated into selenoproteins at in-frame UGA stop-codons and is synthesized from serine in the cognate tRNA, tRNAsec (SELC) by a series of enzymatic steps. In bacteria domain, SELC is aminoacylated with L-serine by the Seryl-tRNA Synthetase, then Seryl-tRNAsec is converted to Selenocysteyl-tRNAsec by the homodecameric complex Selenocysteine Synthase (SELA). The binary complex SELA-SELC interaction has, since 1992, always been described as occurring at a ratio of 5 SELC molecules per 10 SELA monomers. Here we show by electron microscopical symmetry analysis that this stoichiometric ratio is rather of 10 SELC molecules per 10 SELA monomers and show the comparison of cryo preparation using the Jeol 2100 (LNNano) and Titan Krios which were made at Netherlands Center of Electron Nanoscopy (NeCEN), Universiteit Leiden Netherlands. This data set will allow us obtaining the structural model of the complex SELA and the binary interaction system, SELA-SELC, to determination of binding configuration. With the structural models will be possible discuss the structure-function relationships of these assemblies and their regulatory role in bacterial Selenocysteyl-tRNAsec synthesis.

Acknowledgements: This work was supported by FAPESP and CAPES

20S Proteasome: Structural study using SAXS

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The process of intracellular proteolysis (protein degradation) is a regulatory mechanism of cellular homeostasis with the same level of importance as gene expression [1].The proteasome is a proteolytic complex responsible for protein degradation and consists of a catalytic core unit called the 20S(20SPT) where the hydrolysis occurs, engaged in one or both ends by regulatory units, called 19S, responsible for the recognition of poly-ubiquitylated proteins, unfolding and translocation of them to the 20S catalytic chamber. However, the catalytic unit (20SPT) can also degrade not marked proteins with poly-ubiquitin tail, as in the case of oxidized proteins. Oxidized proteins have a tendency to form aggregates (a phenomenon that underlies human neurodegenerative diseases), and therefore they must be effectively removed from the living cell. Interestingly, the cells have approximately 1/3 of proteasome without regulatory units, i.e. only the 20S catalytic unit.
The SAXS technique was used to investigate structural aspects of this system. It is known that the proteasome in solution may have structural changes induced by ligands, the presence and absence of modulators, activators and inhibitors [2], including post-translational modifications. The aim of this investigation is to study the changes on the quaternary structure by the addition of DTT on the sample buffer, which may remove the glutathione-modifier of cysteine residues of the 20SPT. Advanced data analysis and modeling methods can be used to obtain structural information. It was also possible to use atomic resolution structures to modeling of the SAXS data. The models were also correlated with TEM results. As it will be presented, the SAXS data has shown that the presence of DTT induces important conformational changes on the proteasome structure which can be directly correlated with its function and catalytic mechanism [2].

REFERENCES

[1] WEISSMAN AM et al. Nat Rev Mol Cell Biol., 2011 12:605-620.
[2] SILVA G.M et al. Antioxidants & Redox Signaling, 2012, vol 16, doi: 10.1089/ars.2011.4210.

Acknowledgements: FAPESP, USP, CAPES, CNPq, IBU

Preliminary crystal structure analysis of *Canavalia brasiliensis* seed lectin (ConBr) in complex with γ-Aminobutyric Acid (GABA)

SILVA-FILHO, J. C.[1], Nóbrega,R.B.[2], Rocha, B.A.M.[2], Santi-Gadelha, T.[1], GADELHA, C. A. A.[1], Cavada, B.S.[2], and Delatorre, P.[1]

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[2] Universidade Federal do Ceará - Fortaleza CE Brazil

Lectins are defined by its capability in interact with specificity and reversibility with carbohydrates through H-bonds and Van der Waals forces. In 2007, however, Delatorre and coworkers demonstrated that *Canavalia gladiata* seed lectin can interact with the non-protein amino acid α-aminobutyric acid (Abu), and more recently it was observed that this molecule was co-purified with *Canavalia brasiliensis* seed lectin (ConBr). Since Abu is a homolog molecule of γ-Aminobutyric Acid (GABA), and in plant this amino acid is involved with plant defense, as well as seed lectins are proposed to function in this way, we aim verify through X-ray diffraction analysis whether ConBr can interact with GABA. ConBr crystals were soaked with GABA 5 mM. Crystals then were submitted to X-Ray diffraction experiment in MXI beam line of Laboratório Nacional de Luz Sincrotron (LNLS), Campinas, Brazil. Crystals belong to C2 space group, with cell parameters a=120.4, b=72.1 and c=68.4. Matthews coefficient was 2.45 ^{3} Da^{-1} indicating the presence of two molecules in the asymmetric unit. Initial rigid body and restrained refinements lead to an R factor and R free values of 0.28 and 0.31, respectively. Preliminary model analysis showed that ConBr molecule display a canonical dimmer assembly, where GABA encounters in the interface of the two monomers, being stabilized through H-bonds and Van der Waals forces by Ser113, Lys114, Leu115, Leu126, Val179 and His180 from one monomer and by Phe130 and Asp139 from another monomer. Furthermore, GABA interacts with two water molecules. As a dimmeric assembly, there are two GABA-binding sites in the ConBr structure, but GABA encounters only in one site. The other site encounters filled with three water molecules. Model analysis also demonstrated the presence of glycerol molecule in carbohydrate binding site of each monomer and it was observed three electron density maps corresponding to diethylene glycol. After this analyses and molecular modeling, further restrained refinement cycles lead to R factor and R free values of 0.21 and 0.25, respectively. In the present moment, we are finishing structure analysis for improve R free value and for understand some observations viewed in this preliminary study.

Acknowledgements: This work was supported by CNPq and CAPES.

Prospecção de Ligantes para o Receptor Ativador de Proliferação de Peroxissomos

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A pandemia da síndrome metabólica atinge pelo menos 25% da população mundial, sendo caracterizada como um conjunto de patologias de efeitos associados, como diabetes, obesidade, inflamação, aumento de colesterol e hipertensão, o que pode levar a cardiopatias, entre outras doenças. Atualmente, a maioria dos esforços no combate a esta síndrome se reflete em tentativas de controle de receptores nucleares, principalmente TR e PPAR. Porém, a maioria dos fármacos disponíveis no mercado, que utilizam esses receptores como alvos, apresentam efeitos indesejáveis. Portanto, a comunidade científica e as indústrias farmacêuticas estão em busca de novos compostos que possam atuar como ligantes destes receptores, modulando-os de forma seletiva, na tentativa de minimizar efeitos deletérios. Os PPARs regulam a transcrição de genes relacionados ao metabolismo de lipídeos, controle de inflamação e produção de insulina. Seus ligantes, ácidos graxos, eicosanóides e prostaglandinas têm sido muito estudados no tratamento de diabetes e dislipidemias, sendo de grande importância para a indéstria farmacêutica. Neste contexto, este trabalho tem como objetivo buscar alguns compostos que possam atuar como agonistas do PPAR. Para tanto, inicialmente a proteína (PPAR) recombinante foi expressa e purificada por afinidade e alguns compostos, de uma lista de 80 moléculas sintetizadas, foram selecionados para testes, com base na estrutura geral dos ligantes já conhecidos como Rosiglitazona, por exemplo. Foram realizados ensaios de cristalização da proteína com diferentes ligantes e foram obtidos cristais em cerca de 100 condições com 31 ligantes diferentes. Os dados de alguns cristais, referente aos ligantes que apresentaram resultados promissores nos ensaios biofísicos foram coletados. Paralelamente estão sendo realizados ensaios celulares e de diferenciação de adipócitos na busca de ligantes que modulem seletivamente o PPAR e portanto, que possam ser aplicados no desenvolvimento de fármacos para o tratamento de diabetes.

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Inhibition studies of human PTP1B, a phosphatase involved in cancer

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Cancer is a leading cause of death today, and the second cause of non accidental death in Brazil, where government spending with the disease exceeds US$ 1 billion per year. In many cases, anticancer therapies and treatments are not completely effective, and therefore it is extremely important to develop new therapies or to improve the existing ones. The Protein Tyrosine Phosphatase PTP1B (UniProt: P18031) was identified as an important target for the development of anticancer therapies. This protein is involved in cellular signaling pathways through dephosphorylation of protein substrates and is found overexpressed in many types of malignant tumors (Yip, S.C. *et al.*, *Trends Biochem. Sci.*, 2010, **35:** 442–449). The gene for this protein was commercially synthesized and cloned. We have established in our lab protocols for expression, purification, and crystallization of PTP1B, as well protocols for large scale ligand screening. PTP1B cleaves the substrate para-nitrophenolphosphate (pNPP) to yield para-nitrophenol (pNP) and inorganic phosphate. Screening of newly synthesized compounds is performed *in vitro* by quantifying the conversion product by colorimetric methods, recording the absorbance at λ=405 nm. When the enzyme is inhibited, conversion of substrate to product does not occur or occur less efficiently. A series of novel compounds, referred to as RPJ, was synthesized at IQ/UNICAMP. One of the compounds exhibited a high degree of inhibition (RPJ 355 – 99,5%) of enzyme activity. Co-crystallization and soaking of apo crystals were adopted to obtain complexes protein:ligand. Crystals diffracted to $\sim$ 2.0 resolution and belong to the space group $P3_221$, with unit cell parameters $a = b = 88.7$, $c = 104.7$, $\alpha = \beta = 90°$, $\gamma = 120°$. Initial structures were solved by Molecular Replacement using the PDB entry 1AAX (Puius, Y.A. *et al.*, *Proc. Natl. Acad. Sci. USA*, 1997, **94:** 13420–13425) as the search model. In this work, we present the protocols established in our laboratory, along with the results of ligand screening. Although a true complex has not been obtained so far, different conformations were observed at the active site region of the enzyme. Representative structures determined by our group are also presented and discussed on the light of the available knowledge of PTP1B.

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Formação de complexos do TR e TR:RXR com coativador e a modulação pelos ligantes

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A regulação da transcrição gênica é controlada por receptores nucleares (RNs) e é responsável por governar eventos como desenvolvimento, metabolismo e diferenciação, por exemplo. O receptor de hormônio tiroideano (TR) é um destes RNs, que controla diversos aspectos do metabolismo basal. Tais receptores atuam como homo ou heterodímero, sendo modulado pelo ligante cognato T3. Um dos parceiros do TR na formação do heterodímero é o RXR, um RN considerado promíscuo, por interagir com vários receptores na formação de heterodímeros. Neste trabalho foi caracterizado o homodímero de TR e o heterodímero com RXR, na ausência e presença de cada um dos agonistas, T3 e ácido 9-*cis* retinóico (RXR), com o objetivo de descobrir a base molecular da modulação da transcrição pelos ligantes. Além disso, também foram caracterizados complexos maiores, como homo e heterodímeros, na presença de uma proteína coativadora, GRIP 1. É importante mencionar que o coativador utilizado nesta abordagem não foi apenas um peptídeo, tal como na maioria dos estudos envolvendo RNs e coativadores, mas uma construção da proteína contendo 250 aminoácidos, abrangendo os três motivos de interação com RNs (LXXLL). Utilizando anisotropia de fluorescência, SAXS e ensaios celulares de transativação, foi realizado um estudo sistemático sobre o TR, TR-RXR, TR-CoA e TR-RXR-CoA na presença de T3 e ácido 9-*cis* retinóico. A partir dos resultados obtidos foi possível discutir sobre a formação de homo e heterodímero e sobre a estequiometria no recrutamento do coativador. Mais ainda, as afinidades medidas por fluorescência mostraram que a adição do ácido 9-*cis* retinóico não interfere na ligacção a elementos responsivos do DNA, resultado que vai contra a alguns trabalhos da literatura. Os resultados dos ensaios de transativação celular foram condizentes com os resultados de anisotropia, indicando que o ácido 9-*cis* retinóico não interfere na transativação. Pelos resultados de SAXS observou-se que o coativador GRIP 1 estabiliza estruturalmente o heterodímero TR-RXR, conforme visto nas curvas de Kratky. Este estudo traz informação molecular, funcional e estrutural sobre a formação do complexo entre homo e heterodímero do TR, com coativador e ligantes e como os ligantes podem modular este processo. Tais resultados podem contribuir para a melhor compreensão das bases moleculares da ativação do TR.

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Binding studies of substituted 2-oxo-2-(phenylamino)acetic acids and phenylsulfamic acids as potential inhibitors of PTP1B

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According to the World Health Organization, cancer is amongst the three leading causes of death for adults in developing countries, where both incidence and mortality are increasing at alarming rates. By 2020, 10.3 million deaths are estimated worldwide, two-thirds of them in newly-industrialized and developing countries. Protein tyrosine phosphatases (PTPs) are a family of signaling enzymes which play essential roles in intracellular signal transduction by regulating tyrosine phosphorylation thus helping to control cell growth, differentiation and other cellular processes. The protein tyrosine phosphatase 1B (PTP1B) plays an important role in cellular signaling and is implied in many human diseases, including cancer, diabetes, obesity and osteoporosis. In spite of previous studies, it is still a challenging problem to discover specific inhibitors towards each PTP due to the structural homogeneity of active and secondary-binding sites within this family. In this context, small molecule inhibitors of PTP1B can be promising drug candidates[1]. We aim to synthesize a small molecule series of substituted 2-oxo-2-(phenylamino)acetic acids[2] and substituted phenylsulfamic acids[3]. The compounds were docked on the PDB entry 2F71[3] by using OpenEye software FRED[4]. The compounds selected presented good chemical complementarity with the active site, which occurs through hydrophobic interactions with residues F182 and Y46, in addition to hydrogen bonds established with residues R221 and S216 located at the bottom of the active site pocket. The most promising candidates were 2-(4-chlorophenylamino)-2-oxoacetic acid and *para*-methoxy phenylsulfamic acid. In this work, these results are described and discussed in detail, with a comparative study of the mode of binding of the successful candidates. Experimental studies are in course in order to validate the inhibition properties of the compounds designed.

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Using docking studies for the development of LMW-PTP inhibitors based on fragments

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Cancer is currently a leading cause of death, accounting for 7.6 million deaths recorded worldwide. It is believed that in 2020, cancer will kill more than HIV/AIDS, tuberculosis and malaria put together[1]. The search for enzyme inhibitors has become an important way in the design of new drugs against cancer. LMW-PTP is a protein phosphatase involved in critical cell signaling pathways and have been identified as an important target for new anticancer therapies[2]. The present work is aimed at the development of new inhibitors of LMW-PTP. Based on the crystallographic structure PDB entry 5PNT[3], which contains the buffer molecule MES (2-(N-morpholino)-ethanesulfonic acid) in the active site, five molecular fragments were initially synthesized, with molecular weight ranging from 172 to 245 Da, and assayed *in vitro* against LMW-PTP to check possible inhibition. Three of these compounds inhibited the protein in a single concentration assay (compound concentration equal to 5mM), presenting inhibition between 19% and 54% of the enzyme activity. The fragment which inhibited 54% of the enzyme activity was chosen as a starting guide for the design of new compounds, in order to improve inhibitory activity. Molecular docking studies of these new compounds were then carried out using FRED[4] and a recent crystallographic structure of LMW-PTP obtained in our group, which contains a phenylmethylsulfonyl fluoride (PMSF) molecule bound in the active site. According to the docking results, the compounds presenting (i) good shape complementarity with the active site, (ii) hydrophobic interactions with the residue Y131 and (iii) hydrogen bond interactions with the main chain nitrogen atoms located at the bottom of the active site pocket, have been selected for organic synthesis (in course). In this work, inhibitory assays will be presented, along with docking results and the mode of binding of the new molecules proposed for synthesis. This study will contribute for a deeper understanding of molecular recognition by the phosphatase and the identification of novel inhibitors.

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Parte II

Biologia Molecular e Química de Proteínas

Characterization of the Sulfate binding protein Sbp in *Xanthomonas citri*

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Xanthomonas citri is an important phytopathogen that causes the citrus canker disease, which affects most of citrus plants and causes significant economic losses to Brazil, the second largest exporter of orange and juice of the World. Understanding the mechanisms of infection and pathogenesis of this bacteria is an important step for the development of ways to control this disease. In *Xanthomonas citri* genome we identified the *sbpcysUWA* operon, encoding the ABC transporter for sulfate assimilation. Sbp is the sulfate periplasmic-binding protein (Sbp) responsible for the affinity and specificity of the system, which blockade of its activity can lead to the lackness of sulfate inside the cell. In this work we show the first functional and structural characterization of this protein as an attempt to use it as a target for the development of grow inhibitors. Sbp was expressed and purified as a soluble protein from *Escherichia coli* BL21 (DE3) strain with 37.5 kDa. Spectroscopic analyses in presence of sulfate revealed the protein shows secondary structure gain as well as an increasing of almost 10 degrees in the thermal stability. Proteomic analyses and GFP expression controlled by the it sbpcysWUA promotor region revealed the expression of Sbp in different conditions. Crystallization trials produced crystals as needles in different conditions, which need to be refined for difraction experiments. Based on the atomic coordinates from the it Salmonella typhimurium ortholog, which shares more that 60 percent of sequence identity, we built a structural model and mapped the ligand-binding site.

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Proteomic analysis of *Xanthomonas axonopodis* pv. *citri* under different culture conditions

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Xanthomonas citri is an important phytopathogenic bacterium that infects citrus plants causing significant losses for the economy. In our group, we have focused on the identification and characterization of ABC transporter proteins of this bacterium, in order to determinate their function for growth *in vitro* and *in vivo*, infection and pathogenesis. ABC transporters represent one of the largest families of proteins, which transport since small molecules as ions up to oligopeptides and sugars. In prokariotic cells many works have reported the importance of ABC transporters for pathogenesis, resistance, biofilm formation, infectivity and DNA repair, but until our knowledge, there is no data related to these transporters in *X. citri*. In order to determinate which transporters are expressed in *X. citri*, we started a proteomic analysis based on SDS PAGE gels associated to LC MS/MS. After growing *X. citri* in LB, XAM (a citrus mimetic culture medium), minimum media (M9) and M9 with half sulfate, cellular extracts were obtained and used for preparation SDS PAGE gel. Seven bands (14 kDa to 126 kDa) in SDS-PAGE were cut off the gel, treated with trypsin and submitted to the MS for protein identification. The data analysis started by the software Mascot Distiller against *X. citri* database and the results were analysed in Scaffold Q+.

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Cloning, expression and purification of enzymes from natural products biosynthesis of biotechnological interest.

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Natural products represent one of the principal sources of bioactive molecules which can be used therapeutically on humans. Within the natural products, various antibiotics exist which have been utilized throughout many decades against various types of infections. The natural antibiotics are chemically classified by its action mechanism and they are generally complex molecules produced by microorganisms, plants and marine organisms whose chemical manipulation is not simple. These organisms produce bioactive molecules through many enzymatic pathways that may have biotechnological application in the production of known antibiotics derivatives. Meanwhile, for this, the determination of its crystallographic structures is necessary. Among the enzymes related to biosynthesis, the glycosyltransferases are of great importance, since almost every natural product has sugars bonded to the aglycone. Here we will show partial results of cloning, expression and purification of several glycosyltransferases of the biosynthesis of important antibiotics derived from Streptomyces. We have cloned, expressed and crystallization trial is in progress for enzymes of the biosynthesis of macrolides and aminoglycosides. This enzymes may be modified to increase the promiscuity to be applied in the production of new antibiotics.

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Parte III

Ciência Atômica e Molecular

Espectroscopia de multicoincidência da molécula de diclorometano por impacto de fótons UVV e raios-x moles

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A espectroscopia por tempo de voo (TOF- Time of Flight) é uma técnica amplamente utilizada na foto-fragmentação molecular. Dando sequência ao estudo da molécula do diclorometano [1], queremos correlacionar os mecanismos de fragmentação iônica com os elétrons acessados seletivamente através da luz monocromática. Para acessar diferentes estados eletrônicos de diferentes valores de energia e de forma contínua, utilizamos o feixe de luz síncroton na linha TGM do LNLS selecionados através de monocromadores na faixa de Ultravioleta de vácuo (UVV) e raios-X moles (12 eV a 210 eV). Os estados excitados das moléculas possuem curto tempo de vida e uma grande probabilidade de ionização. A complexidade de seu estudo torna-se maior no caso em que ocorrem ionizações múltiplas. Os íons de cargas múltiplas, na maior parte das vezes, também são instáveis e se dissociam gerando espécies de massa menor com carga simples. Para compreender esses mecanismos de dissociação estamos empregando as técnicas de espectroscopia de massa em coincidência com elétrons e íons, PEPICO (coincidência entre o fotoelétron e o foto-íon) e PEPIPICO (coincidência entre o fotoelétron e dois foto-íons que chegam em sequência). Técnicas de multicoincidência permitem uma análise muito completa do processo de fragmentação, dando informações sobre o caminho e padrão da fragmentação e da dinâmica da fotoionização. Neste trabalho comparamos os valores obtidos através das inclinações das ilhas de coincidência no espectro PEPIPICO com valores obtidos para diferentes processos de separação de carga através do modelo [2]. Notamos que para eventos em que o mesmo par de fragmentos é liberado, podem ocorrer diferentes tipos de processos de separação de carga. Observamos também através do rendimento parcial do PEPIPICO que para a molécula de diclorometano, a coincidência mais abundante que corresponde a aproximadamente 25% dos eventos na maior parte das energias, é a chegada de um íon de H^+ seguido pelo íon de Cl^+. Referências - [1] K. F. Alcantara,W.Wolff, A. H. A Gomes. L. Sigaud, S. Soriano, V. Oliveira, A. B. Rocha, A. C. F. Santos, J. Phys. B vol. 44 (2011). [2] M. Simon et al. J Phys. Chem.1993, 97, 5228-5237

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Fotoionização da molécula SF_6 nas proximidades da camada K do enxofre

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O hexafluoreto de enxofre (SF_6) é uma molécula de vasta aplicação industrial. Entre suas propriedades, é um ótimo dielétrico, quimicamente inerte e com alta pressão de vapor em temperatura ambiente, o que o torna um ótimo isolante elétrico de alta voltagem em transformadores, geradores, capacitores e cabos [1]. Também é usado em técnicas de gravação por plasma [1, 2]. Na atmosfera, o SF6 contribui fortemente para o efeito estufa, e por ser muito inerte persiste por um longo tempo na atmosfera [3]. Portanto, a fragmentação dessa molécula por raios-x, que bombardeiam a atmosfera devido á radiação cósmica e solar, é bastante interessante. Excitação e ionização de moléculas em camada interna geralmente resultam na criação de íons moleculares simples ou multiplamente carregados muito instáveis que se fragmentam em espécies mais leves com ou sem separação de carga. A fim de estudar a fragmentação da molécula de SF6 após excitação em camada interna, foram realizadas medidas de fotoionização desta molécula na borda da camada K1s do enxofre. Usando técnicas de coincidência múltipla (PEPICO e PEPIPICO), as medidas foram realizadas na linha SXS do Laboratório Nacional de Luz Síncrotron (LNLS). Foram medidos os rendimentos iônicos parciais em função da energia do fóton. Observou-se um alto grau de fragmentação, com completa fragmentação da molécula e a formação de íons até triplamente carregados. Também foram determinadas as energias cinéticas dos fragmentos produzidos.

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Study of the conformational stability of proteins in solution probed by X-Ray Fluorescence NEXAFS

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Several proteins with essential roles in the human metabolism owe much of their structure stability to the presence of sulfur-containing amino acids and their capability to form disulfide bridges (-S-S- bonding). These sulfur bridges often form between two cysteines that are distant from each other in the polypeptide backbone or even in two separate polypeptides, and help to stabilize the intricate shapes of proteins, particularly those present outside the cells where they are subjected to added physical and chemical stress. The shape of proteins composed of more than one chain may be altered through the action of several agents such as organic solvents, temperature, pH conditions, heat, radiation and so on. In this work we focused on insulin, a small protein produced at the pancreas, responsible for controlling blood sugar levels. Insulin consists of two polypeptide chains and presents three disulfide bridges, two involving cysteines from different chains and the other one involving cysteines from the same polypeptide. We measured NEXAFS spectra of insulin in solution for three different pH conditions, and compared with the spectrum of solid insulin. Preliminary results point to a break in the disulfide bridges in the pH conditions measured. The measurements were taken at the SXS beamline, using a new samples holder designed at the beamline to measure liquid samples. The NEXAFS spectra were recorded around the S 1s edge, using a fluorescence detector. Since these are pioneering measurements of proteins in solution using this instrumentation, we also measured two smaller biomolecules, cystine and methionine.

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Fragmentation Mechanisms of Perfluorinated compounds using Synchrotron Radiation: Study of $CF_3CF_2CF_2C(O)Cl$

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Perfluorinated compounds have been extensively used in industrial applications during the last years. Recently, some perfluorinated species were detected in tissues of animals, in environmental waters, and in the atmosphere. Different processes may be responsible for the presence of these compounds in the environment. For example, the thermolysis of fluoropolymers and the degradation of fluorotelomer alcohols result in the emission of perfluorocarboxylic species to the atmosphere. In this work, and as part of a general project aimed to the elucidation of the photofragmentation mechanisms of compounds relevant for atmospheric chemistry, we present the study of perfluorobutanoyl chloride using synchrotron radiation with energies between 7.3 and 300 eV. The photoexcitation and photofragmentation mechanisms of perfluorobutanoyl chloride were studied in the TGM beamline at LNLS using the chamber for gaseous samples and coincidence techniques. There is no ion in the PEPICO spectra at energies lower than 11 eV, denoting that these energies are below the first ionization potential of the molecule. At 12 eV the only ion in the spectrum is the $ClCO^+$ fragment, while the increment of the excitation energies leads to the formation of $(M\text{-}Cl)^+$ and $(M\text{-}ClCO)^+$. The $CF_3{}^+$ ion appears from 16 eV, becoming the most important fragment at higher energies. The TIY spectrum obtained around the Cl 2p threshold, 211 eV, shows three resonances peaks at 201, 204 and 206 eV, while the C 1s TIY spectrum presents only one resonance at 287 eV below the threshold, occurring at 296 eV. The PEPICO spectra in this energy region were found to be almost independent of the ionization energy, being the CF^+ (the only CF species found so far in the interstellar medium), $CF_2{}^+$ and $CF_3{}^+$ fragments the most abundant of the spectra. The ions FCO^+, CF_2Cl^+, $C_2F_4Cl^+$, $C_3F_6Cl^+$ and $C_3F_7O^+$, also detected in the spectra, denote the importance of frustrated dissociations to radicals followed by intramolecular abstraction reactions. Dissociation mechanisms were elucidated from PEPIPICO spectra.

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Dissociation mechanisms of SO_2- containing molecules after photoexcitation with synchrotron radiation in the energy range between 100 and 1000 eV

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Recent investigations in our research group have been dedicated to the elucidation of photochemical reaction mechanisms between small molecules that are relevant as atmospheric contaminants or components. For example the photochemical gas-phase reaction between SO_2, O_2 and Cl_2 was studied and the reaction mechanisms were proposed on the basis of the isolation and identification of the products. Molecules of the type $ClSO_2(OSO_2)_nCl$, with n=1,2 and the novel peroxide $ClSO_2OOSO_2Cl$ were determined, among others, as the main photoproducts. On the frame of a general project aimed to the elucidation of the photochemical and electronic properties of molecules containing the XSO_2- group, with X=halogen, we present here the study of the of the ionic photofragmentation of three compounds of this family: $(ClSO_2)_2O$, FSO_2NCO and $ClSO_2NCO$, after core-shell excitation of C 1s, N 1s, O 1s, and F 1s electrons. Photoionization and photofragmentation of the compounds in the energy region between 250 and 1000 eV were studied in the SGM beamline at LNLS, using the experimental station for gaseous samples and coincidence techniques. The detection of ionic fragments in coincidence, PEPIPICO techniques, allows the study of unimolecular photofragmentation mechanisms. At the high excitation energies, the most important processes conduct usually to atomic fragments produced through concerted mechanisms. Nevertheless, in the three molecules studied here several polyatomic ionic fragments were detected in coincidence. The NCO^+/SO^+ coincidence was observed for FSO_2NCO and interpreted as a four-body secondary decay after differed charge separation mechanisms. It is worth to mention that this coincidence was not observed in the case of $ClSO_2NCO$, for which most of the fragmentation mechanisms involve atomic fragments. On the other hand, the ${SO_2}^+$ ion was produced from $(ClSO_2)_2O$ by several different mechanisms.

