CNPEM

24th RAU
ANNUAL USERS MEETING LNLS/CNPEM
March 11th and 12th, 2014

Book of Abstracts

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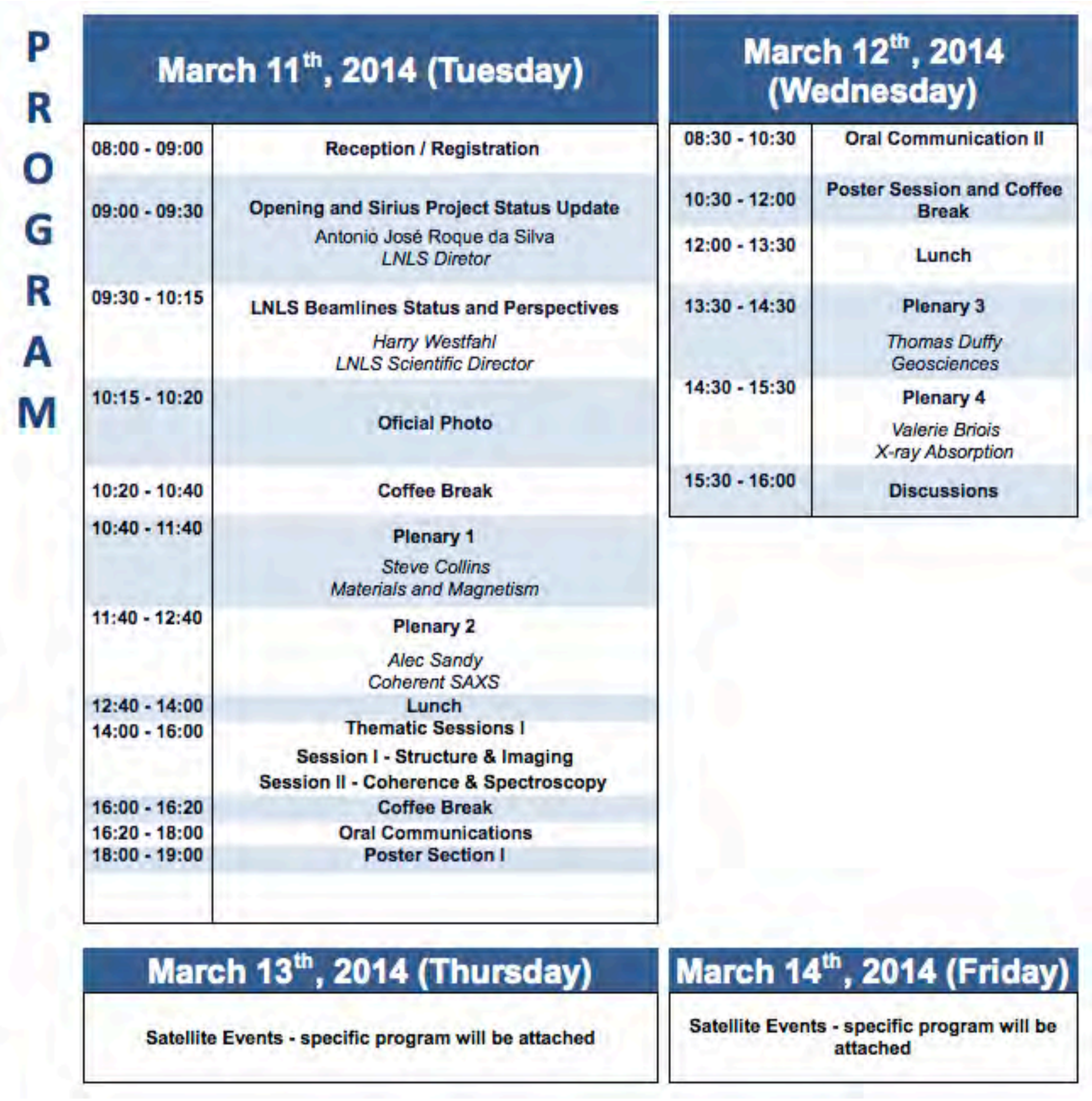
Foreword

The Users Committee welcomes all participants of the 24th Annual Users Meeting of the Brazilian Synchrotron Light Laboratory (RAU/LNLS).

This meeting takes place in concomitantly with the construction of Sirius, our new synchrotron light source. From the beginning South American scientists are excited with the perspective of a revolution in several experimental areas like Physics, Biology and Chemistry. In fact, we expect that this new light source will have a larger positive impact as compared to its antecessor, LNLS, built 15 year ago. It is worth to remind us that Sirius is planned to operate at 3 GeV energy and 0.28 nm.rad emittance, being one of the lowest in the world. Furthermore, 13 beamlines are already planned for the new source. Care was taken to make sure that they would cover most of the on-going LNLS research areas. This new high brilliant source will allow, for example, to study complex systems on a nanometric scale, including also the study of very diluted systems which will be more realistic to environmental challenges of the future and to the field of new energy sources. These anticipated breakthroughs in a few key areas will only become true thanks to the users and their synergy with the new possibilities opened by Sirius. In this context, it is clear the importance of the present user meeting. The meeting coordinator would like to thank the effort of the scientific committee, which helped in the selection of the invited speakers, oral and poster presentations. We would like also to thank the LNLS directors and all their staff which gave strong support to the meeting organization.

We wish all a productive meeting.

24th RAU Users Committee



PROGRAM

March 11th, 2014 (Tuesday)

08:00 - 09:00	**Reception / Registration**
09:00 - 09:30	**Opening and Sirius Project Status Update** Antonio José Roque da Silva *LNLS Diretor*
09:30 - 10:15	**LNLS Beamlines Status and Perspectives** *Harry Westfahl* *LNLS Scientific Director*
10:15 - 10:20	**Oficial Photo**
10:20 - 10:40	**Coffee Break**
10:40 - 11:40	**Plenary 1** *Steve Collins* *Materials and Magnetism*
11:40 - 12:40	**Plenary 2** *Alec Sandy* *Coherent SAXS*
12:40 - 14:00	**Lunch**
14:00 - 16:00	**Thematic Sessions I** **Session I - Structure & Imaging** **Session II - Coherence & Spectroscopy**
16:00 - 16:20	**Coffee Break**
16:20 - 18:00	**Oral Communications**
18:00 - 19:00	**Poster Section I**

March 12th, 2014 (Wednesday)

08:30 - 10:30	**Oral Communication II**
10:30 - 12:00	**Poster Session and Coffee Break**
12:00 - 13:30	**Lunch**
13:30 - 14:30	**Plenary 3** *Thomas Duffy* *Geosciences*
14:30 - 15:30	**Plenary 4** *Valerie Briois* *X-ray Absorption*
15:30 - 16:00	**Discussions**

March 13th, 2014 (Thursday)

Satellite Events - specific program will be attached

March 14th, 2014 (Friday)

Satellite Events - specific program will be attached

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Abstracts

X-ray Absorption and Fluorescence Spectroscopy (XAFS)

INTERPLAY BETWEEN PARTICLE SIZE, ELECTRONIC PROPERTIES, AND STRUCTURE OF MODEL CO-NI CATALYSTS AND THEIR INFLUENCE ON CARBON ACCUMULATION DURING STEAM REFORMING OF ETHANOL

ADRIANO HENRIQUE BRAGA[1]; DANIELA COELHO DE OLIVEIRA[2]; JOÃO BATISTA OLIVEIRA DOS SANTOS[1]; JOSÉ MARIA CORRÊA BUENO[1].

1.UFSCAR, SAO CARLOS - SP - BRASIL; 2.LNSL, CAMPINAS - SP - BRASIL.

Palavras-chave: in situ XAS;catalysis;ethanol

Resumo:

Ethanol produced from biomass is a sustainable feedstock that could be used for the production of H_2, by steam reforming reaction (SRE). Ni is abundant and inexpensive metal to develop very active catalysts for this purpose. A major problem of Ni-based catalyst is the susceptibility to carbon accumulation with time on stream in SRE [2] and the high rates of undesirable methane formation [3].

The analysis of the ED-XANES show simultaneous reduction of Co and Ni oxides in the bimetallic catalyst, suggesting that formation of alloy may occur due to reduction of $M^{2+}(M^{3+})_2O_4$ spinel.

XPS data revealed that the surface of the bimetallic catalyst is enriched of Ni (Ni/Co=2) in both the calcined and reduced samples. Hence, in the bimetallic sample, the Co is in the core of nanoparticle, which prevents severe oxidation (opposed to monometallic Co), and Ni is in the surface. The alloying of the metals change electronic properties of both the metals, leading to a final catalyst more reactive and which can stabilize better the rates of ethanol activation and carbon oxidation. Surprisingly, this catalyst is high tolerant to carbon accumulation, proving the better oxy-reduction properties.

LA0.4SR0.6TI1-XCOXO3-D (0 <= X <= 1) ELECTRODE CARACTERIZATION SIMULATING OPERATION CONDITIONS AT INTERMEDIATE TEMPERATURE SIMMETRIC SOLID OXIDE FUEL CELLS (S-SOFC)

ANALIA SOLDATI[1]; FEDERICO NAPOLITANO[1]; DIEGO LAMAS[2]; JOCHEN GECK[3]; ADRIANA SERQUIS[1].
1.CONICET - CENTRO ATÓMICO BARILOCHE, BARILOCHE - ARGENTINA; 2.CONICET-UNIVERSIDAD DEL COMAHUE, NEUQUEN - ARGENTINA; 3.INSTITUT FÜR FESTKÖRPERFORSCHUNG, DRESDEN - ALEMANHA.

Palavras-chave: solid oxide fuel cell;symmetric electrodes;titanates

Resumo:

In this work, a combined synchrotron X-ray diffraction (XPD), X-ray Absorption Near Edge Spectroscopy (XANES) and Extended X-ray Absorption Fine Structure Spectroscopy (EXAFS) study of LSTC ($La_{0.4}Sr_{0.6}Ti_xCo_{1-x}O_{3-d}$ with 0<=x<=1), intended as symmetric solid oxide fuel cells (S-SOFC) electrode, is presented. Crystallographic and Electronic structure were characterized at room temperature and under reductive and oxidising temperature cycles (20-700ºC) simulating operation conditions in a S-SOFC. LSTC has a perovskite pseudocubic structure with an A-site vacancy concentration related with Co doping level. This result seems to be triggered by the fact that Ti remains in a higher formal valence (around 4+) independent of the Co concentrations. On the contrary, Co K-edge XANES spectra shows a dependency with the doping level but this seems to be related to structural changes. In-situ measurements simulating the working environment show that LSTC undergoes a rhombohedric to cubic perovskite phase transition with critical temperature being dependent of the structural distortion level. On the other side, XANES/EXAFS in situ experiments show that Co oxidation state moves toward more reduced values with temperature, in both oxidising and reductive environments, while Ti remains always close to 4+.

ELEMENTAL DISTRIBUTION IN BONE MATRIX AFTER CHEMOTHERAPY TREATMENT FOR BREAST CANCER USING X-RAY MICROFLUORESCENCE

ARISSA PICKLER OLIVEIRA[1]; DELSON BRAZ[1]; RITA ALESSIO[1]; GABRIELA SENA[1]; ANDRÉ PEREIRA ALMEIDA[1]; CARLA LEMOS MOTA[1]; ANDREA MANTUANO[2]; LIEBERT PARREIRAS NOGUEIRA[2]; REGINA BARROSO[2].

1.COPPE/UFRJ, RIO DE JANEIRO - RJ - BRASIL; 2.INSTITUTO DE FÍSICA/UERJ, RIO DE JANEIRO - RJ - BRASIL.

Palavras-chave: BONE REMODELATION;BREAST CANCER;X-RAY MICROFLUORESCENCE

Resumo:

According to the National Cancer Institute it was estimated 518,510 new cancer cases for the years 2012 and 2013 in Brazil. From this estimative, 52,680 correspond to breast cancer (BC). The most commonly used treatment strategy is surgical intervention, depending on the tumor stage; it may also include chemotherapy or radiation therapy. One of the side effects caused by some chemotherapy drugs is the induction of amenorrhea, temporary or not, in premenopausal women, with consequent decreased production of estrogen. Premenopausal women undergoing chemotherapy for treatment of breast cancer have significant bone loss from the first year after initiation of treatment, especially at the femur.

The aim of this work was evaluated important elements in femur head samples, qualitatively and quantitatively, involved in osteoporosis when rats were subjected to a chemotherapy regimen, irradiation or ovariectomy procedure. Wistar rats females, aging approximately three months, were divided in four groups: control, cyclophosphamide and doxorubicin, and cyclophosphamide, docetaxel and ovariectomized. The measurements were carried out in the X-ray microXRF station at the LNLS. Elemental distribution maps were collected at room temperature.

Acknowledgements: We thank C. Perez for the technical support and the team of the Radiological Sciences Laboratory of State University of Rio de Janeiro (C. Salata, C.B. Andrade, C.E. Veloso) who made the samples available.

ATTEMPTS TO INVESTIGATE PRESSURE-INDUCED PHASE TRANSITION OF NANOCRYSTALLINE ZNS PRODUCED BY MECHANICAL ALLOYING AT LNLS-DXAS BEAM LINE

CARLOS EDUARDO MADURO DE CAMPOS[1].

1.UFSC, FLORIANOPOLIS - SC - BRASIL.

Palavras-chave: High Pressure;ZnS nanocrystals;Mechanical Alloying

Resumo:

Two in situ dispersive x-ray absorption studies on nanocrystalline ZnS samples produced by Mechanical Alloying were carried out under high pressure up to about 15 GPa by using a diamond anvil cell. The phase transition from the wurtzite to the zinc-blende structure reported to occur at 11.5 GPa for nanocrystalline ZnS in XRD experiments studies cannot be seen in our XAS data and no obvious transition to a new phase with rock-salt structure also appeared up to 15 GPa. The pseudo-bulk modulus and the pressure derivative of nanocrystalline ZnS were derived by fitting the Birch–Murnaghan equation. The resulting modulus was higher than that of the corresponding bulk material, indicating that the nanomaterial produced by mechanical alloying has higher hardness than the bulk material.

Education of the author's work during the period of the experiment on the research proposals DXAS - 12527 (mai2012) and 11612 (Oct. 2011): Postdoctoral at UFSCar (2005-6).

THE INTERACTION BETWEEN SIZE, STRUCTURE AND OXIDATION STATE OF CO-CU-BASED CATALYSTS AS A KEY POINT FOR THE CONTROL OF CARBON ACCUMULATION IN STEAM REFORMING OF ETHANOL

CÍCERO NAVES ÁVILA-NETO[1]; CARLA EPONINA HORI[1]; DANIELA ZANCHET[2]; RENATA UEMA RIBEIRO[3]; JOSÉ MARIA CORRÊA BUENO[3].

1.UNIVERSIDADE FEDERAL DE UBERLÂNDIA, UBERLÂNDIA - MG - BRASIL; 2.UNIVERSIDADE ESTADUAL DE CAMPINAS, CAMPINAS - SP - BRASIL; 3.UNIVERSIDADE FEDERAL DE SÃO CARLOS, SÃO CARLOS - SP - BRASIL.

Palavras-chave: Steam reforming of ethanol;Crystallite size;Rate of carbon accumulation

Resumo:

Cobalt-based catalysts supported on magnesium aluminate and promoted with copper were characterized and tested under conditions of steam reforming of ethanol (SRE). The challenge was to verify how the size, crystal structure and oxidation state of Co-Cu nanoparticles affect the rate of carbon accumulation, a major cause of deactivation in SRE. XPS analyses showed that Cu atoms migrate to the surface of nanoparticles after reduction. EXAFS and in situ XRD data demonstrated that Co and Cu form an alloy with face-centered cubic structure at the surface. The superficial Cu atoms promote the reduction of CoO_x species by means of the spillover effect. To estimate the size and structure of the nanoparticles, a model based on EXAFS and XPS data was developed considering the nanoparticles to be spheres with reduced cores and oxidized shells. It was found that both the reduced core and the size of nanoparticles increase proportionally to the load of Cu. The observed apparent dependence of carbon accumulation rate under SRE on Co nanoparticle size is mainly associated with the presence of the element in oxidized state and the nature of the metal on catalyst surface. Since the C-C bond is cleaved on Co^0 sites, the oxidized shell is actually the result of redox equilibrium between the steps of water activation, which oxidizes the particle surface, and oxidation of deposited carbon, which re-reduces the surface.

CHEMICAL CHARACTERIZATION OF RAIN IN CÓRDOBA CITY, A STUDY OF THE DEPOSITION PROCESS

ELDO EDGARDI AVILA[1]; MARIA LAURA LOPEZ[1]; MARIA LILA ASAR[1]; SERGIO ANDRES CEPPI[1]; RODRIGO EXEQUIEL BÜRGESSER[1].

1.FAMAF-UNC, IFEG-CONICET, CORDOBA - ARGENTINA.

Palavras-chave: rainwater;deposition process;, cloud condensation nuclei

Resumo:

Sequential samples of single precipitation event were collected between December-2011 and September-2012 in Córdoba, Argentina. The temporal evolution of the pH value, electrical conductivity and the concentration of the elements S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Rb, Sr, and Pb were analyzed. The samples were analyzed by Synchrotron Radiation Total Reflection X-Ray Fluorescence (SR-TXRF) by using the XRF line at the Brazilian Synchrotron Light Source Laboratory (LNLS). The results show a high variability of the variables (pH, electrical conductivity, concentrations) at the initial stage of precipitation and a sharp decreasing as event progress. The average scavenging coefficients for the analyzed elements were calculated. It is found that for the soluble fraction at the initial state of precipitation, Ca, K and S contribute with ≈ 95% of the mass concentration and they show the highest coefficients for the washout process. For the insoluble fraction, K, Ca and Fe contribute with ≈ 60 % of the mass concentration at the onset of precipitation. Assuming that the amount of pollutants available for scavenging are insignificant for large precipitation depths, the chemical elements (within the analyzed elements) acting as cloud condensation nuclei were inferred.

MICRO-XRF AND XANES STUDY OF ZN-DOPED ORMOSIL PHOSPHOTUNGSTATE HYBRID FILMS WITH ENHANCED PHOTOCHROMIC RESPONSE

ELIAS PAIVA FERREIRA NETO[1]; SAJJAD ULLAH[1]; ORLANDO ARMANDO ELGUERA YSNAGA[1]; UBIRAJARA PEREIRA RODRIGUES FILHO[1].

1.USP, SAO CARLOS - SP - BRASIL.

Palavras-chave: Photochromism;Zn K-edge XANES;Sol-gel

Resumo:

In this study, we report a simple sol-gel preparation of transparent photochromic films based on Zn^{+2} doped Ormosil-phosphotungstate hybrid materials. Compared to the undoped samples, the photochromic response of the Zn^{2+}-doped hybrid films increases by 237%. Micro X-ray fluorescence (research proposal XAFS1-14257) analysis showed a linear increase in intensity of the W $L\alpha_1$ fluorescence line with increase in $Zn(NO_3)_2$ concentration. It therefore turns out that the addition of the addition of Zn^{2+} in the sol-gel preparations leads to an increase in the amount of phosphotungstate ($PW_{12}O_{40}{}^{3-}$) incorporated in dip-coated films thereby enhancing the photochromic response of the hybrid films. We suggest that addition of Zn^{2+} ion can possibly leads to the formation of Zn-phosphotungstate nano-agglomerates which get trapped into the Ormosil network during films preparation. Qualitative analysis of the Zn K-edge XANES spectra suggests that the Zn^{2+} doping cations present octahedral coordination in the hybrid films, most probably in the form of a aqua complex . This result is consistent to the formation of a phosphotungstate salt, since in this kind of compound the counter cation is usually coordinated by water. Therefore the μ-XRF and XANES studies allowed us to understand how the addition of Zn^{2+} cations can lead to the preparation of highly photochromic Ormosil-phosphotungstate films, which are promising candidates for the design of practical UV-sensing devices and dosimeters**.**

INVESTIGATING ARSENIC FORMS IN TAILINGS FROM A GOLD MINE

EVANISE SILVA PENIDO[1]; REGLA TOUJAGUEZ LA ROSA MASSAHUD[1]; FÁBIO BENEDITO ONO[1]; LUIZ ROBERTO GUIMARÃES GUILHERME[1].

1.UNIVERSIDADE FEDERAL DE LAVRAS, LAVRAS - MG - BRASIL.

Palavras-chave: Arsenic;toxicity;EXAFS

Resumo:

High concentrations of total arsenic (As) have been measured in soils/tailings of gold mining areas worldwide. Arsenic is a human health concern because it can contribute to skin, bladder, and other cancers. It occurs commonly in the environment in several oxidation states (−3, −1, 0, +3, and +5) and the mobility and toxicity of As are related to its speciation. This work aimed at analyzing mine tailings using X-ray absorption near edge structure (XANES) and the extended X-ray absorption fine structure (EXAFS) spectroscopy to determine the predominant oxidation state of As and to identify the first As neighbors (first shell and second shell) in four tailings (R1, R2, R3 and R4) from the Delita gold mining area (Cuba). The analyses were conducted at the As K-edge (11,867 eV) at the Brazilian Synchrotron Light Laboratory-LNLS (Campinas, Brazil). The spectra were recorded at room temperature using a Si (111) double crystal monochromator with an upstream vertical aperture of 0.5 mm and calibrated with Au L3-edge (11,919 eV). The XANES spectra in each sample confirmed the predominance of pentavalent As (AsV) in all tailings. The EXAFS analysis showed As-O binding at a distance of 1.4A˚ and As-Fe at a distance of 3.0A˚. These findings indicate a pattern very similar to the reference sample of scorodite for all tailings, except in R4, suggesting that another arsenate mineral is associated with this sample.

QUANTIFICATION OF PHOSPHATE IN PRECAMBRIAN FOSSILS USING X-RAY TECHNIQUES: IMPLICATIONS FOR THE RISE OF ANIMALS' HARD PARTS

FABIO RODRIGUES[1]; MÍRIAN LIZA ALVES FORANCELLI PACHECO[2]; DOUGLAS GALANTE[1].
1.LNLS/CNPEM, CAMPINAS - SP - BRASIL; 2.UFSCAR, SOROCABA - SP - BRASIL.

Palavras-chave: Phosphate;Fossil;Fluorescence

Resumo:

The presence of purely organic or biomineralized carapaces among Precambrian fossils brings important information about the ecological relations and the paleoenvironment. In addition, the biomineralization phenomenon can be used in astrobiology for the search for biosignatures of extant or extinct life on Earth or elsewhere.

A specific problem is the detection of phosphate, an important component of many animals, being also precipitated by several microorganisms. The phosphate is difficult to be studied using spectroscopic techniques such as Raman or X-ray Fluorescence (XRF) due to specific experimental problems.

In this work, the group has developed a synchrotron-based methodology to detect and quantify phosphate in the fossil context, using the phosphorous K-edge XANES spectra (P K XANES).

Calibration curves in many different substrates were built and the results obtained for the fossils were interpolated to determine the concentration of P on the carapace. Several fossils were studied using this technique and the detection limit compared with other spectroscopic techniques, such as Raman and XRF.