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Fragmentation Mechanisms of Trifluoroethanol, CF_3CH_2OH, following Photoexcitation with Synchrotron Radiation between 100 and 1000 eV

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Fluorinated alcohols are industrial alternative compounds for chlorofluorocarbons and hydrochlorofluorocarbons, species responsible for ozone depletion in the stratosphere and with high global warming potentials. Although Trifluoroethanol presents a wide variety of industrial applications, going from pharmaceutical uses as starting material for some inhalation anesthetics, in the preparation and treatment of nylon, as working fluid for heat engines, between others, studies regarding its potential environmental impact are still scarce. In this work, and as part of a general project aimed to the elucidation of the photofragmentation mechanisms using synchrotron radiation of compounds relevant for atmospheric chemistry, we present here the study of Trifluoroethanol using synchrotron radiation between 100 and 1000 eV. Photoionization and photofragmentation of Trifluoroethanol in the energy region between 100 and 1000 eV were studied in the SGM beamline at LNLS, using the experimental station for gaseous samples and coincidence techniques. Photoelectron-Photoion-Coincidence (PEPICO) spectra were taken at each resonance, and bellow and above every resonance. The most intense signals in the PEPICO spectra are the ones assigned to H^+, COH^+, and the peak at $m/z = 31$, that may corresponds to CH_2OH^+, CF^+, or both. Features arising from C^+, F^+, $CF_2{}^+$, $CF_3{}^+$ and OH^+ fragments are also important in the spectra. It is worth to mention the presence of several ions, with relative intensities between 1 and 5 %, explained only by atomic rearrangements: $CH_3{}^+$, H_2O^+, FH^+, $C_2H_3{}^+$, CFH^+, CH_2F^+, FO^+ y $F_2{}^+$. The PEPIPICO spectra are dominated by islands corresponding for the coincidence of H^+ with almost all the possible charged fragments. One of the most important channels leads to the formation of H^+ and $CF_3{}^+$ in a concerted mechanism. Other examples are the coincidences between CF^+/CH_2O^+ and $CF_2{}^+/CHO^+$, that follow Differed Charge Separation mechanisms.

Acknowledgements: This work has been supported by LNLS under Proposal SGM-11670. We thank Arnaldo Naves de Brito and SGM beamline staff for their assistance throughout the experiments, and Facultad de Ciencias Exactas, Universidad Nacional de La Plata, CONICET and ANPCyT for financial support.

Photoionization and photofragmentation study of $ClC(O)OSO_2CF_3$ in the valence-, inner-, and core-electrons energy regions

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As part of a research project dedicated to the study of the electronic properties of molecules containing the SO_2- group and halogen atoms, we present here the fragmentation studies following phoionization of valence, inner-shell and core-shell electrons of chlorocarbonyl trifluoromethanesulfonate, $ClC(O)OSO_2CF_3$. This compound has been prepared by our research group, and its conformational, structural and spectroscopic properties were studied using different experimental and theoretical techniques. Gas electron diffraction and vibrational analysis were interpreted in terms of an equilibrium of two conformers in the gas phase. $ClC(O)OSO_2CF_3$ was prepared by the reaction of ClC(O)SCl with $AgOSO_2CF_3$, according to the literature. The studies were performed using the experimental station for gaseous samples and coincidence techniques, in the TGM and SGM beamlines at LNLS. In the valence electron region, the PEPICO spectra are dominated by signals at m/q = 63/65 and 69, attributable to $ClCO^+$ (with its characteristic isotopic splitting) and $CF_3{}^+$, respectively. If the gaseous sample is irradiated with synchrotron light of higher energies, several new fragments appear in the spectra, with an increasing importance of atomic ions for ionization energies corresponding to core-shell electrons. $SO_2{}^+$, $CF_2{}^+$, SO^+, $CO_2{}^+$, CF^+, CO^+, among others, are the fragment observed for irradiation energies in the region of S 2p and Cl 2p electrons, together with $ClCO^+$ and $CF_3{}^+$. In the C 1s, O 1s and F 1s energy regions, atomic fragments became important in the spectra, being observable also signals originated in double charged species ($CO_2{}^{2+}$, Cl^{2+}, F^{2+}, O^{2+}, and C^{2+}). The PEPIPICO spectra have revealed different photodissociation mechanisms. The most abundant islands in the spectra correspond to the formation of the following pairs of fragments in coincidence: $ClCO^+/CF_3{}^+$, S^+/Cl^+, and O^+/S^+, the fragmentation processes can be interpreted in terms of concerted mechanisms.

Acknowledgements: This work has been supported by LNLS under Proposals TGM-1276 and SGM-1670. We thank Arnaldo Naves de Brito and the TGM and SGM beamlines staff for their assistance throughout the experiments, and Fac. Cs. Ex., UNLP, CONICET and ANPCyT for financial support.

STRUCTURE DETERMINATION OF LASSBIO-1515: A NEW LEAD-COMPOUND CANDIDATE OF THE *N*-ACYLHYDRAZONE CLASS

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The use of X-rays for determination of three-dimensional atomic arrangements in crystal structures of organic and inorganic compounds is an important stage both in the design of new substances and in the development of the new procedures for the synthesis of the already known compounds. In this work, synchrotron X-ray powder diffraction (XRPD) data allowed for structure determination of LASSBio-1515 compound, a *N*-acylhydrazone (NAH) derivative lead-compound candidate, synthesized in Laboratory of Synthesis and Evaluation of Bioactive Substances (LASSBio®) of the Federal University do Rio de Janeiro. The NAH moiety constitutes a pharmacophoric group due to its relation to several biological activities, such as cardioinotropic, anti-inflammatory and analgesic ones. The preliminary results have shown that XRPD is an effective tool for the crystal structure determination of *N*-acylhydrazone derivatives. This technique has been indispensable for unambiguous characterization of the relative configuration of these organic molecules, allowing an accurate understanding of bioactivity profile. The measurement has been performed in the XPD beamline at Brazilian Synchrotron Light Laboratory (LNLS). X-ray powder diffraction data collected in transmission and high-throughput geometries were used to analyze LASSBio-1515. The X-ray wavelength of the synchrotron radiation used in this study was determined to be $\lambda = 1.55054$. The structure of the LASSBio-1515 compound was solved and Rietveld method was used to refine the crystal structure. This compound crystallizes in a monoclinic ($P2_1/c$) space group, with unit cell $a = 11.26255(16)$, $b = 12.59785(16)$, $c = 8.8540(1)$, $\beta = 90.5972(7)^o$ and V = 1256.17(3) ^{3}. The crystal structure of LASSBio-1515 is comprised by four formula units per unit cell (Z = 4), accommodating one molecule in the asymmetric unit (Z = 1). The goodness-of-fit indicator $\chi^2 = 1.04$ and $R_{wp} = 5.006$.

Acknowledgements: This work was performed at the LNLS Brazilian Synchrotron Light Laboratory with support from the LNLS User Program (Projects XPD 12474). We would like to thank the Brazilian agencies CNPq, FAPESP, INCT-INOFAR and FAPERJ for financial support.

1s3d satellites of the K$\beta_{1,3}$ emission spectrum of Zn

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The intensity evolution of the 3d spectator hole satellite of the K$\beta_{1,3}$ emission spectrum of Zn was studied as a function of the excitation energy from threshold to saturation. Emission spectra were measured at the XRD1 beamline using a high resolution X-ray spectrometer in Rowland geometry. Satellite structures associated to 1s3d excitation channels were extracted from the measured spectra by fitting a calculated satellite lineshape, the whole satellite intensity being a fitting parameter. The 1s3d satellite structure was calculated using the GRASP code. Spectrometer resolution effects were included by convoluting with a gaussian response function. The double ionization threshold and the saturation intensity were determined by fitting the Thomas model to the experimental data. The assignment of the satellite structures to 1s3d multielectronic effects was confirmed from the threshold energy of 15.2±0.4 eV, which is close to the prediction of the $Z+1$ model of 17.4 eV. A saturation intensity of 35±2%, relative to the main peak intensity, was observed. Emission spectra could be accurately fitted considering the K$\beta_{1,3}$ diagram lines, 1s3d satellites along with contributions of $KM_{2,3}M_{4,5}$ radiative Auger transitions.

Acknowledgements: This work was partially supported by the National Synchrotron Light Laboratory (LNLS), Brazil and the Secretaría de Ciencia y Tecnología de la Universidad Nacional de Córdoba.

OXIDE NANO-LAYERS STUDIED BY X-RAY RAMAN SCATTERING IN TOTAL REFLECTION GEOMETRY

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Different processes could take place from the interaction of X-ray with matter: photons can be absorbed by the photoelectric effect and decay in florescence process, the photons could also experience coherent or incoherent scattering. Nevertheless, under resonant conditions, another low probability interaction can occur: the x-ray resonant Raman scattering (RRS) [1].

If the angle of the incident radiation is less than a critical angle derived from the Snells law, X-rays are totally reflected due to the refractive index is less than unity [2]. Making use of this fact, different depths of a sample can be studied scanning the incident photon angle through this critical angle. At this respect, studies of characteristic emissions, or reflected intensities, present a tool for the analysis of surface properties, such as variations of electron density with depth with resolutions from ngströms to microns [3].

This work shows experimental results of X-ray Raman scattering at grazing incidence conditions with the aim of recognize chemical environments in different layers of stratified materials using a low resolution energy dispersive system. Multilayer samples of Fe compounds were measured in the XRF beamline of the Brazilian synchrotron facility using monochromatic radiation and an EDS setup. The measurements were performed in total reflection regime with incident photon energy lower and close to the K absorption edge of Fe.

After a simple data processing, the result allowed characterizing oxide nanolayers, not observable with the use of conventional geometries, reaching identification of the oxidation state present in a particular depth of a sample surface with nanometric, or even sub-nanometric, resolution using a low-resolution EDS system.

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Acknowledgements: This work has been partially supported by the Brazilian Synchrotron Light Laboratory (LNLS).

X-ray absorption spectroscopic and multiple scattering formalism investigation of a possible S-Cu interaction in the Cu- sulfenilcarbonilic ligands.

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Chemical, biochemical, biogeochemical, and environmental studies of sulfur have proliferated because of the recognition of its role in many important processes on the earths various ecosystems. For example, the sulfur has an important role in electron transfer systems (ETs), being the ETs an integral component in a diverse range of important biological functions including photosynthesis, respiration, and nitrogen fixation. Sulfur is also present in urea, which is the main end product of protein metabolism in humans and other mammalian animals.

In this work, we published a series of results obtained to investigate the sulfur and copper environments in new synthetic covalent sulfenilcarbonilic compounds which can be used as ligands in the coordination chemistry. Previous studies have illustrated the utility of Cu and S K-edge XAS for establishing the electronic structure of copper-sulfur complexes. The K XANES involving 1s-np transitions, more specifically, the XANES pre-edge region has been identified as providing information on the amount of covalent mixing of sulfur and ligand atomic orbitals in various S-compounds. The shape of XANES spectra will reflect the density of empty states, because in X-ray absorption the excited electron is not free and the dipole transition poses strong selection rules to the final state (i.e., we will sense site and symmetry for S-atom). The Cu K XANES involving 1s-np and 1s-3d transitions, which enables sensing states of hybridization, unoccupied states like symmetries and charge transfers.

Show the differences between S-ligands and Cu-S-ligands in the S K XANES spectra. Using de FDMNES program in multiple scattering formalism, we could attribute these differences to the conformations of sulfur environment and correlated with those obtained by other techniques (XRD and NMR).

The Cu K EXAFS/XANES study allowed us to obtain the coordination numbers and average distances of first neighbors sulfur (Feffit pack), and hybridizations responsible in the complex formation, respectively. Also, using de FDMNES program, we could investigate the electronic state responsible in the charge transfer in the system.

Acknowledgements: This work was supported by PIP 3079 and PICT 2008 - 00038.

Um estudo sobre a formação de dímeros de ácido acético e ácido fórmico duplamente deuterado em fase gasosa na borda K do Oxigênio e do Carbono

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O estudo de moléculas pré-bióticas simples é de fundamental importância para entender a formação de moléculas orgânicas complexas, como os aminoácidos, as proteínas e as nucleobases presentes no DNA e no RNA. Uma hipótese para o surgimento das nucleobases é que elas teriam sido sintetizadas a partir de compostos orgânicos mais simples contidos em meteorito e asteróides que caíram na Terra. Diversos experimentos demonstraram que é possível produzir moléculas pré-bióticas complexas a partir de moléculas mais simples em ambientes que simulam o meio interestelar. Neste contexto, temos realizado um estudo sobre processos de fotoionização e fotofragmentação de moléculas pré-bióticas simples. Neste trabalho, em particular, realizamos a fotoionização e fotofragmentação do ácido acético (CH_3COOH) e do ácido fórmico duplamente deuterado (DCOOD) em fase gasosa. Os dados experimentais foram obtidos no Laboratório Nacional de Luz Síncroton, mas especificamente na linha de luz SGM, com o auxílio de um espectrômetro de massa por tempo voo. Obtemos espectros da produção total de íons (TIY) em função da energia dos fótons e espectros de massa, utilizando a técnica de coincidência entre elétrons e íons, PEPICO. Os diversos espectros TIY e de massa do CH_3COOH e do DCOOD, foram obtidos para diferentes valores de pressão da câmara experimental e para fótons com energia na borda K do oxigênio, 525 a 550 eV e na borda K do carbono, 280 a 330 eV. A variação da pressão é feita na tentativa de verificar se a produção de alguns íons é resultante da fragmentação de dímeros, formados antes da região de ionização do espectrômetro de massa por tempo de voo.

Acknowledgements: LNLS, CNPQ, CAPES

Determinação Teórica-Experimental do Potencial de Ionização de Moléculas de Interesse Biológico na Região do UVV.

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Estudos da interação da radiação com moléculas pré-bioticas incluem a formação de aminoácidos a partir de seus precursores como os ácidos carboxílicos e moléculas do grupo amina, bem como a formação de nucleotídeos que são partes constituintes do RNA e do DNA. As propriedades fotofísicas e fotoquímicas dessas moléculas pré-bióticas nas regiões UV e VUV são, assim, de direto interesse para o entendimento da fotoestabilidade, bem como para contribuição com pesquisas de radioastronomia, ciência dos cometas e para estudos de exobiologia. O estudo da fotoestabilidade dessas moléculas mais simples tanto em fase gasosa como em fase condensada, bem como a possível fotodegradação delas, quando expostas a radiação com comprimentos de onda na região do ultravioleta de vácuo e raios-x moles, são então de grande interesse. Recentemente foram implementadas melhorias na linha de luz D05A-TGM, que passou a fornecer fótons com energia a partir de 7,3 eV. Isto possibilitou estudarmos processos de fotoionização e fotofragmentação de moléculas de ácidos carboxílicos e dos grupos amina e amida em fase gasosa após a interação com fótons com energia no intervalo de 7,3 a 12,0 eV. A estação experimental foi equipada com um espectrômetro de massa por tempo de voo, montado em uma câmara rotativa. Utilizamos técnicas de produção parcial de íons, que permitiu determinar, de forma precisa, a energia de aparecimento dos íons pais (ou potencial de ionização adiabático) do ácido fórmico deuterado (DCOOD), ácido acético (CH_3COOH), formamida ($HCONH_2$), acetaldeído (CH_3COH) e etanolamina (CH_2 (NH_2)CH_2OH) e de outros canais de fragmentação que não puderam ser observados em medidas anteriores devido à limitação da linha de luz. Além dos resultados experimentais, fazemos um tratamento teórico utilizando a Teoria do Funcional da Densidade (DFT) onde obtemos, por exemplo, a energia teórica de aparecimento dos íons coletados no experimento.

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Determinaciones experimentales de Secciones Eficaces de Producción de Fluorescencia

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Valores experimentales de Secciones Eficaces de Producción de Fluorescencia L son necesarios para muchos casos, por ejemplo para ser utilizados en investigaciones básicas y aplicadas, en el análisis elemental no-destructivos, cálculo de dosis, etc. También son requeridos para probar los modelos atómicos utilizados en la predicción de datos, como por ejemplo en la producción de rayos X por fluorescencia.

En este trabajo se han determinado experimentalmente las Secciones Eficaces de Producción de Rayos X por Fluorescencia L para elementos con $45 \leq Z \leq 50$ utilizando radiación sincrotrón a 9 keV.

Los datos obtenidos para las líneas Ll, $L\alpha$, $L\beta_1$, $L\beta_2$, $L\gamma_1$ y $L\gamma_2$, fueron agrupadas considerando el esquema de transición, las energías de las líneas de emisón y la resolución del detector. Los resultados obtenidos fueron comparados con datos teóricos, obteniéndose un buen acuerdo en general.

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X-RAY RESONANT RAMAN SCATTERING EXTENDED FINE STRUCTURE

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When X-ray photons irradiate atoms under resonant conditions, a low probability interaction can arise: the X-ray resonant Raman scattering (RRS). This inelastic process presents some relevant differences compared to other interactions between X-rays and matter; when the exciting photon energy approaches from below to an absorption edge of a target element, the Raman process become dominant over other effects. In a X-ray Raman process for an incident photon energy a variety of emitted photon energies are possible, contrasting, for example, florescent process where the emitted photon has a fixed energy.

In this work we study the oscillations present in the RRS fine structure of diverse metal compounds. In order to understand and explain these oscillation patterns, we also isolated the oscillations of different EXAFS spectra. After a simple data manipulation, a direct comparison between the oscillation of both RRS and EXAFS experiments was performed. A notable similitude between both patterns is present in all the studied compounds.

The experiments were carried out at the XRF Beamline of the Laboratorio Nacional de Luz Sincrotron (LNLS) of Campinas, Brazil.

For the first time interference information, i.e. EXAFS modulations, has been observed in X-ray scattering spectra using a low resolution EDS system.

These results suggest a new spectroscopy technique allowing chemical characterizations using X-ray Raman scattering. In this regard, first results had shown the potentiality of these kinds of experiments. Additionally, due to the adaptability of emission techniques, several possibilities appear from the applications of RRS spectroscopy in different geometries, as in grazing incident conditions for surface studies and even three-dimensional analysis by RRS in confocal arrangements. In these cases, this new tool could obtain meticulous 3D spatially resolved information about constitutive elements and their oxidation states; information not viable to achieve using conventional absorption techniques.

This novel RRS chemical-environment technique will offer an excellent opportunity to study diverse kind of samples in the micro- and nano-regime using a low resolution system.

Acknowledgements: This work has been partially supported by the Brazilian Synchrotron Light Laboratory (LNLS)

X-ray absorption spectroscopic and multiple scattering formalism investigation of a possible S-Cu interaction in the Cu- sulfenilcarbonilic ligands.

Andrini, L.[1], Giovanetti, L. J.[2], Erben, Mauricio F.[2], Della Védova, Carlos O.[2], and Requejo, F. G.[2]

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Chemical, biochemical, biogeochemical, and environmental studies of sulfur have proliferated because of the recognition of its role in many important processes on the earths various ecosystems. For example, the sulfur has an important role in electron transfer systems (ETs), being the ETs an integral component in a diverse range of important biological functions including photosynthesis, respiration, and nitrogen fixation. Sulfur is also present in urea, which is the main end product of protein metabolism in humans and other mammalian animals. In this work, we published a series of results obtained to investigate the sulfur and copper environments in new synthetic covalent sulfenilcarbonilic compounds which can be used as ligands in the coordination chemistry. Previous studies have illustrated the utility of Cu and S K-edge XAS for establishing the electronic structure of copper-sulfur complexes. The K XANES involving 1s-np transitions, more specifically, the XANES pre-edge region has been identified as providing information on the amount of covalent mixing of sulfur and ligand atomic orbitals in various S-compounds. The shape of XANES spectra will reflect the density of empty states, because in X-ray absorption the excited electron is not free and the dipole transition poses strong selection rules to the final state (i.e., we will sense site and symmetry for S-atom). The Cu K XANES involving 1s-np and 1s-3d transitions, which enables sensing states of hybridization, unoccupied states like symmetries and charge transfers. Show the differences between S-ligands and Cu-S-ligands in the S K XANES spectra. Using de FDMNES program in multiple scattering formalism, we could attribute these differences to the conformations of sulfur environment and correlated with those obtained by other techniques (XRD and NMR). The Cu K EXAFS/XANES study allowed us to obtain the coordination numbers and average distances of first neighbors sulfur (Feffit pack), and hybridizations responsible in the complex formation, respectively. Also, using de FDMNES program, we could investigate the electronic state responsible in the charge transfer in the system.

Acknowledgements: This work was partially supported by LNLS and PIP 3079 and PICT 2008 - 00038.

Production of Highly Charged Kr Ions By Synchrotron Radiation: New results

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Charge state spectra of Kr ions generated by photoionization from 1900 to 2000 eV X-ray with Ne atoms have been measured by the PEPICO technique. Relative abundances of Kr(q+) ions in charge state up 5+ were obtained. A comparison with other experimental and theoretical data is presented.

Acknowledgements: LNLS, CNPq

Chemical shifts in X-ray photoelectron spectroscopy caused by pH-induced protonation on methionine and cysteine aqueous solutions

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In the early 70s, Siegbahn and Siegbanh published the first results of experimental electronic states for liquids [1], however, restricted to liquid samples with low vapor pressure (p_v), as formamide. With the development of microjet technique proposed by B. M. Winter and Faubel [3] significantly has increased the possibility to analyze other liquids with higher vapor pressure, such as liquid water ($p_v = 4.6$ Torr). Liquid water is the medium where the main biological reactions occur, therefore, data of electronic states of biological molecules in vapor-liquid interface is of great importance for understanding the subject.

We present the first results of preliminary characterization of R4000 Scienta electron analyser in the study of liquid-vapor interface of methionine and cysteine aqueous solutions, using the microjet technique. We obtain by using x-ray photoelectron spectroscopy the N1s, C1s and S2p chemical shifts of cysteine and methionine in aqueous solutions at different pH values. These shifts are associated with the sequential protonation of the amino and carboxyl groups, which affects both charge state and hydrogen bonding to the surrounding water molecules.

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Acknowledgements: This work was supported by CNPq, FAP-DF, DPP-UnB and LNLS.

Parte IV

Geociência, Meio-ambiente e Aplicações em Materiais Biológicos

Size selective elemental concentration of aerosol particles using SR-XRF

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Trace metals are ubiquitous in urban ambient air, with mass concentrations in the range of a few μg m-3 down to less than a few ng m-3. To measure such low concentrations represents a challenge for chemical and physical analysis. In this study, ambient aerosols were collected in Córdoba (Argentina) from April 2010-June 2012, in 3-h intervals and four size fractions, using a SIOUTAS impactor (SKC). In addition, 24 h samples in the PM2.5 fraction were collected with the DPS-SKC impactor. Aerosol samples were excited with a monochromatic excitation beam at two different energies both, with and without the presence of air to obtain size-segregated elemental aerosol mass concentrations for Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu and Zn under the selected experimental conditions. The high sensitivity of SR-XRF allowed for very low detection limits for most of the above elements. The data obtained with this technique aims to illustrate that there is a considerable gain of relevant information when time resolution for measurements is increased from 1 day to 3 h. The individual size fractions of a specific element seems to indicate different short-term patterns although further analysis need to be performed. The aims of this work were: (1) to present detailed source apportionment results for PM2.5 and the minor fractions (with time resolution) measured in the city, and (2) to compare with samples collected from July 2009-April 2010 to verify possible seasonal and inter annual variability.

Acknowledgements: This research was partially supported by the National Synchrotron Light Laboratory (LNLS), Brazil, by the Agencia Nacional de Promoción Científica y Tecnológica (FONCyT), by the Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), and SECyT (UNC). M. Achad thank FONCyT, and M.L. López and S. Ceppi thank CONICET for graduate fellowships.

Avaliação de substâncias inorgânicas no lodo de algumas estações de tratamento de esgoto da Região Metropolitana de Campinas por SR-TXRF

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O aumento da produção de lodo decorrente do crescimento do volume de esgoto tratado e do número de estações de tratamento de esgotos (ETE) no Brasil tem exigido a busca de alternativas para a sua disposição final. A compostagem e a utilização agrícola são alternativas viáveis uma vez que o lodo é rico em matéria orgânica, macronutrientes (N, P, S, Ca e Mg) e micronutrientes (Cu, Fe, Mn, Zn, B, Mo, Co, Se, Na e Cl) necessários à fertilidade dos solos. Porém devido aos lançamentos clandestinos e despejos industriais nas redes públicas de coleta de esgoto, pode haver a presença de elementos que causam danos à saúde e ao ambiente como Pb, Hg, Cd, As, Cr e Se. Neste projeto foram avaliados os elementos potencialmente tóxicos no lodo previamente desaguado da ETE Camanducaia (Jaguariúna), ETE Vila Flora (Sumaré), ETE Praia Azul e Carioba (Americana), ETE Samambaia, Anhumas, Santa Mônica, Piçarrão e Barão Geraldo (Campinas), através de Fluorescência de Raios X por Reflexão Total com Radiação Síncrotron (SR-TXRF). Os resultados preliminares indicaram que o lodo de esgoto das ETE da Região Metropolitana de Campinas RMC, exceto o lodo da ETE Santa Monica, atende as concentrações máximas permitidas de substancias inorgânicas estabelecidas pela Resolução CONAMA n 375 de 2006, porém, não atende o limite do elemento níquel da Instrução Normativa IN n 27/06 (70 mg.kg^{-1}). Com relação ao lodo da ETE Santa Monica, os elementos potencialmente tóxicos (EPTs) Cu, Ni e Zn excedem a Resolução CONAMA 375/06, e com relação à IN 27/06 excede para o elemento níquel. Os dados analisados indicam que os lodos da RMC não podem ser usados diretamente como fertilizantes. Para o uso agrícola destes resíduos, os mesmos necessitam passar por um processo que reduzam as concentrações das substancias inorgânicas, adequando o produto as legislações brasileiras.

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Study of schizophrenia at embrionary and atomic levels

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Schizophrenia is a chronic, severe, and disabling brain disorder that has affected people throughout history and its causes have not been completely elucidated yet. Oxidative stress, disturbed thinking and irrational behavior which are common to schizophrenic patients may be a result of changes in the levels of certain trace metals. In this work we analyzed induced pluripotent stem cells derived from schizophrenic patients in order to unveil schizophrenias impairments at the embrionary and atomic levels. Multielemental analyses were performed and results revealed high potassium and zinc levels on schizophrenia-derived cells compared to healthy ones. These findings suggest that potassium and zinc are related to the development of the schizophrenia.

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Titanium Diffusion in Shinbone of Mice with Osseointegrated Implants

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The use of Ti-based dental implants to replace lost dental elements is increasingly frequent. Dental implants are composed of Ti IV-type which is an alloy of titanium, aluminum and vanadium. When the implant is contacted with the tissue, a modification in its surface undergoes, releasing particles of titanium in different concentrations. The metabolism of free titanium is not well known. Titanium up-taking mode or movement in the body is not known, nor its toxic dose.

The micro-XRF technique is a suitable method for measuring trace elements in small samples whether liquid or solid. Six adult male Wistar mice of approx. 180 g were studied. Surgical site was prepared in a shinbone of the animals. A vertical incision of 1.5 cm was performed and a single pure titanium foil of 1.5 mm by 0.3 mm and 4 mm thick was introduced inside the bone, in the longitudinal direction. Euthanasia of animals was done after titanium implantation. Animals care and surgery were performed under International Animal Protection Rules.

The experiments were carried out at the microfluorescence station of the XRF beamline of the LNLS. The actual beam size on the sample was 10 x 10 microns. For each sample, XRF spectra were taken by linear scanning in area near the new bone formed around the Ti implant.

The scanning line show a clear effect of titanium diffusion while calcium intensity present a different behavior. Moreover, a clear correlation among the different structures of bones is observed in the Ti and Ca intensities. A more complex data analysis is required in order to find quantitative parameters of diffusion rates. These analyses will require intensities normalization of titanium peaks. This process could be attained by considering the net intensity of calcium, which represents somehow the compact degree of the octocalcium phosphate structure. After normalization, the diffusion rates will be quantified by derivatives procedures.