EVALUATION OF THE INFLUENCE OF MACRONUTRIENTS IN THE BIOACCUMULATION OF LEAD BY EICHHORNIA CRASSIPES

FERNANDO RODOLFO ESPINOZA-QUIÑONES[1]; APARECIDO NIVALDO MÓDENES[1]; ANA PAULA DE OLIVEIRA[1]; GUSTAVO HENRIQUE FIDELIS DOS SANTOS[2].

1.UNIOESTE, TOLEDO - PR - BRASIL; 2.UEM, MARINGA - PR - BRASIL.

Palavras-chave: SR-TXRF technique;heavy metal;bioaccumulation

Resumo:

SR-TXRF measurements was used to study the influence of the macronutrient phosphorus in the lead bioaccumulation process, using the living aquatic macrophyte Eicchornia crassipes in different hydroponic conditions with variations in phosphorus and lead concentrations was investigated. A set of growth experiments in hydroponic media doped with lead and phosphorus within a wide concentration range was performed for 32 days in a greenhouse. All experiments were carried out with periodic replacement of all nutrients and lead. According to the TXRF results, the adsorption/accumulation of lead ions in roots and leaves of the Eichhornia crassipes was slightly favoured by the presence of high phosphorus concentrations in the metal-doping Clark growing solutions. It can be noticed that the lead removal by roots is a quit process, occurring basically a high lead adsorption in the first days, whereas the lead bioaccumulation in leaves is a low process due to ocurr a low transportation rate of nutrients for aerial parts of the aquatic plant. Beside this, high lead concentrations in metal-doping Clark solutions have negatively influenced the accumulation of phosphorous in leaves as well as a low phosphorous adsorption in roots, suggesting that there is a detrimental effect on sorption and transport of phosphourous to the leaves by the presence of lead ions.

EFFECTS OF FORMALIN FIXATION ON QUANTITATIVE SOFT TISSUE VALUES OBTAINED BY GRATING-BASED PHASE-CONTRAST IMAGING

GABRIEL BUENO DE MORAES FIOR[1]; MARIAN WILLNER[1]; MATHIAS MARSCHNER[1]; JONATHAN SCHOCK[1]; BARBARA CERVANTES[1]; MICHAEL CHABIOR[1]; ALEXANDER HIPP[2]; JULIA HERZEN[2]; FRANZ PFEIFFER[1].

1.DEPARTMENT OF PHYSICS AND INSTITUTE OF MEDICAL ENGINEERING, TECHNISCHE UNIVERSITÄT MÜNCHEN, MÜNCHEN - ALEMANHA; 2.INSTITUTE OF MATERIALS SCIENCE, HELMHOLTZ-ZENTRUM GEESTHACHT, HAMBURG - ALEMANHA.

Palavras-chave: Phase-Contrast;Formalin fixation;Soft tissue

Resumo:

Conventional absorption-based X-ray computed tomography presents excellent results for high absorbing structures such as bones, but is incapable of discriminating between various soft tissue types. To overcome this limitation, several phase-contrast imaging techniques have been developed lately. One of them is grating interferometry, which has been successfully translated to work with laboratory X-ray sources and additionally allows for quantitative imaging [1-3]. As the method is still experimental, investigated biomedical tissue samples are mostly fixated in formalin so far.

The objective of our work is to study the influence of formalin fixation on quantitative tissue values to get a better understanding of possible differences between the measurement results of fixated samples and the appropriate in vivo scenario.

A Talbot-Lau interferometer has been employed in combination with a rotating-anode X-ray tube and a photon-counting detector. Tomography scans of porcine fat and rind have been performed to study the effects of formalin fixation. Quantitative phase-contrast Hounsfield Units of adipose tissue, muscle tissue and skin have been determined for all different samples.

[1] Pfeiffer, F. et. al.: Nature Physics, Vol. 2(4), S. 258-261 (2006)

[2] Herzen, J. et al., Optics Express, Vol. 11 (2009)

[3] Donath, T. et al., Investigative Radiology, Vol. 45 (7), S. 445-452 (2010)

CARACTERIZACIÓN MULTIELEMENTAL DE TUMORES DE PERSONAS EXPUESTAS A CANCERÍGENOS AMBIENTALES POR SR-XRF-CT Y SR-XRF EN EL LNLS

GUILLERMINA A BONGIOVANNI[1]; GABRIELA A. MIRABELLI[2]; ROBERTO D PÉREZ[3]; CARLOS A PÉREZ[4].
1.CONICET-UNIV NAC COMAHUE, NEUQUÉN-CINCO SALTOS - ARGENTINA; 2.INST. BAC SPINOZA, CÓRDOBA - ARGENTINA; 3.FAMAF-UNC- CONICET, CORDOBA - ARGENTINA; 4.LNLS, CAMPINAS - SP - BRASIL.

Palavras-chave: bioacumulación;cancerígenos;diagnóstico

Resumo:

El arsénico (As) es un tóxico abundante en la naturaleza y el consumo crónico de agua con este contaminante produce HACRE (hidroarsenicismo crónico regional endémico) y principalmente cáncer de vejiga y pulmón. Se determinó la concentración de As en el agua de red de una localidad de la provincia de Córdoba, Argentina, y se encontraron valores entre 25-50 ug/L de As. A esto se suma una empresa de curtiembre que arroja residuos con cromo (Cr) en un riachuelo en el lado este del poblado. Se obtivieron muestras tumorales de dos habitantes de esa localidad y fueron analizados por microtomografía y micro-fluorescencia utilizando radiación sincrotrón en la línea D09B-XRF del LNLS (SR-uXRF-CT y SR-uXRF) para determinar la composición elemental de los diferentes tejidos que los componen. Estas tecnologías brindan una valiosa información relacionada a distribución de y acumulación de elementos que pueden ser usadas en el diagnóstico y localización de formaciones malignas.

The authors would like to thank LNLS-Campinas, Brazil (proposal D09B-XRF-13421 y 13495), CONICET, UNCo and FONCyT, Argentina.

ASSESSMENT OF THE MECHANISM OF ZN2+ REMOVAL BY USING THE SR-TXRF TECHNIQUE

GUSTAVO HENRIQUE FIDELIS DOS SANTOS[1]; FERNANDO RODOLFO ESPINOZA-QUIÑONES[2]; APARECIDO NIVALDO MÓDENES[2]; CARLOS EDUARDO BORBA[2]; MAURO ANTONIO RAVAGNANI[1]. 1.UEM, MARINGÁ - PR - BRASIL; 2.UNIOESTE, TOLEDO - PR - BRASIL.

Palavras-chave: SR-TXRF;zinc removal;biosorption

Resumo:

In this work the synchrotron radiation total reflection X-ray fluorescence (SR-TXRF) technique was used to study the mechanism of metal sorption by dead biomass. Particulates of Egeria densa biomass were chosen as an adsorbent to remove divalent zinc from an aqueous solution. Several batch zinc-sorption experiments were performed by adding 0.3 g of E. densa dry biomass into 50 mL of aqueous solution containing 4 mequiv. L^{-1} Zn^{2+} at pH 5. SR-TXRF measurements were performed in aqueous and digested samples obtained from aqueous solutions and the treated E. densa biomass, respectively. Based on the mass balance among the major elements in the liquid and solid phases before and after the Zn-removal experiments, an ion exchange process is suggested as the main mechanism.

X-RAY ABSORPTION SPECTROSCOPY OF SR2FEMOO6

HENRIQUE PERIN MARTINS[1]; RODRIGO JOSÉ OCHEKOSKI MOSSANEK[1]; MIGUEL ABBATE[1].
1.UNIVERSIDADE FEDERAL DO PARANÁ, CURITIBA - PR - BRASIL.

Palavras-chave: double perovskite;spectroscopy;multiplet effects

Resumo:

The electronic structure of the double perovskite Sr2FeMoO6 was studied using XANES spectroscopy. The double-perovskite Sr2FeMoO6 is a half-metallic ferromagnet with a high Tc. It also presents a rather large tunneling magnetoresistance (TMR) close to Tc. The experimental XAS spectra were measured at room temperature at the SXS and SGM beamlines in the LNLS. The ligand K and transition metals L absorption spectra were interpreted using an atomic multiplet program. The calculations for the L edges were done considering three possible oxidation states for the transition metals: Fe3+ - Mo5+, Fe4+ - Mo4+ and Fe5+ - Mo3+. Subsequently, we removed the 2p hole structure from these absorption spectra calculations in order to simulate the 3dn+1 - 4dn+1 addition states, which should be similar to the first structures of the ligand K absorption spectra. This three-way comparison clearly indicates that the transition metals in this double-perovskite are in the mixed Fe3+ - Mo5+ valence state.

- Master's student
- Research proposals: SGM10773 and SXS10771

GRAZING-INCIDENCE X-RAY RESONANT RAMAN SCATTERING

HÉCTOR JORGE SÁNCHEZ[1]; JUAN JOSÉ LEANI[1]; CARLOS ALBERTO PÉREZ[2]; ROBERTO DANIEL PÉREZ[1]; JOSÉ ROBLEDO[1].

1.UNIVERSIDAD NACIONAL DE CÓRDOBS, CÓRDOBA - ARGENTINA; 2.LABORATORIO NACIONAL DE LUZ SINCROTRÓN, CAMPINAS - SP - BRASIL.

Palavras-chave: Resonan Raman Scattering;XRF;Energy Dispersive

Resumo:

The GIXRF technique, allows studying different depths of a sample. Resonant Raman Scattering is an inelastic process which presents fundamental differences compared to other interactions. A spectroscopic technique based on this process showed to be useful to distinguish surrounded chemical environments. Both GI and RRS techniques are used in combination to discriminate oxidation state.

ESTUDO DA FORMAÇÃO DE NPS BIMETÁLICAS DE PT-CU POR DXAS IN SITU

JOCENIR BOITA[1]*; MARCUS VINICIUS CASTEGNARO*[1]*; MARIA DO CARMO MARTINS ALVES*[1]*; JONDER MORAIS*[1]*.*

1.UFRGS, PORTO ALEGRE - RS - BRASIL.

Palavras-chave: Pt-Cu;DXAS;in situ

Resumo:

As nanopartículas (NPs) de Pt-Cu desencadearam ao longo dos anos consideráveis investigações em função das suas propriedades eletrônicas, estruturais, mecânicas, ópticas e catalíticas [1-3]. Tais NPs possuem aplicações importantes como catalisadores (mono e bimetálicos) [4,5]. Neste trabalho monitoramos a formação de NPs de Pt-Cu através do método poliol em etilenoglicol por Espectroscopia de Absorção de Raios-X Dispersivo in situ (DXAS) nas bordas K do Cu e L_3 da Pt. 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 Pt-Cu com diâmetro médio de 3,7 ± 0,8 nm.

STUDY OF LI1-XNIO2 OBTAINED BY SOL- GEL WITH CORN STARCH BY X-RAY PHOTOELECTRON SPECTRA

JOSÉ MÁRCIO SIQUEIRA JR[1]; GLAUCIO BRAGA FERREIRA[1]; CLAUDIA VARGAS TORRES DE BARROS[2]; ANTONIO CARLOS DE OLIVEIRA GUERRA[2]; FRANCISCO MANOEL DOS SANTOS GARRIDO[2].
1.UNIVERSIDADE FEDERAL FLUMINENSE, NITERÓI - RJ - BRASIL; 2.UNIVERSIDADE FEDERAL DO RIO DE JANEIRO, RIO DE JANEIRO - RJ - BRASIL.

Palavras-chave: XPS ;sol-gel;lithium ion battery

Resumo:

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[1]. For characterizing of these materials, XPS (X-Ray photoelectron Spectroscopy) have been used: the valence band electronic structure information have been obtained.

In the present work used a combination of sol-gel process and method SHS (Self-Propagating High-Temperature Synthesis) for the synthesis of the precursors, characterized by obtaining the gel and subsequent combustion of the nitrate-starch. Then obtaining green dark solids in the form of fine powder, then were calcined at 750° C for 16h.

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 6×10^{-8} mBar.

The samples obtained at different molar ratios Ni / Li were analyzed from the Li 1s , Ni 3p, Ni 2p, and O1s peaks .

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ESPECIACIÓN DE AS EN CABELLO HUMANO POR SR-XRF-XANES COMO MEDIDA DE EXPOSICIÓN PARA VALORAR LOS RIESGOS ASOCIADOS A SU CONSUMO CRÓNICO

JULIO ALEJANDRO NAVONI[1]; CARLOS A PÉREZ[2]; GUILLERMINA A BONGIOVANNI[3]. 1.CATEDRA. TOXICOLOGÍA Y QUÍMICA LEGAL- FACULTAD DE FARMACIA Y BIOQUÍMICA-UBA, BUENOS AIRES - ARGENTINA; 2.LNLS, CAMPINHAS - SP - BRASIL; 3.CONICET-UNIV NAC COMAHUE, NEUQUEN - ARGENTINA.

Palavras-chave: ARSENIC;ESPECIATION;EXPOSURE

Resumo:

El arsénico (As) es uno de los elementos tóxicos más abundantes de la corteza. Alrededor de 14 millones de personas se encuentran expuestas en América Latina, teniendo aparejado el riesgo de desarrollo de numerosas patologías, entre ellas el cáncer. En la Argentina no hay estudios epidemiológicos relacionados a especiación de As en muestras biológicas.

La metodología SR-XRF-XANES que hemos implementado en la línea D09B-XRF del LNLS nos permite discriminar el contenido de diversas especies químicas del As en muestra de cabello de personas expuestas. Debido a que estas especies son producidas por el metabolismo celular, la metodología SR-XRF-XANES es una herramienta analítica útil, no solo para la evaluación de la exposición, sino también porque evita observaciones erróneas debido a la presencia de As proveniente de la contaminación externa. También podría ser de suma utilidad para estudiar el patrón de metabolización del As y la función de las faneras en la Toxicocinetica/dinamia del As, lo que da un valor agregado en el estudio de población humana expuesta y en la valoración de los riesgos asociados a esta problemática sanitaria.

The authors would like to thank LNLS-Campinas, Brazil (proposal D09B-XRF-15253), CONICET, UNCo and FONCyT, Argentina

XAFS STUDY ON AL-DOPED ZNTE AND ZNSE SEMICONDUCTORS POWDERS

LAURA C. DAMONTE[1]; JOAQUIN HOYA[2]; JUAN IGNACIO LABORDE[2].

1.UNLP-IFLP, CONICET, LA PLATA - ARGENTINA; 2.UNLP, LA PLATA - ARGENTINA.

Palavras-chave: nanocrystalline semiconductors;mechanical milling;solar cell

Resumo:

II-VI semiconductors are of interest due to their potential application as photovoltaic devices like hybrid solar cells. The efficiency of these devices may be improved mainly increasing charge carriers densities and interfacial processes. In order to reach this last purpose nanocrystalline materials are the best option as solar cells constituents. In this study we present zinc based semiconductors powders which optical and electrical properties have been modified by the Al presence acting as small quantities of dopant.

The nanosized doped semiconductors (ZnSe and ZnTe) were obtained by mechanical milling which has been proved to be an effective and simple technique to produce nanocrystalline and large quantities of materials. Metal oxide Al_2O_3 together with ZnSe or ZnTe was milled in adequate proportion to obtain the desired concentration. Parameters such as initial concentrations, atmosphere and milling times were varied. X-ray Absorption Spectroscopy (XAFS) characterization on doped powders was done in order to probe cation sustitution. Undoped ZnSe and ZnTe nanocrystalline powders prepared in a similar way were analyze for comparison. The knowledge obtained can be of use to give direction to the improvement of the performance of hybrid organic/inorganic solar cells.

LOCAL ORDER AND SPECIATION OF PR0.6SR0.4CO0.8FE0.2O3-Δ NANOPOWDERS

LEANDRO MARCELO ACUÑA[1]; FERNANDO FRANCISCO MUÑOZ[2]; RODOLFO OSCAR FUENTES[3]; DIEGO GERMÁN LAMAS[4].

1.CONICET-CITEDEF, VILLA MARTELLI - ARGENTINA; 2.CITEDEF, VILLA MARTELLI - ARGENTINA; 3.CNEA, SAN MARTÍN - ARGENTINA; 4.CONICET, NEUQUÉN - ARGENTINA.

Palavras-chave: nanopowders;perovskite;IT-SOFCs

Resumo:

Materials with perovskite structure ABO_3 have found application as cathodes in solid oxide fuel cells (SOFCs) due to their excellent mixed ionic and electronic conduction properties and electrocatalytic activity for the oxygen reduction reaction (ORR) at high temperatures (900 – 1000°C). Nevertheless, at these temperatures several negative aspects diminish the SOFC performance.

To solve these problems, research is focused in new materials that exhibit the desired features in the intermediate temperature (IT) range of 500-700°C. Our previous works demonstrated that cathodes based on nanostructured powders of $La_{0.6}Sr_{0.4}CoO_{3-\delta}$ (LSC) and $Sm_{0.5}Sr_{0.5}CoO_{3-\delta}$ (SSC) exhibit faster ionic conduction which lowers the polarization resistance, compared to those made by microstructured powders, even in the IT range.

In this work we studied the local order, speciation and crystal structure of $Pr_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (PSCF) nanopowder in the temperature range of 20 – 700°C. Measurements of the Co, Fe and Sr K-edges and Pr L_3-edge were carried out in the D04B – XAFS-1 beamline of the LNLS in transmission mode. In order to analyze the behavior of the powder as function of O_2(g) concentration, measurements were carried out under three different O_2 concentrations for each temperature. The observed variations gave some insight about the capability of this powder to store or release oxygen atoms depending on the surrounding conditions.

STUDY OF PERSISTENT LUMINESCENCE MECHANISMS OF TB3+ AND PR3+ DOPED MATERIALS WITH X-RAY ABSORPTION SPECTROSCOPY

LUCAS CARVALHO VELOSO RODRIGUES[1]; HERMI FELINTO BRITO[1]; JORMA HÖLSÄ[2]; MIKA LASTUSAARI[2]; MARIA CLAUDIA F. C. FELINTO[3]; JOSÉ MIRANDA CARVALHO[1]; PAULA PINHEIRO PAGANINI[3].

1.IQ-USP, SÃO PAULO - SP - BRASIL; 2.UNIVERSITY OF TURKU, TURKU - FINLÂNDIA; 3.INSTITUTO DE PESQUISAS ENERGÉTICAS E NUCLEARES, SÃO PAULO - SP - BRASIL.

Palavras-chave: Persistent Luminescence;Mechanism;Rare Earth

Resumo:

Research on persistent luminescence materials has expanded since mid 1990s due to their versatile applications. Despite the experimental and theoretical advance made for Eu^{2+} doped materials, the similar phenomena arising from trivalent rare earths (R^{3+}) have received much less attention. Among such materials, $CdSiO_3$:R^{3+} show persistent emission from the R^{3+} ions or defects or both when doped with Tb^{3+} and Pr^{3+} or La^{3+}, Gd^{3+}, and Lu^{3+} or Dy^{3+} and Sm^{3+}, respectively. Understanding the mechanism of persistent luminescence of these materials requires the knowledge of dopant's valence and environment and if the photoionization process produces R^{2+} or R^{IV}.

The synchrotron radiation (SR) XANES measurements on $CdSiO_3$:R^{3+} show only the trivalent Pr^{3+}, Eu^{3+} and Tb^{3+}, even if the Tb persistent luminescence was induced by X-rays. The photoionization of Pr^{3+} and Tb^{3+} during charging persistent luminescence thus creates Pr^{3+}-h^{+} and Tb^{3+}-h^{+} pairs instead of Pr^{IV} and Tb^{IV}. The EXAFS data confirmed that R^{3+} replace Cd^{2+} in $CdSiO_3$, requiring charge compensation and formation of defects responsible for storing energy for persistent luminescence. The XANES and EXAFS results aided to design the mechanism of persistent luminescence from Pr^{3+} and Tb^{3+} in $CdSiO_3$. The band gap energy and the $4f^n$ ground energy level positions vis-à-vis the host's band system were determined with the SR VUV-UV excitation spectroscopy. Finally, the trap energies were determined with thermoluminescence measurements.

LUMINESCENT PROPERTIES OF EU DOPED CAAL2O4 PRODUCED BY PROTEIC SOL GEL ROUTE

MANASSES ALMEIDA GOMES[1]; ADRIANO BORGES ANDRADE[1]; MARCOS V. DOS SANTOS REZENDE[2]; MARIO ERNESTO GIROLDO VALERIO[1].

1.UFS, SÃO CRISTOVÃO - SE - BRASIL; 2.IFS, LAGARTO - SE - BRASIL.

Palavras-chave: Luminescence;Sol-Gel-Proteic;nanoparticles

Resumo:

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 (Termo-gravimetry) 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 1200°C 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 Eu3+ 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.

This work was done during the masters.

X-RAY EXCITED OPTICAL LUMINESCENCE (XEOL) SR(1-X)BAXAL2O4:EU PHOSPHORS

MARCOS V. DOS SANTOS REZENDE[1].

1.INSTITUTO FEDERAL DE SERGIPE, ARACAJU - SE - BRASIL.

Palavras-chave: XEOL;rare earth ion;Sr1-xBaxAl2O4

Resumo:

The $SrAl_2O_4$ and $BaAl_2O_4$ have been investigated recently due the several other optical properties. Of all optical properties observed in $SrAl_2O_4$ the most recently finding is the long lasting phosphorescence (LLP) and such property is activated by the presence of rare earth ions. In this work usual EXAFS and XANES measurements were performed and compared to the XEOL results. This combination of experimental techniques allowed us to propose a mechanism of X-ray excitation and de-excitation via luminescence of $Sr_{1-x}Ba_xAl_2O_4$:Eu (x=0, 0.2, 0.4, 0.6, 0.8, 1.0) nanopowders. In this work, we report the optical response of $Sr_{1-x}Ba_xAl_2O_4$:Eu, prepared via new proteic sol–gel method, with selected photon energy near the Ba L_{III}-edges and Eu L_{III}-edge. XEOL spectrum was collected using an optical spectrometer simultaneously to the XAS spectrum and the area of XEOL spectrum is calculated and plotted as a function of the excitation energy. The main results can be summarized as follows: i- Eu is incorporated in the $Sr_{1-x}Ba_xAl_2O_4$:Eu matrix as a mainly trivalent species but a small amount of the Eu^{2+} is also present; ii- both Eu^{3+} and Eu^{2+} are located in two non-equivalent sites; iii- irradiation with X-rays reduces a great part of the Eu^{3+} to Eu^{2+} and the former is not stable in the matrix returning to Eu^{3+}; iv- the Eu^{3+} XEOL emission intensity is approximately constant for X-rays photons around the Eu L_{III} edge and slightly decreased in the X-ray photon energy around the Ba L_{III} edge.

SYNCHROTON RADIATION µXRF STUDY OF VARIABILITY AND SPATIAL DISTRIBUTION OF LEAD AND ANTIMONY IN CORRODED BULLETS USED FOR HUNTING IN CORDOBA, ARGENTINA

MERA M. F.[1], RUBIO M.[1,2,3], GERMANIER A.[1], FAUDONE S.[1], ZAMPAR V.[1], PÉREZ C. A.[4]

[1]CENTRO DE EXCELENCIA EN PRODUCTOS Y PROCESOS DE CÓRDOBA. CEPROCOR. ÁLVAREZ DE ARENALES 230 Bº JUNIOS. CÓRDOBA, ARGENTINA.