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Utilización de las técnicas de SR-XRF para identificar los blancos moleculares del arsénico ambiental

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Utilizando la técnica SR-TXRF determinamos bioacumulación de As en especies de ecosistemas marinos, que son claves dentro de la cadena alimenticia, como el kril. Aunque no está totalmente dilucidado su mecanismo de toxicidad, se ha descripto que el As puede conjugarse a péptidos como el glutatión y a proteínas interaccionando con sus grupos tioles afectando sus actividades biológicas. Sin embargo, muy pocas han sido identificadas, a pesar que podrían estar relacionadas también con el proceso de retención en tejidos y con su transferencia dentro de la cadena trófica. Por ello, hemos iniciado estudios tendientes a identificar los blancos moleculares involucrados en estos procesos. Se encontró As en todas las muestras de tejidos procedentes de animales de ambientes marinos, analizando la composición elemental (16¡Z¡40) por SR-TXRF. En sub-fracciones analizadas por SR-XRF, observamos que algunos elementos mayoritarios como el Cl y K son principalmente solubles. Mientras que una alta proporción del Fe y del Zn estaría interaccionando fuertemente con proteínas. Estos resultados sugieren que la SR-XRF es una técnica apropiada para analizar interacciones metales-biomoleculas. Sin embargo, el As no pudo ser detectado en las bandas proteicas separadas por SDS-PAGE y analizadas por SR-XRF por ser un elemento minoritario. Se están obteniendo sub-fracciones más concentradas para continuar con la identificación de los destinos celulares de este contaminante.

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Parte V

Matéria Mole e Fluídos Complexos

Physical Chemical Properties of Sunflower Oil Stearins: thermal and polymorphic behavior

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The isothermal crystallization behavior of soft (SS) and hard (HS) stearins obtained from high stearic high oleic sunflower oil (HSHOSFO) was studied using polarized light microscopy, differential scanning calorimetry, texture analysis and wide (WAXS) and small (SAXS) angle X-ray scattering with synchrotron source . Samples were crystallized in isothermal conditions at different temperatures. SS samples were crystallized at 5, 15, 16, 17, 18.5, and 19 C; while HS samples were crystallized at 10, 21, 22, 23, 24, and 25 C. Results from this research show that crystallization temperature strongly affects the crystallization behavior of these systems. Both fractions are polymorphic in nature which translates into different crystal morphologies and thermal behavior. The first form obtained when samples were isothermally crystallized to crystallization temperature (T_c) was always the α-form. Polymorphic behavior strongly changed with T_c for both fractions. SS fractions were characterized by β_2' crystals at lower T_c (below and at 15 C) and β_1' at higher T_c (16C and above). Interestingly, neither β_2 nor β_1 crystals were observed for SS samples crystallized at 10C/min in a DSC pan after 90 min at T_c. Similarly, HS samples were mainly characterized by β_2' crystals when crystallized at lower T_c (below and at 23 C) and α and β_1' crystals when crystallized at higher T_c (24 C and above). β_2 and β_1 crystals were only obtained after 48 h of storage at 25C. These results showed that depending on crystallization conditions, sunflower oil stearins had 5 polymorphic forms. These different polymorphic behaviors as a function of T_c are translated in significant differences in morphology and thermal behavior. This article will be submitted for publication sum.

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Silica gels and xerogels prepared by sol gel process: acid catalysts and microstructure

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This work is about the effect of the type of acid used as catalyst on the microstructure of silica hydrogels and xerogels prepared by sol-gel process. Small Angle X ray Scattering (SAXS), BET sorptometry and low resolution nuclear magnetic resonance spectroscopy (H-RMN) were used to characterize the materials. Ethanol, water and tetraethoxysilane in a volumetric ratio 5:7.5:5 were used as precursors. HF, HCl or HNO3 acid were used as catalyst. Sols were turned to gels and xerogels by drying and firing (450 C). SAXS measurements on gels were performed at DO2A-SAXS2, wavelength= 1.7968 , q range: 0.0055 - 0.10 A^{-1}. Fired xerogels were analyzed at DO2A-SAXS1, wavelength= 1.5400 , q range: 0.0177 - 0.4747 A^{-1}. T2 relaxation times were determined with a Minispec, mq60, Brucker. N2 adsorption isotherms were determined with a Micromeritics ASAP 2020. Gelification was 2 orders faster with HF. H-RMN analysis indicated that gels made with HCl or HNO3 have a more open structure containing trapped water. SAXS analysis was performed by 2 approaches. The 1st was based in a fractal arrange of poly-disperse spherical pores, considering sub units poly-dispersity. The 2nd was an empirical model that does not require previous knowledge of the system. Similar trends were obtained with both models. Gels have a fractal structure that depends on the type of acid. Rg2 is larger for HF; these structures may be associated with porous aggregates. HCl and HNO3 produced polymeric type gels with Rg1 and Rg2 smaller than for HF. Gel structure collapsed after firing with an increment in Rg1. Porod slope was 4.0 in the HF-xerogels and 2.7-2.6 for the others, indicating smooth and rough separation surfaces respectively. BET analysis showed that HF-xerogels were mesoporous while the other microporous. The size of microporous determined by BET and SAXS was similar. These results agree with a polymeric structure with rough separation surfaces. Due to the high nucleophilicity of F, HF leads to fast hydrolysis and condensation with formation of particle like units, while HNO3 and HCl produce polymeric type units. The first lead to mesoporous and the 2nd to microporous xerogels.

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The study the properties structurals and elastics of phases lamellar of lipid

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Lamellar systems composed of lipid bilayers have been widely used as model system for investigating properties of biological membranes, interactions between membranes and with biomolecules. The composition of the membrane determines its three dimensional shape and its properties such as rigidity and compressibility which play an important role on membrane fusion, protein adhesion, interactions between proteins, etc. We present a systematic study of a lamellar system composed of lecithin and a commercial co-surfactant (Simusol), which is a mixture of ethoxylated fatty acids. Using X ray scattering and a new procedure to fit X-ray experimental data, we determine relevant parameters characterizing the lamellar structure, varying membrane composition from 100% of lecithin to 100% of Simulsol. We present experimental data illustrating the swelling behavior for the membrane of different compositions and the respective behavior of the Caillé parameter. From and GISAXS experiments on oriented films under controlled humidity we investigate the compressibility of the lamellar phase and the effect of incorporating co-surfactant. Combining the Caillé parameter and compressibility studies we determine the bending rigidity of membranes. The results obtained with this experimental approach and new procedure to fit X-ray experimental allows us to identify structural changes in the bilayer depending both on hydration and co-surfactant content, with implications on elastic properties of membranes.

Acknowledgements:

On the action of surfactants in the protein denaturation: a study by SAXS and ITC

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Proteins are the major constituent of biological systems along with carbohydrates, lipids and nucleic acids (DNA and RNA). According to their structure and composition, proteins perform several functions in the organism, since from the macroscopic level, with participation on the olfaction of animals, to the cellular level, allocated in the membrane and making the connection between extra and intracellular environment. The function of a protein (which may be enzymatic, hormonal, structural, energy, transport etc) is related to several factors including its structure (primary, secondary, tertiary or quaternary). Denaturation occurs when the secondary structure and / or tertiary is lost, which is almost always followed of loss of the biological function. Temperature, pH and the action of surfactants influence the process of the denaturation. This work investigates the latter aspect mentioned before. Therefore we are using an isolated protein, alpha-lactalbumin, that is found in the milk and whose function is related to the synthesis of galactose. The purpose is to characterize, in a thermodynamic-structural point of view, the denaturation of alpha-lactalbumin in the presence of surfactants anionic (sodium dodecyl sulfate SDS), cationic (tetradecyltrimethylammonim bromide TTAB), zwitterionic (2-diheptanoyl-sn-glycero-3-phosphocholine DHPC) and nonionic (decyl-β-D-Maltopyranoside DM). The technique of isothermal titration calorimetry (ITC), which provides information of structural changes from changes in energy, represents the starting point for the study, while the technique of small angle X-ray scattering (SAXS) provides information about the structural characteristics of surfactant-protein complexes formed at each step of the denaturation process. Data analysis is in the initial stage, but it was possible to obtain general parameters related to the complex formed from the correlation of both calorimetric and scattering data. As will be shown, each class of surfactant denatures protein in a particular way, as shown in the literature [1], providing complexes with different characteristics. The studies will provide the basis for a characterization of other protein-surfactant systems (as lysozyme-surfactant), in addition to future correlation of data obtained with those from other techniques such as circular dichroism (CD), nuclear magnetic resonance (NMR) and fluorescence spectroscopy, which provide additional information for these systems.

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Report on the design and test of liquid sample holder for SAXS measurements under static magnetic field

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Here, we aim to present the design and test of a sample holder for liquids to perform SAXS measurement under static magnetic field. This is a modification of the already existing holder available in SAXS2 beam line. The design was discussed at the last RAU [1], the construction is under progress nowadays and the implementation will be carried out under proposal D11A - SAXS1-13714 (Nov. 2012). This device can find applications in the study of induced anisotropy in colloidal magnetic dispersion and rheological problems, among others. The static magnetic field are produced with commercially available NdFeB magnets of remanent field B_r=1.12 T. We have designed two distinct configurations to achieve homogenous field, parallel and perpendicular to the beam direction. Also, the arrangements can be modify to vary the field intensity up to 0.7 T. We choose to keep the original material of the liquid sample holder (stainless steel 316L) because austenitic stainless steels are non-magnetic in the annealed, fully austenitic condition. The magnetic permeability of this material in this condition is generally less than 1.02 at 5 kA/m. To test the effectiveness of the field achieved with the projected magnets arrangements we choose the use of stable colloidal suspensions, consisting of single-domain spherical magnetic nanoparticles (NP) displaying very low polydispersity and dispersed in liquids. The mean primary particle sizes are in the range from 2 to 7 nm and coated with $\sim$ 2 nm oleic acid shell. This ensemble exhibited a nice SAXS pattern [2], which is the result of primary particle pattern superimposed to the power law behavior originated at the NP self organization.

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ESTUDIO SOBRE MICELAS UNIMOLECULARES DERIVADAS DE LA POLIETILIENIMINA HIPERRAMIFICADA: SAXS, XRR, LB

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Las micelas unimoleculares1 son estructuras constituidas por un núcleo polimérico dendrítico rodeado por una coraza (generalmente moléculas pequeñas en relación al núcleo), anclada covalentemente, de distinta características fisicoquímicas. De este modo, la entidad resultante emula a las micelas tradicionales (multiméricas), pudiendo presentar, en función de sus constituyentes, características micelares directas o reversas. El anclaje de ácidos carboxílicos (C8-C18), a través de enlace amida, a núcleos hiperramificados de polietilenimina (HPEI, Mn= 10kda), da por resultado la formación de micelas unimoleculares (HPEI-Cx) con comportamiento reverso, solubles en solventes orgánicos variados (cloroformo, tolueno, THF)2. Las mismas han sido efectivas en una miríada de campos de estudio tanto básicos como aplicados, como pueden ser la transferencia de nanopartículas a fase orgánica y la interacción con colorantes hidrófilos en medio apolar. Previamente, hemos demostrado que HPEI-C16 en tolueno, puede presentarse como micela unimolecular a alta temperatura (¿33C), o agregados supramoleculares estructurados a baja, sufriendo estos últimos expansión térmica negativa (NTE, Negative Thermal Expansion)3. En el presente trabajo se mostraran resultados del estudio de dichos sistemas, evaluando el impacto del largo de cadena presente en la coraza sobre el comportamiento en solución/suspensión utilizando Dispersión de Rayos X Bajo Angulo (SAXS) y la estructura de monocapas en la interfase aire/agua obtenidas en Balanza de Langmuir y caracterizadas mediante Reflectividad de rayos X (XRR).

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COMPLEJOS SUPRAMOLECULARES AUTOENSAMBLADOS IÓNICAMENTE DERIVADOS DE LA POLIETILENIMINA HIPERRAMIFICADA

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El autoensamblado iónico (ISA, Ionic self assembly) ha demostrado ser una versátil herramienta para la formación de complejos supramoleculares, con variados comportamientos y funcionalidades. Dentro de los ISA, las estructuras derivadas de polielectrolitos, se han convertido en un área de gran desarrollo dentro de la materia blanda [1]. Complejos de este estilo, pueden ser generados a partir de la interacción entre ácidos carboxílicos y la polietilenimina hiperramificada (HPEI) [2]. En este caso, la reacción acido base entre los grupos carboxílicos del acido y las aminas del polímero, da origen a la interacción iónica entre los carboxilatos y amonios resultantes, que es muy estable en solventes de baja constante dieléctrica (como cloroformo, tolueno o THF), generándose, por tanto, complejos supramoleculares con un núcleo hidrófilo de HPEI y una coraza constituida por las cadenas alifáticas de los ácidos interactuantes. En el presente trabajo, mostraremos un estudio sistemático de estructuras derivadas de la interacción iónica HPEI (Mn= 10Kda), con ácidos grasos de distinto largo de cadena (C8-C18). Los diferentes complejos fueron caracterizados en fase solida y en suspensión/solución (THF,Tolueno) utilizando Dispersión de Rayos X a Bajo Ángulo (SAXS), evaluando el impacto del largo de cadena y sus mezclas, el grado de recubrimiento (Relación Carboxilato/Amonio) , la mezcla de distintos largos de cadena y el importante efecto de la temperatura en las diversas fases resultantes.

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Caracterización estructural de agregados de asfaltenos mediante el uso de técnicas de dispersión de luz. Dinamic Light Scattering y Small-angle X-ray Scattering.

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La caracterización estructural de asfaltenos es un aspecto importante para entender los procesos físicos y químicos que tienen lugar durante su floculación en las diferentes etapas de los procesos de producción y refinación. La estructura molecular de los asfaltenos puede ser analizada con base en parámetros moleculares promedio obtenidos mediante información de análisis elemental, distribuciones de peso molecular y resonancia magnética nuclear. Durante su floculación o precipitación, la interacción entre unidades moleculares es importante y la formación de agregados tiene lugar. Estos agregados pueden ser caracterizados mediante técnicas de dispersión de luz como DLS en el rango visible o SAXS en la región de los rayos X. En presente trabajo una muestra de asfaltenos obtenida a partir de un crudo pesado, obtenidos mediante técnica SARA, se caracterizó mediante resonancia magnética, espectrometría de masas y espectroscopia de infrarrojo. Difracción de rayos X fue utilizada para caracterizar las muestras en fase sólida y obtener información relacionada con los parámetros cristalinos del material como espaciado interlaminar, diámetro promedio de las láminas aromáticas y diámetro de los agregados de asfalteno. La caracterización de los agregados de asfalteno se estudió mediante DLS a 532 nm en benceno y tolueno como solventes, considerando dos variables experimentales: la concentración de la muestra y la temperatura. Los resultados experimentales mostraron una dependencia directa entre la concentración de las muestras y diámetro promedio de los agregados, mostrando una disminución progresiva a medida que la concentración disminuye. Se observó que el incremento de la temperatura de la muestra disminuye en forma progresiva el diámetro de los agregados en el rango de 30 a 90C. Se requieren experimentos adicionales utilizando la técnica SAXS para establecer una relación con los resultados de XRD y DLS.

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Interactions and structure of lipid membranes by SAXS investigations

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Lipid membranes are present in many structures of living cells, such as the plasma membrane, the Golgi complex and other organelles. Changes in membranes composition can modify their mechanical properties and structure, like the rigidity, which plays a key role in their three dimensional spatial organization. In this work, we investigate interaction and the flexibility of lecithin membranes and the effect of incorporation of fatty acids. An osmotic pressure (P) applied to the membranes is controlled by preparing the lamellar phase in a polymer solution of PVP. Small Angle X- ray Scattering (SAXS) experiments are carried out in lamellar phases in equilibrium with the polymer solution, allowing us to obtain the curves P(D) for each membrane composition, where D is the lamellar period. For a given osmotic pressure, we observe that the lamellar period is shifted to higher values upon incorporation of fatty acids, indicating that repulsive forces are enhanced. An exponential decreasing of P(D) was observed for membranes containing up to 50With fittings of SAXS curves we may obtain structural parameter of the membranes. We may than observe the behavior of Caillé parameter, which is related to the Rigidity Constant and the Compression Modulus of the membrane. We observed that these parameter are sensible to the incorporation of fatty acids, showing some changes in the membrane flexibility. These findings reveal the great potential of this methodology for studies of membranes of biological interest.

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Parte VI

Materiais Estruturais e Aplicações na Indústria

Effect of bambu on the morphology of low density polyethylene/bamboo flour composites

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Bamboo belongs to the grass family. It is an alternative of sustainable material for use in product design, being inserted in the concept of Eco-design as fiber reinforcement in polymer matrix composites. Although, previous reports have shown that it is difficult to extract bamboo fibers having its superior mechanical properties, they also indicated that bamboo cellulose crystals incorporated in the polymeric matrix have the potential to increase the mechanical properties of composites. In this study, we investigate the morphology of low density polyethylene (LDPE)/bamboo flour (BF) composites that were modified with polyethylene-graft-maleic anhydride (PE-g-MA) and glycerol. BF was obtained by grinding samples of 3 years old bamboo Phyllostachys Heterocycla. The samples were ground using sandpaper in carpentry and then the grains which passed through 100-mesh screen were selected. Due to its low processing temperature, LDPE (Braskem-Brazil) was used as matrix. Initially, the raw materials were mixed all together in a torque rheometer at 110^{o}C with rotor speed of 40 rpm for 10 minutes. Then films were obtained using the conventional hot-press method at 110^{o}C for 5 minutes with 2 MPa of pressure. The morphological studies were performed using a monochromatic beam of wavelength 1.55 (exposure time was 300 sec). The scattering intensity was registered using a Pilatus detector (300K, 84 mm X 107 mm) for SAXS with a sample to detector distance of 1976.5 mm. Porod and Guinier analysis were carried out to obtain structural information on the inhomogeneities present in the matrix. Multiplying $I_{(q)}$ by the square q, the Lorentz-corrected scattering curves were obtained and the interdomain spacing L ($L = 2\pi/q$) were estimated from the peak position. SAXS 2D patterns of the PE and composites are isotropic, indicating that the BF are homogeneously distributed in the matrix. Nevertheless, BF introduced affects the structure and morphology of the matrix, changing the initial structure. Although, L is similar for PE and composites, the inhomogeneities present in the matrix are different in shape. Results, from Porod region, indicated a very smooth particle surface ($\alpha = -4$) for PE samples. On the other hand, composite particles presented rough surface($\alpha \sim -3.2$). Guinier analysis, at low angles, at a log($I_{(q)}$) versus log(q) plot, described planar shapes ($\beta = 2$) only for PE samples.

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Luminescent Properties of Eu doped $CaAl_2O_4$ produced by Proteic Sol Gel Route

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In the last years the luminescent properties of aluminates have been investigated for use in a range of applications, varying from use in medicine up to signposts light. The $CaAl_2O_4$ (calcium aluminate) when doped with rare earths ions has shown long lasting phosphorescence due the presence of defects that provide the trapping of the electrons, thus slowing, the emission. In this work, $CaAl_2O_4$ doped with trivalent ions are produced and the luminescent properties are studied. The samples were produced via Proteic Sol-Gel route that consist in using the coconut water as a starting solvent. DTA (Differential Thermal Analyze) and TG (Termogravimetry) were done to seek for the best calcination conditions leading to the formation of the desired phase. XRD (X-Ray Diffraction) was used in the structural characterizations of the nano-powders to know the crystalline phases present in the samples and the results indicated that the samples produced at 1200C for 2h exhibit single crystalline phase. X ray absorption spectroscopy (XAS) was performed around the Eu L_3 edge of the doped samples in the XAFS-2 beam line and around the Ca K edge in the SXS beam line both at LNLS. X ray stimulated optical luminescent (XEOL) was measured simultaneously with XAS in both cases and the luminescence mechanisms were followed. X-ray induced luminescence decay was also measured at the XAFS2 beam line in the single bunch mode. The characteristics transitions of the Eu^{3+} were identified in the emission spectra indicating the presence of Eu^{3+} in the $CaAl_2O_4$ matrix. Preliminary results of photoluminescence of the material will be presented, including the main excitation and emission wavelengths, characteristic decay time, and behavior of the emission intensity as a function of excitation energy.

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Influência das Fases Hexagonal e Monoclínica do $SrAl_2O_4$ nas Propriedades Ópticas de Nanopós Dopados com Eu e Dy

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Os aluminatos são uma classe importante de materiais que apresentam propriedades luminescentes quando dopados com terras raras. O $SrAl_2O_4$ (aluminato de estrôncio) quando dopado com Eu e Dy tem atraído atenção por apresentar fosforescência de longa duração (LLP). O $SrAl_2O_4$ apresenta duas duas fases cristalinas, hexagonal e monoclínica, com transição reversível reportada na literatura em $650°C$. Neste trabalho investigamos a influência das condições de produção das amostras nas concentrações de ambas as fases e nas propriedades ópticas das amostras dopadas. As amostras foram analisadas através das técnicas de Difração de Raios X (DRX), Microscopia eletrônica de Varredura (MEV), Radioluminescência (RL), Luminescência Óptica Excitada com raios X (XEOL) e Espectroscopia de absorção de raios X (XAS). As medidas de XAS e XEOL foram realizadas na linha XAFS-2 (X-ray Absorption Fine Structure) no Laboratório Nacional de Luz Síncrotron, Campinas, Brasil (LNLS). As análises de difração de raios X mostram que a taxa de resfriamento influencia na concentração das fases monoclínica e hexagonal. As amostras puras e dopadas com Dy apresentaram maior quantidade de fase monoclínica quando produzidas com taxa de resfriamento de $10°C/\text{min}$ e as amostras dopadas com Eu, com taxa de $2°C/\text{min}$ induziu a formação da fase monoclínica. Este resultado pode ser interpretado em termos do custo energético envolvido na estabilização das duas fases cristalinas e do custo energético dos defeitos gerados pelos dopantes. As propriedades luminescentes são influenciadas pela razão das fases monoclínica e hexagonal presentes na amostra. Foi possível determinar que o comportamento da resposta radioluminescente em função da concentração das fases cristalinas é na verdade definida pelas propriedades específicas dos defeitos induzidos pelos dopantes e pelo ambiente cristalino que estes se encontram na estrutura do $SrAl_2O_4$. As medidas de RL, combinadas com a XEOL e com medidas de tempo de vida de luminescência excitada com raios X foi possível mostrar que o Dy, ao contrário de modelos propostos na literatura, não é um mero coadjuvante, mas participa ativamente do processo de emissão luminescente definindo as propriedades da LLP para o material.

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XAFS characterization of electrodeposited Ni-W coatings.

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Alloys of tungsten and molybdenum with iron group metals have attracted considerable attention due to their specific magnetic, electrical, mechanical, thermal and corrosion resistance properties. Among them, nickel and tungsten (Ni-W) alloys are particularly interesting because they exhibit good corrosion resistance in different aqueous media, high hardness and ductility, and anisotropic magnetic properties. Therefore, they have been studied as candidates to protect structural metals such as steels and copper, for magnetic recording systems, and for MEMS and NEMS applications. In this work a detailed characterization by X-ray absorption spectroscopy of electrodeposited Ni-W coatings prepared by pulsating electrodeposition on steel and copper substrates is presented. X-ray Diffraction, Atomic Force Microscopy (AFM) and Scanning Electron Microscopy (SEM) results are also presented. These results are discussed in terms of the good hardness and ductility that the coatings present. Different Ni-W coatings were prepared with different pulse programs in order to determine the effect of the preparation conditions on the final structures that were formed. Both XANES and EXAFS experiments at both Ni-K and W-L_3 edges were studied at the XAFS2 beamline of the Laboratorio Nacional de Luz Sincrotron (LNLS), Campinas, Brazil. Experiments were performed in fluorescence mode at room temperature. The results indicate that two main phases are found in the bulk structure: a W-rich amorphous phase and Ni-rich crystalline phases. The crystalline phases consist of crystalline domains of 7-8 nm in size of Ni(W) (fcc) solid solution (12% W content). The amorphous phase exhibits a less compact Ni-W structure and a higher W content. We have found that in both phases the W is under a metallic state without evidence of significant amounts of tungsten carbide, tungstates or citrate-tungsten complexes. The good hardness and ductility of the coatings can be related to the structure consisting of a W-rich Ni-W matrix composite reinforced by the 7-8 nm crystalline domains of the Ni(W) solid solution.

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Impurity Atoms in Electrodeposited Films And Milled Powders of ZnMO (M=Co, Mn)

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(Zn, Mn)O and (Zn, Co)O appears as new promising materials for spintronic. Some authors observed ferromagnetic behavior even at room temperature in these so called diluted magnetic semiconductors (DMS) materials, but the origin of this behavior is still controversial. Although some researchers have claimed that the origin of ferromagnetism is related to the formation of Co-rich clusters, the source of the observed ferromagnetism is far from being clear. In previous works, we have analyzed the magnetic properties of mechanically milled powders [1-3] and electrodeposited films [4] of ZnFeO or ZnCoO samples. In these cases, ZnCoO samples are paramagnetic, what in principle is an indication of a homogeneous distribution of Co into the ZnO matrix. However ZnMnO reveals an antiferromagnetic behavior for high contents of Mn. Therefore taking advantage of synchrotron radiation capabilities for the residual elemental detection inside Mn-rich or Co-rich clusters, we attempt an EXAFS characterization of these $\mathrm{Zn}_{1-x}\mathrm{M}_x\mathrm{O}$ (M: Mn, Fe and Co) samples. The results are discussed taking into account previous studies made by X-ray diffraction, Mössbauer Spectroscopy and magnetic measurements in a Quantum Design MPMS-5S superconducting quantum interference device (SQUID) magnetometer.

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Estudo preliminar de filmes de Ormosis (Silicatos organicamente modificados) por meio de GIXRF assistida por Luz Sincrotron

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O presente trabalho trata sobre medidas de fluorescência de raios-x assistida por luz síncrotron em ângulo rasante de materiais híbridos(ormosis).O alvo deste trabalho é demonstrar o potencial desta técnica na análise quantitativa destes materiais. Silicatos organicamente modificados (ormosis) têm aplicação em diversas ramas da ciência (óptica, biotecnologia, catálise...). Existe muita documentação sobre sua caracterização e avaliação de suas propriedades, mas até o momento não existe uma metodologia analítica que possibilite quantificar sua composição e correlacionar esta com suas propriedades e sua estrutura. A dependência angular da Reflexão Total de Raios-X(TXRF) também conhecida como analise GIXRF (grazing incidence x-ray fluorescence) apresenta um perfil de fluorescência em função do ângulo rasante que é registrado para um determinado intervalo de ângulos,por exemplo de 0 a 0.2 em passos de 0.005(graus sexagesimais).A análise de fluorescência de raios-x em ângulo rasante (GIXRF) tem o potencial de contribuir eficazmente na caracterização de nanopartículas depositadas em superfícies planas assim como fornecer informações sobre a distribuição de profundidade e concentração de elementos nas camadas. Esta técnica é muito sensível, mesmo a profundidades de alguns micrómetros (μm) e os efeitos de absorção são minimizados. Para o desenvolvimento das medidas GIXRF as amostras foram preparadas depositando filmes finos de ormosis contendo Zn sobre substratos de silício monocristalino.Trabalhamos em uma faixa de concentração de Zn de 0.00005M até 0.1M. Fizeram-se medidas a diferentes ângulos (0.05, 0.1, 0.15, 0.2 graus sexagesimais), para obter um perfil dependente do ângulo que forneça informação superficial dos filmes. O espectro GIXRF apresenta ruido de fundo mínimo devido que a luz síncrotron é polarizada.Temos obtido linearidade trabalhando em faixas de concentração de Zn de 0.00005M até 0.01M. Concluimos que esta técnica possibilita a análise quantitativa dos ormosis. References 1) Reinhold Klockenkämper: Total Reflection X-Ray Fluorescence Analysis Chemical Analysis A Series of Monographs on Analytical Chemistry and Its Applications Volume140 John Wiley & Sons New York 1997

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Acknowledgements: Agradecemos a CNPQ e a FAPESP pelo apoio financeiro quanto ao LNLS pelas medidas desenvolvidas

Materiais híbridos siloxano-poliéter como eficientes adsorventes para remoção de poluentes orgânicos e metais pesados.