[2]FACULTAD DE MATEMÁTICA, ASTRONOMÍA Y FÍSICA. UNIVERSIDAD NACIONAL DE CÓRDOBA. FAMAF. CIUDAD UNIVERSITARIA. CÓRDOBA, ARGENTINA.

[3]CONICET. RIVADAVIA 1917. CIUDAD AUTÓNOMA DE BUENOS AIRES, ARGENTINA.
[4]LNLS, LABORATORIO NACIONAL DE LUZ SINCROTRON. CAMPINAS. SP, BRAZIL.

Palavras-chave: µXRF; LEAD; ANTIMONY

Resumo:

We investigated the mineralogical composition and spatial distribution of Pb and Sb species in corroded ammunitions to understand how metallic Pb and Sb reacts in the soil, influencing the bioavailability and the risk of contamination in soil.

Preliminary studies by conventional X-ray fluorescence analysis (XRF) and powder X-ray diffraction (XRD) in soil samples collected from shooting fields of Córdoba were performed in CEPROCOR during 2012. These studies included the quantification of elements in soils and characterization of mineral phases in crust powder removed from corroded Pb bullets. As a continuity of our research we considered the need to use SR µXRF to map the spatial distribution of Pb, Sb and other elements and correlate these spectra with mineral phases on bullets and crust.

The experiment was carried out in August 2013 at the XRF station at LNLS under the proposal *XAFS1-15234.* The samples measured were corroded bullets cemented by epoxy resin and flat polished, crust dust and entire ammunitions. SR µXRF elemental mapping of Pb were performed in selected samples oriented to know process like litharge→ hydrocerussite →cerussite going to more stable phases that immobilizes Pb in soil. It was also explored the micro distribution of Sb in wheathered bullets due to its important incidence in soil contamination, because the low limit accepted for this element in soil by Argentinean agriculture authorities (Law Nº 24051, D 831/93).

Thanks to the high sensitivity of the SR beam and the feasibility to perform micro mapping, it was observed that bullets cores are conformed of few metallic Sb grains dispersed into a metallic Pb matrix, rather than a Pb-Sb alloy. It was also determined the relationship between Sb and Fe in the corrosion process of the bullets observing that Sb was correlated to Fe-compounds in bullet crust material. This was not possible to identify during the preliminary study of CEPROCOR because Sb could be present in an amorphous structure or in concentrations lower than the detection limit.

Further research proposal based on the present scientific project in progress will be oriented to use SR µXANES as an appropriate technique for a better identification of Pb and Sb species in bullets crust material. A more precise characterization of Pb, Sb and even others metallic mineral phases has the aim to develop phyotechnologies for the remediation of contaminated soils.

Acknowledgements: This work was developed at Brazilian National Synchrotron Light Laboratory (Proposta de Pesquisa :XAFS1-15234). The authors would like to thank the LNLS staf for technical support.

ESTUDIO DE LA CINÉTICA DE RETENCIÓN Y LIBERACIÓN DE AS EN LARVAS DEL ANFIBIO *Rhinella arenarum* (SAPO COMÚN ARGENTINO)

MARIANA NOELIA MARDIROSIAN[1]; ROBERTO D PÉREZ[2]; CARLOS A PÉREZ[3]; ANDRES VENTURINO[4]; GUILLERMINA A BONGIOVANNI[1].

1.IDEPA-UNCO-CONICET, NEUQUÉN - ARGENTINA; 2.FAMAF-UNC-CONICET, CÓRDOBA - ARGENTINA; 3.LNLS, CAMPINAS - SP - BRASIL; 4.LIBIQUIMA-UNCO-CONICET, NEUQUÉN - ARGENTINA.

Palavras-chave: ARSÉNICO;BIO-ACUMULACIÓN;SR-XRF

Resumo:

El arsénico (As) es uno de los elementos tóxicos más abundantes de la corteza y es movilizado por el agua exponiendo a más de 130 millones de personas en el mundo y a numerosas especies acuáticas. El As(III) ingresa a las células por acuaporinas y causa estrés oxidativo, también es mono- o dimetilado (As orgánico) para ser excluído por "multidrug resistant proteins" pero una parte se bio-acumula como hemos podido comprobar por SR-µXRF, SR-TXRF y SR-µXRF-CT en ratas o larvas de sapo (*Rhinella arenarum*) expuestos crónicamente a As. Por otro lado, encontramos que si los embriones de sapo son expuestos a As después del día 5, el 70% de los embriones viven en medios con 50 ppm As. La técnica micro-Fluorescencia de Rayos-X utilizando radiación de Sincrotrón (SR-µXRF) disponible en la línea D09B-XRF del LNLS es apropiada para medir As y otros elementos en muestras pequeñas como lo son las larvas de *R. arenarum* expuestas a concentraciones ambientales de As. Para determinar si la mayor susceptibilidad de los embriones desarrollados en As podría deberse en parte a alteraciones de los mecanismos de absorción o eliminación, se midió As en larvas de *R. arenarum* desarrolladas en medios con As desde día 0 o desde el día 5. La liberación de As se midió en larvas expuestas a As durante 14 días y luego incubadas 48 hs en medio sin As.

The authors would like to thank LNLS-Campinas, Brazil (proposal D09B-XRF-15257), CONICET, UNCo and FONCyT, Argentina.

CATALYTIC PROPERTIES OF NI/CEO2-SM2O3 AND NI/CEO2-Y2O3 NANOCOMPOSITES FOR INTERMEDIATE-TEMPERATURE SOLID-OXIDE FUEL CELLS

MARINA SOLEDAD BELLORA[1]; REBECA BACANI[2]; LUCIA MARÍA TOSCANI[3]; ROGÉRIO JUNQUEIRA PRADO[4]; TEREZA DA SILVA MARTINS[5]; MARCIA CARVALHO DE ABREU FANTINI[2]; SUSANA ADELINA LARRONDO[3]; DIEGO GERMAN LAMAS[1].

1.CONICET-UNIVERSIDAD NACIONAL DEL COMAHUE, NEUQUÉN - ARGENTINA; 2.UNIVERSIDADE DE SÃO PAULO-DEPARTAMENTO DE FÍSICA APLICADA, SÃO PAULO - SP - BRASIL; 3.UNIVERSIDAD DE BUENOS AIRES-FACULTAD DE INGENIERÍA - LABORATORIO DE SÓLIDOS AMORFOS, BUENOS AIRES - ARGENTINA; 4.UNIVERSIDADE FEDERAL DE MATO GROSSO-INSTITUTO DE FÍSICA, CUIABÁ - MT - BRASIL; 5.UNIVERSIDADE FEDERAL DE SÃO PAULO-DEPARTAMENTO DE CIÊNCIAS EXATAS E DA TERRA, DIADEMA - SP - BRASIL.

Palavras-chave: IT-SOFC anodes;CATALYTIC PROPERTIES;CeO2-based materials

Resumo:

CeO2-based materials have received great attention due to their excellent catalytic properties for oxidation reactions. In the field of intermediate-temperature solid-oxide fuel cells (IT-SOFCs), CeO2-based anodes are subject of intense study because they have proven to exhibit excellent catalytic properties for both partial oxidation of hydrocarbons in single-chamber SOFCs and direct oxidation of hydrocarbons in conventional (two-chamber) SOFCs. Besides, excellent performance in hydrogen-fueled SOFCs has also been found. These excellent performance of CeO2-based anodes is related to the fact that they are mixed ionic/electronic conductors (MIECs) under reducing atmosphere and, therefore, fuel oxidation takes place on its entire surface, while it only occurs in the [anode/electrolyte/gas] triple-phase boundaries for electronic conductors. It is important to point out that the number of active points for fuel oxidation should be dramatically increased in nanostructured, high specific surface area MIECs.

In this work, we present an in-situ study of Ni/CeO2-Sm2O3 and Ni/CeO2-Y2O3 nanocomposites for IT-SOFC anodes by DXAS technique. We studied the Ni-K and Ce-L3 edges under different operating conditions for H2 or CH4 oxidation. In this way, we monitor the Ni0/Ni2+ and Ce3+/Ce4+ ratios, which are strongly related to the catalytic properties of these materials. In all cases, the reactions were monitored with a mass spectrometer.

EXAFS CHARACTERIZATION OF PTNI BIMETALLIC CATALYSTS APPLIED IN THE AQUEOUS-PHASE REFORMING OF GLYCEROL

MARTÍN MIZRAHI[1]; JOSÉ MARTÍN RAMALLO LOPEZ[1]; MARÍA LAURA BARBELLI[2]; FRANCIASCO POMPEO[2]; GERARDO SANTORI[2]; NORA NICHIO[2].

1.INIFTA, FACULTAD DE CIENCIAS EXACTAS, UNIVERSIDAD NACIONAL DE LA PLATA. CCT LA PLATA- CONICET, LA PLATA - ARGENTINA; 2.CINDECA, FACULTAD DE CIENCIAS EXACTAS, UNIVERSIDAD NACIONAL DE LA PLATA. CCT LA PLATA- CONICET, LA PLATA - ARGENTINA.

Palavras-chave: EXAFS;Catalyst;Reforming of glycerol

Resumo:

The aim of this work is to evaluate the catalytic properties and stability of PtNi bimetallic catalysts supported on Ce-Zr-α-Al_2O_3 (CZA) in the aqueous-phase reforming reaction (APR) of glycerol and to relate them to the results of the EXAFS characterization. The Ni/CZA catalyst presents low conversion to gaseous products and low selectivity to H_2, whereas the Pt/CZA catalyst presents higher selectivity to the glycerol reforming (SCO_2= 45%). The bimetallic catalyst PtNi/CZA presents the highest global activity and promotes the formation of liquid oxygenated hydrocarbons, mainly acetol and 1,2-propylene glycol, which are formed from glycerol hydrogenolysis. By means of EXAFS studies, it was determined that in the PtNi/CZA catalysts three phases are present: a Pt-Ni nano-alloy, unalloyed metallic Pt with high dispersion and unalloyed metallic Ni with low dispersion. The highest activity of the PtNi/CZA catalyst could be assigned to the presence of the Pt-Ni alloy which results in a more active phase than the Pt and Ni sites separately. However, the selectivity to the reforming is lower and the cleavage of C-O bond reactions are favored. The PtNi/CZA catalyst is the more stable and the EXAFS results show that this behavior would be associated to the higher resistance to sintering of the metallic particles, whose structure is stabilized after the first hour of the reaction.

EVALUATION OF THE EFFICIENCY OF PROTEIC SOL-GEL PROCESS TO SYNTHESIS LUMINESCENT NANOPOWDERS OF THE (Y1-XREX)3AL5O12(RE= EU3+, CE3+)

MARIO ERNESTO GIROLDO VALERIO[1]; DANIEL FELIX DIAS DOS SANTOS[1].

1.UNIVERSIDADE FEDERAL DE SERGIPE, ARACAJU - SE - BRASIL.

Palavras-chave: YAG nanopowders;rare earth dopants;synchrotron radiation

Resumo:

YAG nanopowders doped with Eu^{3+} and Ce^{3+} were prepared via Proteic Sol-Gel route. DTA and TGA results indicated the range of tempertures that should be used for the calcination step. Powder XRD results confirmed the formation of the YAG single phase for calcination at 950°C for 3 hours or 1050°C for 2 hours. XANES was used to follow the dopant valence and the results indicated that Eu kept the trivalent state but Ce is incorporated mainly as e tetravalent dopant. PL and RL results indicated that the Eu-doped YAG presented the typical Eu^{3+} emissions. The RL results on Ce-doped samples indicated the presence of the 5d^{1}à4f^1 transitions of the Ce^{3+} species. SEM analysis indicated that the particles showed rod like shapes and their average size were around 70 nm. EDS confirmed the presence of contaminants in all samples, although the optical properties of the Eu-doped YAG were not affected by them. The Ce-doped samples, however, were very sensitive to this contamination and this is the main reason for the oxidation of the almost all Ce^{3+} to Ce^{4+} in the samples. Although the Ce^{3+} concentration is not high, an intense time resolved RL were observed with a lifetime constant around 50ns, which is consistent with the typical decay time for 5d^1→ 4f^1 transitions of the Ce^{3+}. All this results pointed out the potential application of the Ce-doped nanopowders as fast scintillators and the Eu-doped YAG nanopowders as fluorescent probes.

“GRAZING INCIDENCE AND TOTAL REFLECTION X-RAY FLUORESCENCE ANALYSES OF

ORLANDO ARMANDO ELGUERA YSNAGA[1].

1.INSTITUTO DE QUÍMICA DE SÃO CARLOS, SAO CARLOS - SP - BRASIL.

Palavras-chave: Grazing Incidence;Ormosil;Zn,TiO2

Resumo:

Organically modified Silicates (Ormosil) offer many applications in the different branches of the science. Ormosil are based in modified silicate precursors (TEOS or TMOS) with various organic substituents have been used to prepare a whole range of materials with different structures and properties.

We performed GIXRF (X-ray Fluorescence at Grazing Angle) measurements in the first semester of 2012 at LNLS of ormosil thin films doped with ZnO nanoparticles (samples) deposited on monocrystalline silicon substrates via Drop-Coating(semiquantitative analyses) as also of ormosil thin films doped with TiO2 nanoparticles (qualitative analyses).

In our experiments at LNLS we managed concentration levels of ZnO in ormosil films between 0.000005M-0.01M, but we get linearity for a ZnO concentration range between 000005M-0.0001M. We performed GIXRF measurements at LNLS in the first semester of 2013 in order to complete the semi-quantitative analyses of Ormosil doped with ZnO and TiO2 , this latter could not be detected by EDX because is present in small quantity(tenths of ppm) and randomly distributed.

GIXRF/TXRF has demonstrated to be a useful methodology in order to accomplished qualitative and semi-quantitative analyses for ormosil contained Zn and TiO2.

XAS IN SITU DE CATALISADORES DE CU/CEO2-AL2O3 APLICADOS NA REAÇÃO DE DESLOCAMENTO GÁS-ÁGUA: "ESTUDO DO EFEITO DO CÉRIO"

PAULA CRISTINA DE PAULA CALDAS[1]; RENATA UEMA RIBEIRO[1]; SANTIGO J. A. FIGUEIROA[2]; JOSE MARIA CORREA BUENO[1]; JOSÉ MARIA CORRÊA BUENO[1].

1.UFSCAR, SAO CARLOS - SP - BRASIL; 2.LNLS, CAMPINAS - SP - BRASIL.

Palavras-chave: Reação de deslocamento gás água;catalisadores de cobre/céria;catálise

Resumo:

Os catalisadores a base de cobre e céria apresentam uma alta atividade catalítica na reação de deslocamento gás água, contudo, o papel exercido pela céria não está totalmente esclarecido e ainda é motivo de debate. Com o intuito de contribuir para o entendimento do papel da céria catalisadores de Cu/Al_2O_3 foram preparados com teores de 5, 10 e 15% m/m de Cu e modificados com céria (12% m/m). Observou-se ao longo da reação, a partir dos resultados de EXAFS, que os catalisadores não modificados apresentam uma diminuição da razão Cu^+/Cu^0 com o aumento tamanho de partícula de Cu de 0,65 para 0,91 nm, quando se varia o teor do cobre de 5 para 15% m/m, respectivamente. Notou-se um aumento da frequência de reação-TOF (s^{-1}) com a diminuição do tamanho da partícula de cobre, o qual é atribuído a um aumento da quantidade do par redox Cu^+/Cu^0 na superfície do metal. A adição do cério acarretou em um pequeno aumento do TOF (s^{-1}). Através dos espectros de XANES verificou-se que ambos os íons Ce^{3+} e Ce^{4+} estão presentes na estrutura da céria em condições reacionais. A presença de ambos os íons gera vacâncias de oxigênio na superfície da céria, as quais poderiam ativar a água mais facilmente, contribuindo assim, para o pequeno aumento da atividade observada. Contudo, ainda esta sendo desenvolvido a partir dos resultados de EXAFS um modelo metal/óxido que permita o melhor entendimento do efeito da céria. (N° Proposta: XAFS1 – 14327)

WATER QUALITY ASSESSMENT OF THE BEZERRA STREAM TRIBUTARY OF SÃO FRANCISCO RIVER (CASCAVEL/BRAZIL) USING SR-TXRF TECHNIQUE

PHALLCHA LUIZAR OBREGON[1]; FERNANDO RODOLFO ESPINOZA-QUIÑONES[1]; APARECIDO NIVALDO MÓDENES[1].

1.UNIOESTE, TOLEDO - PR - BRASIL.

Palavras-chave: Physico-chemical parameters;element concentrations;statistical analysis

Resumo:

The present study aims to assess the water quality of the Bezerra river. Physico-chemical parameters such as turbidity, dissolved oxygen and chemical oxygen demand (COD) were monitored, as well as element concentrations in six sampling sites. It is noteworthy that the mean annual values of conductivity, turbidity and COD have progressively increased along the stream. From the 13 detected elements, Cr, Mn, Fe, Cu and Zn have shown concentrations above the maximum limits recommended by Brazilian environmental legislation as consequence of highly polluting anthropogenic sources. Applying correlation analyses, collection sites were grouped into two clusters, with the element composition in the first cluster (sites 1, 2 and 6) being due to strong anthropogenic activities. The study of the Bezerra stream water quality could help to develop municipal environmental policies and help with the management of water conservation in the Bezerra stream basin.

REDOX PROPERTIES OF NANOSTRUCTURED LANTHANIDE-DOPED CERIA SPHERES

RODOLFO OSCAR FUENTES[1]; *FERNANDO FRANCISCO MUÑOZ*[2]; *LEANDRO MARCELO ACUÑA*[2]; *ANA GABRIELA LEYVA*[1]; *RICHARD THORTON BAKER*[3].

1.CNEA, SAN MARTIN - ARGENTINA; 2.CITEDEF, VILLA MARTELLI - ARGENTINA; 3.UNIVERSITY OF ST ANDREWS, ST ANDREWS - REINO UNIDO.

Palavras-chave: Ceria;Lanthanide;Redox properties

Resumo:

In the present work, we report the influence on the redox properties on ceria doped with univalent (Gd^{3+}) and multivalent ($Pr^{4+,3+}$) cation with a controlled morphology. Nanostructured $Gd_{0.1}Ce_{0.9}O_{1.95}$ (GDC10), $Gd_{0.2}Ce_{0.8}O_{1.9}$ (GDC20), $Pr_{0.1}Ce_{0.9}O_{2-y}$ (PrDC10) and $Pr_{0.2}Ce_{0.8}O_{2-y}$ (PrDC20) spheres were synthesized by microwave assisted hydrothermal homogeneous co-precipitation technique (HMW) [7]. In situ XANES (D04B-XAFS1 beamline; Ce L_3-edge and Pr L_3-edge) and XRD (D010-XPD beamline) experiments were carried out under reducing and oxidizing atmospheres at different temperatures. The sample was heated at a rate of 10 C/min, and a soak time of 10 min was employed at each temperature step before the scan. The thermal behavior of the materials was studied in 5% H_2/He and in dry synthetic air. At 500 C in reducing conditions, an expansion in lattice parameters was observed compared with the corresponding samples obtained under oxidizing conditions at the same temperature. The largest differences were observed in ceria doped with multivalent cation (Pr).

Proposals: XAFS1-13435; XAFS1-14354; XRD1-13437; XRD1-13563

LOCAL STRUCTURES AND PHOTOCATALYTIC ACTIVITY OF CUO/SRTIO3

SAYONARA ANDRADE ELIZIARIO NUNES[1]; RUTH H. G. A. KIMINAMI[1]; SANTIGO J. A. FIGUEIROA[2].
1.UFSCAR, SAO CARLOS - SP - BRASIL; 2.CNPEM/LNLS, CAMPINAS - SP - BRASIL.

Palavras-chave: XAFS;PHOTOCATALYSIS;RIETVELD

Resumo:

The heterostructured photocatalyst was prepared by hydrothermal method, in which cooper and strontium nitrates solutions were added separately into sodium hydroxide solution, according to specific molar ratio. The morphology and structure of the as-prepared individual phases and heterostructured samples were characterized by XRD, SEM, HRTEM and EXAFS. The experimental results revealed that the samples have phases with good crystallinity, monoclinic CuO (JCPDS no. 21-1276) and cubic SrTiO3 (JCPDS no. 41-1049). A quantitative phase analysis using the Rietveld method confirmed the same proportions for the two phases on the sample. Thus, the successful sample one-step preparation and good homogeneity of the material by hydrothermal method become evident. The surface morphologies of the as-synthesized photocatalysts displayed nanoparticles uniformly distributed throughout the sample with plates and cubic shapes. These plates have an average width of about 250 nm and the cubics between 20 at 100 nm with good dispersity. The heterostructured photocatalyst shows high photocatalytic activity than your individual phases during the degradation of Methyl Orange. By means of this ex situ EXAFS experiments we were able to observe structural changes on this ST based materials. We found that the CuO/ST samples have of less disorder first oxygen neighbors and doping Cu second neighbors, this structural changes can ascribed as responsible for the differences on photocatalytical activity.

DEFECT STRUCTURE AND LUMINESCENCE MECHANISM OF CDSIO3 DETERMINED BY EXAFS, XANES AND XEOL

ZELIA SOARES MACEDO[1]; CAROLINA MELO DE ABREU[1].

1.UNIV. FEDERAL DE SERGIPE, ARACAJU - SE - BRASIL.

Palavras-chave: EXAFS;XANES;XEOL

Resumo:

The defect structure and luminescence of cadmium silicate ($CdSiO_3$) were studied by a combination of EXAFS, XANES and XEOL measurements (Proposals XAFS2-9349/15177/15233). $CdSiO_3$ is a phosphorescent material of high technological interest, with potential applications in areas such as emergency lights, opto-electronic devices and coating of ceramic tiles for radiodiagnostic rooms. In this work, $CdSiO_3$ was produced by sol-gel route. The samples were doped with transition metals (Mn, Ni, Cr, Zn, Fe, Co, Cu) and rare earths (Gd, Tb). Characterization by XEOL in normal and single bunch modes and also by EXAFS and XANES were performed for pure and doped samples. The XEOL spectra presented broad bands at 420, 496 and 590 nm with relative intensities that depend on the dopant and pH. From the EXAFS results, it was concluded that the dopants substitute Cd sites. To understand the charge compensation, the valence of the dopants inserted in the host matrix was investigated by XANES. It was observed that the ions Ni, Zn, Co and Cu assume the valence 2+, while Cr, Gd and Tb present the oxidation number 3+ and Mn and Fe have a mixing of 2+ and 3+ states when inserted in $CdSiO_3$. Lifetime measurements were performed in single-bunch mode and revealed the existence of a fast decay component in the long-lasting emission of $CdSiO_3$. Gathering all the results it was possible to tailor the properties as to obtain phosphorescent materials with violet, blue, green, orange and white emission.