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A presença de poluentes orgânicos e metais pesados na água, oriundos de uma variedade de fontes de efluentes, vem se tornando excessiva, e desta forma preocupante no meio ambiente. Fontes poluentes de Cu, Ni e Cr incluem os efluentes de indústrias do setor elétrico, de fungicidas, de polpa de papel, fertilizantes, curtumes e de alimentos.O uso de híbridos da classe siloxano-poliéter podem levar à preparação de novos dispositivos multifuncionais para eficiente adsorção de corantes e íons metálicos. Esses materiais apresentam propriedades únicas como boa resistência mecânica, transparência e flexibilidade, são insolúveis em água e podem se comportar como hidrogéis, absorvendo grande quantidade de água. O objetivo deste trabalho é estudar o ambiente químico dos íons metálicos Cu2+, Ni2+ e Cr6+ após os ensaios de adsorção na matriz. Uma vez que as propriedades desses materiais parecem estar relacionadas ao sinergismo entre o metal e a matriz, esse mecanismo de interação merece ser estudado. Para isso utilizamos a técnica de XAS (Beamline XAFS1) que fornece informações as quais podem nos permitir sugerir mecanismos para remoção dos íons metálicos estudados, já que esta matriz apresenta diferentes sítios de interações entre metal-matriz. O híbrido siloxano-poliéter a base de PEO com massa molar 500 g.mol-1, mostrou-se eficiente para remoção de espécies iônicas. Após algumas horas de contato com a solução de acid red 114 (aniônico) ou azul de metileno (catiônico) a matriz híbrida adsorveu todo o corante, mudando sua característica física de transparente para colorida, neste caso, azul ou vermelho dependendo da espécie iônica utilizada. A matriz híbrida mostrou-se também eficiente na remoção dos cátions Cu2+, Ni2+ e Cr6+ em solução aquosa. O pH, assim como, o balanço hidrofílico/hidrofóbico apresentaram importante influência na capacidade de remoção. Um estudo inicial por absorção de raios-X usando três diferentes matrizes híbridas a base de PEO e PPO , confirmam que o ambiente ao redor do metal (Ni, Cu e Cr) é formada em grande parte por nitrogênio e oxigênio. No caso dos materiais adsorvidos com Ni a analise dos espectros XANES revela que a estrutura da pré borda é característica de uma coordenação octaédrica.

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XAFS studies on Ni (II) hydroxide nanoparticles obtained by eletrochemical synthesis applied as electrode material for rechargeable batteries

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Its widely known that the Nickel Hydroxide is an important and functional material with multiple applications, principally in battery technology as the positive electrode of so called Cd/Ni, Zn/Ni,H2/Ni, Fe/Ni and MH/Ni cells, also as a precursor of catalysts, and in electrochromic devices. Particular emphasis is placed on the structural (and textural) characterization of the phases involved in nickel hydroxide electrodes as a prerequisite to a rational approach to their redox behavior and understand the relationship between the structural features and the charge storage capacity. Nickel hydroxide has a hexagonal layered structure with two polymorphs forms, namely α and β. The α-form is isostructural with hydrotalcite (HT)- like compounds and consists of a stacking of positively charged $\mathrm{Ni(OH)}_{x-2}$ layers, with intercalated anions (e.g., carbonate, nitrate, etc.) and water molecules in the interlayer space to restore charge neutrality; if the slabs are oriented randomly with respect to one another, leading to turbostratic disorder. The β-form possesses a brucite like $\mathrm{Mg(OH)}_2$ structure and does not contain any intercalated species. In this structure, the OH^- ions are hexagonally packed and the nickel ions occupy alternate rows of octahedral sites leading to layered structure which can be described as an ordered stacking of charge neutral layers of $\mathrm{Ni(OH)}_2$. The HT and the brucite structures are not very much different. In most cases, the active material of positive electrodes belongs to the β-form. It is generally accepted that α-nickel hydroxide will exhibit superior electrochemical properties compared to the β-form. However, the α-nickel hydroxide is a metastable phase and is difficult to synthesize because it changes rapidly to the β-form during synthesis or on storage in a strong alkali. Actually its recognized that the overall performance of nickel cathodes depends on the microstructure, textural characteristics, and the crystallite size of the active material. In this work we explore la possibility of obtain α and/or β nickel hydroxide at semi micro level using a high area platinum mesh as cathode and following the changes with Co hydroxide doping.

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Estudo eletro-morfológico de compósitos eletroativos utilizando SAXS

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Os compósitos de polímero ionomérico e metal (IPMC) são materiais funcionais que deformam em resposta a um estímulo elétrico, amplamente estudado como atuadores robóticos. O IPMC estudado é composto por uma membrana de Nafion® entre eletrodos de ouro. O Nafion® é um copolímero em bloco que combina uma fase hidrofóbica baseada de uma cadeia principal de PTFE e grupos laterais hidrofílicos de perfluor éter-sulfonados. Na forma hidratada, estes grupos laterais se organizam na forma de aglomerados iônicos conectados por canais os quais são responsáveis pela capacidade de transporte iônico deste material. Os aglomerados iônicos possuem uma forte correlação com um pico em torno de $q=2\pi/(4\text{nm})$ que varia em função do grau de hidratação do polímero, e os cristalitos de PTFE, com um ponto de inflexão em baixos ângulos. Considerando estas características estruturais do Nafion®, quando um campo elétrico é ativado sobre a fase polimérica do IPMC, cátions solvatados migram em direção do cátodo através dos canais. A mudança de volume das faces causada pela diferença de concentração de água resulta no dobramento do material. O objetivo deste trabalho foi estudar as variações morfológicas da fase de Nafion® causadas pela influência do campo elétrico e que estão relacionadas com os mecanismos de deformação do IPMC. Para evitar variações morfológicas causadas pela variação do grau de hidratação da amostra durante os experimentos, as medidas foram realizadas dentro de uma câmara com temperatura e umidade controlada, equipada com janelas transparentes ao feixe de raio-X (Myler®). As membranas de Nafion® N117 (forma de H^+) foram mergulhadas em uma solução de HCl por um período longo o suficiente para garantir o H^+ como única espécie catiônica presente na fase polimérica. As membranas foram secadas em uma estufa (90^o) por 12 horas e metalizadas com ouro em uma evaporadora, formando eletrodos com espessura de 150nm. O espalhamento causado pelos eletrodos e a atmosfera de controle de umidade foram subtraídas do sinal espalhado. Após a aplicação da tensão elétrica uma sequência de padrões de espalhamento foi obtida em intervalos de 6 segundos durante 180 segundos. Em uma análise preliminar foi possível observar uma mudança na posição e na intensidade do pico atribuído aos aglomerados iônicos. Simulações utilizando o pacote IRENA do IgorPro estão sendo realizadas para uma análise mais detalhada dessas mudanças morfológicas.

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Parte VII

Métodos e Instrumentação

The limit of perfect-like mosaic crystals in Back-diffraction

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X-ray diffraction at angles close and exactly equal to 90 degrees (back-diffraction) has been applied for a variety of experiments which requires high energy resolution. Among them, thermal expansion measurements and inelastic X-ray scattering are some applications. Few years ago, has been demonstrated that mosaic crystals show like perfect crystals in back-diffraction condition. There are some limits where this is entirely true. Such limits are exploited here. A back-diffraction experiment was mounted at XRD2 beamline at LNLS. A high-energy resolution 4-Crystal Si 551 monochromator was used to have a divergence of 8 μrad and energy resolution of 24 meV at 9.2 keV. This monochormator was employed in order to have a plane and monochromatic X-ray wave beam for a LiF 600 crystal in back-diffraction condition, avoiding any rocking curve broadening due to the beam divergence and/or chromaticity. The 90 μm thick LiF 600 crystal was prepared at the Crystal Laboratory at the ESRF. It was characterized by X-ray topography showing a mosaicity of 200 μrad in an area of 2 cm^2. The back-diffraction measurements on this crystal were done by detecting the transmitted diffracted o-beam profile. The results show diffraction profiles much broader than the ones predicted for a perfect crystal. By making some simulations we show that a mosaic-chromatic effect is the main contributor for this effect. A perfect-like condition is achieved only if the back-diffraction bandwidth ($\delta\lambda/\lambda$) is smaller than the crystal mosaicity (δd/d). Even with this limitation, we show that such mosaic crystals can be used for low energy resolution inelastic X-ray scattering analyzers and/or for a high angular acceptance X-ray back-diffraction monochromator with energy resolution similar to a conventional double crystal monochromator.

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Development of a Two-Dimensional Detector for X-Ray Experiments

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The detection system is one of the most important aspects of any experimental apparatus. The data quality is a direct consequence of the efficiency and resolution of the detector. One example are the proportional counters which, in its simplest conception, are composed of a wire, placed between two plates, with a kilovolt voltage between them. When a photon passes, it ionizes the gas. The created ions are accelerated by the difference of potential, which can be detected as charge pulses in each end, permitting a precise determination the event position [1]. Several methods have been developed to determine the position of the event in a proportional detector [2]. In this project we will work on the development, characterization and control of a two-dimensional multiwire gas detector that will be used for X-Rays experiments (5-8 KeV). This project is been developed in collaboration with the Department of Nuclear Physics of University of Sao Paulo, which has experience with two-dimensional multiwire gas detectors used for heavy ions research [2]. One of the first goals will be to perform modifications in currently available detectors for X-Ray experiment. The modification of the detectors carries several implications, which corresponds to the design of an appropriate window, choice of the internal pressured gas mixture and the setup of the operation and control system [3]. For the windows, some alternatives would be Kapton or Mylar since both materials have low X-Ray absorption and also sufficient high mechanical strength to support the pressure difference (4 atm), even using thin windows. Since the detector will have a reasonable large area (10x10cm or larger), the fixation and sealing of the window is an additional problem. As will be shown, several tests have been already performed both for the test of the electronics and control of the system and also the development of solutions for window fixation and sealing. [1] G. F. Knoll, Radiation Detection and Measurement, John Wiley and Sons, New York, Chicester, Brisbane, Toronto, Singapure (1979). [2] M.M de Moura et al, Nucl. Instr. and Meth. 433 (1999) 623-629A [3] A. Gabriel et al, Nucl. Instr. and Meth. 152 (1978) 191-194

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Calibration method for confocal x-ray microanalysis simplified by Montecarlo simulation

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The confocal setup consists of x-ray lenses in the excitation as well as in the detection channel. in this configuration, a probing volume defined by the overlap of the foci of both x-ray lenses is analyzed. Scanning the sample through this micro volume, 1-3 dimensional studies can be performed. An elemental analysis is obtained by the detection of the x-ray fluorescence produced in the micro volume.

The fundamental parameters method (FP) applied at the confocal configuration relies on a three- dimensional model for the probing volume which depends on the characteristics of both x-ray lenses. The model describes the sensitivity of the spectrometer which relates the theoretical and measured XRF intensities in every pixel of the sample. For the particular case of polychromatic excitation, the theory shows that the focalization properties of the excitation lens for all incident energies affect the x-ray fluorescence intensity. Therefore the traditional calibration method for FP based on the measurement of standard samples becomes unstable since the number of required fitting parameters is too high. To overcome this problem a previous characterization of the excitation lens is recommended. In this work Montecarlo radiation transport simulation was tested as a low cost solution for the characterization of the excitation lens. An own programming code was written in FORTRAN language considering the multiple Fresnel reflections and refractions of the incident beam in the walls of the excitation lens.

The proposed calibration method simplified by Montecarlo simulation was applied for a confocal spectrometer implemented in the Brazilian Synchrotron Radiation Source (LNLS) with white beam. The experimental parameters of the sensitivity were obtained by means of depth profile analysis of several thin films (Micromatters^{TM}). The calibrated confocal setup was used to quantify reference standards in order to validate the calibration procedure. Our results for elemental concentrations had good match with the nominal values of light matrix reference standards with relative error less than 15.

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Microscopic X-ray fluorescence analysis of Spheroid Culture Model of Human Prostate Cells

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Diseases of the prostate gland such as Prostate cancer (PCa) and Benign prostate hyperplasia (BPH) are the most frequently health problems in men past middle age. Spheroid Culture Model are a useful culture technique for tissue engineering or regenerative medicine research, pharmacological and toxicological studies, and fundamental studies in cell biology. Synchrotron Radiation micro X-Ray Fluorescence (μSRXRF) was used to investigate two-dimensional spatial distributions of Fe, Cu and Zn in spheroids derived from prostate tissue with PCa and BPH. The measurements were carried out in the X-ray microfluorescence station of the XRF beam line at the Synchrotron Light National Laboratory (LNLS). The distribution of the elements Fe, Cu and Zn was determined. The results showed that the elements analyzed presented non-uniform distribution.

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Setup for inelastic x-ray scattering at the XDS beamline

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Since a decade ago, inelastic x-ray scattering (IXS) experiments have been performed at the XRD1 beamline of the LNLS with high energy resolution but with a very limited photon flux. The construction of the new wiggler beamline at the LNLS (XDS) will open up the possibility of carrying out new IXS experiments with even better resolution and much higher photon fluxes thanks to the superior x-ray beam quality provided by this source. In this work we present a new setup to be mounted at the XDS beamline to perform IXS experiments with sub-eV energy resolution along with high counting rates. This beamline has a 6+2 circle goniometer which will allow measurements on horizontal, vertical and oblique scattering planes to be performed, while the momentum transfer will can be continuously modified by changing the scattering angle. In order to improve even more the energy resolution we propose to extend the spectrometer arm to 1 m and at the same time to construct analyzer crystals with larger curvature radius. The implementation of the dispersion-compensation method, along with a linear detector, has been considered. The setup design is aimed to two configurations, a high energy resolution mode (~ 0.5 eV, with an incident beam intensity of 2×10^{11} photons/s/100mA) and a high flux mode (1×10^{13} photons/s/100mA with an energy resolution of ~ 1 eV). This setup will provide access to the experimental study of valence and core electronic excitations in condensed matter by means of the inelastic x-ray scattering spectroscopy both using resonant and non-resonant regimes.

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A plug flow microreactor for operando X-ray studies

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There is an increasing importance of apply operando techniques to study heterogeneous catalysis to explore the often complex structure-property relationships. This cannot be overemphasized, it is only by measuring the reactant conversion or the rate of formation of products that one can be sure that the catalysts behaves and performs as expected. Moreover as the surface and sometimes bulk structure of catalysts can be modified under reaction conditions, it is strongly necessary use techniques, like the spectroscopic ones, that able us to investigate catalysts under the actual conditions of operation. This kind of characterization enhancing our overall understanding of the catalytic process and allows an association of the catalyst properties with the activity and/or selectivity provides clues to determine the active reaction site. The core of an X-ray operando study is the reaction cell that holds the catalyst in the beam and make possible that the reaction medium flow to the catalyst at a given reaction condition. The reactor cell designs for X-ray studies is one of the most active areas of development as Clausen et al introduced the first XRD adapted plug flow reactor in 1991. Here the innovation for diminish the thermal gradients coming from the use of this circular aluminum shield around the capillary. The excellent properties given by the aluminum for reflect the infrared radiation generated on the heaters are combined with a geometrical structure that focalize the radiation onto the catalyst, the hole effect is traduced in minimize the temperature gradients along the bed reaching mean values of $\sim$1.7 K/mm up to temperatures of 973 K. These last modifications give us additional benefits as lower potency consumption and a fast temperature response. With these additions the microreactor can be used in XAFS beamlines in tramission or fluorescence geometries and also is able to be used in XRD beamlines.

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X-ray imaging of biomolecules: different resolutions achieved with crystallography, SAXS and coherent diffraction imaging

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In Biosciences, the knowledge about the biomolecule structures, in special the proteins, can provide very important insight about their functions which makes this field of research very attractive. The interests in those information are enormous that many efforts have been done to obtain the best possible resolution, at least, considering the experimental conditions. And it is about those experimental conditions that this work concerns. The classical and robust method to get atomic resolution structure of biomolecules is the crystallography, but it requires crystals that diffract quite well, which it is not always the case. When crystals are not feasible to get, Small-Angle X-ray Scattering (SAXS) may be an alternative. Although SAXS can only provided quite low-resolution, i.e., molecular envelopes, this technique can help the understanding of the protein conformation in solution. If we combine SAXS with in silico calculations, we can obtain fairly detailed models of the domains assembling or quaternary structures of the proteins, considering that the proteins deposited in the Protein Data Bank are fully representative of all other proteins that are not there yet. However, the resolution obtained with SAXS is too low that the Biologists claim for higher resolution without massive protein crystallization essays. So, this made us think about alternative methods for this aim. The promising technique in this case is the Coherent Diffraction Imaging (CDI), in which the light coherence has yielded a great evolution of X-ray scattering techniques. In this work, we present the differences between those three techniques (crystallography, SAXS and CDI) and what we can do with each one. We will discuss the data oversampling that is needed for phase retrieval and information content in the case of SAXS. Crystallography and SAXS data of standard samples were obtained in the MX1 and SAXS2 beamlines from LNLS, respectively, and CDI data come from computational simulations. At the end, we would like to present the new ideas that have come out with the advent of the 4th generation X-ray Sources (i.e., Free-electron lasers) for single molecule structural analysis. This comprise the ideas of non-crystalline X-ray diffraction technique proposed by Dr. David Sayre several years ago. He was also responsible for the introduction of the Shannon sampling theorem to X-ray diffraction techniques to quantify the information content in the data and its resolution.

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Reactive sputter magnetron reactor for preparation of thin films and simultaneous in-situ structural study by X-ray diffraction

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Reactive Sputter Magnetron (RSM) is a widely used technique to thin films growing of compounds both, in research laboratories and in industrial processes. The nature of the deposited compound will depend then on the nature of the magnetron target and the nature of the ions generated in the plasma. One important aspect of the problem is the knowledge of the evolution of the film during the process of growing itself. In this work, we present the design, construction of a chamber to be installed in the Huber goniometer in the XRD2 line of LNLS in Campinas, which allows in situ growing kinetic studies of thin films.

The purpose of the designed reactor is (i) to obtain polycrystalline and/or amorphous thin films by controlled deposition induced by a reactive sputtering magnetron and (ii) to perform a parallel in situ structural study of the deposited thin films by X-ray diffraction, in real time, during the whole growth process. The designed reactor allows for the control and precise variation of the relevant processing parameters, namely magnetron target-to-sample distance, DC magnetron voltage, nature of the gas mixture, gas pressure and temperature of the substrate. On the other hand, the chamber can be used in different X-ray diffraction scanning modes, namely $\theta - 2\theta$ scanning, fixed $\alpha - 2\theta$ scanning and also low angle techniques such as grazing incidence small angle X-ray scattering and X-ray reflectivity. The chamber was mounted on a standard four circle diffractometer located in a synchrotron beam line and firstly used for a preliminary X-ray diffraction analysis of AlN thin films during their growth on the surface of a (100) silicon wafer.

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Parte VIII

Propriedades Estruturais, Eletrônicas e Magnéticas de Sólidos

In situ Ce L_3-edge XANES studies on the effect of Sm content and Pd incorporation on reduction behaviour in 2 wt% Pd/samaria-doped ceria catalysts.

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In the present work, the Sm-doped ceria (SDC) system was studied. SDC is one of the best ionic conductors in this class of materials. SDC nanopowders with three Sm contents were prepared and these were studied as the bare supports (i.e. with no metal function) and as supported metal catalysts, that is, after addition of a 2 wt% Pd metal function by incipient wetness impregnation. All samples were characterized by XRD, X-ray absorption near-edge spectroscopy (XANES) and scanning and high resolution transmission electron microscopy (SEM and HRTEM). In order to determine the effects of Sm content and of Pd incorporation on reduction behaviour, the three support nanopowders and the three corresponding catalysts were studied using in situ XANES experiments at the Ce L_3-edge carried out under a 5%H_2/He atmosphere. A Sm content of x=0.2 resulted in the largest fractional reduction among the supports and the catalyst samples. The incorporation of Pd considerably increased the reducibility of the Ce in the SDC mixed oxide nanopowders. This was demonstrated by analysis of in situ XANES spectra obtained under reducing conditions.

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Phase stability and structural distortions of nanostructured titanium-cobaltite

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In this work we report the synthesis (by a low-temperature chemical route) and the structural characterization of lanthanum strontium titanates based oxides. These materials with perovskite-type crystal structure are good candidates for symmetrical solid-oxide fuel cell electrodes. The room temperature crystal structure of $La_{0.4}Sr_{0.6}Ti_{1-y}Co_yO_{3-\delta}$ ($0.0 \leq y \leq 0.5$) oxides, not previously reported before for $y \neq 0$, was studied by XPD. Structural parameters obtained by Rietveld refinements of synchrotron X-ray powder diffraction data allowed to identify that A-site vacancies creation is the dominant charge compensation mechanism at low cobalt content level but, as Co concentration is increased from $y = 0.0$ to 0.3 there is a transfer to another mechanism (e.g. Co oxidation state changes). For $y \geq 0.3$ the Sr content (and consequently A-site vacancies) stabilizes. A correlation was found between A-site vacancy concentration and lattice parameter evolution as a function of Co content. A rhombohedric to cubic ($R\bar{3}c$ at room temperature to $Pm\bar{3}m$ at 750°C) phase transition was established for $La_{0.4}Sr_{0.6}Ti_{0.7}Co_{0.3}O_{3+\delta}$ composition from high temperature measurements. Meanwhile, no further structural changes was observed as the atmosphere was changed from synthetic air to 5%H_2/95%He at 750°C, simulating cathode and anode working condition, respectively. Besides, no significant differences on lattice parameters were found comparing samples synthesized at 850 and 1100 °C. The same dependence in perovskite A-site vacancy concentration and structural distortion level were observed for both sample series, but the charge compensation mechanism shift was favored and the structural distortion level was increased in the series of higher synthesis temperature.

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Electronic structure of $SrRuO_3$

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The electronic structure of the $SrRuO_3$ ruthenate was studied using several spectroscopic techniques. The Ru 4p core-level and valence band were probed with high energy photoemission spectroscopy (PES), and the conduction band with x-ray absorption spectroscopy (XAS). The experimental results were interpreted with an extended cluster model, which was solved using the configuration interaction method. The theoretical results are in good agreement with the experiments, and were able to reproduce all the spectra with the same set of parameters. The calculations yielded a metallic and ferromagnetic ground state dominated by the $4d^5\underline{L}$ configuration, showing that the compound is in the negative charge transfer regime. The core-level spectrum presents structures at low and high binding energies related to well- and poorly-screened states, respectively. In the valence band spectrum, the Ru 4d region, near the Fermi level, shows the coherent and incoherent features, associated with the well-screened $4d^5\underline{LC}$ and $4d^5\underline{L}^2$ states. On the other hand, the O 2p region, at higher energies, presents some ruthenium contribution associated with the poorly-screened $4d^3$ and $4d^4\underline{L}$ states. This shows that the screening mechanisms in the core-level and valence band regions are similar, as previously suggested. We were also able to extract the Ru 4d contribution for the valence band spectrum by performing Ru L_3 resonant photoemission spectroscopy (RPES). The O1s x-ray absorption spectrum showed the O 2p contribution to the conduction band. The structures in this spectrum are attributed to the unoccupied parts of the t_{2g} and e_g sub-bands. The effects in this region are governed by the relatively large crystal field splitting (10 Dq) and intratomic exchange interaction (J). Therefore, the electronic structure of $SrRuO_3$ is dominated by a strong Ru 4d - O 2p covalent character, and the oxygen states play an important role in the physical properties of this system.

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Resonant photoemission of Sr_2FeMoO_6

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The electronic structure of the double perovskite Sr_2FeMoO_6 was studied using X-ray Photoemission Spectroscopy (XPS). The Sr_2FeMoO_6 material is a ferrimagnetic half-metal with $\mu \approx 4.0\mu_B$. The experimental spectra were measured at room temperature at the SXS beamline at the Laboratório Nacional de Luz Síncrotron (LNLS) - Brazil, and were interpreted with band structure calculations using the LDA method with correlation in the Fe sites (LDA+U). The Fermi level is dominated by Fe 3d and Mo 4d states, which are covalently mixed with O 2p states. We used high energy Mo L_3 resonant photoemission (RPES) to identify and separate the Mo 4d contribution near the Fermi level. The partial density of states (DOS) of molybdenum agrees very well with the RPES spectrum. We also studied the spectra taken at different photon energies, which shows changes in the relative peak intensities. These results help to explain the magnetic ordering and the magnetotransport properties of this material, and provide a more reliable and bulk sensitive technique than the Cooper minimum method.

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Energy conversion evaluated from structural parameters of $BaHfZrO_3$: The convolution of theoretical and experimental insights.

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The input task of hafnium as a substitution element into barium zirconate cubic lattice was preformed through microwave-assisted hydrothermal method. Regardless of hafnium concentration, all diffraction patterns remain reporting a single cubic phase identified as barium zirconate compound, even that the induced first order Raman active modes were significantly changed. Scanning and transmission electronic microscopy revealed the mesocrystalline nature of self-assembled BHZO nanoparticles under dacaoctahedral shape. The detection and quantification of hafnium amounts was possible via light energy conversion supported by analytical and physical analysis. Their luminescence emission was strong dependent of the temperature and improved as hafnium contends was introduced, producing a specific green-yellow light emission, improving its promissory applications. Furthermore, X ray absorption spectroscopy (XAS) over k and L-edge of zirconium found local symmetry breaks associated with specific ordering degree. The K and L_{III}-edges is very sensitive to overlapping of 4d 2p orbital regarding the Zr-O bond and/or 5d 2p, regarding Hf-O bound. Besides the EXAFS simulations of Hf L_{III}-edge indicate that the hafnium contends replaces preferentially zirconium at octahedral sites. For instance, ab initio theoretical approach was used to available the main electronic features of high doped BZO host lattice, via super-cell conduction under DFT methodology.

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Reduction behaviour of nanostructured rare earth-doped ceria solid solutions: XRD and Ce L_3-edge XANES in situ studies.

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Ceria (CeO_2) and rare earth (RE)-doped ceria ($Ce_{1-x}RE_xO_{2-x/2}$) mixed oxides are important materials in significant environmental applications such as the three-way catalysts (TWC) and the electrolyte and anode materials for solid oxide fuel cell (SOFC) technology. In the present work, the RE-doped ceria (RE: Gd, Sm, Tb and Pr) system was studied. All samples were characterized by XRD, X-ray absorption near-edge spectroscopy (XANES) and scanning and high resolution transmission electron microscopy (SEM and HRTEM). In order to determine the effects of RE content on reduction behaviour, catalysts were studied by in situ XRD and XANES (Ce L_3-edge) experiments carried out under a 5%H_2/He atmosphere. The results obtained were fundamental to understand the influence of Ce^{4+}/ Ce^{3+} redox couple in nanostructured RE-doped ceria for catalytic applications.

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Exchange spring coupling in NiFe/IrMn/Co heterostructures

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Exchange bias (EB) [1] is one effect characterized by a shift in the hysteresis loop along the magnetic field axis (H_{ex}) and it is present in several devices for technological applications. Here, it has been studied the spring spin structure formed inside the AF layer when it is coupled to two different FM materials and the EB exists [2,3]. Si(100)/Cu(10nm)/NiFe(20nm)/IrMn(t)/Co(10nm)/Cu(5nm) and Si(100)/Ta(10nm)/ /NiFe(20nm)/IrMn(t)/Co(10nm)/Ta(5nm) multilayers (t= 4, 6, 8, 12, 15, 18, 20, 25 e 30 nm) were deposited by magnetron sputtering and the EB was set by a field cooling of only 10 Oe, since 400 K up to the room temperature (about 300 K). Being NiFe a soft magnet and Co a hard one, one domain wall can be formed inside the AF when and external magnetic field is applied, resulting in the so called exchange spring system [4]. The behavior of the spiral spin structure torsion angle in function of the AF layer thickness was investigated by magnetometry and ferromagnetic resonance. The torsion angle varies from 0^o to 180^o, gradually, as the AF layer thickness changes since 4 nm up to 15 nm, keeping 180^o for ticker spacers. The system with Ta buffer layer becomes more stable. In order to refine the magnetic spin structure of the layers, asymmetry ratios in function of both energy and angles, as well as, element specific hysteresis loops in different incident angles were obtained by resonant magnetic X-ray diffraction in the SGM beam line of LNLS. In our knowledge, it is the first time this technique is applied to multilayers with success in Brazil.

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Local structure of $Pb(Fe_{1/2}Nb_{1/2})O_3$ and $Pb(Fe_{2/3}W_{1/3})_{1-x}Ti_xO_3$ multiferroic materials probed by X-ray absorption spectroscopy at Pb L_{III}-edge

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A material is generally considered functional if it possesses a physical property that is usable in applications. In recent years, much attention has been paid to multiferroics materials which simultaneously exhibit magnetic and electric ordering. The interaction of the electric and magnetic subsystems can manifest itself as the magnetoelectric effect and the effect of mutual influence of the polarization and magnetization. Among the multiferroic materials, a large number of Pb-based perovskites present the formula $Pb(B_1B_2)O_3$ with excellent dielectric, electromechanical and pyroelectric properties, make these and their solid solutions suitable for high performance materials with potential applications as sensors and actuators. The $Pb(Fe_{1/2}Nb_{1/2})O_3$ (PFN) and $Pb(Fe_{2/3}W_{1/3})_{1-x}Ti_xO_3$ (PFW-PT) are multiferroic compounds from this kind of materials showing ferroelectric to paraelectric phase transitions and paramagnetic to G-type antiferromagnetic respectively. These materials have attracted the attention of many researchers because it can be used in multilayer ceramic, capacitors and other electronic devices due to its high dielectric constant, by presenting a diffuse phase transition and low sintering temperature. Although the long distance structure and magnetic/electric properties of these compounds have been characterized by numerous researchers in order to better understand the processes of phase transition and electrical behavior of these compounds, few studies were conducted to verify the existence of a correlation between these properties and local order and electronic structure of materials. Thus, the aim of this study is probe the local structure of PFN and PFW-PT materials by X-ray absorption spectroscopy at Pb L_{III}-edge. In addition, it is not well established in the literature whether PFN composition undergoes a transition from a tetragonal ferroelectric phases to a rhombohedral or a monoclinic phase as the temperature decreases. Our EXAFS measurements at Pb L_{III}-edge for this material have shown that the local structure in lower temperatures is compatible to a monoclinic structure Moreover, EXAFS measurements at Pb L_{III}-edge for PFW compound are relative to a rhombohedral structure in lower temperatures. This result is in agreement to our ferroelectric hysteresis loops, which show a typical behavior of ferroelectric material, although the structure for PFW compound has been described as a cubic phase.

Acknowledgements:

ELECTRONIC PROPERTIES OF THE COORDINATION COMPOUNDS OF THE LIGANDS TRITHIOCARBONATE, PERTHIOCARBONATE AND XANTHATE IN THE S 1s REGION

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The synthesis and characterization of coordination compounds containing sulfur heterocyclic ligands have been object of intense studies in the last decades[1]. The dithiolene is the most important representative of this class of compounds. However, other polisulfurs as perthiocarbonate (CS_4), trithiocarbonate (CS_3) and xanthate ($S_2COEthyl$) are also detached as intermediaries of several chemical reactions. They also act as addictive, anticorrosive and antioxidant species for lubricating oils and greases[2]. These properties were not elucidated and explored in the literature yet. The studies are still limited to the structural characterization of some few complexes[3]. In this work photoabsorption and photoelectron spectra in the S 1s and long scan regions of CS_4, CS_3 and $S_2COEthyl$ ligands have been measured for $[Ni(S_2COEthyl)_2][Net_4]$, $[Ni(CS_3)_2][Net_4]_2$ and $[Ni(CS_3)(CS_4)][Net_4]_2$ compounds. All of them were synthesized following the literature[1-3]. TEY spectra have been acquired at Soft X-ray Spectroscopy (SXS) beamline at LNLS-Campinas (research proposal SXS-13665). The compounds were introduced into the main chamber as solid samples using a carbon sticky tape. The work pressure was kept at 5.0×10^{-8} mbar. The spectra analysis of these species indicates different chemical environment for the S 1s region. Ab initio and DFT calculations, associated with improved virtual orbital (IVO) method and half-core-hole (HCH) method, carried out with the GSCF3 and StoBe-deMon programs, were used to help us to establish the assignments. The geometric parameters were optimized using the GAMESS program.

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X-RAY PHOTOELECTRON SPECTRA OF $\mathbf{LiMn_2O_4}$ OBTAINED BY SOL-GEL ASSISTED BY CORN STARCH

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Lithium-ion batteries are attracting extensive attentions for the use in high-power applications such as electric vehicles, plug-in hybrid electric vehicles, and hybrid electric vehicles. $LiMn_2O_4$ has been considered a promising candidate cathode material due to its low cost, low toxicity and environment friendliness [1,2]. For the characterization of these materials, XPS (X-Ray photoelectron Spectroscopy) has been used and the valence band electronic structure information has been obtained. In the present work we used a sol-gel process for the synthesis of the metal-starch precursor, characterized by the formation of the gel. Then we combine this method with a subsequent combustion of the metal-starch precursor, using a SHS method (Self-Propagating High-Temperature Synthesis). Then we have obtained very dark solids in the form of very fine powder, and then these solids were calcined at 300, 500 and 700 C for 16h. MnO_2 (Aldrich) was used as a reference material for XPS. The XPS measurement with the synchrotron radiation was performed at beamline SXS on the LNLS-Campinas-SP synchrotron facility. The samples were introduced into the chamber as a solid using a carbon sticky tape. The work pressure was kept at 6.0×10^{-8} mBar. The samples heated treated at different temperatures were analyzed for photoelectron spectra in long scan regions of Li 1s, Mn 3p/2p and O 1s.

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Element specific XMCD hysteresis loops of iron oxides

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X-ray magnetic circular dichroism (XMCD) is one of the most useful types of measurement to investigate magnetic properties using synchrotron radiation X-rays. XMCD is measured at the X-ray absorption edge of a specified element in a sample, which enables element-selective measurement. The intensity of XMCD is proportional to the mean magnetic moment projected onto the direction of the incident X-ray, and the sign reflects the direction of the probed moment relative to that of the total magnetization. Due to contributions of Fe3+ occupying octahedral sites and Fe3+ occupying tetrahedral sites in iron oxides are clearly distinguishable in XMCD signal it is possible to obtain hysteresis loops for each iron site. In this work we present XMCD hysteresis loops taken at Fe L-edge on maghemite and Zn ferrites nanoparticles and thin films in total electron yield at LNLS (PGM beamline). The results will be compared with hysteresis loops taken by a vibrating sample magnetometer in the same conditions.

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Influence of co-dopant in the Europium reduction in $SrAl_2O_4$ host

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Rare-earth-doped aluminates serve as an important class of phosphor for commercial applications, especially in the areas of safety improvement and energy saving. The $SrAl_2O_4$:Eu^{2+}, RE^{3+} (RE^{3+}= Gd, Dy, Er and Y) is a materials that may exhibit long lasting phosphorescence and luminescence when doped with trivalent and divalent rare-earth ions. Most aluminates are activated by Eu^{2+} ions, and to obtain the rare earth with this valence, the trivalent rare earth oxide is usually used as the starting material. To reduce the rare earth from Eu^{3+}/Eu^{2+} it is necessary to use particular schemes in the production of the rare earth containing sample. The duration of the long lasting phosphorescence emission is increased by co-doping with rare earth ions, in especial the Dy^{3+} ions. Many studies have been dedicated to understanding the relationship between Dy^{3+} ions and hole traps. However, this relationship is still not fully understood. Therefore, was investigated the effect of the trivalent rare earth ions RE^{3+} (such Gd, Dy, Er and Y) as co-dopant in Eu-doped $SrAl_2O_4$ material. In this work, the DXAS technique (Dispersive X-ray Absorption Spectroscopy) is used to follow the XANES spectrum of the Eu ions during the calcinations program in different atmospheres. Analysis of the reduction dynamics can give information of the synthesis process and DXAS technique can be used to follow it. The pre-calcined samples of SrO:Al_2O_3:Eu, RE were prepared at 600 C via a sol-gel proteic route. DXAS spectra were obtained as a function of temperature excited at the LIII edge of Eu ions during the synthesis. The results shows that the Gd codopant was found to be the most efficient on stabilization of Eu ion in the valence 2+ after annealing cycles. The results suggest that all Eu ion are reduced at 1100C but that part of the Eu return to Eu^{3+}. The Eu reduction processes are explained by a proposed model based on the charge compensation. The reduction of Eu ion occurs due to two charge compensation schemes: one involves the creation of reversible defect and the other involves the reaction of H2 forming water vapor. The comparison of the IPs of the dopant Eu^{2+} and the codopants RE^{3+} can to explain the stabilization of Eu^{2+} ion in the $SrAl_2O_4$:Eu^{2+} when codoped with the other rare earth.

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Caracterización Fe/Co-K-XAFS de $CoFe_2O_4$ en función del tamaño de partícula.

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En la última década ha cobrado fundamental relevancia el desarrollo de nuevos materiales nanoparticulados con propiedades especiales. El estudio de estos sistemas reviste especial interés tanto por sus aplicaciones diversas, como desde un punto de vista estrictamente científico básico. Especialmente interesantes son las nanopartículas de óxidos de Fe por sus múltiples aplicaciones en la industria, en medicina, farmacología, etc.. Actualmente diferentes óxidos de hierro están siendo investigados por sus propiedades interesantes como filtros naturales de spin. La caracterización cuantitativa del entorno cercano del Fe en nanoestructuras, es esencial para comprender sus propiedades magneto-termodinámicas especiales observables a escala macroscópica. Aún no ha sido estudiado con suficiente amplitud el cómo se refleja el tamaño de partícula de óxidos de hierro en el perfil de un espectro XAFS. Unos pocos trabajos aislados en casos muy particulares han sido reportados en la bibliografía [1,2], y en ellos solo describen aspectos cualitativos. Un estudio exhaustivo y sistemático se hace necesario para un análisis cuantitativo mediante la técnica XAFS. La técnica XAFS ha mostrado ser altamente sensible a cambios en la estructura electrónica y topología de vecinos próximos del Fe. Nuestro grupo se ha propuesto investigar de manera sistemática el patrón Fe-K-XAFS característico en nanoestructuras de óxidos de hierro en general en función del tamaño. Presentamos aquí los resultados Fe/Co-K-XAFS obtenidos sobre ferritas de cobalto en función del tamaño de partícula (2, 4, 21, 36, 49 nm).

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Estudo das propriedades estruturais e ópticas do polifosfato LiLaP_4O_{12} dopado com Európio trivalente

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O LiLaP_4O_{12} (LLP) pertencente a família dos MLn(PO_3)$_4$ (sendo M íons de metais alcalinos e Ln íons lantanídeos) tem despertado interesse devido as propriedades ópticas quando dopado com íons terras raras. Compostos fosfatos apresentam gap óptico em comprimentos de onda muito pequenos, sendo transparentes até a região do ultravioleta. O sistema LLP foi produzido pela rota sol-gel proteico. Este método de produção baseia-se na rota sol gel convencional usando como solvente para os reagentes a água de coco, no qual os íons metálicos são ancorados nas cadeias de moléculas orgânicas. Após processos de secagem e calcinação são obtidos nanopós do composto LLP. As fases cristalinas presentes nas amostras foram identificadas através da difração de raios X da amostra comparada com o padrão do banco de dados cristalográficos (ICSD). A distribuição do tamanho médio das partículas foi analisada através da técnica de microscopia eletrônica de varredura. As propriedades ópticas foram avaliadas através do espectro de emissão fotoestimulada (PL) e emissão estimulada por raios X (XEOL). O estado de oxidação do dopante foi avaliada através de medidas de XANES (X-ray Absorption Near Edge Structure). As medidas de EXAFS, XANES e XEOL forma realizadas na linha XAFS2 do LNLS. Os resultados mostram que a rota sol gel proteico é eficiente na produção de materiais luminescentes de alta eficiência de cintilação.

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CORRELACIÓN DEL COMPORTAMIENTO ESTRUCTURAL DE NANOPARTÍCULAS DE OXIDOS DE HIERRO DE 3 Y 9 NM: EL ROL DE LA RELACIÓN SUPERFICIE/VOLUMEN

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XAFS se presenta como una técnica de gran sensibilidad a cambios en la estructura electrónica y topología del ambiente químico del Fe. Especialmente en la región de pre-picos situada entre 15-20 eV antes del umbral de ionización. La estructura de dicha región está relacionada con transiciones electrónicas 1s a 3d (cuadrupolar) y/o 1s A 4p (dipolar) en metales. El pre-borde se desplaza hacia mayores energías cuando el estado de oxidación del Fe aumenta. Esto refleja la transferencia de estados disponibles en la estructura electrónica de sub-bandas entre el Fe y el O. En los últimos años este efecto ha sido utilizado para determinar el estado redox y coordinación del Fe en diversos materiales naturales y sintéticos [1]. Numerosos trabajos han sido reportados empleando esta metodología para el estudio del entorno del Fe (a corto y mediano rango) en óxidos para cristales de gran tamaño. Unos pocos trabajos cualitativos han sido reportados en la bibliografía empleando caracterización XANES en óxidos de Fe a escala nanométrica. Cada tipo cristalográfico de óxido de Fe tiene una estructura electrónica característica, una nanoestructura presenta propiedades particulares que es preciso investigar. En partículas de dimensiones nanométricas los efectos de borde son dominantes y gobiernan la geometría de la estructura. En consecuencia la estructura electrónica de los átomos constituyendo nanoestructuras presenta características propias bien diferentes a la de agregados de mayor tamaño. Esto se ve reflejado mediante un patrón Fe-K-XAFS característico. Con el fin de potenciar el alcance de la técnica XAFS en el estudio cuantitativo de este tipo de sistemas, nuestro grupo ha comenzado a investigar de manera exhaustiva y sistemática un amplio conjunto de óxidos de Fe en función del tamaño de partícula. Dentro de este marco, presentamos en este trabajo los primeros resultados obtenidos sobre maghemita de 3 y 9 nm obtenidos mediante nuevas estrategias en el tratamiento de datos XAFS.

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XAFS characterization of electrodeposited Ni-W coatings

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Alloys of tungsten and molybdenum with iron group metals have attracted considerable attention due to their specific magnetic, electrical, mechanical, thermal and corrosion resistance properties. Among them, nickel and tungsten (Ni-W) alloys are particularly interesting because they exhibit good corrosion resistance in different aqueous media and high hardness and ductility. Therefore, they have been studied as candidates to protect structural metals such as steels and copper. In this work a detailed characterization by X-ray absorption spectroscopy of electrodeposited Ni-W coatings prepared by pulsating electrodeposition on steel and copper substrates is presented. X-ray Diffraction, Atomic Force Microscopy (AFM) and Scanning Electron Microscopy (SEM) results are also presented. These results are discussed in terms of the good hardness and ductility that the coatings present. Different Ni-W coatings were prepared with different pulse programs in order to determine the effect of the preparation conditions on the final structures that were formed. Both XANES and EXAFS experiments at both Ni-K and W-L_3 edges were studied at the XAFS2 beamline of the Laboratorio Nacional de Luz Sincrotron (LNLS), Campinas, Brazil. Experiments were performed in fluorescence mode at room temperature. The results indicate that two main phases are found in the bulk structure: a W-rich amorphous phase and Ni-rich crystalline phases. The crystalline phases consist of crystalline domains of 7-8 nm in size of Ni(W) (fcc) solid solution (12% W content). The amorphous phase exhibits a less compact Ni-W structure and a higher W content. We have found that in both phases the W is under a metallic state without evidence of significant amounts of tungsten carbide, tungstates or citrate-tungsten complexes. The good hardness and ductility of the coatings can be related to the structure consisting of a W-rich Ni-W matrix composite reinforced by the 7-8 nm crystalline domains of the Ni(W) solid solution.

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Si local order at $Ca_2Al_2SiO_7$ and XEOL studies in doped systems

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$Ca_2Al_2Si\ O_7$ (CAS) is a stable matrix that can be used to produce scintillators and phosphors. To synthesize this material a new methodology that combines solid state and proteic sol-gel method was applied. In the new method SiO2 was the silicon source and soluble precursor were added to the starting suspension. Ce, Eu, and Mn ions were used for dopping the samples. The aims of the work are: i- the effect of the calcination temperature on the Si local order and ii- the effect of the dopants on the optical properties of the samples. Powder XRD, EXAFS and X-ray excited optical luminescence (XEOL) measured around the Si K edge were used as the main investigation techniques. Results obtained by XRD indicated that single crystalline CAS phase were obtained at 1300C for the pure, doped and co-doped samples. Si local order was studied to samples dried and calcined at 100, 700, 950 and 1300C. EXAFS measurements were done by total electron yield and X-ray fluorescence at SXS beamline. The results showed that the Si local order is different in each one of the calcined temperature. Optical properties were analyzed by total XEOL yield around the Si K edge in the XANES region. All samples showed an inverted absorption edge behavior in the XEOL indicating that the increasing in the absorption due to the Si ions are competing with the mechanisms generating the light yield in the samples. XEOL spectra presented the characteristic emission spectra of the dopant ions, and it confirms the added impurities are the CAS luminescent centers. XEOL lifetime decay measurements done in the single buch mode at LNLS in the SXS and XAFS2 beamlines, showed the same decay curve tendency when the samples were excited with different X-ray photon energies. The Ce-Mn and Ce doped samples showed shorter lifetime decay constant indicating that these samples can be used in fast scintillator devices.

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The Effect of the Organic Precursor on the Structural and Magnetic Properties of Nanoparticles $CoFe_2O_4$ Synthesized by Co-precipitation Method

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In the last few decades, the study of metal-oxides with nanometer size has attracted considerable attention among the scientific community due to their scientific and technological importance. The spinel ferrite (AFe_2O_4, A = Mn, Co, Ni, Cu, Zn) nanoparticles have been subject of intensive theoretical and experimental investigations due to their remarkable electrical and magnetic properties and wide practical applications to information storage system, ferrofluid technology, magnetic resonance imaging (MRI) enhancement, magnetically guided drug delivery etc. Among these compounds the cobalt ferrite ($CoFe_2O_4$) has been actively investigated because this material to present high chemical stability, moderate magnetization and high coercivity [2], these attractive properties makes $CoFe_2O_4$ nanostructured is a good candidate for many applications [3]. In this work, we report the synthesis process of $CoFe_2O_4$ in nanostructured form using co-precipitation method with addiction different organic precursor to investigate the influence of organic material in structural properties of the $CoFe_2O_4$ nanoparticles and to correlate with their magnetic properties. The analysis of X-ray diffraction (XRD) data confirms that all $CoFe_2O_4$ samples have a single phase identified in a cubic crystalline system belonging to the space group *Fd-3m.* The peaks increasingly broadened in of XRD patterns with the addition of the organic precursor indicate a decrease in the average crystallite size. From point of view magnetic, we have verified that magnetic properties of $CoFe_2O_4$ changes significantly with decreasing of crystallite size (FAPITEC).

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$Ca_2Al_2SiO_7$ synthesis, local order and optical properties studied using synchrotron radiation

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$Ca_2Al_2SiO_7$(CAS) is a very interesting oxide that can be used as host material for rare earth and transition metal dopant ions. When doped, CAS exhibit optical properties such as scintillation and fluorescence allowing several applications. This oxide is generally synthesized by solid state reaction, sol-gel routes or crystal growth. The silicon source used to prepare CAS usually SiO_2, for solid state reaction and crystal growth, or TEOS in sol-gel or other chemical routes. In previous works new methodology which combines solid state reaction and proteic sol-gel method was proposed, where coconut (*Cocos nucifera*) water is used as the starting solvent and the polymerizer agent mixed with non soluble reactants as SiO_2. This work aimed the full characterization of the CAS samples produced with this hybrid route starting with the in situ XRD measurements of the synthesis process. These kinetic studies were performed in the XRD2 beamline at the LNLS. Previous DTA/TG results showed a crystallization onset around 927^oC that may be related to the formation of CAS, and that confirmed by conventional powder XRD. XRD in situ showed that up to 700^oC SiO_2 in quartz structure is preserved. Above 800^oC, intermediate phases are formed and diffuse by thermal effect and react among themselves producing in the end the CAS phase. The kinetic studies also showed at 1160^oC all SiO_2 diffused and react with other phases. Morphological and structural studies were carried out in the synthesized samples by electron microscopy at LME/LNNano and CMNano-UFS. The results indicated that nanoparticles were obtained by this synthesis process. EXAFS studies around the K edges of matrix elements, Ca and Si, showed the local order around them in samples calcined at different temperatures. XANES results around the Mn K edge and Ce and Eu L_{III} edges were used to check the dopant oxidation states. XEOL spectra showed typical emission of the dopants and different behaviors for XEOL excitation spectra when different absorption edges were measured. These results can be used to build up a model to explain the scintillation mechanism of the doped CAS samples. Decay time constants of the XEOL could be measured using the LNLS single bunch mode at both SXS and XASF2 beamlines. The XEOL decay curves showed characteristic decay constant around few tenths of nanosecond sputting these materials in the group of the fastest known scintillators.

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Caracterização estrutural do sistema LaPr(CaSr)MnO a baixas temperaturas

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A manganita $La_{0.225}Pr_{0.4}Ca_{0.375}MnO_3$ é um sistema protótipo para o estudo da separação de fases, por apresentar diferentes tipos de ordenamento de spin e de carga coexistindo em equilíbrio [1]. A proporção entre as fases ferromagnética (FM) e antiferromagnética (AFM) pode ser alterada se as características estruturais do sistema são manipuladas. Neste trabalho fizemos uma dopagem do composto $La_{0.225}Pr_{0.4}Ca_{0.375}MnO_3$, substituindo o íon Ca^{2+} por um de maior tamanho como o Sr^{2+}, mantendo assim fixas as concentrações de íons Mn^{3+} e Mn^{4+}. Neste estudo serão apresentados resultados de medidas de DRX feitas na linha XPD do LNLS, para amostras policristalinas com fórmula geral $La_{0.225}Pr_{0.4}(Ca_{1-x}Sr_x)_{0.375}MnO_3$, com $x = 0.00$ e 0.05, em diferentes temperaturas na faixa de 10 a 300 K. Ajustes dos difratogramas a temperatura ambiente feitos pelo método de Rietveld mostraram a presença de fases cristalográficas únicas nas duas amostras. Comprovou-se que a simetria é ortorrômbica correspondendo ao grupo espacial *Pnma*. A partir das posições atômicas obtidas foi possível comprovar o incremento do ângulo das ligações Mn-O-Mn com a inclusão do dopante, aproximando-o do valor ideal de 180° [2]. Como resultado, o crescimento fase FM foi favorecido, tal como foi observado em medidas de magnetização em função da temperatura feitas no sistema PPMS. Abaixo de 145 K, contrário ao que acontece na amostra $x = 0.00$, na amostra $x = 0.05$ foi observado nos difratogramas o desdobramento dos picos com índices (202) e (242), dando lugar a novos picos fora das posições de Bragg observadas na mesma estrutura à temperatura ambiente. Esse fenômeno vem acompanhado da formação da fase FM de baixa temperatura [1], o que sugere uma correlação dessa fase com o aparecimento de uma nova estrutura cristalográfica. Adicionalmente uma análise previa dos parâmetros de rede mostra uma rápida contração da célula unitária ao esfriar de 100 até 30 K. Os resultados obtidos mostram uma clara correlação entre as propriedades estruturais de baixa temperatura e a formação da fase FM. Análises quantitativas que vem sendo feitas pelo método Rietveld devem ser concluídas com o intuito de determinar a simetria e a proporção da nova fase observada, assim como a correlação entre a simetria e as propriedades estruturais.

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Room temperature A and B-site magnetic contributions in ferrimagnetic $ZnFe_2O_4$ thin film and nanoparticles studied using XMCD

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To investigate the source of magnetism in nanostructured zinc ferrite, we present a study using x-ray absorption (XAS) and magnetic circular dichroism (XMCD) at the $L_{2,3}$ edges of Fe on zinc ferrite samples of different morphology (films and nanoparticles), all showing a relatively large magnetization at room temperature. The samples consist of: a) a zinc ferrite thin film grown at low $O_2$2 pressure of 10^{-5} mbar, the film thickness being 57 nm (ZFO1), b) nanostructured $ZnFe_2O_4$ particles obtained by mechanically milling hydrothermally prepared nanoparticles (sample 2ZF10H, average grain size $D = 13$ nm) and c) nanostructured ferrite particles obtained by mechanical grinding bulk $ZnFe_2O_4$ (BZF10H, $D = 14$ nm). In all cases, the x-ray diffraction patterns indicate that all the samples have the spinel structure with cubic symmetry.

Our results show that the XMCD signals at room temperature display the typical features observed for ferrites, i.e., a positive peak A_1 assigned to magnetic contributions from Fe^{3+} at tetrahedral A-sites of the spinel structure, and two negative peaks B_1 and B_2 related to Fe^{3+} ions at octahedral B-sites. The dichroic signal of film ZFO1 is markedly higher than those of nanoparticles 2ZF10H and BZF10H. Particularly, XMCD of ZFO1 shows markedly intense B_1 and B_2 peaks. This fact results in a larger magnetic moment m per iron ion, which is about 40% higher than the m found for nanoparticles. The results are interpreted in terms of differences observed on the distribution of cations, the absence of nonmagnetic ions at B sites added to overpopulation of A sites that took place in ZFO1 film and the role of oxygen vacancies.

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Relationship between structural and morphological properties of LSC powders and electrochemical performance of porous LSC thick films for IT-SOFCs

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Solid oxide fuel cells (SOFCs) represent a very interesting alternative technology for electric power generation. However, the high operation temperature (900-1000^{o}C) of this device entails expensive fabrication costs and accelerated aging, among other negative aspects. So a great effort is dedicated to the development of new materials that show high performance in the intermediate temperature range of 500-700^{o}C (IT-SOFCs) [1,2]. Particularly, nanostructured mixed ionic-electronic conductors (MIECs) perovskites represent promising materials for IT-SOFCs applications as cathodes [3]. This work deals with the structural and morphological properties of nanostructured powders (15-30 nm) of $La_{0.6}Sr_{0.4}CoO_{3-d}$ (LSC) relative to microstructured powders of LSC and relates these features to the electrochemical performance exhibited by cathodes made of LSC powders in symmetric cell configuration on samaria-doped ceria electrolytes (SDC). Measurements of the X-ray diffraction pattern and XAS spectrum of the powders were performed in the D10B-XPD and D04B-XAFS1 beamlines of the LNLS, in static air and in function of temperature, in the range of 20 - 500^{o}C. Results show that the observed enhancement of the electrochemical activity in nanostructured LSC cathodes is due to the higher SSA (14 m^2/g) and the retention at room temperature of the LSC high temperature cubic phase. Also we found that while Co is in 3+ and 4+ oxidation states at room temperature in microstructured LSC powders, so low vacancies concentration is present, XANES analyses of nanostructured LSC powders showed the presence of Co^{2+} in the same amount at 20 and 500^{o}C, implying that at room temperature, nanostructured LSC powders exhibit the same characteristics as they do at IT-SOFC working temperature.

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Análisis superficial de cintas de $Nd_yFe_{(86-y-x)}B_{14}M_x$ (M=Ti, Nb, Mo) con la técnica XPS usando radiación sincrotrón

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Los ferromagnetos de Nd-Fe-B, con bajas concentraciones de Nd, han despertado el interés tecnológico en los últimos años, debido a sus interesantes propiedades magnéticas tales como alta remanencia y producto de energía elevando así su performance. La baja concentración de Nd, y el uso de elementos refractarios, minimizan el riesgo de oxidación, controlan respectivamente, la obtención de la nanoestructura en el proceso de solidificación con tratamientos térmicos posteriores. Se han explorado tres sistemas de $Nd_yFe_{(86-y-x)}B_{14}M_x$ (x=2, 4; y=7,8; M=Ti, Nb, Mo) en forma de cinta con la técnica XPS usando radiación sincrotrón. Las muestras fueron preparadas por la técnica de solidificación rápida con 2% o 4% del aditivo (M) as quenched (amorfas) y luego con tratamiento térmico a 700C (cristalinas). En las dopadas con Ti y Nb se hallaron sobre la superficie, óxidos de estos elementos. Para estas muestras, se encontró Ti^{+4} y Nb^{+5}, con poca presencia de Ti^0 y Nb^0. Mientras que para las cintas con molibdeno, el aditivo se encontró notoriamente en estado metálico.