LOCAL ENVIRONMENTS OF FE AND NI IN (FE0.5NI0.5)90ZR7B3 MECHANICALLY ALLOYED

VÍCTOR ANTONIO PEÑA RODRÍGUEZ[1]; JUSTINIANO QUISPE MARCATOMA[2]; JOSE MEDINA MEDINA[1]; CHACHI ROJAS AYALA[2]; ELISA MARIA BAGGIO-SAITOVITCH[3].

1.UNIVERSIDAD NACIONAL MAYOR DE SAN MARCOS, LIMA - PERU; 2.CENTRO BRASILEIRO DE PESQUISAS FISICAS, RIO DE JANEIRO - RJ - BRASIL; 3.CENTRO BRASILERIO DE PESQUISAS FISICAS, RIO DE JANEIRO - RJ - BRASIL.

Palavras-chave: EXAFS;MECHANICAL ALLOYING;NANOCRYSTALLINE ALLOYS

Resumo:

During the milling process, Fe and Ni local environments and magnetism in mechanically alloyed $(Fe_{0.5}Ni_{0.5})_{90}Zr_7B_3$ powders (Nanoperm type) were systematically investigated using Extended X-ray Absorption Fine Structure (EXAFS), ^{57}Fe Mössbauer Spectroscopy, X-ray diffraction, and Vibrating Sample Magnetometer. Fe-edge and Ni-edge EXAFS results suggest that the milled-end sample (30 h-sample) shows a new chemical short-range order (CSRO) around Fe and Ni atoms. Conversely, the constant low fluctuation of the interatomic distances from Fe and Ni absorbing atoms, inside the first coordination shell, reflects no changes on the topological short range order (TSRO) for all milled samples. EXAFS, Mössbauer data and X-ray diffraction results suggest that the milled end-sample consists of nanostructured fcc FeNi ferromagnetic solid solution and the changes of the lattice parameters are due to the presence of Zr and B atoms.

The magnetization measurement show that the behavior of the milled-end sample corresponds to a soft ferromagnetic phase.

LUMINESCENCE IN NANOSTRUCTURED CERAMIC SCINTILLATORS

VERÔNICA DE CARVALHO TEIXEIRA[1]*; MARIO ERNESTO GIROLDO VALERIO*[1]*.*

1.UFS, SÃO CRISTÓVÃO - SE - BRASIL.

Palavras-chave: Scintillators;luminescence lifetime decay;aluminosilicate

Resumo:

Pure, doped and co-doped with Ce, Eu, Mn samples of $Ca_2Al_2SiO_7$ (CAS) were produced using a hybrid methodology that combines proteic sol-gel and solid state methods. Powder XRD results confirmed that only the CAS phase was produced and TEM analysis indicated that nanoparticles were obtained. XANES results proved that the most abundant valences of dopants were identified as Ce^{3+}, Eu^{3+} and Mn^{2+}. XEOL and PL emission spectra showed typical transitions associated to the dopants.

The luminescence lifetime decay was measured for all samples using the single bunch operation mode at LNLS. The results indicated that the samples doped with Ce, Ce and Eu and Ce and Mn exhibit more than 90% of total luminescence associated with a decay time constant smaller than 40 ns. Samples doped with Eu^{3+} and Mn^{2+} have longer decay time constants, however samples co-doped with Eu and Mn have a characteristic decay time shorter than the singled doped samples. Results in the literature reports that the Ce and Mn or Eu and Mn co-doped samples presented quite long and persistent luminescence and that was attributed to the d-d transitions of Mn, but in the present work CAS:CeMn nanoparticles exhibited quite shorter decay time constant. An interesting feature of the co-doped CAS is the possibility produce scintillators with tunable spectra. The CAS:CeMn samples has two large emission bands, the first one associated to the Ce^{3+}, from 350 up to 510 nm, and the second one, related to Mn^{2+}, from 530 to 730 nm.

GRAPHICAL USER INTERFACE FOR MODELING GRAZING INCIDENCE XRF (GI-XRF) DATA: A NEW TOOL USED AT THE XRF BEAMLINE OF THE BRAZILIAN SYNCHROTRON LIGHT LABORATORY

VANESSA ISABEL TARDILLO SUAREZ[1]*; CARLOS A PÉREZ*[1]*; EDUARDO XAVIER SILVA MIQUELES*[1]*; CLAUDIA RODRIGUEZ TORRES*[2]*.*

1.LNLS, CAMPINAS - SP - BRASIL; 2.UNIVERSIDAD NACIONAL DE LA PLATA, LA PLATA - ARGENTINA.

Palavras-chave: GIXRF;TXRF;modeling

Resumo:

A Graphical User Interface (GUI) using a code, written in Python, has been developed for simulating Grazing Incidence X-Ray Fluorescence (GI-XRF) Data for layered thin films. Perfectly sharp interfaces have been considered although interfacial diffusion and roughness can be included as well. Initial tests showed that our code is in a good approximation with experimental data. Previous results were presented in Praga**[1]**, as well as in Osaka**[2]** where simulations involving Co-doped SnO_2 thin films deposited on $LaAlO_3$ (LAO) were calculated in order to study thickness-dependent distribution of Co metal ions. In this work we present GI-XRF simulations for a set of samples measured at the XRF beamline of the Brazilian Synchrotron Light Laboratory.

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CHARACTERIZATION OF LILA(XO4)2:ND3+ (X = MO, W) MICROCRYSTALS GROWN BY THE MICRO-PULLING DOWN TECHNIQUE

JAIR RICARDO DEMORAES[1]; SONIA LICIA BALDOCHI[1].

1.INSTITUTO DE PESQUISAS ENERGÉTICAS E NUCLEARES - IPEN, SÃO PAULO - SP - BRASIL.

Palavras-chave: FIBRAS MONOCRISTALINAS;FLUORESCENCIA R-x;TERRAS RARAS

Resumo:

The growth and characterization of $LiLa(XO_4)_2$:Nd^{3+} (X = Mo, W) microcrystals as single crystal fibers was studied for future laser development. Materials with two or more constituent cations, that present superposed X-ray fluorescence energies, cannot be accurately quantified by the traditional energy dispersion X-ray spectroscopy (EDX). This is the case of the energy lines of Nd^{+3} and La^{+3} ions on the Nd:LLX host. For this reason, the real concentration along the Nd:LLX single crystal fibers were evaluated by a synchrotron X-ray fluorescence microprobe system (μ-XRF). The undoped and Nd-doped LLX crystalline fibers were grown by the micro-pulling-down technique (μ-PD). Nd:LLX powders were obtained by the appropriate mixtures of both $LiLa(XO_4)_2$ (LLX) and $LiNd(XO_4)_2$ (LNX). The content of neodymium is described by the following relation: $LiLa_{1-x}Nd_x(XO_4)_2$ with x = 0.01, 0.02, 0.05 and 0.10. The μ-XRF experiments were performed in an X-ray Fluorescence beam line at LNLS, Campinas, Brazil, using a monochromatic beam for sample´s excitation. In this case, the selective energy excitation of Nd absorption edge reduces the overlapping of the fluorescence lines of La and Nd, allowing a more accurate determination of the incorporated dopant. The collected data analyzed with the PyMca software available at LNLS. The results showed that the LLM host supports the doping by Nd ions without strong segregation and its distribution is quite homogeneous along the fiber length.

STUDY OF DEFECT IN LI DOPED ZNO NANOWIRES TO ELUCIDATE THE ORIGIN OF INTRINSIC MAGNETISM.

SILVIA PEREZ PEREZ DE HELUANI[1]; BENJAMIN STRAUBE[1]; CLAUDIA RODRIGUEZ TORRES[2]; MANUEL VILLAFUERTE[1].

1.UNIVERSIDAD NACIONAL DE TUCUMAN, TUCUMAN - ARGENTINA; 2.UNIVERSIDAD DE LA PLATA, LA PLATA - ARGENTINA.

Palavras-chave: nanowires;ZnO;doped

Resumo:

Here we report structural characterization, X rays absorption, structural and luminescence measurements in Li doped ZnO nanowires and microwires (Fig.1). The nanowires (Nws) were grown on Si/SiO2 substrates, without catalyst, by simple carbothermal evaporation of ZnO. The microwires (Mws) were prepared by carbothermal process. The studied Nws have a diameter between 50nm and 130nm and the Mws between 80 and 150 mu m. To the aim of study the nature of defects and obtain evidence of hole doped in ZnO, X-ray absorption ne structure data were collected at the Zn K edge, 9659 eV (Fig.2). The measurements were carried out in fluorescence mode at the XRF Fluorescence beamline of the LNLS (Campinas, Brazil). A monochromatic X-ray beam of 9.7 keV in transmission mode was used.

Spectroscopy techniques were combined with luminescence measurements to elu-cidate, considering the defects influence in electronic structure and local environment of Zn ions, the relationship between defects, structure and doped.

The characterization of the local environment of impurities (coordination, distances to nearest neighbors, valence state, etc) is vital to approach the understanding of the problem. These data will be used as a basis for theoretical simulations by FDMNES code. We found a correlation between the increase of intrinsics defects (Zn and O vacancies) and the content of Li in both, Nws and Mws.

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March 11th and 12th, 2014

Abstracts

X-ray Diffraction (XRD)

STRUCTURE AND MORPHOLOGY OF CUO NANOWIRES PRODUCED BY RESISTIVE HEATING

ALEJANDRO ZUNIGA[1]; DENISE CRIADO[1].

1.UFABC, SANTO ANDRE - SP - BRASIL.

Palavras-chave: Electron Microscopy;Nanowires;Copper Oxide

Resumo:

In this work we report the formation of copper oxide nanowires via oxidation using a fast and low-cost technique: resistive heating. Copper wires were resistively heated for different times and electrical currents in air, resulting in the formation of copper oxide nanowires due to the oxidation of the copper surface. The nanowires were characterized using electron microscopy, which indicated that the electrical current played an important role on the morphology and density of the copper oxide nanowires.

ÓXIDO DE CÉRIO COMO PADRÃO DIFRATOMÉTRICO PARA DETERMINAÇÃO DA LARGURA INSTRUMENTAL

ANDERSON MARCIO DE LIMA BATISTA[1]*; FÁTIMA ITANA CHAVES CUSTÓDIO MARTINS*[1]*; JOSÉ MARCOS SASAKI*[1]*.*

1.UNIVERSIDADE FEDERAL DO CEARÁ, FORTALEZA - CE - BRASIL.

Palavras-chave: Material Padrão de Referência;Óxiso de cério;Difração de raios X

Resumo:

O uso de Materiais Padrão de Referência (Standard Reference Material - SRM) em difração de raios X é sumamente importante para ter-se uma boa caracterização. Em todas as medidas feitas em um difratômetro de raios X é necessário retirar de seu difratograma o valor da largura intrumental. Essa largura é determinada com o uso de SRM's. Atualmente, o hexaboreto de lantânio é usado como SRM com essa finalidade. Neste trabalho propõe-se o uso do óxido de cério como material padrão para determinação da largura intrumental dos difratômetros. Algumas das principais características do SRM são: partículas com dimensões da ordem de µm, homogêneo e baixa microdeformação. Tamanhos dessa ordem produzirão picos de difração com largura a meia altura estreita, de tal modo, que essa largura represente a largura do instrumento. Tanto os perfis dos picos de difração quanto suas larguras estão associados aos efeitos instrumentais (divergência, fendas, dispersão espectral e etc.). Considerando esses efeitos, o uso de uma fonte síncrotron é adequada para a caracterização de um SRM, tendo em vista a alta intensidade proveniente de tal fonte de radiação, um vasto espectro em energia e baixa divergência do feixe, que são características essenciais para uma boa caracterização das partículas. O óxido de cério foi sintetizado a partir de sulfato de cério tetrahidratado e apresentou características compatíveis com as de um SRM. O autor realizou as medidas durante o mestrado sob a proposta XRD1-14557.

STRUCTURAL STUDY OF LIQUID SURFACES USING LANGMUIR TROUGH AT LNLS

CARLOS EDUARDO PINHEIRO VIEIRA[1]; XIMENA ELIZABETH PUENTES MARTINEZ[1]; ANTONIO AUGUSTO MALFATTI GASPERINI[2]; LEIDE PASSOS CAVALCANTI[3].

1.UNIVERSIDADE FEDERAL DE SÃO PAULO, SÃO JOSÉ DOS CAMPOS - SP - BRASIL; 2.EUROPEAN SYNCHROTRON RADIATION FACILITY, GRENOBLE - FRANÇA; 3.LABORATÓRIO NACIONAL DE LUZ SÍNCROTRON, CAMPINAS - SP - BRASIL.

Palavras-chave: Langmuir trough;grazing incidence synchrotron techniques;beam deflector

Resumo:

Liquid surfaces and interfaces such as Langmuir and Langmuir-Blodgett films, wetting films and polymer films have been intensively studied in different domains like pharmaceutical, electronics, food and paintings. Surface sensitive techniques like grazing-incidence diffraction (GID), X-ray reflectivity (XRR) and grazing-incidence small-angle X-ray scattering (GISAXS) are powerful tools to investigate the molecular structure of surfaces and interfaces. This work shows the status of an experimental setup for grazing incidence synchrotron techniques that is in construction at XRD2 beamline at LNLS. The main idea is to insert new optical elements at the experimental hutch, and a Langmuir trough for studying Langmuir monolayers in situ. It will be necessary to deflect the incoming beam downward for studies at the liquid surfaces. Generally, a mirror or a monochromator is used to deflect the beam and the choice depends on the deflection angles required on specific studies. Given this point of view, 600 nm platinum-coated mirror was produced in order to get small incident angles about 0,2° in liquid surface. Platinum has an excellent reflectivity between the energy interval of 5 – 11 keV. An apparatus was designed to support and to move the mirror and is composed of positioning devices, two linear-stages and one 2-circle-segment. In combination with a beam deflector, the Langmuir trough will be integrated on the beamline electronics for automation and control of Langmuir monolayers.

SYNCHROTRON RENNINGER SCANNING AS A PROBE OF STRUCTURAL CHANGES IN DOPED NSH SINGLE CRYSTALS

CLÁUDIO MÁRCIO ROCHA REMÉDIOS[1].

1.UFPA, BELEM - PA - BRASIL.

Palavras-chave: X-ray;multiple diffraction;Doping of crystals

Resumo:

Doping of single crystals are processes often employed to alter the physical properties, widening their use in many technological applications. Small structural changes induced by doping can be hard to detect and, therefore, characterization methods susceptible to such small changes are of great importance. X-ray multiple diffraction provides a physical tool for invariant phase measurements. Intensity profiles provide information on invariant phases, while angular positions of the multiple diffractions allow accurate determination of lattice parameters. In this work X-ray multiple diffraction has been applied to study the substitutional incorporation of Mg^{2+} ions into NSH crystals (nickel sulfate hexahydrate: $NiSO_4.6H_2O$). By increasing the atomic disordering only of O^{2-} sites in model structures of doped NSH, the sense and magnitude of induced phase shifts match those necessary to justify the observed changes in the intensity profiles. Causes of disordering and lattice parameter variation are discussed. Although the amount of extra oxygen disordering are relatively large regarding the small difference in ionic radii of metallic ions.

TUNING THE SURFACE MAGNETIC ANISOTROPY IN CR,FE-DOPED NIO NANOPARTICLES

CRISTIANO TELES MENESES[1]; KAROLINE OLIVEIRA MOURA[2]; RODRIGO JOSE SILVA LIMA[3]; JOSE GERIVALDO SANTOS DUQUE[4].

1.DEPARTAMENTEO DE FÍSICA - UNIVERSIDADE FEDERAL DE SERGIPE, ITABAIANA - SE - BRASIL; 2.INSTITUTO DE FISICA GLEB WATAGHIN - UNIVERSIDADE ESTADUAL DE CAMPINAS, CAMPINAS - SP - BRASIL; 3.UNIDADE ACADÊMICA DE FÍSICA - UNIVERSIDADE FEDERAL DE CAMPINA GRANDE, CAMPINA GRANDE - PB - BRASIL; 4.UNIVERSIDADE FEDERAL DE SERGIPE, ITABAIANA - SE - BRASIL.

Palavras-chave: Surface Anisotropy;Nanoparticles;Magnetic Properties

Resumo:

In this work, we have used studied the magnetic and structural properties of obtain Cr,Fe-doped NiO nanoparticles (for dfferent doping concentrations) obtained the co-precipitation method. X-ray diffraction analyses using Rietveld refinement show a slightly decreasing in the microstrain and mean particle size as function of the doping. Transmission electronic microscopy images show that particles change the morphology from a shape faceted to nanorod-like with increasing of doping. X-ray photoelectron spectroscopy (XPS) analyses show an increasing of the amount of Fe^{3+} with increasing of emission angle, indicating that the surface particle present a more amount of Fe^{3+} than the Fe^{2+}. The Zero-Field-Cooling and Field-Cooling (ZFC-FC) magnetization curves show a superparamagnetic behavior at high temperature and low temperature peak (at T = 10 K) which is enhanced with increasing of the doping concentration. An unusual behavior of the coercive field was also observed. We argue that these behaviors can be linked with the strengthening of surface anisotropy caused by the incorporation of doping ions. Based on the magnetizations results, the core particle present a spin configuration like-antiferromagnetic and the composition on the particle surface close to ferrimagnetic strucuture. Besides we have observed the exchange Bias phenomenon at low temperature region which can be associated to the interaction between the core (AF) and the shell (FM). (CNPq, FAPITEC-SE)

IN-SITU CHARACTERISATION AND CATALYTIC TESTING OF CO AND PD PROMOTED TUNGSTEN CARBIDE CATALYSTS

DEAN H BARRETT[1]; CRISTIANE B RODELLA[1]; LUIZ A SANTAROSA[1]; GLAUCO F LEAL[1].
1.LNLS, CAMPINAS - SP - BRASIL.

Palavras-chave: catalysis;in-situ x-ray dirffraction;promoted tungsten carbide

Resumo:

Transition metal carbides are obtained when carbon atoms are incorporated into transition metal interstitial sites. It has been shown that these tungsten carbide catalysts can be used to convert cellulose which is the most abundant source of biomass into value added products which presents great potential for sustainable production of fuels and chemicals. In-situ PXRD studies of the effects of Pd and Co promoters on tungsten carbide catalysts showed the promoters effect not only the temperature that carburization occurs but also the phase of tungsten carbide that occurs. Carburization temperatures decreased in the following series non-promoted > Pd > Co. The non-promoted carburization produced both W_2C and WC phases. These phases were also present in the Pd promoted catalyst but absent in the Co promoted case. The Co promoter not only produced a phase pure W_2C but was also able to perform the carburization at the lowest temperature, some 110°C lower than the catalyst produced without a promoter. Both Ni and Pd promoters were able to lower the carburization temperature and formed a mixture of W_2C and WC phases with the Pd promoter being the only one of the promoters identifiable in the PXRD scans. This may imply that the Pd is present in the catalyst in a different manner to that of the Co promoter. Co was found to be the best promoter as it acts to lower the carburization temperature while producing a phase pure product of W_2C which is the most active tungsten carbide phase.

STRUCTURAL AND TRANSPORT PROPERTIES OF NANOSTRUCTURED CATHODES FOR INTERMEDIATE-TEMPERATURE SOLID-OXIDE FUEL CELLS

DIEGO GERMAN LAMAS[1]; LEANDRO MARCELO ACUÑA[2]; AUGUSTO ENRIQUE MEJÍA GÓMEZ[3]; MARÍA BELÉN VIGNA[4]; EDUARDO QUEZADA LÓPEZ[4]; JOAQUÍN SACANELL[3]; MARCIA CARVALHO DE ABREU FANTINI[5].

1.CONICET-UNIVERSIDAD NACIONAL DEL COMAHUE, NEUQUÉN CAPITAL - ARGENTINA; 2.CINSO-UNIDEF-CITEDEF-CONICET, VILLA MARTELLI - ARGENTINA; 3.DEPARTAMENTO DE FÍSICA DE LA MATERIA CONDENSADA, CAC-CNEA, SAN MARTÍN - ARGENTINA; 4.UNIVERSIDAD NACIONAL DEL COMAHUE, NEUQUÉN CAPITAL - ARGENTINA; 5.INSTITUTO DE FÍSICA-UNIVERSIDADE DE SÃO PAULO, SÃO PAULO - SP - BRASIL.

Palavras-chave: SOFC cathodes;Nanomaterials;cobaltites

Resumo:

Fuel cells are one of the most promising technologies for environmentally-friendly and high-efficiency power generation. Among them, solid-oxide fuel cells (SOFCs) have the unique capability to use different fuels such as hydrocarbons or hydrogen. However, several issues have to be overcome in order to reduce the operation costs. The reduction of their high operating temperatures, typically around 900-1000ºC, is one of the most important ones. For this reason, extensive research work has been conducted in order to find novel materials to produce SOFCs capable to work at intermediate temperatures (IT-SOFCs). Cathodes based on mixed ionic/electronic conductors (MIECs) have received great attention because the active sites for the oxygen reduction reaction extend the whole surface of the cathode, while in conventional electronic conducting materials it only takes place in the [oxygen/cathode/electrolyte] triple phase boundaries (TPBs).

In the last years, our research group proposed a novel family of high-performance cathodes based on nanostructured MIECs, mainly cobaltites and cobalto-ferrites of perovskite-type structure, dramatically increasing the number of active sites. In this work, we present high-temperature XPD and XANES studies on nanostructured MIEC cathodes, under operating conditions, and correlate them with the transport and electrocatalytical properties. In particular, we will discuss the retention of the high-performance cubic phase in nanocrystalline cobaltites.

CHARACTERIZATION OF ANTIMALARIAL OLIGONUCLEOTIDE/CATIONIC NANOEMULSION COMPLEXES BY MEANS OF ENERGY DISPERSIVE X-RAY DIFFRACTION

FERNANDA BRUXEL[1]; ÂNGELO MALACHIAS[2]; CARLOS A PÉREZ[3]; ROGÉRIO MAGALHÃES-PANIAGO[2]; MÔNICA CRISTINA OLIVEIRA[2]; HELDER FERREIRA TEIXEIRA[4].

1.UNIPAMPA, URUGUAIANA - RS - BRASIL; 2.UFMG, BELO HORIZONTE - MG - BRASIL; 3.LNLS, CAMPINAS - SP - BRASIL; 4.UFRGS, PORTO ALEGRE - RS - BRASIL.

Palavras-chave: nanoemulsion;oligonucleotide;EDXD

Resumo:

Antisense oligonucleotides (ON) targeting P. falciparum topoisomerase II seem to be an interesting strategy against malaria. Due to the low stability and intracellular penetration of free ON, cationic nanoemulsions (NE) have been proposed for the delivery of this kind of molecules, inhibiting parasite growth (up to 80%), causing a delay in the P. falciparum life cycle. The structural characterization of the NE/ON complexes still remains poorly studied and understood. In this study, NE were complexed to ON in various [+/-] charge ratios. The final complexes were characterized (droplet size and zeta potential) and their structural organization was investigated by energy dispersive X-ray diffraction (EDXD). Both NE and NE/ON complexes displayed a mean droplet size in the 200-300 nm range (PDI < 0.2). NE exhibited a highly positive zeta potential (+50 mV), which inverted to negative values (-20 mV) after ON complexation. In EDXD experiments, blank NE presented well-defined diffraction peaks, corresponding to a lamellar structure organization of the dispersed system (lattice spacing of 63 Å). The lamellar organization was maintained in NE/ON complexes. However, ON provoked the disorganization of the lipid arrangement and the increase in the lamellar periodicity (82.7Å) of blank NE. These findings lead us to suppose that ON may be inserted in the lamellar arrangement, expanding the lattice spacing at high concentrations.