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Electronic structure and magnetic states in $La_{1-x}Sr_xCoO_3$ investigated by photoemission and x-ray absorption spectroscopy

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Studies concerning Co perovskites $La_{1-x}A_xCoO_3$ ($a = Ca, Sr, or Ba$) have recently been of a great interest because these systems show a fairly large magnetoresistance both in bulk and thin films. The parental compound $LaCoO_3$ is known to be a nonmagnetic (low-spin) semiconductor at low temperatures but it undergoes a gradual transition from a nonmagnetic ground state to a paramagnetic ground state above 90K and then to a metal above 500K. It is still controversial whether the 90K transition is a low-spin to a high-spin one or not. In addition, it is known that by replacing La by Sr one introduces holes into $LaCoO_3$, leading the system to a transition from a nonmagnetic semiconductor to a ferromagnetic metal. In order to understand this behavior we study the electronic structure of $La_{1-x}Sr_xCoO_3$ by photoemission and x-ray spectroscopy. The experimental data where obtained at SXS and SGM beamlines of Brazilian Synchrotron Light Laboratory (LNLS). It is shown that Co2p core-level and valence-band spectra exhibit charge-transfer satellites. By replacing Sr by La in $LaCoO_3$, we observe that the valence-band spectra do not exhibit rigid-band behavior but change systematically, reflecting a semiconductor to metal transition which occurs with hole doping. The combination of band structure and cluster model calculations on $LaCoO_3$ are compared with the experimental data, leading us to suggest that an intermediate spin state is realized in the ferromagnetic phase.

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Speciation of Ti and Co in nanostructured titanates of composition (La,Sr)Ti1-yCoyO3-d used as electrodes in symmetric SOFCs

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ABO3 perovskites with Ti in the B site are promising materials for new solid oxide fuel cells (SOFC) with symetric designs. These compounds, widely recognized as good anodes, enhance their ionic conductivity by replacing small amounts of Ti with other transition metals. Thus, enabling their use as SOFC cathodes. However, substitution of polyvalent atoms in the ABO3 structure might induce oxidation and reduction processes in the components or even creation of vacancies of oxygen or A atoms to compensate for charge and size changes. We investigated here the perovskite family $La_{0.4}Sr_{0.6}Ti_{1-y}Co_yO_{3-\delta}$ with (0.1 $\leq y \leq$ 0.5 (LSTC) prepared by a chemical route of citrates and sintered at 750 °C and 1100 °C. XANES and EXAFS analysis at the transition metals K-edges supported by Density Functional Theory calculations reveled that Co dramaticaly changes its oxidation state, while Titanium stays as Ti^{4+}, as the dopant fraction increases. This seems to be independent of synthesis parameters as the sinterization temperature or grain size. These results are of significant importance to understand the charge compensation mechanisms in this system and will allow to find the optimal LSTC composition for symetric fuel cell designs.

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ON THE CATION SUBSTITUTION SITE OF Ca-DOPED LAYERED COBALTITES $YBaCo_2O_{5.5}$ STUDIED BY NEUTRON DIFFRACTION AND X-RAY ABSORPTION SPECTROSCOPY

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The layered compounds $RBaCo_2O_{5+\delta}$ (R being a rare earth or yttrium) have been intensively studied in the past few years, as they allow for a wide range of oxygen non-stoichiometry controlling the mixed valence state of Co ions, and therefore many novel physical properties may be tuned. An insteresting variable to explore regards the substitution with other non-magnetic cations. Recently, we reported a neutron diffraction study of the Ba-site substituted cobaltites [1], showing that even a small addition of Sr or Ca in the Ba-site (5 to 10%) produces a dramatic effect on the magnetization of the samples, on the Seebeck coefficient and on the resistivity. However, recent reports on substituted cobaltites have opened up the possibility that the substitution site for Ca atoms might not be obvious. Motin Seikh *et al.* [2] presented a study of Ca substituting at the Y site, showing very similar magnetic properties as our nominally Ba-site substituted samples. The structure of layered cobaltites has been shown to allow the accommodation of cations with a wide range of ionic radii at the lanthanide site, which in addition to the wide oxygen non-stoichiometry range and three possible oxidation states for Co, renders an extreme versatility to the formation of the compound. Therefore, it can easily accommodate a host ion even if the charge and/or radius of the dopant is quite different. More recently [3], the possibility of any of both substitution sites has been suggested. All these studies motivated the careful synthesis of Ca- and Sr- substituted layered cobaltites with nominal substitution sites at Ba and at Y. We performed X-ray absorption spectroscopy at the Ca and Sr K-edges to study the local environment around the dopant ions and arrived to a picture showing inequivocally that Ca is replaced at the Y site, whereas the Sr substitution site seems to be influenced by the dopant concentration. [1] G. Aurelio et al. J. Phys.: Condens. Matter 23 315403 (2011) and references therein [2] M. Motin Seikh, V. Caignaert, V. Pralong, C. Simon, and B. Raveau, J. of Phys.: Cond. Matter 20, 015212 (2008). [3] T. Sarkar, V. Pralong, and B. Raveau, Physical Review B 83, 214428 (2011).

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Hydrothermal synthesis of ZnO: Correlation between structural properties and photocatalytic activity.

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Zinc oxide (ZnO) has been studied for decades and in recent years it had renewed interest due to its potential applications in many fields. In the micro and nano scales, ZnO displays unique properties, which have been successfully exploited in many technological applications. The particle size and morphology control has been reported as a major challenge in tuning ZnO devices performances. ZnO has a wurtzite structure and a band gap of 3.37 eV. Its relatively open crystalline structure offers the possibility of incorporation of impurities, contaminants or dopants. In addition, ZnO arises as an alternative to TiO2, a well know photocatalyst that has similar band gap energy. Nowadays, its use in photocatalysis became one of the most investigated applications of ZnO. In this work we report on the structural and optical properties of ZnO powders and ZnO films deposited on carbon. The samples were characterized by XAS, UV-VIS and photoluminescence. The correlation between the structure and photocatalytic activity will be presented.

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Estudo da Estrutura Atômica e eletrônica de Materiais ferroelétricos cerâmicos através da técnica de XAS: É possível avançar mais?

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Os materiais ferroelétricos tem sido objeto de intensas investigações científicas nos últimos anos devido ao grande espectro de aplicações tecnológicas e na busca de um melhor entendimento das interessantes propriedades apresentadas por esta classe de materiais. O estudo de suas propriedades ferroelétricas, piroelétricas, piezoelétricas e ópticas tem ampliado cada vez mais o potencial de aplicação tecnológica desses materiais. Nos últimos 10 anos, através da técnica de Espectroscopia de Absorção de raios-X (XAS), realizamos uma quantidade significativa de trabalhos sobre a estrutura local e eletrônica de uma serie de materiais ferroelétricos baseados nos compostos ferroelétricos $PbTiO_3$, $PbZrTiO_3$ e $BaTiO_3$ [1-6]. Neste trabalho, mostraremos as avanços obtidos durante este periodo na tentativa de melhor compreender as propriedades elétricas destes materiais através da técnica de XAS e se ainda é possível avançar nesta área de conhecimento utilizando esta técnica de analise estrutural.

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Structural, Optical and thermal properties of NSH crystals doped with manganese ions.

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Nickel sulfate hexahydrate NiSO4.6H2O (NHS) crystals are known to possess an optical transmission spectrum which has attracted much attention because it presents two regions with high transmission, the first region being between 200 and 350 nm and the second between 400 and 600 nm, and a high absorption efficiency in other regions of the UV-VIS spectrum1,2. A light transmission spectrum with these characteristics is similar to an optical filter. Unfortunately, this material loses stability at a relatively low temperature, 73 C. This low thermal stability is associated with the large amount of water in the composition of these materials which has an ionic complex formed by ions consisting of nickel bonded to six water molecules in a covalent manner. A single nickel sulfate hexahydrate crystal doped with manganese ions was grown. The green block was grown by the slow evaporation method. Its structural, optical and thermal properties were studied using a Raman spectroscopy, X-ray multiple diffraction using synchrotron radiation transmission spectrometry, and TGA. A careful investigation of the crystal structure showed that doped samples of nickel sulfate hexahydrate have the same tetragonal structure as the pure crystal. The dehydration temperature of doped crystal was found to be about 82 oC, higher than that of pure crystal. High-resolution Renninger Scans of NSH crystals were carried out at XRD1 station of the Brazilian Synchrotron radiation facility (LNLS). A three-axes Huber goniometer was used in order to provide Renninger scans. The (008) primary reflection was chosen for these experiments. The results show that the crystals symmetries are practically the same regardless of the incorporation of manganese ions. Accurate calculation of the unit-cell parameters revels that there is relative dilation of the lattice parameters following Mn dopant. The results have also demonstrated that reflection phases are sensitive to presence of dopant ions in the lattice of NSH. Structural changes causing the phase shifts are discussed.

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The formation studies of NiO and Cr2O3 by X-ray diffraction with synchrotron light source

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The interest in the physical of nanoparticles has increased in the last decades because of the different properties encountered in the nanocrystalline materials and their corresponding bulk. Chromium oxide nanoparticles have several applications such as catalysis of CO [1] and H2S [2], green pigments [3], thermal protection [4], wear resistance [5,6] as in advanced digital recording systems [7] that depend on the crystalline size and morphology. Reduced particle size is also needed for improved sintering abilities, that means decreased sintering temperatures and increased density of sintered powders [8]. Several methods have been implemented in order to obtain the nanocrystalline chromium oxide, including microwave plasma [9], sol-gel [10,11] and mechanochemical processing [12]. From the idea of using coconut water [13] as a precursor to obtain metal oxide, in this work we used commercial gelatin thinking that both precursors are constituted of the protein in its composition. In this work we use a simple method to obtain nanoparticles of oxides by means of gelatin using salts of Ni and Cr in aqueous solutions. We present here the results of X-ray powder diffraction (XRPD) as a function of temperature to see the initial formation of NiO and Cr2O3 [14] nanoparticles even the experimental setup is not properly mounted to study the kinetic of the system.

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Sol gel synthesis, structural and luminescent properties of $YVO_4:Eu^{3+}$

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$YVO_4:Eu^{3+}$ is interesting material due to their luminescence properties, and they have potential applications as TV phosphors, plasma display panels (PDPs), lamps, lasers, cathode ray tubes (CRTs), field emission displays (FEDs), X-ray detectors, and scintillators in medical image detectors. In this work the non-hydrolytic sol-gel methodology was employed in the preparation of $YVO_4:Eu^{3+}$. The influence of temperature with respect to the attainment of a material consisting of pure phases and displaying excellent luminescence properties was investigated by thermal analyses (TG/DTG/DTA), X-ray diffraction (DRX), small angle X-Ray scattering (SAXS), transmission electron microscopy (TEM), photoluminescence of the Eu^{3+} ion (FL), lifetime of the Eu^{3+} ion excited state, and quantum efficiency. The TG/DTG curves displayed peaks relative to mass losses of solvent molecules, pyrolysis of organic matter remaining from the synthesis, and structural arrangement. The DTA curve presented an exothermic peak at 660 °C, indicating crystallization of the oxide. The XRD data demonstrated that the YVO_4 phase was formed at 600 °C, and that at 800 °C only the pure matrix is present, with crystallite size of about 60 nm. The samples treated at 800 and 1000 °C, the peaks relative to impurities disappeared, suggesting that only the crystalline phase YVO_4 was present in the samples. The SAXS results evidenced a power law behavior extended for one decade (0.01 to 1 nm^{-1}). Moreover, these curves followed the q^{-4} scaling law, indicating that the samples treated a 600, 800, and 1000 °C for 4 h obeyed the Porod law and presented smooth and nonfractal interfaces, typical of ideal two-phase systems with sharp boundaries. The excitation spectra of the samples displayed the charge transfer band (CTB) and sharp lines (f-f transitions) of Eu^{3+} ions. The photoluminescence data evidenced the characteristic transition bands arising from the $^5D_0$ - ^7F_J (J = 0, 1, 2, 3, and 4) manifolds under maximum excitation at CTB and $^5L_6$ level of the Eu^{3+} ion. The lifetime and quantum efficiency were about 0.70 ms and 50 %, respectively, corroborating literature data. The process reported here is promising for the preparation of phosphors, since it gives rise to a material with strong luminescence in the red region of the electromagnetic spectrum.

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Effect of metallic composition of Ni and Co based catalysts towards steam reforming of ethanol

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Ethanol appears to be interesting for production of hydrogen (to be used as fuel on fuel cells or in industrial process) because of its availability and because the reaction can occur on lower temperatures. The metallic nature of catalysts leads to very different catalytic properties in materials mostly because of the electronic properties of the metals. The major problem of any reforming reaction is carbon accumulation. So, achieve catalysts resistant to this problems remains a challenge in catalysis field. Co and Ni are good catalysts for this purpose, although their suffer carbon accumulation in large extent. The strategy to avoid this is to increase the amount of oxide species available to oxidize the carbon, equilibrating the rates of ethanol adsorption and carbon oxidation, which can be done by decreasing of particle size and the formation of bimetallic systems. Our results show that lower metal loadings (from 15 to 8 wt % of metal) lead to Co smaller particles, observed by a decreasing on the coordination number (CN) of Co-Co scattering and by the appearance of Co-O scattering. In the Ni case, no changes regarding the CN and no significant Ni-O were present. But in the bimetallic CoNi catalyst, EXAFS spectra showed that smaller CNs were found in the low metal loading, in both the Ni and Co K-edges. Also, there is presence of oxidized species. Interestingly, at the monometallic catalysts the amount of carbon formed is quite similar in both loadings; in the bimetallic catalyst at high loading, it follows the order Ni more than CoNi more than Co, this intermediate profile its believed to the changes in electronic properties of the alloy CoNi formed. Although, at low loading, very insignificant amounts of C were found, showing that the electronic changes are enriched by the combination of smaller particles and metallic composition, leading to stable catalysts.

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In-situ XANES experiments on Ni K-edge in mesoporous ZrO_2-CeO_2:Ni

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Ordered mesoporous ZrO_2-CeO_2 mixed oxides are potential candidates for catalytic applications. These systems, used as anodes in solid oxide fuel cells (SOFC), may lead to better performance of SOFCs, due to an enhancement on surface area, aiming to achieve a lower working temperature. The aim of this studies is to evaluate the reduction capacity of Ni^{2+} to Ni in ZrO_2-x(mol)%CeO_2 (x=50 and 90) samples impregnated with 60(wt.)%NiO.

The synthesis was made with Zr and Ce chloride precursors, HCl aqueous solution, Pluronic P123, NH_4OH to adjust the pH (3-4) and a teflon autoclave to perform a hydrothermal treatment (80^oC/48h). The samples were dried and calcined, until 540^oC in N_2 and 4 hours in air. The NiO impregnation was made with an ethanol dispersion of $Ni(NO_3)\times 6H_2O$. The powder was calcinated in air until 350^oC for 2 hours. Temperature-resolved XANES data at the Ni K-edge were collected at the DXAS beam line of the LNLS in transmission mode, using a Si(111) monochromator and a CCD detector. Sample preparation consisted of mixing ~6mg of the powder samples with boron nitride and pressing into pellets. The data were acquired during an experiment of temperature programmed reduction (TPR) under a 5% H_2/He until 600^oC and mixtures of 20%CH_4:5%O_2/He, at temperatures from 400 to 600^oC. All the reactions were monitored with a mass spectrometer. The data was analyzed with a linear combination fit of 2 standards for each valence number using Athena software.

The Ni K-edge experiments demonstrated that for both contents of CeO_2, NiO embedded in the porous zirconia-ceria matrix reduces at lower temperatures than pure NiO, revealing that the ZrO_2-CeO_2 support improves the reduction of impregnated NiO. Ni was oxidized to NiO after all reactions with methane and oxygen. Hydrogenated carbonaceous species were detected, but under reducing conditions, the hydrocarbon compounds are removed. The reaction of total oxidation of methane CH_4:O_2 (1:2 ratio) was observed at lower temperatures (around 400^oC) for both samples.

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Parte IX

Superfícies, Interfaces e Nanossistemas

Site-selective photofragmentation of chlorinated polymeric films observed around the chlorine K-edge

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Photon stimulated ion desorption (PSID) and Near-Edge X-ray Absorption Fine Structure (NEXAFS) studies have been performed on poly(vinyl chloride) (PVC) and poly(vinyl dichloride) (PVDC) around the chlorine 1s-edge. The experiments were performed using a synchrotron source operating in the single-bunch mode and a time-of- flight mass spectrometry for ion analysis. Desorption ion yield curves were determined as a function of the photon energy. Cl^+ ion yields reproduce photoabsorption spectra, showing significant increase at the 1s-resonance. Edge-jump ratios for Cl^+ ion yield were much higher than the equivalent electron yields, indicating site-selectivity in C-Cl bond breaking for both polymers, as a result of efficient spectator Auger decay. 3:1 isotope ratio of chlorine was measured for the PVC. For other ionic species the indirect X-ray induced electron stimulated desorption (XESD) process seems to play an important role. The interpretation of NEXAFS spectra were assisted by quantum mechanical calculations at a multireference perturbation theory level.

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SYNTHESIS AND CHARACTERIZATION OF CALCIUM PHOSPHATE MACRO AND MESOPOROUS FOR DRUG RELEASE SYSTEMS

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The aim of the present work is the characterization of calcium phosphates, especially hydroxylapatite (HAP - Ca_{10} $(PO_4)_6$ $(OH)_2$) and β-tricalcium phosphate (β-TCP - $Ca_3(PO_4)_2$) with hierarchical arrangement of pores obtained via organic templates formed by two compounds: cetyltrimethylammonium bromide (C_{16}TAB) surfactant and gelatinized corn starch. The IUPAC-International Union of Pure and Applied Chemistry ranked the pores according to their diameters as: mesopores (2 nm $< \phi <$ 0 nm) or macropores ($\phi >$ 50 nm). Structures containing hierarchical pores arrangement are useful in many areas of biomaterial engineering such as drug delivery, bone repayments and bone reconstruction. The incorporation of a luminescence probe such as Eu^{3+} in porous HAP and β-TCP increases the applicability of the ending product for drug delivery since the fluorescent probes is already nucleation sites in the inorganic scaffold hosting the drug. The synthesis of pure HAP and β-TCP as well as doped HAP and β-TCP with 6 mol% Eu^{3+} was also investigate. The samples were structural and morphological characterized via powder X-ray diffraction (XRD), Extended X-ray absorption fine structure of (EXAFS), scanning electron microscopy (SEM) and Small angles X-ray scattering (SAXS). The XRD results indicated that the type of organic template employed promotes variations in the dimensions of the nanoparticles of calcium phosphate in crystalline phases. EXAFS results showed that the local symmetry of the Eu^{3+} incorporated in hydroxyapatiteis consistent with incorporation of Eu^{3+} in larger scale at the Ca(1) sites of HAP. The SAXS and SEM results indicated that meso and macropores were not obtained on addition of C_{16}TAB alone, whereas the samples produced with the combination of starch and C_{16}TAB have a pore size distribution.

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Estudo de propriedades elásticas e ópticas de nanomembranas de GaAs:InAs

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Nanomembranas de semicondutores com espessuras entre 5nm e 300nm tem atraído crescente interesse científico [1-3]. Tal atratividade deve-se à excepcional combinação de maleabilidade mecânica com a alta qualidade cristalina de filmes semicondutores crescidos por técnicas epitaxiais e a possibilidade de transferi-los para qualquer substrato, fornecendo novas rotas para desenvolvimento de dispositivos.

Neste trabalho investigamos deformações sofridas por camadas finas de GaAs/AlGaAs com pontos quânticos de InAs em sua estrutura. As estruturas são crescidas em substratos de GaAs (001) cobertos por uma camada sacrificial de AlAs de 50nm. Sobre esta camada depositamos membranas com 30nm e 60nm de espessura e pontos quânticos de InAs com cobertura nominal de 1.8 monocamadas, centrados em uma estrutura de barreiras de AlGaAs. As membranas são então liberadas por métodos de litografia ótica e ataque químico, que permitem uma definição da estrutura a ser removida, sua corrosão vertical e eliminação da camada de AlAs por HF:H_2O.

Após serem extraídas de seus substratos originais as membranas são transferidas para qualquer substrato por diferentes técnicas. A primeira consiste em liberar a membrana em solução e depositá-la por elevação [3]. Este método permite obter membranas de áreas grandes, mas com formato lateral aleatório. Dois outros processos que permitem uma melhor definição da forma da membrana utilizam fita dupla face ou um substrato coberto por PMMA para que as membranas possam ser aderidas a novas superfícies.

Medidas de difração de raios-x sob incidência rasante permitem avaliar modificações do strain dos pontos quânticos de InAs e da camada de GaAs, comparando a qualidade das membranas extraídas por cada processo. Os estados de deformação gerados também induzem alterações na estrutura de bandas das camadas extraídas, que podem ser averiguadas por medidas de fotoluminescência. Deste modo podemos comparar informações acerca da qualidade da rede cristalina e da estrutura eletrônica. Os resultados obtidos revelam o potencial de cada método de transferência para uso no processamento e fabricação de novos dispositivos.

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On the chemical state of the Pd_XCu_{1-X} nanoparticles' surface atoms

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Synthesis and characterization of bimetallic systems have attracted great interest in nanoscience, since they have revealed novel physical and chemical properties, different of those presented by monometallic counterparts. Thereby, much effort has been dedicated to investigate the shape, size, crystal and electronic structure, as well surface properties of bimetallic nanoparticles (NPs). The main goal of our study is to synthetize and characterize Pd_XCu_{1-X} (X= 0.7, 0.5 and 0.3) NPs obtained via wet chemical reduction. The average size of NPs obtained by this method is about 4 nm (varying with the value of X), as observed by TEM. The XRD patterns of the NPs present the peaks related to Pd-Cu alloy and none of the peaks characteristics of pure Pd^0 or Cu^0, indicating the formation of crystalline PdCu alloy with average crystallite size of about 4.1 nm (varying with the value of X). Surface investigation made by XPS measurements provided the relationship between the Pd concentration and the oxidation state of the nanoparticles' surface atoms.

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Characterization and catalytic activity of Palladium nanoparticles during NO decomposition

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The catalytic decomposition of NO_X over noble metals supported catalysts has become one of the most attractive ways of controlling the emissions of these noxious gases. In this work, we obtained Pd nanoparticles (NPs) by wet chemical reduction and we studied the catalytic activity of Pd NPs supported on carbon in the direct decomposition of NO. The formation of NPs was monitored by *in-situ* UV-visible absorption. By HRTEM, the morphology of the NPs was revealed as a worm-like system, formed by linked crystallite clusters with an average short axis diameter of 5.42 nm. XPS and XRD analysis confirmed the NPs metallic state. During the decomposition reactions, the effluent gases from the reactor were analyzed by *in-situ* IR absorption. The Pd/C catalysts proved to be active in the temperature range of 323 K to 673 K.

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The influence of oxidation state, size and electronic properties of Co-Cu crystallites on carbon deposition during reforming of ethanol

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Production of hydrogen gas from reforming of ethanol via Co-based catalysts is a matter of global concern. In spite of reportedly high activities and selectivities, these catalysts still undergo significant deactivation, which is generally attributed to sintering, carbon deposition and oxidation of Co metallic particles. It is known that Co^0 and CoO_x species coexist and that control of deposited carbon can be accomplished by manipulating the Co^0/CoO_x ratio. However, the nature of active sites is still a challenge and requires *in situ* studies. In this work we examine the phase changes of Co by means of XAFS, XPS and XRD studies during steam reforming of ethanol, highlighting its correlation with resistance to carbon deposition. Co-Cu/$MgAl_2O_4$ catalysts containing 12 wt. % of Co and 0.5 to 3 wt. % of Cu were prepared by incipient wetness impregnation of the supports with aqueous solutions of the respective salts. After reducing the catalysts, there is a migration of Cu atoms to the surface of crystallites. These atoms partially replace the Co atoms in the Co face-centered cubic lattice, thus forming a Co-Cu alloy. The oxidation of carbon filaments by water is hindered in Cu-promoted catalysts due to the strong interaction between the filaments and the surface alloy. The rate of carbon deposition is also dependent on the oxidation state of Co and decreases with the coordination number of Co-Co scattering. Above 673 K, the fraction of reduced Co is greater than the fraction of CoO and the products of ethanol reforming are observed. This fact reflects a predominant reduction of CoO in the presence of ethanol above 673 K when compared to oxidation of Co^0 in the presence of water. The size of Co crystallites can be controlled by changes in the nature of support, Co loading or addition of Cu, which associated to the right composition of reactants results in catalysts with tunable Co^{2+}/Co^0 ratio. The presence of both Co^0 and Co^{2+} sites on catalyst surface helps to equilibrate the steps of ethanol activation and carbon oxidation, resulting in stable catalysts free of carbon.

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Structure of Silver-Containing Sol-Gel Hybrid Materials and its Performance as Biocide Coatings

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Development of thin biocide coatings is acquiring higher meaning since it brings the possibility to functionalize surfaces exposed to biologic contamination and, therefore, to inhibit the spreading of contagious infections provoked by different microorganisms. In this work, hybrid organic-inorganic sol-gel materials were functionalized with silver ions in order to analyze the relationship between the hybrid structures, silver ion stability and biocide effect as a function of the organic component and densifying thermal treatments. Hybrid silica-methyl and silica-epoxy coatings were synthesized, through the sol-gel method, by hydrolytic condensation of tetraethoxysilane (TEOS), methyl-trimethoxysilane (MTES) and glycidoxypropyltrimethoxysilane (GPTMS) under acidic conditions. Silver ions were added in the sol stage by a silver nitrate solution. Stable and colorless sols were obtained. Through dip-coating at a constant withdrawal rate, homogeneous and cracks-free coatings were obtained and thermally treated at 50, 100, 150 and 200 °C in air and oxygen atmospheres. Hybrid structures and thermal evolution of silver nanoparticles were analyzed by Small Angle X-ray Scattering (SAXS) at the SAXS1 beamline of LNLS. A spinodal-like phase separation was resolved in each one of the hybrid matrixes. Analysis of SAXS curves were compared with results from Fourier Transformed Infrared Spectroscopy (FTIR), UV-visible spectroscopy and Transmission Electron Microscopy (TEM). Biocide effect was evaluated, against *Escherichia coli*, through the inhibition halo in agar diffusion tests.

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Photon and electron stimulated ion desorption on thiophene-based polymers

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Photon (PSID) and electron (ESID) stimulated ion desorption studies have been performed on thiophene-based polymers at LNLS and at the Surface Chemistry Laboratory, UFRJ. For poly(thiophene) (PT) and poly(3-methylthiophene) (P3MT), it was found that sulfur K-shell photoexcitation produces S+ desorption efficiently. On the other hand, S2+ desorption is enhanced at higher energy excitations. These results were interpreted in terms of the Auger-stimulated ion desorption mechanism. For poly(3-hexylthiophene) (P3HT), the S+ desorption seems to be suppressed, which may be due to the hexyl side-chains. PSID spectra for P3HT and P3HT/CNT show great similarity and exhibit desorption of the polymer fragments only. This is in accordance with previous morphological studies on these materials, which suggested that the nanotubes are highly dispersed and involved by the polymer. PT was also studied by the electron stimulated ion desorption (ESID) technique with variable electron energy and the results explained in terms of the Auger stimulated ion desorption process and secondary electrons. Atomic sulfur ions could be clearly measured and isotopic contributions identified. PSID spectra of PT at different thicknesses are also presented, and together with ESID studies it was possible to investigate the influence of secondary electrons in the desorption process, which is highly desirable, since they involve lower energy levels (valence electrons), affecting the properties of interest of photovoltaic materials.

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Estudo da formação de NPs de Cu e Pt por DXAS *in situ*

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As nanopartículas (NPs) de cobre (Cu) e platina (Pt) desencadearam ao longo dos anos consideráveis investigações em função das suas propriedades eletrônicas, estruturais, mecânicas, ópticas e catalíticas [1-2]. Tais NPs possuem aplicações importantes como catalisadores (mono e bimetálicos), por exemplo, na reação de oxidação de CO e em células combustíveis [3]. Neste trabalho monitoramos a formação de NPs de Cu e Pt através de Espectroscopia de Absorção de Raios X Dispersivo *in situ* (DXAS). O monitoramento *in situ* foi possível através do uso de um reator específico, o qual permite acompanhar a formação de NPs em solução com resolução temporal, e um dosador de reagentes com acionamento remoto. Após a realização dos experimentos *in situ*, foram medidos os espectros de EXAFS *ex situ* das NPs formadas. As medidas de DXAS *in situ* e XAS *ex situ* foram realizadas nas linhas de luz DXAS e XAFS-1 do LNLS, respectivamente. As NPs formadas também foram caracterizadas por Difração de Raios X (XRD) e Microscopia Eletrônica de Transmissão (TEM). Os resultados mostraram claramente a evolução da estrutura eletrônica dos íons em solução até a formação de NPs. Foram sintetizadas NPs de Cu com diâmetro médio de 2,5 ± 0,70 nm, e NPs de Pt com 2,7 ± 0,55 nm.

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Characterization of titanium and titanium nitride coatings obtained with a PIII&D system

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Ti and TiN coatings on stainless steel are proposed to improve the hardness and tribological properties of the surface of this material. Cathodic arc deposition is an efficient technique to produce thin films due to its high deposition rate. In these devices, a high current (100 A) runs between the electrodes generating the emission of a metallic plasma jet from the cathode. When a substrate is located intercepting the plasma jet, a metallic coating is obtained. Applying a pulsed negative bias to the sample, the ion impinging energy on the surface can be increased and if the bias voltage is high (kV) the ions achieve enough energy to be implanted. When the high negative potential is on ions are accelerated towards the surface and are implanted, while the bias is off ions condense on the surface resulting in the deposition of a coating or a film. In this way plasma immersion ion implantation is combined with deposition (PIII&D). PIII&D has demonstrated to be useful for the fabrication of nanostructure coatings. The use of high voltage pulses to bias the substrate allows to obtain denser films and to relax internal stress improving the adhesion. The aim of this work was the characterization of Ti and TiN thin films obtained with a PIII&D system. The system was constituted by a dc cathodic arc with a Ti cathode of 5 cm in diameter and an annular copper anode of 8 cm in diameter. The discharge was run continuously at 100 A. The substrate was biased with a pulsed generator. Pulse amplitude was varied from 1 to 15 kV, the pulse rate was fixed at 200 Hz with a pulse duration fo 35 μs. Films deposited on stainless steel and silicon substrates with different ion implantation conditions were study at the XRD2 beamline of the LNLS. A theta/2theta geometry similar to Bragg Bentano configuration and grazing incidence were employed. By means of XRR, the film density was determined. The PIII&D technique has not introduced significant changes in the morphology of the films compared with coatings deposited with a cathodic arc without pulsed bias. However, XRD diffractograms showed clear differences, as shifts in the peak position broadening and splittingof the peaks, indicating that PIII&D has affected the film structure. The lattice parameters and crystallite size were compared among films obtained without and with implantation.

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Estudo de XANES in situ durante o crescimento de estruturas de ZnO

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Óxido de zinco (ZnO) é um semicondutor que possui uma banda de energia proibida de 3,3 eV, e alta energia de ligação excitônica (60 meV) que assegura a emissão excitônica eficiente à temperatura ambiente. Também possui uma estrutura cristalina do tipo Wurtzita (hexagonal) com espaçamento de rede a = 0,325 nm e c = 0,521 nm. Trata-se de um material com ampla aplicabilidade na área da óptica, na microeletrônica e em biosensores devido as suas importantes propriedades químicas, elétricas e ópticas [1]. Considerando que a morfologia destes materiais influencia suas principais propriedades físicas têm-se produzido nanomateriais com dimensões e formas bem controladas. Por exemplo, são obtidas estruturas de ZnO na forma de nanofios, nanotubos, nanocolunas, nanoflores, nanoesferas, etc. De acordo com a literatura, há pouco esclarecimento do mecanismo e fatores que governam o tipo de morfologia formada. Na deposição por CBD (Chemical Bath Deposition) a morfologia cristalina é fortemente influenciada pelas condições experimentais, como: a temperatura, o tempo de deposição, pH, tipo do substrato e solvente. O controle do tamanho, a forma e a orientação dos cristais de ZnO no substrato é um pré-requisito para criação de materiais de alta área superficial para uso em muitos tipos de dispositivos, incluindo os dispositivos fotovoltaicos e optoeletrônicos [2]. No presente trabalho serão apresentados estudos da formação e caracterização de filmes de ZnO. O estudo com a técnica XAS in situ na borda K do Zn, foi empregado para monitorar a formação do filme de ZnO durante a deposição sobre o substrato de grafite. Na caracterização das amostras empregamos a DRX (Difração de Raios X) para obter a estrutura cristalina dos filmes, enquanto que MEV (Microscopia Eletrônica de Varredura) forneceu detalhes da morfologia das estruturas. Os resultados de XPS (Espectroscopia de Fotoelétrons induzidos por Raios X) permitiram sondar o ambiente químico dos elementos presentes na superfície da amostra.

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Observation of an anomalous van der Waals gap near the surface of Bi_2Te_3 by scanning tunneling microscopy and X-ray crystal truncation rod scattering

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Bi_2Te_3 is part of a very specific group of materials known as topological insulators. The motivation of the study of these materials comes from their conductivity: they are insulators in the bulk and conductors at the surface, features that are very important for electronic applications. They are simple to be obtained through techniques already established to semiconductor materials such as silicon. The atomic structure of Bi_2Te_3 is similar to graphene, since van der Waals interactions keep the layers of the material connected. However, its stable configuration includes five monolayers at the following order: Te-Bi-Te-Bi-Te. Bi_2Te_3 is a promising material and its atomic and electronic configurations are not completely determined. In this experimental study we have observed different terraces at the atomic level of the sample surface using scanning tunneling microscopy (STM). Using STM we have concluded that after being cleaved, Bi_2Te_3 does not break only into five monolayers, but also in smaller atomic steps. A theoretical simulation will be carried out to explain its electronic structure (i.e., why Bi_2Te_3 is cleaved also in steps where the covalent bonds are at first stronger than van der Waals interactions). The sample was also characterized using X-ray diffraction at beamline XRD2 (LNLS). Reciprocal space maps perpendicular to the substrate surface were carried out, along the 00L, 01L and 10L lines. These data were analyzed and compared to a five-monolayer periodic model. The final fit reveals a significant aproximation between intensity peaks allowed and the experimental data. We conclude that the surface van der Waals gap is different from the bulk one.

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Ultrafast charge transfer in poly(thiophene) probed by resonant Auger spectroscopy

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Charge transfer dynamics is a topic of highly importance in fundamental and in many applied areas like femtochemistry, surface photochemistry, molecular electronics, solar energy, and so on. Besides pump-probe optical experiments, Auger decay spectra following core excitation emerges as an alternative with major advantages. Firstly, because the core hole lifetime probed by core level spectroscopy can be used as a fast internal clock and in so far very low timescales can be achieved, the so-called core hole clock (CHC) method. Secondly, because of the inherent atomic specificity of core levels. For some applications, the surface sensitivity of low energy electrons adds up. Ultrafast electron transfer dynamics in the low-femtosecond regime was evaluated for poly(thiophene) by resonant Auger spectroscopy (RAS) using the core-hole clock method. Sulfur *KLL* Auger decay spectra were measured as a function of the photon energy. Remarkable changes developed by tuning the photon energy along the sulphur 1s edge, depending on the nature of the intermediate core excited states. It was possible to disentangle transitions to pi*, sigma* and Rydberg states by RAS not resolved by XAS. Competing Raman and Auger channels could be separated and charge transfer times derived.

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Deposition and Characterization of Thin Films of Ti-Nb-Zr Deposited on Si(111) and Stainless Steel

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Ti-6Al-4V is one of the main biomaterial alloys employed as implants, but the release of Al and V ions is associated to health problems and adverse tissue reactions. A new class of Ti alloys employs Zr for solid-solution hardening and Nb as β phase stabilizer. Metals such as Ti, Nb, and Zr, known as valve metals, usually have their surfaces covered by a thin oxide film spontaneously formed in air. This oxide film constitutes a barrier between the metal and the medium. The Ti-Nb-Zr alloys have mechanical and corrosion resistance characteristics which make them suitable for use as implants. It is relevant to investigate the surface properties which are adequate for clinical applications, and an interesting option for tuning surface functionality is thin film technology. The Ti-Nb-Zr films were grown by magnetron co-sputtering deposition onto cleaned (111) silicon and stainless steel substrates at room temperature from zirconium, titanium, and niobium metal targets. The morphology and chemical composition of the films were analyzed by means of atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS). The AFM images showed the low roughness and the nanometric grain sizes of the films, which can be described by the parameters (Ra and grain size) extracted from the image analyses over a surface region of 500 nm x 500 nm. In the case of the silicon substrate, the film showed a lower grain size (53 nm) than the stainless steel substrate (70 nm), both films exhibit roughnesses with Ra = 3 nm. The Ti 2p, Nb 3d, and Zr 3d core level spectra were obtained by XPS for both films and the results showed the formation of mixed oxides on the surfaces of the Ti-Nb-Zr films deposited on Si(111) and stainless steel substrates.

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Fotodegradação de gelos astrofísicos induzida por radiação síncrotron

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Acetonitrila (CH_3CN), Formamida ($HCONH_2$) e Acetona (CH_3COCH_3) são moléculas relevantes do ponto de vista pré-biótico. Todas essas moléculas foram identificadas por sua emissão em radiofrequência na direção da nuvem molecular Sagitário B2 (Sgr B2), uma região quimicamente rica de gás e poeira nas proximidades da região central da Via Láctea. Acetonitrila foi também detectada no cometa Kohoutek. De maneira análoga, formamida foi identificada no cometa Hale-Bopp e, tentativamente, em objetos estelares jovens, tais como W33 A e NGC 7538 IRS9. Todos estes ambientes estão sujeitos à ação de agentes ionizantes, tais como fótons, elétrons e raios cósmicos, provocando a fragmentação e consequente dessorção de espécies neutras e iônicas, podendo levar à formação de moléculas mais complexas. Com o objetivo de simular a realidade astrofísica em laboratório, foram preparados gelos de acetonitrila, formamida e acetona condensados a uma temperatura de 10 K em uma câmara de ultra-alto vácuo. Estes gelos foram expostos à radiação síncrotron em ordem zero (não monocromática) na linha SGM do LNLS. A degradação do gelo foi acompanhada por espectroscopia de fotoabsorção nas bordas 1s do carbono, nitrogênio e oxigênio.

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Understanding the stability of $Ni/CeO_2/Al_2O_3$ catalysts for reforming of ethanol as addressed by temperature-resolved XANES analysis

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Hydrogen can be produced by steam reforming (SRE) and oxidative steam reforming of ethanol (ORE) catalyzed by metal surfaces. In this study we tried to elucidate the nature and the stability of the Ni species during ORE. We analyzed a 15%Ni/Al_2O_3 sample using XANES-ORE temperature-resolved spectra. The results demonstrated that metallic nickel particles were oxidized by the feed. The increase in temperature caused a decrease in the number of Ni metallic sites up to 673 K. After this temperature, when the increase in ORE activity, and consequent production of H_2, starts, there is a steady increase on the Ni^0/Ni^{2+} ratio. Spatial-resolved XANES-ORE of 15%Ni/Al_2O_3 showed that near the entrance of the catalytic bed, the Ni^0/Ni^{2+} ratio reaches a minimum due to the oxidizing nature of the feed. This ratio increases continuously along the reactor length, reaching a value around 90% at the exit. Ni^0/Ni^{2+} ratio is strongly sensitive to the degree of Ni reduction. The control of Ni^0/Ni^{2+} ratio by manipulating Ni clusters sizes and composition of the feed can equilibrate the steps of ethanol activation and carbon oxidation, resulting in stable catalysts. Therefore, we decided to study catalysts with different nickel loadings (5, 10 and 15 wt.%) supported on CeO_2/Al_2O_3 for ORE. Temperature-resolved analyses of XANES indicated that the smallest nickel content presented the highest oxidation state in all temperature range during ORE. The oxidation state of nickel particles submitted to reaction conditions decreased with an increase of nickel content. The highest deactivation during ORE was observed for 5%$Ni/CeO_2/Al_2O_3$. On the other hand, 10%$Ni/CeO_2/Al_2O_3$ catalyst presented the largest stability for ORE, as well as, the best hydrogen yield. The excellent performance obtained for 10%$Ni/CeO_2/Al_2O_3$ catalyst can be attributed to a good balance among active phases and redox capacity that the support CeO_2 supplies to the catalyst.

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Caracterización mediante Fe K XANES del entorno local del Fe en catalizadores Fe-Si aptos para la producción de nantubos de carbono

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En este trabajo se presentan los resultados del estudio de un conjunto de catalizadores aptos para la producción de nanotubos de carbono (NTC) y de sus precursores, con el objetivo de obtener información que pueda correlacionar la eficiencia catalítica de cada catalizador con la estructura local del Fe presente en el mismo. En los últimos años el estudio de las noveles propiedades de los NTC ha llevado a optimizar las rutas de síntesis de estos materiales, tanto como a ensayar nuevas vías de obtención. Estudiar los constituyentes del proceso, a la vez que el proceso, permite obtener información cualitativa y cuantitativa importante tanto para el diseño como para la optimización de este tipo de materiales y sus productos. Mediante el método sol-gel se sintetizaron nanopartículas de óxido de hierro en matrices de SiO2, para luego usarlos como catalizadores en la síntesis de NTC por Deposición Química en Fase Vapor (CVD). Mediante la técnica XANES (X-ray Absorption Near Edge Spectroscopy) en el borde de absorción K del Fe (7112 eV) se caracterizó al entorno local del Fe estudiándose la simetría y la valencia (estado de oxidación) de las nanopartículas de óxido de hierro en matrices de SiO2. El estudio de los prepicos Fe-K XANES reveló que las nanopartículas de óxido de hierro en todos los catalizadores, previo a su uso en el proceso de catálisis, se encuentran en la fase alfa-Fe2O3, con una simetría de la naturaleza de este óxido, en tanto que para los precursores existe una tendencia a un orden más centrosimétrico. Este hecho descarta la presencia de silicatos de Fe, que afectan los rendimientos catalíticos, cuando los catalizadores ingresan al reactor. En estos momentos se están realizando experiencias Fe K XANES con los materiales en condiciones de reacción catalítica y posteriores a la reacción para ver si existen posibles modificaciones del entorno local del Fe y poder comprender las grandes diferencias de la eficiencia catalítica mostradas por este conjunto de catalizadores.

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Magnetic properties, electronic structure and morphology of PtCo and PtCo/Au dumbbell nanoparticles

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Multicomponent nanocrystals (MNCs) became an important class of materials due to their abilities to carry multiple functions that can be utilized simultaneously [1-3]. Recent progress in synthesis of MNCs allows obtaining different types of nanoparticles such as core-shells [1], dumbbells, or other geometries [3]. Characterization of PtCo and PtCo/Au alloys was performed using electron microscopy (TEM), X-ray absorption (XAS), X-ray scattering at low angle (SAXS), global magnetic measurements (MM) and magnetic circular dichroism measurements (XMCD). Combination of TEM and SAXS results show spherical particles with a size dispersion of about 5% for Pt_3Co system. SAXS reveals that the addition of Au modifies the stability of MNCs in solution producing NPs agglomerates. XAFS measurements at the Pt $L_{2,3}$ edges and Co K reveal changes in the oxidation state of Co after Au deposition. XAFS previous results [3] have shown that the Au addition removes the Co atoms from the surface of the PtCo NP. XANES at the Pt $L_{2,3}$ edges show a charge transfer from Pt 5d level after Au deposition respect to the Pt configuration in the MNCs used as seed. From MM is observed that all samples exhibit superparamagnetic behavior at RT with a blocking temperature which decreases in smaller Pt_3Co MNCs. XMCD at the Pt-$L_{2,3}$ edges measurements show that there is a transfer of magnetic moment from Co atoms to Pt and also reveals that addition of Au does not affect the magnetic behavior for the Pt atoms. The variation of the XMCD intensity signal with temperature is in accordance with changes in the magnetization of the PtCo alloy. This shows that the Co atoms in the alloy are main responsible for the appearance of the XMCD signal, but can not rule out a contribution to this effect from the size of NPs.

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Alkanethiols Adsorbed on Platinum, Palladium and Bimetallic Pd/Au Surfaces

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The study of thiol self-assembly on platinum group metals is difficult since different reaction pathways, involving molecule decomposition and S adsorption, could take place along with SAM formation. We have analyzed Pd, Au-Pd and Pt surfaces by means of XPS, using both a conventional X-ray source (Mg K α) and synchrotron radiation (SGM beamline).

In every case we have spectroscopic or electrochemical evidence of the presence of sulphide or atomic sulphur as coadsorbates of thiolates. The origin of the sulfide in the different surfaces has been rationalized considering the ability of the metals to induce the C-S bond cleavage, due to the high population of the electronic states near the Fermi Level. On the contrary, Au surfaces are not able to induce the formation of sulfide upon adsorption of alkanethiols. Thus, it is expected that Pd-Au bimetallic surfaces would show intermediate behavior, depending on the Pd content. The S2p signals showed both sulfide and alkanethiolate components. However, our query about the existance of a minimun Pd coverage neccesary to induce the C-S bond scission remains to be answered.

The possibility of C-S bond scission was considered and it was proposed as an explanation for the electrochemical behaviour of hexanethiol-modified Pt surfaces. For this metal, the atomic sulphur and thiolate signals are expected to lie at very similar binding energies. Thus, although atomic sulphur might be responsible of the poor barrier properties of the short-chained alkanethiols on Pt, high resolution XPS showed only one component located at 162 eV.

These results show that SAMs on platinum group metals and bimetallic surfaces have intriguing properties and should be considered from a new perspective.

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Redox behaviour of $Ce_{0.9}Zr_{0.1}O_2$ and NiO(60wt%)/$Ce_{0.9}Zr_{0.1}O_2$ nanocatalyst

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In this work, the reduction of Ce(IV) to Ce(III) in $Ce_{0.9}Zr_{0.1}O_2$ (GS) and NiO(60wt%) /$Ce_{0.9}Zr_{0.1}O_2$ (ZDC6) nanocatalysts, and the subsequent reoxidation, were studied by time-resolved in situ XANES technique. GS nanopowder was synthesized via the glycine-nitrate gel-combustion method. Nickel was incorporated via incipient impregnation with alcoholic solutions of $Ni(NO_3)_2.6H_2O$ with the appropriate concentration to get the final nominal composition. The in-situ XANES experiments were carried out at the LNLS, Campinas, Brasil, in the D06A-DXAS dispersive line equipped with a Si(111) monochromator and a CCD detector. The data were collected near the absorption edges L_{III} of Ce and K of Ni, in the transmission mode. While collecting the transmitted signal, samples were heated at 10°C/min from 20°C to 800°C, with a 30 min isothermal period at 800°C, in a continuous flow of Hydrogen (H_2) (5mol%-He balance) or Oxygen (O_2)(5mol%-He balance) in reduction or reoxidation experiments, respectively. In the reduction process, no significant difference in the Ce(IV) in GS and ZDC6 samples was observed up to 700°C, while complete reduction of NiO to Ni $^\circ$ was achieved. At 700°C, Ce(IV) cations in ZDC6 sample started to reduce faster and deeper than in GS sample. This effect could be associated to the dissociation of H_2 molecules over the Ni° formed, facilitating the reduction of Ce(IV) cations. During the reoxidation process, GS sample increases the reoxidization percentage almost linearly with temperature, while ZDC6 sample showed a two-step process: the first one from room temperature to 300°C and the second one in the 600°C-800°C temperature range. From 300°C up to 600°C, the reduction percentage remained unchanged, while the main part of the reoxidation of Ni° to Ni(II) took place. Above 700°C and up to 800°C, the remaining Ce(III) and Ni° centers were completely reoxidized.

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Produção de gás de síntese a partir da oxidação parcial do metano em presença de catalisadores de níquel derivados de perovskitas do tipo $La_{1-x}Ca_xNiO_3$.

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Precursores catalíticos do tipo perovskitas $La_{1-x}Ca_xNiO_3$ com x = 0; 0,15; 0,3 e 0,5 foram sintetizados pelos método do citrato, sendo os precursores $LaNiO_3$ também preparados por impregnação por via úmida e co-precipitação utilizando NaOH ou Na_2CO_3 como agentes precipitantes. Os catalisadores foram avaliados na oxidação parcial do metano (OPM) em testes de 24 horas de duração. As amostras foram caracterizadas por análise termogravimétrica (ATG), infravermelho com transformada de Fourier (FT-IR), TPR e difração de raios X (DRX) a temperatura ambiente. Também foram realizados experimentos DRX in situ sob atmosfera redutora, com aquisições em temperaturas exatamente anteriores ao início dos principais eventos de redução observados por redução a temperatura programada (TPR-H_2), estudos estes conhecidos por hot-stage diffraction (HSD). As amostras também foram caracterizadas por reação superficial a temperatura programada (TPSR), Oxidação a Temperatura Programada pós-teste catalítico (TPO) e também por Espectroscopia fotoeletrônica de raios X (XPS). Todas as amostras se apresentaram seletivas a gás de síntese e a presença de cálcio favoreceu a formação de carbono filamentoso em detrimento do carbono amorfo em toda a faixa de estudo (x = 0 a x = 0,5).

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Caracterização estrutural e magnética de nanopartículas de $\alpha - Fe_2O_3$

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Atualmente, o estudo de materiais com dimensões nanométricas tem atraído considerável atenção, principalmente devido ao seu forte potencial para aplicações tecnológicas. Neste sentido, a síntese de nanomateriais com um tamanho e morfologia específica tem sido o principal desafio para os pesquisadores. Dentre os vários métodos de síntese existentes na literatura, o método da coprecipitação vem se destacando por sua praticidade e o uso de reagentes não nocivos ao meio ambiente[1,2]. Neste trabalho, utilizamos a técnica de coprecipitação aliada à adição de agentes quelantes para produção de nanopartículas de $\alpha - Fe_2O_3$. Os precursores foram tratamos termicamente nas temperaturas de 200, 300 e 400^oC para obtenção das nanopartículas de $\alpha - Fe_2O_3$. As caracterizações das amostras sintetizadas foram realizadas através de difração de raios-x (DRX), espalhamento de raios-x a baixos ângulos (SAXS), espectroscopia de absorção de raios-x (XAS), microscopia eletrônica de varredura (MEV), microscopia eletrônica de transmissão (MET) e medidas de magnetização. Os resultados de DRX e refinamento Rietveld, confirmam a formação das nanopartículas para todas as temperaturas de tratamento térmico. As nanopartículas produzidas com adição de agente quelante possuem tamanhos médios de domínios cristalinos variando entre 4 e $27nm$[1]. Adicionalmente, observamos que a concentração do agente quelante pode induzir um crescimento preferencial das partículas. Os resultados de MEV, MET, DRX e SAXS mostram claramente que houve um melhor controle da morfologia, tamanho e largura da distribuição de tamanhos das nanopartículas obtidas com adição do agente quelante. Os resultados de MET e XAS dispersivo mostram que as nanopartículas são formadas já na etapa da secagem. Os resultados de magnetização no modo Zero-Field-Cooling e Field-Cooling (ZFC-FC) exibem claramente uma dependência entre a temperatura média de bloqueio e o tamanho médio das nanopartículas.

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Structure of Hollow Iron Oxide Nanoparticles modified with Mo addition studied by XAFS and SAXS

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The large capacity resulting from reducing iron oxide to iron is promising for lithium battery anodes; however, this conversion during the electrochemical cycling is accompanied by fading of the electrode performance due to material pulverization and subsequent loss of electrical contacts between the active material and current collector. On the other hand, cycling of iron oxide-based electrodes in the high voltage range where only intercalation of Li ions occurs has been recently found to be promising to design cathodes.[1] The unique nature of hollow metal oxide nanoparticles (NPs)[2] such as a thin shell, large internal void, and doubled surface area[3] and cation vacancies has raised a lot of interest for their applications in energy storage. Recently Shevchenko et al.[4] reported the role of the high concentration of cation vacancies in hollow iron oxide NPs in lithium intercalation reactions. This report explains significantly higher capacities observed in the case of hollow NPs as compared with their bulk analogues and emphasize the importance of morphology of NPs for targeted applications. Very recently it was found that Mo-substituted γ-Fe_2O_3 also enhanced lithium ion battery performance by generating additional cation vacancies[1]. These studies motivated us to analyze the structure and morphology of hollow iron oxide NPs similar to the ones reported by Shevchenko et al. modified by the addition of Mo for lithium ion storage. In this work we report the analysis of samples before and after annealing process and after Li cycling by transmission electron microscopy (TEM), small angle X-ray scattering (SAXS) and X-ray absorption fine structure (XAFS). SAXS experiments were performed in order to follow changes in morphology and NPs arrange with the Mo addition and after Li intercalation process. XAFS experiments at the Fe K edge and Mo L_{23} edges were performed in order to understand the origin of the change in Fe vacancies with Mo addition.

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Óxido-reducción en nanopartículas de óxido de Fe producida por irradiación con rayos X blandos

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En este trabajo presentamos un estudio mediante XANES y XMCD realizado sobre nanopartículas de óxido de magnetita de 9-12 nm de diámetro, recubiertas con ácido cítrico, preparadas por coprecipitación química de sales. Las medidas en los bordes L_2 y L_3 del Fe se realizaron en la línea PGM (SGM-12490 Proposal) del LNLS. Se observó que los espectros XANES cambiaban con el tiempo de irradiación. El XANES de partida evidenció una alta proporción de Fe_2O_3 en la capa superficial de las nanopartículas, consistente con la oxidación de la fase original (magnetita). A medida que aumenta el tiempo de irradiación, los espectros evolucionan en el sentido del incremento de una fase tipo hierro metálico conjuntamente con la reducción del remanente de óxido de hierro. Se observó que la transformación se completó en 90 min de irradiación.

En las mismas condiciones se realizaron medidas de dicroísmo con polarización circular de aproximadamente 80% y campos de 0.6 T. Las medidas se realizaron tanto invirtiendo la polarización como la dirección del campo aplicado. Se observó que la señal XMCD presentaba dos picos negativos (componentes paralelas al campo aplicado) y uno positivo (antiparalelas al campo). Estos picos pueden asignarse a Fe en diferentes sitios cristalinos y estados de oxidación: Octaédrico (B) 2+ (pico negativo) o Fe metálico, Tetraédrico (A) 3+ (pico positivo) y Octaédrico (B) 3+ (pico negativo). La cinética de transformación se registró realizando medidas de dicroísmo en función del tiempo a la energías para las cuales la señal XMCD presentaba máximos y mínimos. Los resultados indican que la interacción de la radiación con las nanopartículas rompe los enlaces de ácido cítrico lo cual deja la superficie de las nanopartículas reducidas en oxígeno, originándose la reducción de parte de parte del Fe de las nanopartículas de Fe^{3+} a hierro metálico.

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Size-dependent phase transitions in nanostructured zirconia-scandia solid solutions

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Size effects on phase stability and phase transitions in technologically relevant materials have received growing attention. Several works reported that metastable phases can be retained at room temperature in nanomaterials, these phases generally corresponding to the high-temperature polymorph of the same material in bulk state. Additionally, size-dependent shifts in solubility limits and/or in the transition temperatures for on heating or on cooling cycles have been observed.

ZrO_2-Sc_2O_3 (zirconia-scandia) solid solutions are known to exhibit very high oxygen ion conductivity provided their structure is composed of cubic and/or pseudocubic tetragonal phases. Unfortunately, for solid zirconia-scandia polycrystalline samples with typical micrometrical average crystal sizes, the high-conductivity cubic phase is only stable above 600°C. Depending on composition, three low-conductivity rhombohedral phases (β, γ and δ) are stable below 600°C down to room temperature, within the compositional range of interest for SOFCs. In previous investigations, we showed that the rhombohedral phases can be avoided in nanopowders with average crystallite size lower than 35 nm.

In this work, the dependences of phase stability and solid state phase transitions on the crystallite size in ZrO_2-10, 12 and 14 mol% Sc_2O_3 nanopowders were investigated by X-ray powder diffraction (XPD) at the D10B-XPD beamline of the LNLS [1]. The average crystallite sizes were within the range of 35 to 100 nm, approximately. At room temperature these solid solutions exhibit mixtures of a cubic phase and one or two rhombohedral phases, β and γ, with their fractions depending on composition and average crystallite size, while at high temperatures these solid solutions become cubic single-phased. The size-dependent temperatures of the transitions from the rhombohedral phases to the cubic phase at high temperature were determined through the analyses of a number of XPD patterns. These transitions were studied on cooling and on heating, exhibiting hysteresis effects whose relevant features are size and composition dependent.