ACKNOWLEDGMENTS: LNLS (XRF 11751) and CAPES/COFECUB (540/06).

THE EFFECTS OF CE AND Y DOPPING IN A CA2MNREO6 DOUBLE PEROVSKITE

JANAINA BASTOS DEPIANTI[1]; MARCOS TADEU D'AZEREDO ORLANDO[1]; ARTHUR SANTANA CAVICHINI[1].
1.UNIVERSIDADE FEDERAL DO ESPÍRITO SANTO, VITORIA - ES - BRASIL.

Palavras-chave: double perovskite;XANES;XRD

Resumo:

We have studied the effects of Ce and Y dopping in Ca-site of Ca_2MnReO_6 double perovskite up to 10% and 15% respectively. The Rietveld refinement of X-ray diffraction pattern showed a change in the lattice parameters of the doped without change in the space group $P2_1/n$. The X-ray Absorption Near Edge (XANES) spectra at the Mn K-edge and the Re L_3-edge showed a non-integer valence for Mn and Re in all samples. The Mn average valence was +2.3. It was invariant for all samples. The Re average valence decrease with the Y content. Taken into account that the Mn average valence was invariant for all samples, the frustration temperature shift was associated with the values for Re average valence.

We thank LNLS for concession of beamlines (XRD1 and XAFS1 #5441 and DXAS #9195).

CHARACTERIZATION OF CAF2/SI(111) THIN FILMS BY SYNCHROTRON X-RAY DIFFRACTION AND HIGH-RESOLUTION TRANSMISSION ELECTRON MICROSCOPY

JEFFERSON SUELA[1]; EDUARDO ABRAMOF[2]; PAULO H O RAPPL[2]; SUKARNO O FERREIRA[3]; JOAQUIM P GOMES[1]; ÂNGELO MALACHIAS[4].

1.DEPARTAMENTO DE FÍSICA, INSTITUTO FEDERAL DE EDUCAÇÃO, CIÊNCIA E TECNOLOGIA DO NORTE DE MINAS GERAIS, JANUARIA - MG - BRASIL; 2.LABORATÓRIO ASSOCIADO DE SENSORES E MATERIAIS, INSTITUTO NACIONAL DE PESQUISAS ESPACIAIS, SÃO JOSÉ DOS CAMPOS - SP - BRASIL; 3.DEPARTAMENTO DE FÍSICA, UNIVERSIDADE FEDERAL DE VIÇOSA, VIÇOSA - MG - BRASIL; 4.DEPARTAMENTO DE FÍSICA, UNIVERSIDADE FEDERAL DE MINAS GERAIS, BELO HORIZONTE - MG - BRASIL.

Palavras-chave: Calcium Fluoride;GID;HRTEM

Resumo:

This work reports on the structural characterization of calcium fluoride thin films by synchrotron x-ray diffraction in co-planar and grazing incidence diffraction (GID) configurations, high-resolution transmission electron microscopy (HRTEM) and transmission electron diffraction were also used to characterize the samples. The films (10 and 30 nm thick) were grown by molecular beam epitaxy on [111]-oriented Si substrates at temperatures from 400 to 700 °C. The x-ray measurements were performed at the XRD2 beam line of LNLS, while transmission electron diffraction and HRTEM characterization were made at the LNNano facilities using a model JEN 3010 URP transmission electron microscope. Omega-2theta scans in co-planar configuration around (111) diffraction Bragg peak indicated that calcium fluoride films grown at 400 and 450 °C temperatures are almost fully relaxed, while films grown at substrate temperatures higher than 500 °C accumulated all or part of the thermal strain. According to omega-2theta scans in grazing incidence diffraction configuration, the (2-20) calcium fluoride Bragg splits into two peaks. This splitting is more evident for higher growth temperatures or thicker layers. Transmitted electron diffraction showed rotated crystallites inside the calcium fluoride layers that were clearly seen in a high-resolution transmission electron microscopy image. The splitting of the (2-20) calcium fluoride diffraction peak is probably due to these rotated crystallites.

MINERAL COMPOSITION ANALYSIS OF URINARY STONES BY X-RAY MICROTOMOGRAPHY AND X-RAY POWDER DIFFRACTION

LETICIA KUPLICH[1]; MARCOS VINICIUS COLAÇO[1]; LIEBERT PARREIRAS NOGUEIRA[1]; FANNY NASCIMENTO COSTA[2]; DELSON BRAZ[2]; RAFAEL ARRUDA PINTO[3]; FABRICIO BORGES CARRERETTE[3]; ROOSEVELT DROPPA JUNIOR[4]; REGINA BARROSO[1].

1.UERJ/ DFAT, RIO DE JANEIRO - RJ - BRASIL; 2.LABORATÓRIO DE INSTRUMENTAÇÃO NUCLEAR/COPPE/UFRJ, RIO DE JANEIRO - RJ - BRASIL; 3.SERVIÇO DE UROLOGIA, HOSPITAL UNIVERSITÁRIO PEDRO ERNESTO/UERJ, RIO DE JANEIRO - RJ - BRASIL; 4.CENTRO DE CIÊNCIAS NATURAIS E HUMANAS/ UFABC, SÃO PAULO - SP - BRASIL.

Palavras-chave: XRPD;Urinary calculi;micro-CT

Resumo:

In this work microtomography (μ-CT) and Synchrotron X-ray powder diffraction (XRPD) was used to study the phase composition of human urinary calculi. The stones were collected from Department of surgical specialty (Service of Urology) of Pedro Ernesto Memorial Hospital, State University of Rio de Janeiro - UERJ, Brazil

Computed microtomography (μ-CT) is an imaging technique that allows volumetric measurements of attenuation of X-rays for non-destructive evaluation of materials. The images were obtained using an X-ray source geometry with "cone-beam" at the TOMOLAB station of Elettra Synchrotron Facility, Trieste, Italy. It is equipped with a microfocus sealed tube ensures that a focal point of at least 5 microns. Due to geometry "cone-beam", it is possible to reach a spatial resolution near the size of the focal point.

Synchrotron XRPD data were collected at the Brazilian Synchrotron Light Laboratory (LNLS), under approval research proposal 14521. Measurements were carried out with λ = 1.2398 Å (E=10 keV) and diffraction patterns were collected in the 2θ region ranging from 8º to 80º, with step scans of 0.005º and counting time of 100 s/step and were recorded by a linear detector (Mythen1K). Rietveld refinements of the XRPD data was performed using GSAS software and EXPGUI package. Our preliminary results showed that the samples comprises many phases (multiphase), such as hydroxyapatite, struvite, uric acid and calcium oxalate monohydrate.

ESTIMATION OF MEAN CRYSTALLITE SIZES OF XRD STANDARD REFERENCE MATERIALS PRODUCED AT IPEN BY XLPA

LUIS GALLEGO MARTINEZ[1]; RODRIGO UCHIDA ICHIKAWA[1]; KENGO IMAKUMA[1]; XABIER TURRILLAS[2]; MARCOS TADEU D'AZEREDO ORLANDO[3].

1.IPEN, SAO PAULO - SP - BRASIL; 2.ICMAB - CSIC, BARCELONA - ESPANHA; 3.UFES, VITÓRIA - ES - BRASIL.

Palavras-chave: Standard Reference Materials;Line Profile Analysis;Crystallite Sizes

Resumo:

Standard reference materials (SRM) are used to certify the alignment of diffractometers by calibrating peak positions and its shapes. SRM's are also used in X-ray Line Profile Analysis to correct the instrumental contribution to the experimental line breadth, which permits the determination of mean crystallite sizes and microstrains of materials. For this purpose the SRM must have a large crystallite size (generally greater than 300 nm) and almost zero or none microstrains. Since the profiles of the SRM are usually very narrow, the determination of its size are generally difficult to perform which leads to the application of the simplest XLPA method, the Scherrer method. However this method does not take into account a possible contribution of the microstrains. To overcome this problem the Single-Line method was applied to determine the mean crystallite sizes and microstrains of the SRM's Y_2O_3, CeO_2 and Al_2O_3 produced at IPEN to provide a more refined method to estimate size-strain of these standard reference materials. For this purpose a sample of LaB_6 SRM from NIST was used to correct the instrumental contribution since it presented the narrowest profile among the SRM's. The analysis was performed on synchrotron radiation data measured at the Brazilian Synchrotron Light Source - LNLS.

ANÁLISE QUÍMICA DO FILME FORMADO SOBRE O AÇO 441 QUANDO OXIDADO EM ALTAS TEMPERATURAS

MARIA DE FATIMA SALGADO[1].

1.UEMA, CAXIAS - MA - BRASIL.

Palavras-chave: oxidação ;aço ferritico 441;altas temperaturas

Resumo:

A pressão parcial de oxigênio da atmosfera pode afetar não só a cinética de oxidação, mas também as propriedades físicas e químicas dos filmes de óxidos formados sobre os aços inoxidáveis, sendo assim, importante conhecer o comportamento de oxidação dos aços inoxidáveis ferríticos a altas temperaturas em diferentes pressões parciais de oxigênio. O comportamento de oxidação do aço Inoxidável ferrítico, AISI 441, foi investigado em temperaturas entre 850 ^{o}C e 950^{o}C em atmosfera de Argônio, através de caracterização química e microestrutural dos filmes de óxidos formados. As amostras do aço utilizadas neste trabalho, com dimensões (0,5 x 0,5 x 0,6)mm, fornecidas pela ArcelorMittal Inox do Brasil, foram desbastadas com Lixas de carbeto de silício de granas 1000, 1200 e 2400. Posteriormente polidas, com pastas de diamante de granulometria 3 e 1 µm. apresentando um acabamento especular, Após polimento e limpeza com acetona em ultra-som, foi realizado tratamento de oxidação isotérmica em Termobalança, com sensibilidade de ± 1µg, com temperaturas variando de 850°C a 950°C, em atmosfera Argônio por um tempo de 50horas . Caracterização microestrutural e química dos filmes por Microscopia Eletrônica de Varredura (MEV), Espectroscopia de Energia Dispersiva (EDS). Utilizando-se a técnica de DRX, no LNLS, observou-se espectros, nos quais, os filmes crescidos sobre o aço AISI 441 apresentaram o Óxido de Cromo majoritariamente, seguido por espinélios manganês e ferro.

TUCANO: *in situ* temperature- humidity-controlled experiments using powder X-ray diffraction at LNLS

NUNES, R. S.1,2, FONTOURA, A. F. M.3, CANOVA, H. F.3, SCHERER, J. A.3, YOKAICHIYA, F.4, FRANCO, M. K. K. D.4, PAIVA-SANTOS, C. O.1, EVANS, J. S. O.2

1UNIVERSIDADE ESTADUAL PAULISTA - ARARAQUARA SP BRAZIL

2UNIVERSITY OF DURHAM - DURHAM UNITED KINGDOM

3LABORATÓRIO NACIONAL DE LUZ SÍNCROTRON - CAMPINAS SP BRAZIL

4INSTITUTO DE PESQUISAS ENERGÉTICAS E NUCLEARES - SÃO PAULO SP BRAZIL

Palavras-chave: Pharmaceuticals;In situ Relative humidity experiments;Chamber

Resumo:

Organic products such as pharmaceuticals are very susceptible to environmental conditions (temperature and relative humidity), process such as dehydration/rehydration is a constantly recurring situation, and in many cases, it is a reversible process that *ex situ* measurements are not effective at tracking. This work reports the design, construction and implementation of a chamber with temperature and humidity control for *in situ* X-ray powder diffraction (PXRD) experiments, called TUCANO. It combines features of available and inexpensive commercial devices with easy maintenance; the design of the sample holder support allows vertical translation in order to align the sample in the X-ray beam. The relative humidity is produced and controlled, inside the chamber, by a mixing gas flux of dry N2 and wet N2 (created by passing dry N2 through water at controlled temperature). In order to characterize the temperature behaviour in this furnace thermal distribution simulations were performed on the sample holder and data set of Al2O3 were collected and analysed with Parametric Rietveld refinement for sample temperature correction. As relative humidity behaviour depends of temperature, the maximum RH is limited by the temperature applied to the sample, thus a characterisation of this limitation was performed to determine the maximum RH applicable at each temperature. The furnace efficiency for RH *in situ* PXRD experiments is demonstrated from the deliquescence effect of NaCl.

STUDY OF THE MICROSTRUCTURE IN REMELTED ZIRCALOY BY SYNCHROTRON DIFFRACTION LINE PROFILE ANALYSIS

RODRIGO UCHIDA ICHIKAWA[1]; LUIS GALLEGO MARTINEZ[1]; LUIZ ALBERTO TAVARES PEREIRA[1]; KENGO IMAKUMA[1]; XABIER TURRILLAS[2].

1.NUCLEAR AND ENERGY RESEARCH INSTITUTE (IPEN/CNEN), SÃO PAULO - SP - BRASIL; 2.MATERIALS SCIENCE INSTITUTE OF BARCELONA (ICMAB/CSIC), BELLATERRA - ESPANHA.

Palavras-chave: Warren-Averbach Method;X-ray Line Profile Analysis;Zircaloy

Resumo:

Zirconium alloys, especially those known as Zircaloys, are extensively used both as fuel cladding and as core parts in PWR nuclear reactors. These alloys composed basically of Zr, Sn and minor contents of other elements, present good mechanical and corrosion properties allied to low thermal neutron absorption. In this work X-Ray Diffraction Line Profile Analysis was applied to study mean crystallite sizes and RMS microstrains in Zircaloy ingots produced by VAR (vacuum arc remelting) of machining chips generated in the fabrication of nuclear fuel elements for the Brazilian power reactors. The VAR remelted samples were also submitted to heat treatments in order to study changes in the microstructure, resulting in “as cast”, “annealed” and “quenched” samples. The X-ray diffraction measurements were performed using synchrotron radiation at the Brazilian Synchrotron Light Source (LNLS). The XRD line broadening was corrected by the deconvolution of the instrumental breadth from the experimental one by the Stokes method, using Y_2O_3 as standard sample. The Fourier space method of Warren-Averbach was used to determine the mean crystallite sizes and RMS microstrains from the corrected XRD profile. The results show the influence of heat treatments on the microstructures of the studied samples.

Acknowledgements: The autors acknowledge to CNEN for the scholarship of R. U. Ichikawa and to LNLS (Project number: D10B - XPD 11833)

INTERACTION OF NUCLEIC ACIDS WITH LIPID MONOLAYER USING X-RAY DIFFRACTION TECHNIQUES.

XIMENA ELIZABETH PUENTES MARTINEZ[1]; CARLOS EDUARDO PINHEIRO VIEIRA[1]; ANTONIO AUGUSTO MALFATTI GASPERINI[1]; LEIDE PASSOS CAVALCANTI[1].

1.BRAZILIAN SYNCHROTRON LIGHT LABORATORY, CAMPINAS - SP - BRASIL.

Palavras-chave: EPC/DOTAP/DOPE ;X ray diffraction ;Langmuir monolayers

Resumo:

Cationic lipids are of major interest as drug delivery systems of negatively charged drugs, proteins, biopolymers, genes, or the use of vaccines for prevention and treatment of infectious diseases. The insertion of a nucleic acid (DNA or RNA) in a target cell aiming at the production of a specific protein or the modification of metabolic pathways. Plasmid DNAs, different types of RNA (messenger, micro, silence) can be used, depending on the application. Liposomes composed of the ternary lipid composition of egg phosphatidylcholine (EPC), 1,2-dioleoyl-sn-glycero-3-phosphoethanolamine (DOPE) and 1,2-dioleeoyl-3-trimethylammonium-propane (DOTAP) have been successfully tested in vivo as DNA carriers against Hepatits B.

Despite the promising in vivo results, there is a lack of information about of the ternary EPC/DOTAP/DOPE interaction with plasmid DNA, which could help to improve the formulations. In this work, we study a system formed by nucleic acids and Langmuir monolayer of EPC/DOTAP/DOPE using thermodynamic methods and X ray diffraction techniques.

The X ray diffraction techniques on Langmuir monolayers are convenient in this case, plays an important role in determining the properties of the molecular structure and packing of the membrane with the flexibility of in situ sample preparation varying subphase composition and surface pressure.

STRUCTURAL STUDY OF CE0.9ZR0.1O2 NANOCATALYSTS UNDER REDOX CONDITIONS

MARIA GENOVEVA ZIMICZ[1]; FERNANDO DANIEL PRADO[1]; DIEGO GERMAN LAMAS[2]; SUSANA ADELINA LARRONDO[3].

1.IFISUR-CONICET, BAHÍA BLANCA - ARGENTINA; 2.CONICET Y UNCOMA, NEUQUÉN - ARGENTINA; 3.UNIDEF-CONICET, BUENOS AIRES - ARGENTINA.

Palavras-chave: XPD;REDOX PROCESS;CeO2-ZrO2

Resumo:

The aim of this work is to achieve a better understanding of the structural changes experienced by ZrO_2-CeO_2 mixed oxides under reducing and oxidizing conditions. Two samples, with $Ce_{0.9}Zr_{0.1}O_2$ nominal composition, were studied. One of them with low surface area and the other with high surface area (samples LS and GS respectively). In–situ X-ray powder diffraction (XPD) experiments using synchrotron radiation were performed in different atmospheres (5 mol%H_2/He, 5 mol% O_2/He, and 2mol% CH_4 – 4 mol% O_2 He balance) in the r.t to 900°C temperature range. XPD patterns were collected at the D10B-XPD beam-line of the Brazilian Synchrotron Light Laboratory (LNLS, Campinas, Brazil) using a high-intensity and low-resolution configuration, without crystal analyzer. The energy was set at 7997.43 eV and the X-ray wavelength was 1.55031 Å.

Sample LS did not show any structural change under the studied conditions. On the contrary sample GS showed cubic fluorite structure until 870°C, with a segregation of a new phase for temperatures up to 900°C. After the reoxidation treatments in 5mol% O_2this segregated phase disappeared at 750°C, recomposing the original cubic structure. Finally, during in-situ XPD studies in 2 mol%CH_4 – 4 mol%O_2 atmosphere, GS XPD pattern revealed a new peak centered at 26.5°, which appears at 450°C and could be assigned to graphitic carbon formed during methane oxidation.

Acknowledgements: To LNLS (proposal XRD1-14413), PIDDEFN°011/11 and ANPCyT (PICT 2010-0322).

PHASE IDENTIFICATION OF CU-IN ALLOYS WITH 45 AND 41.25 AT.% IN COMPOSITIONS

SILVANA SOMMADOSSI[1]; LAURA BAQUÉ[2]; GABRIELA AURELIO[2]; DIEGO GERMAN LAMAS[1]; SERGIO ARICÓ[3]; ALDO CRAIEVICH[4].

1.CONICET/UNCOMA, NEUQUÉN - ARGENTINA; 2.CONICET/CAB-CNEA, BARILOCHE - ARGENTINA; 3.CAC-CNEA/INST. SABATO, BUENOS AIRES - ARGENTINA; 4.INSTITUTE OF PHYSICS, UNIVERSITY OF SÃO PAULO, SAO PAULO - SP - BRASIL.

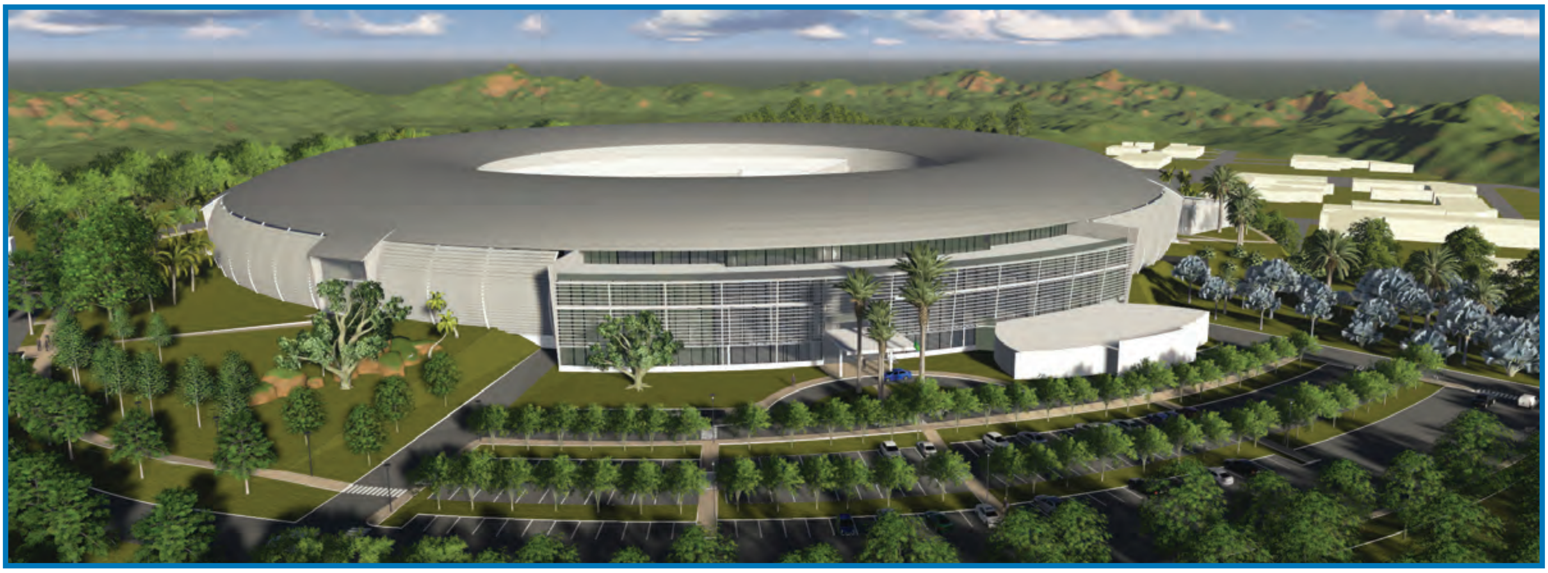
Palavras-chave: Intermetallic;Powder diffraction;Phase transitions

Resumo:

The Cu-In-Sn system has been intensively investigated for its use as a Pb-free solder in the electronic industry. Nevertheless, there are still some controversial regions in the Cu-In-Sn, Cu-In and Cu-Sn equilibrium phase diagrams. In this work, the thermal stability of Cu-In alloys with 45.0 and 41.2 at.% In nominal compositions was investigated by differential scanning calorimetry (DSC), scanning electron microscopy (SEM), wavelength dispersive spectroscopy (WDS) and in-situ synchrotron X-ray powder diffraction (S-XPD) over a temperature range from 25 up to 400 °C. The studied samples are mainly composed of a $Cu_{11}In_9$ phase together with minor amounts of the B phase and, in one of the samples, with pure In. No evidence of the $Cu_{10}In_7$ (41.2 at.% In) phase was detected, not even in the sample with 41.2 at.% In nominal overall composition. The combined use of the S-XPD and DSC techniques allowed us to identify two phase transitions involving the $Cu_{11}In_9$ phase, one of them corresponding to the B + $Cu_{11}In_9$ « h’ reaction at T = 290 °C and the other to the peritectic $Cu_{11}In_9$ « h’ + L reaction at T = 311 °C.

Abstracts

UV and Soft X-Ray Spectroscopy (EUV)



ZNO FILMS CHEMICALLY DEPOSITED ON STAINLESS STEEL WITH CONTROLLED MORPHOLOGY AND THICKNESS

ADRIANA RODRIGUES[1]; MARCUS VINICIUS CASTEGNARO[2]; MARIA DO CARMO MARTINS ALVES[2]; JONDER MORAIS[2].

1.UFRGS, VIAMAO - RS - BRASIL; 2.UNIVERSIDADE FEDERAL DO RIO GRANDE DO SUL, PORTO ALEGRE - RS - BRASIL.

Palavras-chave: Zinc oxide ; nanostructures;morphology

Resumo:

Zinc oxide (ZnO) is a direct wide band gap (3.37 eV) semiconductor that has attracted much interest in fundamental research due to its potential applications [1]. Considerable efforts have been devoted to design effective methods to synthesize ZnO films with well-defined controlled morphology using a variety of physical or chemical methods. A remarkable diversity of morphologies may be obtained simply by changing the reaction parameters and introducing organic additives. Several substrates have been tested, including stainless steel, which is an attractive option due to its high corrosion resistance, high conductivity, thermal stability and relatively good biocompatibility. ZnO deposited on stainless steel (ZnO/SS) has promising applications on electronic and optoelectronic devices, which have not been extensively explored. We report on the hydrothermal synthesis and characterization of nanostructured ZnO/SS films with controlled morphology and thickness, provided by changing the concentration of diaminopropane (DAP) in the reaction solution. The films were characterized with the XRD technique to study the crystal structure, while SEM and TEM provided details of the morphology of the anostructures. XPS allowed probing the chemical environment of the elements present on the surface of the sample. Our results corroborate the fact that the

STUDY OF CE3+ AND EU3+ EMISSION DOPANTS ON LILAP4O12 SCINTILLATOR

ADRIANO BORGES ANDRADE[1]; MARIO ERNESTO GIROLDO VALERIO[1].
1.UNIVERSIDADE FEDERAL DE SERGIPE, SAO CRISTOVAO - SE - BRASIL.

Palavras-chave: Scintillators;Luminescence;Sol-Gel route

Resumo:

The $LiLaP_4O_{12}$ (LLP) belongs to the family of $M_ILn\ (PO_3)_4$ (where M_I are alkali metal and Ln lanthanide ions) phosphates and the interest in these systems are due the optical properties when doped with rare earth ions. Phosphate compounds exhibit optical absorption edges at small wavelengths, as compared to oxides, and some of them are transparent in the ultraviolet region. La and Y based phosphates are interesting materials due to its excellent properties as fast or long response scintillators. . In this work, pure and doped LLP samples were produced via Sol-Gel route using polyvinyl alcohol (P.V.A) as the chelating agent. The material was pre-calcined at 500°C for 1h followed by calcination at 750°C for 4h. The emission and excitation spectra of the trivalent cerium and europium ions as dopants on $LiLaP_4O_{12}$ host were measured using excitation bellow and above the band gap of the LLP matrix. The characteristic decay time of the transitions were also measured for each transition, showed decay times of the order of ns and µs. The X-ray Excited Optical Luminescence (XEOL) is show and the dependence of the luminescence intensity whit the excitation energy, also were measurement the absorption spectra in broad gap region this material, which proved to be close to 7.0 eV.

Acknowledgments: INCT-inami, CNPq, LNLS and FAPITEC

ESTUDO DA FRAGMENTAÇÃO DA MOLÉCULA SF6 POR FOTOIONIZAÇÃO DE CAMADA INTERNA E CAMADA DE VALÊNCIA

ANDERSON HERBERT DE ABREU GOMES[1]; KATIANNE FERNANDES DE ALCANTARA[1]; ANTONIO CARLOS FONTES DOS SANTOS[1].

1.UFRJ, RIO DE JANEIRO - RJ - BRASIL.

Palavras-chave: Fotoionização;SF6;TOF

Resumo:

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 SF_6 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 à radiação cósmica e solar, é bastante interessante.

Neste trabalho, foram realizadas medidas de fragmentação da molécula de SF_6 pela técnica de Espectroscopia por Tempo de Voo (TOF - Time of Fligth), usando técnicas de coincidência simples (PEPICO) e múltipla (PEnPICO). Usando fótons num espectro de energia entre 20eV e 280eV, podemos analisar diversos fenômenos relacionados à fotoionização e excitação da molécula tanto em ressonâncias de camada interna (F 1s, S 2s e S 2p) quanto em camadas de valência. As medidas foram realizadas na linha SXS do Laboratório Nacional de Luz Síncrotron (LNLS).

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STUDY OF GRAPHENE ON IR(111) BY X-RAY PHOTOELECTRON SPECTROSCOPY AND DIFFRACTION

CAIO CÉSAR SILVA[1]; LUÍS HENRIQUE DE LIMA[1]; RICHARD LANDERS[1]; ABNER DE SIERVO[1]. 1.UNICAMP, CAMPINAS - SP - BRASIL.

Palavras-chave: Graphene;photoelectron diffraction;metal intercalation

Resumo:

Graphene has a whole set of fascinating properties like high mobility of relativistic charge carriers, ballistic transport, high mechanical strength, and ideal surface to mass ratio [1]. An alternative system that allows the study of these properties is quasi-free-standing graphene, i.e. graphene that preserves its properties even when it is supported by a substrate. Recent studies could demonstrate that Ir(111) does indeed allow for the preparation of extended graphene with high structural quality [2], and the band structure of graphene on Ir(111) is almost identical to the one of pristine graphene [3]. Metal intercalation between graphene and different substrates has been intensively used either to functionalize the electronic properties of graphene or to enhance the physical-chemical properties of the intercalating metal. The aim of this work is determine the structure of graphene on Ir(111) and Fe intercalation between epitaxial graphene and the Ir(111) substrate by X-ray photoelectron spectroscopy (XPS) and diffraction (XPD). The XPS and XPD experiments were carried out at the PGM beamline of LNLS and complementary STM measurements were performed at UNICAMP. The preliminary surface structure determination based in a comprehensive multiple scattering calculation approach will be presented.

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HIGH RESOLUTION VALENCE BAND PHOTOEMISSION SPECTRA OF MOO2 SINGLECRYSTALS

EDUARDO BONINI GUEDES[1]; MIGUEL ABBATE[1]; RODRIGO JOSÉ OCHEKOSKI MOSSANEK[1].
1.DEPARTAMENTO DE FÍSICA - UFPR, CURITIBA - PR - BRASIL.

Palavras-chave: Photoemisson;Valence Band;MoO2

Resumo:

Molybdenum ions can assume a valence ranging from 2+ to 6+, depending on the chemical environment it is inserted, allowing Mo atoms to form one of the biggest materials families known. One of the simplest members of this family is the molybdenum dioxide. The ideal MoO_2 bulk sample crystallizes in the TiO_2 (monoclinic) structure, presents weak paramagnetism and conventional metallic behavior. In this work, we report high-resolution valence band photoemission spectroscopy (PES) on MoO_2 singlecrystals. The measurements were performed in the PGM beamline, at Laboratório Nacional de Luz Síncrotron (LNLS, Campinas – SP, Brazil). The overall energy resolution was about 100meV with photon energy of 200eV. Liquid He and a cryostat were used to cool the chamber and control the temperature from 50K to room temperature (RT). The RT results show that the two-peak structure near the Fermi energy present in polycrystals, due to the x^2-y^2 and xy/xz orbitals, turned into a single-peak structure in the singlecystal sample spectrum. The detailed view of this peak reveals the presence of two features, addressed to the coherent and incoherent parts of the spectral function, which are not observed in other spectra found in the literature. As the temperature is lowered, the coherent/incoherent intensity ratio increases due to the decrease of quasiparticle scattering. Moreover, these high resolution experimental results indicate that many-body effects are indeed present in this compound.

SÍNTESIS Y CARACTERIZACIÓN DE PELÍCULAS DELGADAS DE ÓXIDO DE GRAFENO REDUCIDO OBTENIDAS POR LANGMUIR-BLODGETT

FACUNDO CARLOS HERRERA[1]; CECILIA DOS SANTOS CLARO[1]; JOSE RAMALLO LOPEZ[1]; GUSTAVO MORALES[2]; FELIX REQUEJO[1]; JOSE AVILA[3]; MARIA CARMEN AVILA[3]. 1.INIFTA-UNLP, LA PLATA - ARGENTINA; 2.UNRC, RIO CUARTO CORDOBA - ARGENTINA; 3.SYNCHROTRON SOLEIL,, SAINT-AUBIN - FRANÇA.

Palavras-chave: Oxido de grafeno;XPS;Langmuir Blodgett

Resumo:

El objetivo del presente trabajo es estudiar métodos de deposición de películas de óxido de grafito (GO) empleando la técnica de Langmuir-Blodgett (L-B) y posteriormente producir la reducción de la película empleando distintos métodos térmicos para obtener el óxido de grafito reducido (RGO). Finalmente, con el objetivo de caracterizar el RGO obtenido por los distintos métodos, las estructuras obtenidas son caracterizadas mediante espectroscopía fotoelectrónica de rayos X (XPS) con resolución espacial nanométrica, Difracción de rayos X en incidencia rasante (DRX), micro-Raman y microscopía de fuerza atómica (AFM). El GO se sintetizó mediante el método de Hummers, y se depositó sobre Si(100) empleando la técnica de L-B. Los depósitos se analizaron en la línea ANTARES del Sincrotrón SOLEIL, donde se estudió la evolución in-situ durante un tratamiento térmico en ultra alto vacío y en presencia de hidrógeno. Se estudiaron los films de GO en la línea DRX2 del Sincrotrón LNLS. Del análisis de los espectros Raman se aprecia una disminución de la banda D asociada a sitios defectuosos de la red. Se estudió el espesor de las láminas de GO previo y posterior al tratamiento(RGO), encontrándose para una lámina de RGO un espesor de 0,37±0,05nm, valor de espesor cercano al esperado para una lámina de grafeno. Los datos experimentales demuestran la posibilidad de realizar depósitos de GO por L-B y la eficiencia del proceso de reducción térmico para producir RGO con un nivel bajo de defectos

EXTREME UV FRAGMENTATION STUDY OF NOVEL CHEMICALLY HYBRID RESISTS FOR THE NEXT LITHOGRAPHY GENERATION

FELIPE KESSLER, FRANCINE R. SCHEFFER, VIKRAM TOMAR, SUBRATA GHOSH KEN E. GONSALVES AND DANIEL E. WEIBEL

Palavras-chave: Extreme UV fragmentation;chemically hybrid resists;lithography

Resumo:

MAPDST homopolymer, and copolymers were studied to evaluate their fragmentation processes under EUV radiation. Films were synthesized, characterized, and prepared in the Indian Institute of Technology Mandi (IITM), and the Laboratory of Photochemistry and Surfaces (UFRGS). Thin films were prepared in a glove box under red light. XPS, QMS, and NEXAFS were used for film irradiation and characterization in the PGM beam line. Films were irradiated at different energies (92 eV to 684 eV) between 1.5 and 15 min. After irradiation the samples were oxidized by O_2 for 20 min. XPS and NEXAFS analysis after irradiation at 104.7 eV showed that for the MAPDST, the irradiation strongly decreased the concentration of the triflate group. The O 1s NEXAFS spectrum of the untreated film almost disappeared after 1 min of irradiation. F 1s NEXAFS spectra also revealed same results. S 2p NEXAFS showed than the two main signals observed in the pristine film of the 2p sulfur excited species mainly to the σ^*_{C-S} transitions. Only one of the signals resisted the irradiation: the terminal sulfur atom bonded to the phenyl ring resisted. S 2p XPS spectra evolution during irradiation confirmed one signal remained after irradiation, corresponding to the S atom from phenyl group. Desorption of fragments were monitored during irradiation confirming the degradation of the triflate group after about 30s of irradiation, reflecting a very efficient photo degradation process of the new synthesized resins.

ZR-ENVIRONMENT DISTORTIONS IN ZR1-XSIX MESOPOROUS THIN FILMS PROBED BY ZR L AND SI K-XANES SPECTROSCOPY

FELIX REQUEJO[1]; LEANDRO RUBEN ANDRINI[1]; PAULA CECILIA ANGELOME[2]; GALO ARTURO SOLER-ILLIA[2].
1.INIFTA, LA PLATA - ARGENTINA; 2.GERENCIA QUÍMICA (CNEA), BUENOS AIRES - ARGENTINA.

Palavras-chave: mesoporous;nanomaterials;XANES

Resumo:

We synthesized, characterized and investigated the ion local structure of large-pore mesoporous $Zr_{1-x}Si_xO_2$ (x between 0.0-0.3 and 0.7-1.0) thin films obtained by Evaporation Induced Self Assembly (EISA). The main goal was to understand the effect of the Zr:Si molar relation on the fundamental or local ion local structure and their correlation with the final properties of the material. We have substantially improved the more traditional characterization methodologies (FTIR, TEM, 2D-SAXS) by using of X-ray Absorption Spectroscopy (XAS) at the Zr and Si L and K edges respectively.

According to the obtained average Zr-O distances by Zr L23-XANES, it can be inferred that the Zr surrounded by SiO_2 is morphologically forced to adopt a configuration similar to the Si in SiO_2, by reducing the distance of the first neighbouring oxygen. Thus, Zr coordination can be tuning between 6 and 8 by Zr:Si ratio in homogeneous samples (the Zr coordination number increases when its molar percentage increases). In addition, Si K-XANES experiments indicate that the Si adopts a different electronic configuration as more Zr is introduced in the mixed oxide, indicating a mixture between the two cations. These results are consistent with a distribution of Zr in the absence of phase segregation which causes more distortion of the SiO_2 network than phase separation of ZrO_2 for large Zr concentrations.

IONIZAÇÃO E FRAGMENTAÇÃO DO CH$_3$CHO POR FÓTONS, PRÓTONS E ÍONS DE LÍTIO

FREDERICO VASCONCELLOS PRUDENTE[1]; ÍTALO PRAZERES[1]; MANUELA SOUZA ARRUDA[1]; ANTONIO CARLOS FONTES DOS SANTOS[2]; NELSON VELHO DE CASTRO FARIA[2]; RICARDO DOS REIS TEIXEIRA MARINHO[1]; LUIZ ANTONIO VIEIRA MENDES[1]; ALINE MEDINA[1]. 1.UNIVERSIDADE FEDERAL DA BAHIA, SALVADOR - BA - BRASIL; 2.UNIVERSIDADE FEDERAL DO RIO DE JANEIRO, RIO DE JANEIRO - RJ - BRASIL.

Palavras-chave: Moléculas Pré-Bióticas;TOF;Coincidência entre elétrons e Íons

Resumo:

Uma hipótese para explicar a origem da vida sugere que as biomoléculas foram formadas no espaço pela recombinação de moléculas orgânicas mais simples submetidas a radiação e a colisões com partículas como prótons, elétrons e íons, e então trazidas para a Terra por meteoros e cometas. Assim, o estudo de moléculas pré-bióticas é de fundamental importância para entender a formação de moléculas orgânicas complexas. Esse trabalho é um estudo experimental de uma dessas moléculas pré-bióticas, o acetaldeído (CH$_3$CHO). Apresentamos os espectros resultantes da ionização e fragmentação do acetaldeído por fótons, prótons, e os íons Li$^+$ e Li^{2+}. As medidas com prótons e íons de Lítio foram obtidas no Laboratório de Colisões Atômicas e Moleculares da UFRJ com energias que variam entre 200 eV e 2,0 MeV. Os fragmentos iônicos produzidos após a interação são analisados por um espectrômetro de tempo de voo (TOF) em coincidência com o projétil incidente. As medidas com fótons com energias de 10 eV a 22 eV foram obtidas no Laboratório Nacional de Luz Síncrotron com o auxílio de um espectrômetro TOF e utilizando a técnica de coincidência entre elétrons e íons, PEPICO. Será apresentada uma comparação entre os espectros obtidos com os diferentes projéteis.

Este trabalho é financiado pelo LNLS, pela UFBA e pelo acordo PROCAD/Casadinho (CAPES, CNPq).

ELECTRONIC PROPERTIES OF THE COORDINATION COMPOUNDS OF THE LIGAND DIMETHYLDITHIOCARBAMATE IN THE S 1S REGION

GLAUCIO BRAGA FERREIRA[1]*; ANTONIO CARLOS DE OLIVEIRA GUERRA*[2]*; CÁSSIA CURAN TURCI*[2]*; NADIA MARIA COMERLATO*[2]*.*

1.UNIVERSIDADE FEDERAL FLUMINENSE, NITEROI - RJ - BRASIL; 2.UNIVERSIDADE FEDERAL DO RIO DE JANEIRO, RIO DE JANEIRO - RJ - BRASIL.

Palavras-chave: dithiocarbamates;Photoabsorption;Photoelectron

Resumo:

The sulphur heterocyclic systems are important coordination ligands because their electrical conduction, ferromagnetism and non-linear optic (NLO) properties[1]. The dithiolenes are the main representative of this class of compounds. However, other polisulfurs as dithiocarbamates are also detached as versatile chelating agents for the separation of metals. They also show biological effects [2]. However, the elucidation of inner shell properties still was not explored[3]. Photoabsorption and Photoelectron spectra in the S 1s and long scan regions of Dimethyldithiocarbamate ligand have been acquired for $[Sb(S_2CNMe_2)_3]$ and $[Bi(S_2CNMe_2)_3]$ neutral compounds. All compounds were synthesized following the literature[2]. TEY spectra have been acquired at Soft X-ray Spectroscopy beamline at the LNLS-Campinas (research proposal SXS-14393). The compounds were introduced into the main chamber as solid samples using a carbon sticky tape. The work pressure was kept at ~5 x 10^{-8} mBar. The spectra analysis of these species indicates different chemical environment for the S 1s region. Ab initio and DFT calculations were used to help us to establish the assignments.

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PHOTOESTABILITY OF ASTROPHYSICAL ICES DUE TO SOFT X-RAY IRRADIATION: RELEVANCE TO SOLID PHASE ASTROCHEMISTRY

GUILHERME CAMELIER ALMEIDA[1]; ALEXANDRE BERGANTINI[2]; SÉRGIO PILLING[2]. 1.UFRJ, RIO DE JANEIRO - RJ - BRASIL; 2.UNIVAP, SÃO JOSÉ DOS CAMPOS - SP - BRASIL.

Palavras-chave: White Beam;IV-TF;Ices

Resumo:

The aim of this work was to investigate the photostability of astrophysical ices due to exposure to different doses of a white beam of synchrotron radiation at the SGM beamline. Pure ices of acetone, acetonitrile and ethanol were prepared, in situ, in an UHV chamber. These ices were irradiated with different doses of a white beam (1-1200 eV). The degradation of the ice matrix was followed, in situ, by Fourier transform infrared spectroscopy. Applying this methodology we could estimate the destruction cross sections, σ_d, which allowed us to estimate the half-life for these molecules in the ice phase and extrapolate this behavior to astrophysical environments where soft X-rays play an important role on the development of interstellar chemistry complexity.

ESTUDO COMPARATIVO DA FRAGMENTAÇÃO POR FÓTONS DE MOLÉCULAS ISOELETRÔNICAS DE INTERESSE BIOLÓGICO

MANUELA SOUZA ARRUDA[1]; LUIZ ANTONIO VIEIRA MENDES[2]; ALINE MEDINA[2]; JOSENILTON DO NASCIMENTO DE SOUZA[2]; RICARDO DOS REIS TEIXEIRA MARINHO[2]; FREDERICO VASCONCELLOS PRUDENTE[2].
1.UFRB/UFBA, CRUZ DAS ALMAS/SALVADOR - BA - BRASIL; 2.UFBA, SALVADOR - BA - BRASIL.

Palavras-chave: moléculas biológicas;fotofragmentação;PEPICO

Resumo:

Colisões de fótons com moléculas podem ter diversas aplicações como, por exemplo, na astrofísica, em estudos relacionados à evolução físico-química de espécies moleculares presentes nos primórdios da existência do universo. Moléculas contendo átomos de carbono, oxigênio, nitrogênio de hidrogênio têm sido de especial interesse no estudo da evolução-físico química do universo. Desta maneira, no presente trabalho, fazemos um estudo comparativo da interação de fótons na região do UVV e raio-X moles com moléculas isoeletrônicas de interesse biológico: ácido fórmico (HCOOH), formamida (HCONH$_2$) e acetaldeído (HCOCH$_3$). Em particular, acrescentamos informações experimentais e teóricas relacionadas ao entendimento dos processos de fotofragmentação destas moléculas em fase gasosa devido à ionização de elétrons da valência e do caroço. Os espectros experimentais foram obtidos no Laboratório Nacional de Luz Síncrotron (LNLS), nas linhas de luz TGM e SGM, com o auxílio de um espectrômetro de massa por tempo voo e utilizando a técnica de coincidência entre elétrons e íons, PEPICO. Fazemos, também, uma análise teórica dos processos de fotofragmentação e fotoionização, utilizando a Teoria do Funcional da Densidade e a Teoria do Funcional da Densidade Dependente do Tempo.

SILVER AND PLATINUM NANOPARTICLES SUPPORTED ON CARBON: SYNTHESIS, CHARACTERIZATION AND CATALYTIC ACTIVITY TOWARDS NO REDUCTION

M. V. CASTEGNARO (M)[1], J. ALEXANDRE[2], M. C. M. ALVES[2], I. M. BAIBICH[2] AND J. MORAIS[1]

[1]IF, UNIVERSIDADE FEDERAL DO RIO GRANDE DO SUL (UFRGS), PORTO ALEGRE, RS, BRAZIL}

[2]IQ, UNIVERSIDADE FEDERAL DO RIO GRANDE DO SUL (UFRGS), PORTO ALEGRE, RS, BRAZIL}

Palavras-chave: Environmental Catalysis;Metal Nanoparticles;XPS

Resumo:

Noble metal nanoparticles (NPs) have been widely applied to several catalytic processes due to the unique physical and chemical properties induced by their nano-scale dimensions. Therefore, in the last years, the synthesis and characterization of metal NPs have gained ground in materials science. In this work, Ag and Pt NPs have been successfully obtained by wet chemical reduction. The shape and size of the resulting NPs were investigated by TEM.

The Ag and Pt NPs were later supported on activated carbon (AC) in order to obtain heterogeneous catalysts, which were characterized by SEM to observe the dispersion of the NPs on the support. The structural properties of the formed catalysts were investigated by XRD, and the electronic properties of their surfaces were probed by synchrotron-excited XPS. The results confirmed the formation of metallic NPs with sizes of about 4 nm and with high crystallinity.