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Nanohilos magnéticos preparados por síntesis química

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Hemos sintetizado nanohilos magnéticos en sustratos de alúmina anodizada. Para ello hemos utilizado un método sol-gel modificado, que nos ha permitido la obtención de hilos de maghemita (gamma Fe2O3). Como molde para los mismos fueron utilizados sustratos de alúmina nanoporosa, fabricados por un proceso de doble anodización. Hemos medido las propiedades magnéticas de estas estructuras a través de curvas de magnetización vs temperatura y magnetización vs campo magnético aplicado, donde se ve claramente la existencia de una textura magnética, compatible con la existencia de nanohilos. Las imágenes de microscopía SEM muestran estas estructuras de un diámetro de 45 nm y de hasta 1,5 micrómetros, alojadas en los poros de la alúmina. La microscopía de transmisió de alta resolución (HR-TEM) muestra que las estructuras están formadas por nanopartículas orientadas de tamaños del orden de los 10 nm.

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Chemical and structural characterization of Hf-based high-k dielectrics by X-ray spectroscopy

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For years, silicon oxide (SiO_2) had been used as gate dielectric for field effect transistors; however, in sub-100nm devices, this material presents high leakage currents, due to loss of their dielectric properties. For this reason, different highk materials have been suggested as candidates to substitute the SiO_2 and SiO_xN_y as gate dielectric. The most promising candidate to substitute the conventional gate dielectrics is the HfO_2, although its low crystallization temperature ($\approx 500^oC$) is an important restriction so that to improve its thermal stability, the incorporation of Al or Si in the phase of the HfO_2 has been proposed. Usually, when these ones are thermally treated, the nanoparticles formation takes place. In order to investigate the conditions that allow the formation of nanoparticles, $50-mol\%Hf$ mixed with Al and O were deposited on silicon substrate by atomic layer deposition and annealed at 1000^oC in two different environments (N_2 and $N_2+5\%O_2$) during 60 s by two methods: rapid thermal processing (RTP) and laser annealing. Following, the films were chemical and structurally characterized by X-ray reflectance (XRR, $\lambda = 1.749$), grazing incidence small angle scattering (GISAXS, $\lambda = 1.749$), and x-ray diffraction (XRD, $\lambda = 1.542$). The results show that the thickness of the deposited layers was about 28.8 nm and the surface roughness varied as function of the annealing environment. The roughness of the film annealed in $N_2+5\%O_2$ was larger (1.3 nm) than that for the films annealed in N_2 ($\approx 0.9nm$). For the case of the critical angle (θ_c), it is larger for the film annealed by laser ($\theta_c = 0.430^o$) compared to those annealed by RTP (0.413 and 0.414^o). On the other hand, the GISAXS analysis shows the formation of spheroidal nanoparticles with different radius (R) and height (H) depending on both thermal method and environment. The largest nanoparticles are formed when the films are annealed by laser (R=2.0 nm; H=4.4 nm) while the smallest ones are obtained when the film is treated by RTP in N_2 (R=1.41 nm; H=2.94 nm). The addition of 5% of O into the annealing environment yields slight variation of the size (R=1.45 nm; H=2.85 nm). XRD reveals larger formation of HfO_2 phases for films annealed by RTP, whereas after annealing by laser the films remain predominantly amorphous with the lowest nanoparticles of $Al_{2.4}O_{3.6}$. In summary, the most adequate thermal treatment to avoid the nanoparticle formation was shown to be the annealing by laser.

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Structural and chemical analysis of low-k dielectric films for MOS integrated Circuits

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Low-k dielectric materials has been employed in the microelectronics industry for advanced CMOS technologies, enabling the continuous miniaturization of the MOS devices. In recent years, Porous $SiCOH$ low-k films have been introduced in modern integrated circuit fabrication to reduce the parasitic capacitance between interconnect metal lines. In this sense, advanced low-k $SiCOH$ (ALK) films with k-value of about 2.0, open porosity of 45 %, and mean pore diameter of 3 nm were prepared on 300 mm silicon wafers. The thickness of them was around 180nm and some them were subsequently treated in N_2 plasma for 20 s or $Ar - H_2$ plasma, also for 20 s. According to ellipsometry, the refractive index of the as-deposited films is slightly lower (1.254) compared to the films treated in N_2 plasma (1.263) or in $Ar - H_2$ plasma (1.258) and their thickness c.a 170 nm. From the X-Ray Reflectometry (XRR) analysis, the critical angle remains almost constant for as-deposited and plasma-treated films (0.138-0,146 degrees). From the GISAXS spectra, it was determined the mean radius and the geometrical features of the pores of the ALK films. Firstly, the two-dimensional GISAXS pattern (2D-GISAXS) was transformed to one-dimensional ones (1D-GISAXS). The 1D-GISAXS profiles were extracted along the q_y direction for different q_z points (from 0.69 to 1.52 nm^{-1}), then they were analyzed with the aid of the Kratky curves. The form of the Kratky curves showed the coexistence of different types of pores, with a characteristic polydispersive behavior of the typical scattering. The fitting procedure of these curves were performed by modeling the ALK film with one, two or three types of non-interacting pores. A fitting with an excellent agreement was only possible if three types of pores were included in the model: two spheres and an elongated like-cylinder. Each feature was associated to an Ornstein-Zernike relation. For all cases, the mean pore radius was close to 1.2nm. On the other hand, porosity slightly decreased after plasma treatment in N_2 or $Ar - H_2$ (from 47% to $\approx$ 40%) as estimated by integrating the Kratky curves along with the electron density of porous matrix. Therefore, the structural and chemical properties of ALK films can be well characterized by x-ray spectroscopy together with ellipsometry method.

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Study of the structural properties of ultra-thin films of (Fe_3O_4) by photoelectron diffraction (PED).

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The structural knowledge of a material is of fundamental importance because from it we can obtain the band structure, density of states, electrical, thermal and mechanical. Generally the atomic arrangement of the surface of the material differs from volume structure. In this work we perform the in-situ structural study of an ultra thin film (20) of magnetite (Fe_3O_4) grown on Pd (111) in an environment of ultra-high-vacuum (UHV) in LNLS (Brazilian Synchrotron Light Laboratory - Campinas, Brazil). Interest in the study of this compound is due to its applications in spintronics and magnetic recording [1].
The chemical characterization was performed using X-ray photoelectron spectroscopy (XPS) and structural study was performed using the technique of photoelectron diffraction (XPD) using conventional x-ray source (Al_{K_α}) and photon energy hv = 300eV from the beamline SGM. We compare the diffraction data with models for the surface structure with the help of the program MSCD (Multiple Scattering Diffraction Calculation). The surface $Fe_3O_4(111)$ presents alternating planes of Fe and O and has six possible endings. Our results indicate that the ultra-thin film prepared is completed in 1/4 tetrahedral layer of iron with high relaxations in the first atomic layer and the coexistence of two domains $Fe_34O_(111)$ rotated 60 degrees. Our results are in good agreement with studies of ultra-thin films of magnetite via technical LEED (Low Energy Electron Diffraction) [2,3].

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Structure of Hollow Iron Oxide Nanoparticles modified with Mo addition studied by XAFS and SAXS.

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The large capacity resulting from reducing iron oxide to iron is promising for lithium battery anodes; however, this conversion during the electrochemical cycling is accompanied by fading of the electrode performance due to material pulverization and subsequent loss of electrical contacts between the active material and current collector. On the other hand, cycling of iron oxide-based electrodes in the high voltage range where only intercalation of Li ions occurs has been recently found to be promising to design cathodes [1]. The unique nature of hollow metal oxide nanoparticles (NPs) [2] such as a thin shell, large internal void, and doubled surface area [3] and cation vacancies has raised a lot of interest for their applications in energy storage. Recently Shevchenko et al. [4] reported the role of the high concentration of cation vacancies in hollow iron oxide NPs in lithium intercalation reactions. This report explains significantly higher capacities observed in the case of hollow NPs as compared with their bulk analogues and emphasize the importance of morphology of NPs for targeted applications. Very recently it was found that Mo-substituted γ -Fe_2O_3 also enhanced lithium ion battery performance by generating additional cation vacancies[1]. These studies motivated us to analyze the structure and morphology of hollow iron oxide NPs similar to the ones reported by Shevchenko et al. modified by the addition of Mo for lithium ion storage. In this work we report the analysis of samples before and after annealing process and after Li cycling by transmission electron microscopy (TEM), small angle X-ray scattering (SAXS) and X-ray absorption fine structure (XAFS). SAXS experiments were performed in order to follow changes in morphology and NPs arrange with the Mo addition and after Li intercalation process. XAFS experiments at the Fe K edge and Mo L_{23} edges were performed in order to understand the origin of the change in Fe vacancies with Mo addition.
[1] Hahn, B. P., et. al R. Energy Environ. Sci. 2011, 4, 1495 1502. [2] Yin, Y. D., et. al. Science 2004, 304, 711 714. [3] Cabot, A., et. al.Phys. Rev. B 2009, 79, 094419. [4] Koo, B., et. al. Nano Lett. 2012, 12, 24292435.

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Structure of Hollow Iron Oxide Nanoparticles modified with Mo addition studied by XAFS and SAXS.

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The large capacity resulting from reducing iron oxide to iron is promising for lithium battery anodes; however, this conversion during the electrochemical cycling is accompanied by fading of the electrode performance due to material pulverization and subsequent loss of electrical contacts between the active material and current collector. On the other hand, cycling of iron oxide-based electrodes in the high voltage range where only intercalation of Li ions occurs has been recently found to be promising to design cathodes [1]. The unique nature of hollow metal oxide nanoparticles (NPs) [2] such as a thin shell, large internal void, and doubled surface area [3] and cation vacancies has raised a lot of interest for their applications in energy storage. Recently Shevchenko et al. [4] reported the role of the high concentration of cation vacancies in hollow iron oxide NPs in lithium intercalation reactions. This report explains significantly higher capacities observed in the case of hollow NPs as compared with their bulk analogues and emphasize the importance of morphology of NPs for targeted applications. Very recently it was found that Mo-substituted γ -Fe_2O_3 also enhanced lithium ion battery performance by generating additional cation vacancies[1]. These studies motivated us to analyze the structure and morphology of hollow iron oxide NPs similar to the ones reported by Shevchenko et al. modified by the addition of Mo for lithium ion storage. In this work we report the analysis of samples before and after annealing process and after Li cycling by transmission electron microscopy (TEM), small angle X-ray scattering (SAXS) and X-ray absorption fine structure (XAFS). SAXS experiments were performed in order to follow changes in morphology and NPs arrange with the Mo addition and after Li intercalation process. XAFS experiments at the Fe K edge and Mo L_{23} edges were performed in order to understand the origin of the change in Fe vacancies with Mo addition.

[1] Hahn, B. P., et. al R. Energy Environ. Sci. 2011, 4, 1495 1502 [2] Yin, Y. D., et. al. Science 2004, 304, 711 714 [3] Cabot, A., et. al.Phys. Rev. B 2009, 79, 094419 [4] Koo, B., et. al. Nano Lett. 2012, 12, 24292435

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Magnetic properties, electronic structure and morphology of PtCo and PtCo-Au dumbbell nanoparticles.

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Multicomponent nanocrystals (MNCs) became an important class of materials due to their abilities to carry multiple functions that can be utilized simultaneously [1-3]. Recent progress in synthesis of MNCs allows obtaining different types of nanoparticles such as core-shells [1], dumbbells, or other geometries [3]. Characterization of PtCo and PtCo-Au alloys was performed using electron microscopy (TEM), X-ray absorption (XAS), X-ray scattering at low angle (SAXS), global magnetic measurements (MM) and magnetic circular dichroism measurements (XMCD). Combination of TEM and SAXS results show spherical particles with a size dispersion of about 5% for Pt_3Co system. SAXS reveals that the addition of Au modifies the stability of MNCs in solution producing NPs agglomerates. XAFS measurements at the Pt $L_{2,3}$ edges and Co K reveal changes in the oxidation state of Co after Au deposition. XAFS previous results [3] have shown that the Au addition removes the Co atoms from the surface of the PtCo NP. XANES at the Pt $L_{3,2}$ edges show a charge transfer from Pt 5d level after Au deposition respect to the Pt configuration in the MNCs used as seed. From MM is observed that all samples exhibit superparamagnetic behavior at RT with a blocking temperature which decreases in smaller Pt_3Co MNCs. XMCD at the Pt-$L_{3,2}$ edges measurements show that there is a transfer of magnetic moment from Co atoms to Pt and also reveals that addition of Au does not affect the magnetic behavior for the Pt atoms. The variation of the XMCD intensity signal with temperature is in accordance with changes in the magnetization of the PtCo alloy. This shows that the Co atoms in the alloy are main responsible for the appearance of the XMCD signal, but can not rule out a contribution to this effect from the size of NPs.

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Study of expanded austenite formed in plasma nitrided AISI 316L using synchrotron radiation diffraction- II

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Plasma nitriding of stainless steels improves some tribological properties, as a result of the nitrided layer, which is formed on the surface. When using temperature lower than 450 °C, an expanded austenite phase is formed, whose diffraction peaks are broader and shifted to lower angles, when compared to γ-phase reflections. The $\gamma_N(200)$ peak position is more deviated relatively to $\gamma(200)$ than other planes, demonstrating a distortion ϵ from the cubic fcc unit cell. In a recent study of AISI 316L nitrided samples using synchrotron diffraction, Fewell et al tested ten plausible candidate structures in order to propose a structure for this phase(1). They concluded that the triclinic lattice has the fewest deformation-split components of the candidate structures before the (440) reflections. For the current study, synchrotron diffraction using photon energy of 6.5 keV was used for measuring diffractograms up to the (222) reflection, from eight nitrided AISI 316L samples. They were nitrided at different conditions of time (3, 4 and 5 h) and temperature (350, 400 and 450°C), and consequently, showed different properties, such as nitrogen concentration C_N and nitrided layer thickness. Fewells model (1) was assumed on the diffractogram fittings, using the Le Bail method. Moreover, the nitrided layer thickness was correlated to the radiation penetration for the different reflections in two aspects: 1) The austenite reflections are observed for all the samples because the penetration of the lowest A(111) reflection is greater than the largest thickness of the nitrided layer. In spite of this, if the thickness increases, the A(111) reflection intensity decreases; 2) Two different expanded austenite phases were used in fittings of the samples nitrided at 350 and 400 °C fittings, and only one for those nitrided at 450 °C. Moreover, when the time used in the process is fixed, if the temperature increases, the C_N values also rise for all of the γ_N phases. Finally, the distortion ϵ increases in both cases, when the time and the temperature increase. Ref: (1) M.P. Fewell et al, Surf. Coat.Technol. 202 (2008) 1802.

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Caracterización mediante Fe K XANES del entorno local del Fe en catalizadores Fe-Si aptos para la producción de nantubos de carbono.

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En este trabajo se presentan los resultados del estudio de un conjunto de catalizadores aptos para la producción de nanotubos de carbono (NTC) y de sus precursores, con el objetivo de obtener información que pueda correlacionar la eficiencia catalítica de cada catalizador con la estructura local del Fe presente en el mismo. En los últimos años el estudio de las noveles propiedades de los NTC ha llevado a optimizar las rutas de síntesis de estos materiales, tanto como a ensayar nuevas vías de obtención. Estudiar los constituyentes del proceso, a la vez que el proceso, permite obtener información cualitativa y cuantitativa importante tanto para el diseño como para la optimización de este tipo de materiales y sus productos. Mediante el método sol-gel se sintetizaron nanopartículas de óxido de hierro en matrices de SiO_2, para luego usarlos como catalizadores en la síntesis de NTC por Deposición Química en Fase Vapor (CVD). Mediante la técnica XANES (X-ray Absorption Near Edge Spectroscopy) en el borde de absorción K del Fe (7112 eV) se caracterizó al entorno local del Fe estudiándose la simetría y la valencia (estado de oxidación) de las nanopartículas de óxido de hierro en matrices de SiO_2. El estudio de los prepicos Fe-K XANES reveló que las nanopartículas de óxido de hierro en todos los catalizadores, previo a su uso en el proceso de catálisis, se encuentran en la fase alfa-Fe_2O_3, con una simetría de la naturaleza de este óxido, en tanto que para los precursores existe una tendencia a un orden más centrosimétrico. Este hecho descarta la presencia de silicatos de Fe, que afectan los rendimientos catalíticos, cuando los catalizadores ingresan al reactor. En estos momentos se están realizando experiencias Fe K XANES con los materiales en condiciones de reacción catalítica y posteriores a la reacción para ver si existen posibles modificaciones del entorno local del Fe y poder comprender las grandes diferencias de la eficiencia catalítica mostradas por este conjunto de catalizadores.

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X-ray absorption spectroscopy study on $La_{0.6}Sr_{0.4}CoO_3$ and $La_{0.6}Sr_{0.4}Co_{1-y}Fe_yO_3$ nanotubes and nanorods for IT-SOFC cathodes

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In the last years, extensive research has been devoted to develop novel materials and structures with high electrochemical performance for intermediate-temperatures solid-oxide fuel cells (IT-SOFCs) electrodes. In recent works, we have investigated the structural and electrochemical properties of $La_{0.6}Sr_{0.4}CoO_3$ (LSCO) and $La_{0.6}Sr_{0.4}Co_{1-y}Fe_yO_3$ (LSCFO) nanostructured cathodes, finding that they exhibit excellent electrocatalytic properties for the oxygen reduction reaction [1,2]. These materials were prepared by a pore-wetting technique using polycarbonate porous membranes as templates. Two average pore sizes were used: 200 nm and 800 nm. Our scanning electronic microscopy (SEM) study showed that the lower pore size yielded nanorods, while nanotubes were obtained with the bigger pore size. All the samples were calcined at 1000^{o}C in order to produce materials with the desired perovskite-type crystal structure.

In this work, we analyze the oxidation states of Co and Fe and the local atomic order of LSCO and LSCFO nanotubes and nanowires for various compositions. For this purpose we performed XANES and EXAFS studies on both Co and Fe K edges. These measurements were carried out at the D08B-XAFS2 beamline of the Brazilian Synchrotron Light Laboratory (LNLS). XANES spectroscopy showed that Co and Fe only change slightly their oxidation state upon Fe addition. Surprisingly, XANES results indicated that the content of oxygen vacancies is low, even though it is well-known that these materials are mixed ionic-electronic conductors. EXAFS results were consistent with those expected according to the rhombohedral crystal structure determined in previous X-ray powder diffraction investigations.

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In-situ DXAS study of NiO/CeO_2-Gd_2O_3 nanocomposites for IT-SOFC anodes

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Fuel cells are promising devices for environmentally clean energy production by directly converting chemical energy into electricity. Among them, solid oxide fuel cells (SOFCs) have the unique capability to use different fuels such as hydrocarbons or H_2. However, several issues have to be solved in order to improve their efficiency and reduce their costs. The reduction of their working temperature, which is typically around 900-1000^{o}C, is one of the most important issues. For this reason, extensive research has been devoted to develop novel materials for intermediate-temperature SOFCs (IT-SOFCs).

CeO_2-based anodes have proven to exhibit excellent catalytic properties. Besides, these materials are mixed ionic/electronic conductors (MIECs) under reducing atmosphere and, therefore, fuel oxidation can take place on its entire surface, while it only occurs in the [anode/electrolyte/gas] interphase (triple-phase boundaries) for electronic conductors.

In recent works, we investigated the performance of nanostructured CeO_2-based anodes for IT-SOFCs. Nanomaterials are not employed in conventional SOFCs since grain growth is expected to occur at high temperature, but their use in IT-SOFCs is currently under evaluation. Anodes based on nanostructured MIECs are very interesting because the number of active sites for fuel oxidation is expected to increase dramatically. For example, we have found that NiO/GDC (GDC: Gd_2O_3-doped CeO_2) nanocomposites exhibit excellent performance under H_2, with enhanced properties with decreasing grain size.

The aim of this work was to study the influence of the crystallite size on the reducibility of NiO/GDC nanocomposites under diluted H_2 by the DXAS technique. We found that NiO/GDC nanocomposites of smaller crystallite size exhibit much higher reducibility for both Ni and Ce atoms, which is probably related to the excellent performance of nanostructured NiO/GDC anodes.

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Evaluation of Structural Features of Crystalline and Amorphous Ta_2O_5 NTs by X-ray Spectroscopy: Effects of Structural Disorder on the Photocatalytic Activity

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Recently the electrochemical anodization for the manufacturing of high ordered and self-organized semiconductors with nanotubular (NTs) structures has attracted great scientific interest. The main advantages of the anodization encompass a simple synthetic procedure, a cost-effective scale-up process and an art to control the structures sizes as well as their charge transport properties. Because of its wide range of applications and potential chemical, electrical, electronic, biocompatible and optical properties the Ta_2O_5 nanostructures have been extensively studied both experimentally and theoretically over the past three decades. The as-anodized Ta_2O_5 NTs are usually amorphous and heat treatment is often performed to convert the amorphous phase to crystalline phase. However, it has been shown that the heat treatment parameters affect the crystalline structure and morphology of semiconductor NTs. Furthermore, for many technological applications such as photocatalysis (water splitting) and solar cell (Grätzel solar cell) the crystallinity of the semiconductor nanotubes has a vital effect. In this work, we choose the EXAFS and XANES techniques to evaluate the electronic structure and structural disorder of the Ta_2O_5 NTs. The results will be correlated to the photocatalytic activity for hydrogen production by the reaction of water splitting.

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MATERIAIS HÍBRIDOS CONTENDO NANOPARTÍCULAS DE ZnO DOPADAS COM Mn OU Co PARA LIBERAÇÃO CONTROLADA DE MEDICAMENTOS

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Matrizes hibridas siloxano poliéter apresentam propriedades únicas como elevada resistência mecânica, transparência e flexibilidade sendo um material de grande potencial para várias áreas científicas e tecnológicas, incluído o uso em dispositivos de liberação controlada de farmoquímicos [1]. Nanopartículas semicondutoras de ZnO despertaram grande interesse dos pesquisadores devido as suas propriedades eletrônicas, luminescentes, catalíticas, de conversão de energia e optoeletrônicas [2]. Outro fato relevante é a possibilidade de dopagem deste semicondutor com elementos magnéticos originando uma nova classe de materiais conhecidos como semicondutores magnéticos diluídos (SMD), um material multifuncional com propriedades magnéticas e óticas [3]. O objetivo deste trabalho é preparar um dispositivo de liberação controlada de fármacos conjugando as propriedades individuais de cada componente num mesmo material, usando as propriedades magnéticas dos SMD para guiar o dispositivo de liberação de droga até o órgão doente, e as propriedades luminescentes do ZnO para monitorar a posição do dispositivo dentro do corpo humano. A técnica de espalhamento de raios-X a baixo ângulo (SAXS) permitiu obter informações sobre a distância de correlação entre os grupos siloxanos e a influência da incorporação das nanopartículas nesta distância e o raio de giro (Rg) das partículas siloxano. Os dados estão sendo compilados na forma de artigo cientifico para publicação em breve

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Avaliação da sílica CTA-MCM-41 contendo polímero no interior dos seus canais utilizando SAXS

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A utilização de catalisadores heterogêneos básicos para produção de biodiesel, ao invés de homogêneos, desperta interesse pela redução do número de operações de separação e neutralização envolvidas, pela redução do impacto ambiental decorrente dos rejeitos líquidos da lavagem, e pelo fato deles não serem corrosivos, dando assim, uma vida útil muito maior para a planta industrial [1]. A pesquisa industrial e acadêmica têm se dedicado na busca de catalisadores heterogêneos mais eficientes de modo a aumentar os rendimentos em biodiesel na reação de transesterificação. Assim, nosso grupo tem estudado a sílica mesoporosa com cátions CTA ocluídos (CTA-MCM-41) para a transesterificação [2]. Segundo Fabiano e colaboradores [2] há uma diminuição da atividade catalítica após sucessivos usos na transesterificação devido a lixiviação dos cátions CTA (cetiltrimetilamônio) do interior dos canais do material. Desta forma, perdem parte da basicidade necessária para este tipo de reação; visto que o sítio ativo provém da interação do cátion CTA com o ânion silóxi. A fim de promover a melhoria da estabilidade catalítica foram feitas sínteses [3] com modificações em que se adicionou monômero e fotoiniciador e depois realizou-se a polimerização. Espera-se que os polímeros formados irão interagir com o tensoativo localizado no interior dos canais da CTA-MCM-41 e dessa forma melhore a estabilidade catalítica. A técnica de espalhamento de raios X a ângulos pequenos (SAXS) pode comprovar a presença do polímero no interior dos canais do material. Sendo assim, o espalhamento q aproximadamente 1,7 nm^{-1} mostrou que, em relação ao material que foi sintetizado sem polímero (R=0), nos sólidos que contem o polímero há um deslocamento da curva (100) para q menor. Esse deslocamento aumenta com o tamanho da cadeia alquílica do monômero que foi utilizado para síntese e comprova que, pelo menos parte dele encontra-se no interior dos canais da CTA-MCM-41 e consequentemente houve a expansão desses. As condições utilizadas para análise foram: 1) Comprimento de onda λ=0,15498 nm; distância amostra-detector de 562,5359 mm (curta distância). Para as amostras sólidas a taxa de aquisição de 30s (2 x 15s).

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The influence of chondroitin sulfate and chitosan on structural and superficial properties of composite multilamellar liposomes.

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A composite multilamellar liposome containing chitosan attached to the inside and outside of the membrane as well as an opposite charged polyelectrolyte, chondroitin, adsorbed at the surface was developed. Not only the chitosan/chondroitin ratio but also the concentration of them were varied. The structure and superficial properties of the liposomes were studied through a combination of light scattering, ζ-potential, and small-angle X-rays scattering techniques. While the chitosan/chondroitin ratio affected the superficial charge distributions, the concentration of polyelectrolytes affected the structural properties of the liposomes, as the rigidity of the phospholipid layers. The superficial charge of the resultant composite liposome was influenced by the type and concentration of the polyelectrolyte. Information about the charge density could be obtained by the treatment of ζ-potential data, and it was used to estimate the amount of chondroitin adsorbed to the liposome surface. Applying the modified Caillé theory to the X-rays scattering curves, information about the internal structure of the liposomes was accessed. The ability to control the properties of composite multilamellar liposomes is an important issue when they have to be applied as a biomaterial device component.

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Use of operando XAS-Raman-Mass Spectroscopies to evaluate catalytic behavior of Cu/Al_2O_3 catalysts on ethanol dehydrogenation reaction

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The targets for reducing greenhouse gas emissions have a significant increase in the consumption of biofuels in coming years, especially ethanol. Ethanol is highlighted, because, besides being used as a direct fuel source in automotive, may be used to produce hydrogen, ethyl acetate, n-butanol and other chemical products by dehydrogenation reactions. In this investigation, catalytic behavior of copper supported on hierarchical porous alumina was accompanied using operando XAS-Raman-Mass Spectroscopies in ethanol dehydrogenation reaction. This reaction was investigated in Soleil Synchrotron Laboratory - France, on reduced and calcined 10wt.%Cu/Al_2O_3 catalysts between 200-400^{o}C. XANES data during the reduction treatment at 250^{o}C for 30 minutes showed that copper starts to reduce around 210^{o}C, with the formation of about 60% of intermediate Cu^+ species. At the end of the reduction, the copper is nearly completely reduced. For this reduced catalyst, the formation of H_2, acetaldehyde and ethyl acetate as the main products at 300^{o}C in ethanol flow was observed. At higher temperature, an increase in ethylene and ethyl ether products was detected, related to acid sites of alumina. For unreduced Cu catalyst, XANES data showed that the reduction only starts at a temperature of 250^{o}C on ethanol stream. At this temperature, an induction period with a high increase the ethanol conversion and formation of H_2 and acetaldehyde as main products was observed. Above 300^{o}C, products selectivity is similar to reduced sample. For this reaction, unreduced copper catalysts showed more active and stable than reduced sample, probably related to agglomeration of copper nanoparticles during the reduction treatment.

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Índice Remissivo

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