Moreover, we studied the catalytic activity of Ag/CA and Pt/AC during the direct decomposition of NO (nitric oxide), since it is one of the most important and challenging reactions in environmental catalysis. During the catalytic tests, the effluent gases were analyzed by *in-situ* IR absorption in order to determine the gas composition at the reactor exhaust. From these reactions, we verified that both catalysts are active in the temperature range of 323 K to 673 K. We also compared the Ag/AC and Pt/AC catalytic behavior with previous results obtained for Pd/AC catalysts.

This work was funded by CAPES, CNPq, FAPERGS, LNNano (TEM-HR-15294) and LNLS (SXS-14437 and SXS-15314 proposals). M. V. Castegnaro thanks CAPES for his PhD fellowship.

THE INTERPLAY OF ELECTRONIC STRUCTURE, ORIENTATION AND CHARGE TRANSPORT IN ORGANIC SEMICONDUCTORS: THIOPHENE-BASED POLYMERS

MARIA LUIZA ROCCO[1]; YUNIER GARCIA-BASABE[1]; BRUNO GABRIEL ALVES L. BORGES[1]; CAROLINE ARANTES[2]; LUCIMARA STOLZ ROMAN[3].

1.IQ-UFRJ, RIO DE JANEIRO - RJ - BRASIL; 2.INMETRO, DUQUE DE CAXIAS - RJ - BRASIL; 3.DF-UFPR, CURITIBA - PR - BRASIL.

Palavras-chave: Semicondutores orgânicos;método core-hole clock;transferência de carga

Resumo:

Ultrafast electron dynamics is a relevant topic to many applied areas like femtochemistry, surface photochemistry, molecular electronics, solar energy, and so on. Resonant Auger spectroscopy following core excitation emerges as an alternative with major advantages. Firstly, the core hole lifetime probed by core level spectroscopy can be used as a fast internal clock and in so far very low timescales in the range of femtoseconds (10-15 s) down to hundred attoseconds (10-18 s) can be achieved, the so-called core-hole clock (CHC) method. Ultrafast electron dynamics in the low-femtosecond regime was evaluated for thiophene-based polymers by resonant Auger spectroscopy using the core-hole clock method. Sulfur $KL_{2,3}L_{2,3}$ Auger decay spectra were measured as a function of the photon energy. Remarkable changes developed by tuning the photon energy along the sulphur 1s absorption edge, depending on the nature of the intermediate core excited states. Competition between core hole decay and delocalization of the photoexcited electron was monitored. Branching ratios of Raman (spectator) and normal Auger channels were calculated and electron delocalization times for the different polymeric films derived as a function of the excitation energy. Photoabsorption measurements were also conducted and molecular orientation derived, which corroborated the proposed conduction mechanism.

TIOMALIC ACID ADSORBED ON AU (111) AND NANOPARTICLES SURFACES

MARÍA ÁNGELA ALVAREZ MANSO[1]; JULIO CESAR AZCÁRATE[1]; MARÍA ALEJANDRA FLORIDIA ADDATO[1]; ALDO ALBERTO RUBERT[1]; GASTÓN CORTHEY[1]; GERMÁN SEBASTIÁN KÜRTEN MORENO[1]; GUILLERMO ALFREDO BENITEZ[1]; EUGENIA ZELAYA[2]; ROBERTO CARLOS SALVAREZZA[1]; MARIANO HERNÁN FONTICELLI[1].

1.THE RESEARCH INSTITUTE OF THEORETICAL AND APPLIED PHYSICAL CHEMISTRY (INIFTA), UNLP-CONICET, LA PLATA - ARGENTINA; 2.BARILOCHE ATOMIC CENTER (CAB), NATIONAL ATOMIC ENERGY COMMISSION (CNEA) - CONICET, SAN CARLOS DE BARILOCHE - ARGENTINA.

Palavras-chave: Gold (111), gold nanoparticles;tiomalic acid, atomic sulfur;selective bond cleavage

Resumo:

The self-assembly of thiomalic acid (TMA) on Au(111) and on Au nanoparticles (AuNPs) of different sizes have been studied by X-ray photoelectron spectroscopy (XPS) and electrochemical techniques. Results shows that TMA is adsorbed on the Au(111) surface as thiolate species with a small amount of atomic sulfur (~10%) and a surface coverage lower to that found for alkanethiol on Au(111) due to steric factors. The amount of atomic sulfur markedly increases when the TMA is self-assembly on AuNPs (3-4 nm and 6 nm in size) by the ligand exchange method. We propose that the atomic sulfur is produced as a consequence of C-S bond cleavage, a process that is more favorable at defective sites of the AuNPs surface. The bond scission is also assisted by the presence of an electron withdrawing group, as it is the case of the carboxyl moiety, in alpha position, with the consequent formation of a resonance-stabilized carbanion. The presence of a high local concentration of positive charged molecules increases the stability of negative charged leaving group. Our results demonstrate that the terminal functionalities of thiols are conditioning factors in the final structure and composition of the adlayers.

Acknowledgements: This work has been supported by the LNLS under proposals PGM-SGM 14387 y SGM 14243. We also acknowledge financial support from Agencia Nacional de Promoción Científica y Tecnológica (PICT 2010-0423, PICT 2010-2554), CONICET (PIP 11220090100139), UNLP, Argentina.

SYNTHESIS AND CHARACTERIZATION OF GRAPHENE OXIDE AND GRAPHENE.

MERI DOMINGOS VIEIRA[1]; DIEGO GEMINO C. DA SILVA[1]; GLAUCIO BRAGA FERREIRA[1]; CÁSSIA CURAN TURCI[1]; ALINE ZUANY CARDOSO[1].

1.UNIVERSIDADE FEDERAL FLUMINENSE, NITEROI - RJ - BRASIL.

Palavras-chave: GRAPHENE OXIDE;GRAPHENE;XPS SPECTROSCOPY

Resumo:

Graphene has been widely studied due to its unique properties[1] which are dependent on its structure then, the control of its synthesis is important. A modified Hummer 's method[1] and thereafter reduction with aluminum in acidic media were used to obtain graphene oxide and graphene[2] respectively, showing to be easy and reproducible. However, oxidation and reduction times and washing must be optimized to obtain pure materials with controlled properties.

The characterization methods were X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) with the facilities of the LDRX-UFF, the Soft X-ray Spectroscopy (SXS) beamline at the LNLS-Campinas (SXS-14393) and the XPS- RECAT-UFF.

The x-ray diffraction can be roughly used as a fast method to monitor the synthesis with posterior more accurate XPS analysis.

The graphene oxide samples analyzed in the XPS - LNLS showed C_{1s} binding energies at 284.4-285 eV, 286.5 eV and 287.9 accoding to C-C or C-H bond, C-OH and C = O, respectively. The graphite mineral used as a starting material presents a slightly oxidized surface, with a very intense band at approximately 284.4 eV and a little one at 285 eV . However, the C_{1s} band for the reduced graphene oxide on the 287.9 e 286.5 eV region is diminished but not removed showing that the reduction is not complete.

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STUDY OF MOMENTUM-TRANSFER DEPENDENCE OF BORON K-EDGE BY MEANS OF X-RAY RAMAN SCATTERING

SERGIO ANDRES CEPPI[1]; OSCAR ARIEL PAREDES MELLONE[1]; GUILLERMO STUTZ[1].
1.FAMAF-UNC, CÓRDOBA - ARGENTINA.

Palavras-chave: x-ray Raman scattering;B K-edge; FEFF 9.6 program

Resumo:

Inelastic x-ray scattering spectra have been measured for energy losses around the B K-edge in a polycrystalline sample. The B K-edge was investigated for momentum transfers q going from qa<1 to qa>1, where a is the orbital radius for the K shell. The experiments were measured at XDS beamline using a high energy-resolution spectrometer for inelastic x-ray scattering spectroscopy.

The experimental x-ray Raman spectra show clear differences between spectra measured for different momentum transfers, which are related to deviations from the dipole approximation of the x-ray Raman scattering process. In order to explain these differences, ab initio theoretical calculations were performed of the projected density of state and also of q-dependent Raman spectra using the FEFF 9.6 program. Main changes at high momentum transfers can be assigned to the contribution of monopole transitions to s-type empty states.

EFFECT OF ANNEALING ON PSIF AND PSIF:PCBM NANOSCALE MORPHOLOGY AND CHARGE TRANSFER DYNAMICS PROBED BY RESONANT AUGER SPECTROSCOPY

YUNIER GARCIA-BASABE[1]; BRUNO GABRIEL ALVES L. BORGES[1]; LUCIMARA STOLZ ROMAN[2]; MARIA LUIZA ROCCO[1].

1.IQ-UFRJ, RIO DE JANEIRO - RJ - BRASIL; 2.DF-UFRJ, CURITIBA - PR - BRASIL.

Palavras-chave: Semicondutores orgânicos;Efeito do tratamento térmico;Dinâmica de transferência de carga

Resumo:

X-ray absorption (XAS) and Auger decay measurements on poly[2,7-(9,9-bis(2-ethylhexyl)-dibenzosilole)-alt-4,7-bis(thiophen-2-yl)benzo-2,1,3-thiadiazole] films and blends with PCBM were performed following sulphur 1s absorption edge. Distinct morphologies and electrical properties were observed in these materials as a function of the annealing treatment. In order to probe the differences in molecular dynamics and structural order, ultrafast electron dynamics in the low-femtosecond regime was evaluated by resonant Auger spectroscopy using the core-hole clock methodology. Electron delocalization times for the different polymeric films were derived as a function of the excitation energy. Photoabsorption measurements were conducted and molecular orientation derived. These results corroborated with the morphology found for these films and thus the performance of these polymeric films in the devices, and with the proposed conduction mechanism.

24th RAU
ANNUAL USERS
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March 11th and 12th, 2014

Abstracts

Small Angle X-ray Scattering (SAXS)

SAXS CHARACTERIZATION OF NANOSTRUCTURED SYSTEMS FOR NIFEDIPINE NASAL ADMINISTRATION

ALYNE DANTAS LIMA[1]; AMANDA REZENDE LIMA[1]; SARAH GUERRA FERREIRA[1]; JOYCE KELLY MARINHEIRO DA CUNHA GONSALVES[1]; VICTOR HUGO VITORINO SARMENTO[1]; MARIO ERNESTO GIROLDO VALERIO[1]; ANA AMÉLIA MOREIRA LIMA[1]; ROGÉRIA DE SOUZA NUNES[1]; MARCIO ROBERTO VIANA DOS SANTOS[1].
1.UFS, ARACAJU - SE - BRASIL.

Palavras-chave: Drug delivery systems;microemulsion;SAXS

Resumo:

Nifedipine drug used for hypertension control. However, due to its low bioavailability after oral administration it has been suggested the development of a stimuli-sensitive drug delivery system for nifedipine nasal administration. Systems composted by surfactant, oil and water can form a range of aggregates, as microemulsions (MEs) and liquid crystals (LCs). Therefore, the purpose of this study was to develop and evaluate the LC phase behavior of nifedipine formulations. The systems were composed of procetyl AWS® (surfactant), oleic acid (oil phase) and phosphate buffer (aqueous phase - AP) in different proportions and were characterized by Polarized light microscopy (PLM) and Small Angle X-ray Scattering (SAXS) at bean line 1 of Brazilian Synchrontron Light Laboratory (LNLS). The results showed that the systems are isotropic and with the increase of water content, they exhibited transition to anisotropic systems. There were observed wide peaks typical of micelar structures for isotropic systems. Samples with higher AP content exhibited the appearance of new peaks, indicating the beginning of phase transition to lamellar structures. The presented results showed that this systems have a great potential for NF nasal administration due to a possible mucoadhesion. Being structured systems they can promote a drug controlled release.

SÍNTESE E CARACTERIZAÇÃO POR SAXS DE SÍLICA MESOPOROSA CONTENDO MONÔMERO E POLÍMERO ENCAPSULADOS

ANA FLÁVIA PINHEIRO DE CAMPOS[1]; FERNANDA TÁTIA CRUZ[1]; JAILSON ARRUDA DE ARAÚJO[1]; DILSON CARDOSO[1].

1.UFSCAR, SÃO CARLOS - SP - BRASIL.

Palavras-chave: CTA-MCM-41;Polimerização;Transesterificação

Resumo:

Existe um crescente interesse mundial no uso de biodiesel como aditivo ao diesel petroquímico. A utilização deste combustível implica em importantes benefícios ambientais por ser biodegradável, livre de enxofre e compostos aromáticos. Nosso grupo de pesquisa tem estudado o catalisador heterogêneo CTA-MCM-41 para a transesterificação. Assim, a fim de promover a melhoraria da estabilidade catalítica foram feitas sínteses com modificações em que se adicionaram monômeros (acrilatos e metacrilatos) juntamente com o fotoiniciador e depois realizou a polimerização por radiação ultravioleta. Espera-se que os polímeros formados interajam 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) comprovou a presença do monômero ou do polímero no interior dos canais do material. Essa evidência foi constatada pelo deslocamento da curva (100) para q menores em relação ao q ~ 1,7 nm^{-1} da MCM-41 sem aditivo. Esse deslocamento também foi observado quando se aumentou o tamanho da cadeia alquílica dos monômeros utilizados e comprovou-se que parte do polímero encontrava-se no interior dos canais da CTA-MCM-41, provocando a expansão de seus diâmetros.

KINETICS OF FORMATION AND GROWTH OF NANOPARTICLES ON PB 52PBO - 45B2O3-3SNO GLASS

ANDREIA GORGESKI[1]; GUINTHER KELLERMANN[2]; ALDO FELIX CRAIEVICH[3]; LUCIANO A MONTORO[4].
1.UFRGS/UFPR, PORTO ALEGRE - RS - BRASIL; 2.UFPR, CURITIBA - PR - BRASIL; 3.USP, SÃO PAULO - SP - BRASIL; 4.UFMG, BELO HORIZONTE - MG - BRASIL.

Palavras-chave: nanoparticulas;SAXS;vidro

Resumo:

In this work the formation and growth of metallic Pb nanodroplets embedded in 52PbO-45B_2O_3-3SnO_2 glass was investigated. The glass samples were prepared by the melt of PbO, B_2O_3 and SnO powder in an electrical furnace during 1 hour and fast quenching of the melt down do room temperature using the splat-cooling technique. SnO was used as a reducing agent to partially reduce PbO molecules leading to formation of Pb and SnO_2 homogeneously dispersed in the glass. The glass samples were then studied by in situ small-angle x-ray scattering in isothermal conditions. Since the annealing temperatures (649 - 679 K) are above the melting temperature of Pb the nanoparticles are expected to be liquid during the thermal treatment of the glass. Transmission electron microscopy (TEM) measurements performed in the glass-Pb nanoparticles composite showed that Pb particles are crystalline having face centered cubic lattice and the same lattice parameter of macroscopic Pb crystals.SAXS analysis on samples treated at lower temperatures (649 K e 670 K) showed the existence of a depleted zone in the glass evolving the droplets. From the analysis of the SAXS curves at different annealing times, the radius distribution functions of nanodroplets as a function of the annealing time $D_N(R,t)$ were determined.

A proposta de pesquisa é a SAXS1-12504 - Study by SAXS of the formationand growth of Pb nanoparticles embedded in a lead-borate glass.

MATCHING DEI-CT AND SAXS SCANNING TO ASSESS THE MORPHOLOGICAL CHANGES IN BREAST TUMOURS

ANDRÉ LUIZ COELHO CONCEIÇÃO[1]; MARTIN EDUARDO POLETTI[2].

1.UTFPR, CURITIBA - PR - BRASIL; 2.FFCLRP - USP, RIBEIRÃO PRETO - SP - BRASIL.

Palavras-chave: Breast cancer;SAXS;DEI-CT

Resumo:

Nowadays, there is a wide interest on studying of structural features of breast tissues, which could be used as marker of pathological state. Then, in this work we have combined the Diffraction Enhanced Imaging Computed Tomography (DEI-CT) and Small Angle X-ray Scattering (SAXS) scanning to study the transition between healthy and pathological tissue, which included benign and malignant breast lesions.

DEI-CT and SAXS was implemented at the National Synchrotron Light Laboratory in Brazil. The first one, was carried out in the XRD2 beamline using 11keV x-rays and a filtered backprojection algorithm to reconstruct the tumour slice. After localizing the tumour region on the sample, both the lesion and its surroundings were scanned by SAXS technique at SAXS-1 beamline. An x-ray beam of 8.05 keV and size of 0.4 × 0.3 mm^2 (h × v) was used to scan the sample with step size of 0.4 mm covering the whole tumour and its peripheral healthy region.

It was clearly the differences between healthy and pathological tissues related to changes in arrangement and diameter of collagen fibrils. The 2nd order of collagen reflection arises only in the healthy region neighboring the benign lesion, while a broader peak at $q=0.16nm^{-1}$ seems to characterize the malignant lesions.

Finally, based on these information, it was mapped the transition between healthy and pathological human breast tissues which provided to get insights about the changes promoted by the tumours during growth and progression.

SODIUM CASEINATE STRUCTURAL CHANGES DURING HOMOGENEOUS ACIDIFICATION

CRISTIAN HUCK-IRIART[1]; JAIME ALBERTO RINCÓN-CARDONA[2]; CRISTIANO LUIS PINTO DE OLIVEIRA[3]; MARIA LIDIA HERRERA[4]; ROBERTO JORGE CANDAL[2].

1.INQUIMAE-UBA, BUENOS AIRES - ARGENTINA; 2.UNSAM, BUENOS AIRES - ARGENTINA; 3.INSTITUTO DE FÍSICA-USP, SAO PAULO - SP - BRASIL; 4.FCEN-UBA, BUENOS AIRES - ARGENTINA.

Palavras-chave: SODIUM CASEINATE;GEL;HOMOGENEOUS ACIDIFICATION

Resumo:

Structuring liquid oils has become an active area of research in the past decade. Recent strategies to impart solid-fat functionality to liquid oils include gelification of protein emulsions. The aim of this work was to study the effect of sucrose addition on physical properties of acidified sodium caseinate/sunflower oil gels. Gels were prepared from sodium caseinate (NaCas) emulsions with the following composition: 5 wt.% sodium caseinate, 10 wt.% sunflower oil, and 0, 5, 10, 15, 20, and 30 wt.% of sucrose. Emulsions were acidified with glucono-δ-lactone (GDL) acid added in a ratio of GDL/protein 1:5 (1 g of protein and 0.2 g of GDL) and 2:5. Small Angle X-Ray Scattering (SAXS) technique was applied to investigate sodium caseinate supramolecular´s structure during the homogeneous acidification. The experimental data was analyzed using advanced modeling approaches. The Form Factor for the NaCas micelle subunits was described by an ellipsoidal core shell model and the structure factor by the particle-particle interactions. For this term the hard sphere structure factor using the Percus-Yevick approximation for closure relation was used. Data analysis provided an increase of the average distance between the subunits after acidification. This is affected by sucrose addition . As will be presented, these nanoscale structural results provided by scattering experiments is consistent with macroscopic results obtained from several techniques.

HIGH-TEMPERATURE CHAMBER FOR IN SITU GISAXS EXPERIMENTS

DANIEL DA SILVA COSTA[1]; GUINTHER KELLERMANN[1]; IRINEU MAZZARO[1]; ALDO FELIX CRAIEVICH[2]; RENAN GERALDES[3]; VESNA STANIĆ[3]; JOACIR EDMIR DOS SANTOS[3]; FÁBIO ROBERTO ZAMBELLO[3]; FELIX G. REQUEJO[4]; LISANDRO JOSE GIOVANETTI[5]; REGIS TERENZI NEUENSCHWANDER[3].
1.UFPR, CURITIBA - PR - BRASIL; 2.USP, SÃO PAULO - SP - BRASIL; 3.LNLS, CAMPINAS - SP - BRASIL; 4.UNLP, LA PLATA - ARGENTINA; 5.INIFTA, LA PLATA - ARGENTINA.

Palavras-chave: GISAXS;DRX;High-temperature

Resumo:

We here describe the project of a chamber specially designed for in situ experiments of small-angle X-ray scattering at grazing-incidence (GISAXS) during thermal annealing of flat samples. This chamber will operate from room temperature up to 1000 °C and was designed to minimize changes in sample position as a consequence of thermal expansion during the heating and cooling cycles. A changeable Kapton (or Be) window is placed in the upper part of the chamber for simultaneous GISAXS and X-ray diffraction (XRD) measurements. A turbomolecular vacuum pump, directly connected to the body of the chamber, will keep the sample under low pressure (~10^{-6}-10^{-7} Torr, depending on the type of X-ray window used for XRD measurements) during GISAXS and/or XRD experiments. A pre-chamber also connected to the main chamber through a gate valve will allow for changing the sample without vacuum breaking. The chamber makes possible all necessary movements for alignment of the sample with respect to the direct X-ray beam. This project is a cooperation of the X-ray Optics and Instrumentation Laboratory (LORXI), University Federal of Paraná, with LNLS. The designed chamber can be adapted to different X-ray diffractometers of LNLS.

UREASIL-POLY(ETHYLENE)OXIDE HYBRID MATERIAL FOR SELECTIVE ADSORPTION AND SEPARATION OF DYES FROM WATER

EDUARDO FERREIRA MOLINA[1]; RENATO LUIS TAME PARREIRA[1]; EMERSON HENRIQUE DE FARIA[1]; EDUARDO JOSE NASSAR[1]; KATIA JORGE CIUFFI[1].

1.UNIVERSIDADE DE FRANCA, FRANCA - SP - BRASIL.

Palavras-chave: Ureasil-polyether ;small-angle X-ray scattering;Water cleaning

Resumo:

We obtained a cross-linked ureasil-polyether-siloxane hybrid (labeled PEO500) that can function as a stimuli-sensitive material—it swells or shrinks in response to changes in the environmental conditions, can remove dyes effectively and selectively, and is potentially applicable in water purification and treatment. We also developed a methodology to separate a mixture of cationic and anionic dyes present in water. We used in situ small-angle X-ray scattering (SAXS) to evaluate the nanostructure of PEO500 as well as the effect of swelling-shrinkage on this structure. After the swelling equilibrium,the matrix underwent a reversible process, to return to its initial structure. Addition of PEO500 to an aqueous solution of the anionic orange II (OII) or the Ponceau S (PS) dye rendered the solution colorless, but an aqueous solution of cationic Methylene Blue (MB) remained unchanged after 2h of contact with the insoluble matrix. In situ UV-vis adsorption experiments furnished the kinetic parameters for the pseudo-first-order and pseudo-second-order kinetic models; we found that the kinetics of OII and PS removal followed a pseudo-first-order rate equation. On the basis of the experimental and theoretical investigations, we proposed some mechanisms to explain how PEO500 adsorbs anionic dyes efficiently. This “smart” matrix is potentially applicable as an efficient, fast, selective, and convenient device in water treatment and stimuli-sensitive response materials.

STUDY OF THE CITRUS SINENSIS ESSENTIAL OIL MICROEMULSION FORMATION AND EVALUATION OF THE NIFEDIPINE INFLUENCE IN THE SYSTEMS ORGANIZATION

GABRIELA DAS GRAÇAS GOMES TRINDADE[1]; QUÊNNIA GARCIA MORENO RESENDE[1]; JOYCE KELLY MARINHEIRO DA CUNHA GONSALVES[1]; ALYNE DANTAS LIMA[1]; SARAH GUERRA FERREIRA[1]; VALÉRIA SANTOS CONCEIÇÃO[1]; ANA AMÉLIA MOREIRA LIMA[1]; VICTOR HUGO VITORINO SARMENTO[1]; ROGÉRIA DE SOUZA NUNES[1].

1.UNIVERSIDADE FEDERAL DE SERGIPE, ARACAJU - SE - BRASIL.

Palavras-chave: Microemulsions;SAXS;permeation enhancers in the skin

Resumo:

The aim of this work was to evaluate the influence of cosurfactants (ethanol – ET, isopropanol – ISO and propylene glycol – PG) in mixture with surfactant in microemulsions (ME) and evaluate the nifedipine (NF) influence in the systems. The MEs were obtained by pseudo-ternary diagram and characterized by Polarized Light Microscopy (PLM), electric conductivity (EC) and SAXS, droplet size (DS) and polydispersity index (PDI). Two samples of each diagram was chosen and was evaluated the NF influence. Comparing the three diagrams, it was observed a bigger ME zone in the ISO above 40% of mixture. For ET and PG, was above 60% and 70% of mixture, respectively. The MEs showed to be stable, isotropic, with DS between 16-34 nm and PDI below 0,5. EC analysis indicated that the increase of aqueous content provided an increase in the samples EC. SAXS curves showed that all systems were micelar structures, where it can be observed wide peaks centered in q region and with aqueous phase increase the peaks were shifted to higher q values,. SAXS data combined with EC confirmed ME structure as O/ W and bicontinuous. The selected samples pH were compatible with the skin, in the range of 5,64 to 6,07 and for NF stability. The EC didn't alter ME structure, they continued as bicontinuous and O/W. Therefore, the results elucidated the cosurfactant influence in the ME region formation. The obtained systems didn't suffer drug interference, suggesting its use as NF permeation enhancers in the skin.

AVALIAÇÃO DA ALTERAÇÃO DA ESPESSURA DE FIBRAS DE BAGAÇO DE CANA PRÉ-TRATADA EM FUNÇÃO DA UMIDADE ATRAVÉS DE MICROSCOPIA ELETRÔNICA DE VARREDURA EM MODO AMBIENTAL

GEORGE JACKSON DE MORAES ROCHA[1]; DEBORA LEE SIMOES CORSO[1]; VIVIANE MARCOS NASCIMENTO[1].

1.LABORATÓRIO NACIONAL DE CIÊNCIA E TECNOLOGIA DO BIOETANOL (CTBE)/CNPEM, CAMPINAS - SP - BRASIL.

Palavras-chave: MEV;bagaço de cana;umidade

Resumo:

A ação enzimática nas biomassas vegetais é dificultada devido à estrutura recalcitrante do complexo celulose-hemicelulose-lignina. Uma alternativa é o emprego de processos de pré-tratamento, levando ao maior intumescimento das fibras, facilitando o acesso da enzima a estrutura. Neste contexto se faz necessário a análise morfológica para se compreender o comportamento da fibra em função da umidade, afim de escolher condições que irão favorecer o aumento da área superficial e, consequentemente, a maior difusão das enzimas. A técnica de microscopia eletrônica de varredura em modo ambiental é de importante aplicação na investigação deste comportamento, pois permite a observação clara e objetiva deste intumescimento, permitindo a quantificação deste ganho da largura dos pacotes fibrilares com o aumento da umidade. Neste trabalho a biomassa pré-tratada foi obtida em um reator de 350 L (POPE Scientific) no CTBE e as fotomicrografias de MEV foram obtidas em um Microscópio FEI®, Quanta 650, FEG modo ambiental, disponível no LNNano. Os resultados preliminares mostraram um aumento de 13% na largura do pacote de fibras quando a umidade variou de 0 a 100%, evidenciando que acima de 50% este intumescimento é exponencial. As imagens mostram claramente as alterações morfológicas devido à ação da umidade. Conclui-se que para a etapa de hidrólise enzimática se faz necessário que a biomassa pré-tratada contenha uma umidade mais próxima de 100% para uma melhor difusão dos reagentes biológicos.

STUDY BY SAXS OF THE SOLID-TO-LIQUID AND LIQUID-TO-SOLID TRANSITIONS OF PB NANOPARTICLES EMBEDDED IN A LEAD-BORATE GLASS

GUINTHER KELLERMANN[1]; ANDREIA GORGESKI[1]; ALDO FELIX CRAIEVICH[2]; LUCIANO A MONTORO[3].
1.UNIVERSIDADE FEDERAL DO PARANÁ, CURITIBA - PR - BRASIL; 2.UNIVERSIDADE DE SÃO PAULO, SÃO PAULO - SP - BRASIL; 3.UNIVERSIDADE FEDERAL DE MINAS GERAIS, BELO HORIZONTE - MG - BRASIL.

Palavras-chave: nanoparticles;melting;crystallization

Resumo:

The solid-to-liquid and liquid-to-solid transitions of Pb nanoparticles embedded in a lead-borate glass were studied by small-angle x-ray scattering (SAXS) during heating of the glass-Pb nanocrystal composite from room temperature up to 650 K – above the melting temperature of bulk Pb (600.61 K) - and later cooling of the composite down to room temperature. TEM analysis at room temperature showed nanoparticles have nearly spherical shape and average size equal to 13 nm. From the analysis of the SAXS curves, the dependence of the Guinier average gyration radius $<R_g>$ and integrated SAXS intensity Q on temperature were obtained. The behavior of these parameters with the temperature allowed us to precisely determine the melting and crystallization temperatures of a set of nearly spherical Pb nanoparticles using only SAXS measurements. The melting and crystallization temperatures of the nanoparticles, determined from the behavior of the $<R_g>$ and Q(T) experimental functions, are 581 K and 433 K, respectively. These results show Pb nanoparticles having 13 nm radii melt at approximately 19 K below the melting temperature of bulk Pb and exhibit a large undercooling.

COMPOSITES OF NIOBIUM OXYHYDROXIDE/POLYPROPYLENE: EFFECT ON PHASE SEPARATION AND CRYSTALS FORMATION

IACI MIRANDA PEREIRA[1], PATRÍCIA SANTIAGO DE OLIVEIRA PATRICIO[2], SAMARA DURÃEZ DE SOUZA[2], LUIZ CARLOS ALVES DE OLIVEIRA[3], HENRIQUE DOS SANTOS OLIVEIRA[3], RODRIGO LAMBERT ORÉFICE[4]

[1]LABORATÓRIO DE MATERIAIS, DIVISÃO BÉLICA, CENTRO TECNOLÓGICO DO EXÉRCITO, AV. DAS AMÉRICAS, 28750 – BARRA DE GUARATIBA – RIO DE JANEIRO, RJ, 23020-470.

[2]DEPARTAMENTO DE QUÍMICA, CENTRO FEDERAL DE EDUCAÇÃO TECNOLÓGICA DE MINAS GERAIS, AV. AMAZONAS, 5253 – NOVA SUIÇA – BELO HORIZONTE, MG, 30421-169.

[3]DEPARTAMENTO DE QUÍMICA, UNIVERSIDADE FEDERAL DE MINAS GERAIS, AV. ANTÔNIO CARLOS, 6627 – PAMPULHA – BELO HORIZONTE, MG, 31270-901.

[4]DEPARTAMENTO DE ENGENHARIA METALÚRGICA E DE MATERIAIS, UNIVERSIDADE DE FEDERAL DE MINAS GERAIS, AV. ANTÔNIO CARLOS, 6627 – PAMPULHA – BELO HORIZONTE, MG, 31270-901.

Keywords: *Polypropylene, niobium, modified Porod´s Law*

Abstract: Our research group has developed a material based on niobium. They are: (i) hydroxide niobium (Ni H_2O_2), (ii) niobium oxyhydroxide (Ni hyd) and (iii) amphiphilic niobium oxyhydroxide (Ni amp). The three compounds were dispersed on a polypropylene (PP) matriz and characterized using SAXS. Due to cell distortion, a small degree of orientation was observed in the final morphology of PP/Ni hyd, and PP/Ni amp. PP lamellar structure originated a peak at $0.531nm^{-1}$. The peak position of PP/Ni compounds slightly shifts to lower $0.410nm^{-1}$ values, suggesting an increase of the spacing of the periodical lamellar structure and smaller degree of order. Lorentz corrected SAXS patterns for the obtained PP and its composites exhibited a scattering maximum and a second-order peak as a 'bump' at larger q-values. The invariant quantity, Q, was used to calculate the degree of crystallinity, the contribution of crystalline and amorphous phase were separated by a deconvolution. The degree of crystalline phase that contributes to the scattering decreased mainly in the presence of Ni hyd and Ni amp particles. The higher Q observed for PP/Ni hyd might be associated with higher degree of phase separation indicating the presence of crystalline domain with a higher ordering. Results indicated that the introduction of Ni H_2O_2 particle produces a crystalline domain with rather smooth surface and thicker transition zone. PP/Ni hyd and PP/Ni amp composites hold a similar configuration with rough surface.

PHASE BEHAVIOR OF PROCETYL/ OLEIC ACID SYSTEM USED TO PREPARE CITRUS SINENSIS ESSENTIAL OIL EMULSIONS

JOYCE KELLY MARINHEIRO DA CUNHA GONSALVES[1]; ADÉLIA DOS SANTOS[1]; SARAH GUERRA FERREIRA[1]; ALYNE DANTAS LIMA[1]; VICTOR HUGO VITORINO SARMENTO[1]; ROGÉRIA DE SOUZA NUNES[1].

1.UNIVERSIDADE FEDERAL DE SERGIPE, SÃO CRISTÓVÃO - SE - BRASIL.

Palavras-chave: emulsions;rheology;SAXS

Resumo:

Emulsions (EM) are defined as droplets dispersion of two immiscible liquids that are thermodynamically unstable. The interactions between their compounds may induce formation of other self-assembled structures. Citrus sinensis essential oil (CSEO) presents biological activity against Aedes aegypti larvae. Thereby, the aim of this work was to obtain EM from CSEO, procetyl AWS®, oleic acid and water and characterize by rheology, Small Angle X-ray Scattering (SAXS) and evaluate its larvicidal activity. Four EM were selected for characterization (E1, E2, E3, E4) in the same dilution line. Samples rheology analysis exhibited flow index (n) values between $0<n<1$ and consistency index (K) greater than zero, proving the pseudoplastic behavior. Decreasing aqueous phase in the samples induced an increase in the viscosity. SAXS: E1 and E2 exhibited broad peaks typical of less organized structures. Sample E3 presented more pronounced. E4 exhibited a more organized structure, with peaks q max values in the ratio 1:2:3, indicating lamellar periodicity. It was observed in the biological larvicidal assay that the sample with higher water content (E1) obtained smaller CSEO retention consequently an improved larvicidal activity. Conclusion, there were obtained four stable EM and the characterization showed that decreasing water content increases viscosity and system organization that interfered in the biological activity.

Supported by: CNPq, FAPITEC, LNLS, NUESC/ UNIT

INFLUENCE OF PROTIC IONIC LIQUID ON STRUCTURE OF PROTON-CONDUCTING SPEEK-ZIRCONIA MEMBRANES FOR ANHYDROUS FUEL CELL APPLICATION

JOÃO ARTHUR LUNAU BATALHA[1]; RÔMULO SAMPAIO[1]; KARIM DAHMOUCHE[1]; AILTON SOUZA GOMES[1].
1.INSTITUTO DE MACROMOLÉCULAS PROFESSORA ELOISA MANO / UNIVERSIDADE FEDERAL DO RIO DE JANEIRO, RIO DE JANEIRO - RJ - BRASIL.

Palavras-chave: PEFC;sPEEK;Protic Ionic Liquid

Resumo:

Operation in higher temperatures, under anhydrous conditions, is vital for the future of Polymer Electrolyte Fuel Cell (PEFC) technology. In this work, hybrid sPEEK / ZrO_2 membranes, comprising the protic ionic liquid (PIL) diethylmethylamine triflate in different contents were synthesized via sol-gel method. The membranes showed good thermal stability and the presence of ZrO_2 nanoparticles enabled PIL retention. Their structural features have been investigated at 70 ^{o}C by XRD and SAXS. For pure sPEEK, a SAXS broad peak is observed, attributed to spatial correlation between polymer nanodomains rich in SO_3H groups, consistent with a Guinier regime. Incorporation of ZrO_2 (4 wt.%) increases the crystallinity of sPEEK, but does not affect the correlation between SO_3H-rich nanodomains, suggesting weak interactions between ZrO_2 and SO_3H groups. PIL interacts with SO_3H domains, illustrated by the SAXS peak intensity decrease. Another interesting feature is that incorporation of 10 and 40 wt.% PIL leads to an increase in conductivity by the membranes: the former shows a decrease in spatial correlation between ZrO_2 nanoparticles. The structure of the latter exhibits small spatial correlation between ZrO_2 nanoparticles, lower polymer crystallinity and higher conductivity. A study of the evolution of structure, thermomechanical properties and proton conductivity of the membranes in temperatures up to 160 ^{o}C is in course, aiming the practical use of these materials in PEFCs.

SELF-ASSEMBLING GELLING FORMULATION BASED ON LIQUID CRYSTALLINE PHASE AS A NON-VIRAL VECTOR FOR SIRNA DELIVERY

MARCIA CARVALHO DE ABREU FANTINI[1]; LIVIA NEVES BORGHETI-CARDOSO[2]; LIVIA VIEIRA DEPIERI[2]; MARIA VITÓRIA LOPES BADRA BENTLEY[2].

1.INSTITUTO DE FÍSICA-USP, SAO PAULO - SP - BRASIL; 2.FACULDADE DE CIÊNCIAS FARMACÊUTICAS DE RIBEIRÃO PRETO, UNIVERSIDADE DE SÃO PAULO, RIBEIRÃO PRETO - SP - BRASIL.

Palavras-chave: liquid crystal;gene therapy;siRNA

Resumo:

Liquid crystalline systems (LCSs) form interesting drug delivery systems such as in situ gelling delivery systems, which present several advantages to be used as a self-assembling system for local drug delivery. The aim of this study was to develop and characterize in situ gelling delivery systems for local siRNA delivery. The influence of the components that form the systems were investigated and the systems were characterized by polarized light microscope and SAXS. The system containing a mixture of monoolein, oleylamine, propylene glycol and tris buffer (8.16:0.34:76.5:15, w/w/w/w) was considered the most appropriate for local siRNA delivery purpose. The system was characterized as hexagonal phase. The system formed complex with siRNA and remained it in a stable form. The developed liquid crystalline delivery system shows appropriate characteristics to be used as a local siRNA delivery in gene therapy.

EFFECT OF COOLING RATE ON POLYMORPHIC BEHAVIOR OF SUNFLOWER OIL STEARINS

MARIA LIDIA HERRERA[1]; JAIME ALBERTO RINCON CARDONA[2]; ROBERTO JORGE CANDAL[2]. 1.UNIVERSIDAD DE BUENOS AIRES, BUENOS AIRES - ARGENTINA; 2.UNIVERSIDAD NACIONAL DE SAN MARTIN, BUENOS AIRES - ARGENTINA.

Palavras-chave: polymorphism;sunflower stearins;cooling rate

Resumo:

Many factors influence lipid crystallization: cooling rate, initial and final temperatures, agitation rate, cycling, aging, and triacylglycerol organization. Kinetics of crystallization is important in the food industry to produce the desired product characteristics. The aim of this work was to study the effects of cooling rate on polymorphism in two high stearic high oleic sunflower oil stearins (soft and hard), following crystallization behavior by SAXS, WAXS and NMR. The type of polymorphic forms and the kinetics of polymorphic transformations were quantified cooling the samples at three different rates: 0.5, 1, and 10°C/min or applying several heating/cooling cycles. Selected crystallization temperatures (T_c) were 5, 16, 17, 18.5, and 19°C for soft stearin and 10, 21, 22, 23, 24, and 25°C for hard stearin. Three polymorphic forms were observed when samples were crystallized at 10 °C/min to different T_c: α, β'_2, and β'_1. The β polymorphs were not obtained during the times selected for isothermal crystallization. However, β_2 form appeared at least after 6 h at T_c while after 48 h of storage at 25 °C the β_1 polymorph was the main form. The β_2 polymorphic form, which is required for chocolate manufacture, has a very short life and it was isolated from β_1 form by applying cooling/reheating cycles. For slower cooling rate more stable polymorphic forms crystallized. The β_2 polymorphic form crystallized when cooling at 0.5°C/min and its life was elongated.

EFFECT OF THE STEARIC SUCROSE ESTER S-170 ON THE POLYMORPHIC BEHAVIOR OF HIGH STEARIC HIGH OLEIC SUNFLOWER OIL STEARINS

ROBERTO JORGE CANDAL[1]; JAIME ALBERTO RINCON CARDONA[1]; MARIA LIDIA HERRERA[2]. 1.UNIVERSIDAD DE SAN MARTÍN, SAN MARTÍN - ARGENTINA; 2.UNIVERSIDAD DE BUENOSAIRES, BUENOS AIRES - ARGENTINA.

Palavras-chave: Lipids;Polymorphism;sucrose esters

Resumo:

Sucrose esters (SEs) can be used in foods as emulsifiers because they are nontoxic, tasteless, and odorless. In addition to their major function of producing and stabilizing emulsions, SEs have numerous other functional roles such as modifiers of crystallization of lipids. The aim of the present work was to analyze the effect of the SE S-170 on polymorphic behavior of high stearic high oleic sunflower oil stearins during isothermal crystallization with the aim of adding more evidence that improves the understanding of the mechanism of action. Two stearins were analyzed by SAXS and WAXS. S-170 effect was strongly dependent on crystallization temperature. At lower temperatures, when the a form was the main polymorphic form present, the effect was acceleration of crystallization. At higher temperatures, where the β’2 form did not crystallize, and stearins crystallized in the β’1 form, the effect was an acceleration of the formation of the a form and a notorious delay of the appeareance of β’1 form. The polymorphic forms with patterns that strongly differ from the S-170 pattern, such as the β’2 form, were not able to crystallize under the conditions used in this study. S-170 accelerated the polymorphic transition of unstable forms to the β2 form during storage. Taken into account that the β2 form is the required form for confectionary, S-170 effect is very relevant regarding industrial applications.

MICROESTRUCTURE CHARACTERIZATION OF CITRUS SINENSIS ESSENTIAL OIL SURFACTANT SYSTEMS

SARAH GUERRA FERREIRA[1]; VALÉRIA SANTOS CONCEIÇÃO[1]; NAYARA DE SOUZA GOUVEIA[1]; ALYNE DANTAS LIMA[1]; JOYCE KELLY MARINHEIRO DA CUNHA GONSALVES[1]; VICTOR HUGO VITORINO SARMENTO[1]; ROGÉRIA DE SOUZA NUNES[1].

1.UNIVERSIDADE FEDERAL DE SERGIPE, SÃO CRISTÓVÃO - SE - BRASIL.

Palavras-chave: SURFACTANTS SYSTEMS;PHASE TRANSITION;SAXS

Resumo:

Surfactant systems (SS) can undergo into phase transition (PT) in aqueous solution (AS) and become more structured aggregates which can be used as controlled release systems. Citrus sinensis (L.) Osbeck essential oil (CSEO) presents larvicidal activity against Aedes aegypti and was used as oil phase of these SS. The aim of this study was obtain and characterize SS composed by procetyl (P), oleic acid (OA), CSEO and water (W) for Aedes aegypti larvae control. The formulations were prepared by magnetic stirring with different proportions of P:OA 2:1/CSEO/W. The samples were evaluated by Polarized light microscopy (PLM) and SAXS measurements were held at the Brazilian Synchrontron Light Laboratory (LNLS), bean line 1. The phase diagram showed four different phases: microemulsion (ME), liquid crystal (LC), emulsion and phase separation. Ten samples were chosen for characterization. Samples A1-A3 exhibited dark field typical of ME isotropic behavior. Malthese crosses and oil streaks were observed in samples A5-A10 and fan shape texture in sample C4, typical of anisotropic lamellar (L) and hexagonal (H) LC respectively. SAXS measurements confirmed PLM structures, with broad bands of low intensity for MEs, phase transition (A4) and for LLC structure, the positions of the peaks obey the relationship 1:2:3 (A5-A10) and 1:√3:√4 for HLC (C4). In conclusion, the SS were successfully obtained and the two techniques combined were essential for their microstructure characterization.

ESTUDO DA FORMAÇÃO DE MICELAS E MICROEMULSÕES CONTENDO FÁRMACOS: UM ESTUDO DE INTERAÇÃO POR SAXS

DAYANE XAVIER DE OLIVEIRA[1], ROGÉRIA DE SOUZA NUNES[2], MARCELO LEITE DOS SANTOS[1], LEANDRO RAMOS SOUZA BARBOSA[3], VICTOR HUGO VITORINO SARMENTO[1]

[1]DEPARTAMENTO DE QUÍMICA – CAMPUS PROF ALBERTO DE CARVALHO- UFS – ITABAIANA/SE
[2]DEPARTAMENTO DE FARMÁCIA – CAMPUS PROF ALOISIO DE CAMPOS – UFS- SÃO CRISTOVÃO/SE
[3]DEPARTAMENTO DE FÍSICA GERAL - INSTITUTO DE FÌSICA – USP- SÃO PAULO

As micelas (MIs) e as microemulsões (MEs) são como sistemas estabilizados por tensoativos e se assemelham bastante com relação a sua estrutura e propriedades físico-químicas. Quanto a sua aplicabilidade, elas têm sido destacadas por serem capazes de veicular fármacos que possuem uma biodisponibilidade sistêmica limitada por via oral. O objetivo do presente trabalho foi a obtenção de sistemas micelares e microemulsionados (contendo óleo essencial de *Citrus sinensis* (L.) Osbeck como fase oleosa), estabilizados por um tensoativo não iônico (Tween 80) e um cotensoativo de cadeia curta (álcool etílico), que possam ser utilizados como sistema de liberação para a nifedipina (NFD, um fármaco modelo), buscando verificar a interação do fármaco na estrutura desses sistemas. Os aspectos macro e microscópicos foram avaliados utilizando microscopia de luz polarizada (MLP), medidas de pH e condutividade elétrica, tensão superficial e espalhamento de raios-x a baixos ângulos (SAXS). Os resultados demonstraram que esses sistemas são estáveis, isotrópicos e opticamente transparentes na ausência e presença de fármaco. Os modelamentos das curvas de SAXS para as MIs e MEs mais diluídas foram realizados e mostraram a interação existente entre a NFD e os sistemas.

24th RAU

ANNUAL USERS MEETING LNLS/CNPEM

March 11th and 12th, 2014

Abstracts

Macromolecular Crystallography (MX)

CRYSTALLIZATION AND PRELIMINARY X-RAY DIFFRACTION ANALYSIS OF TSA1^{R146Q} MUTANT FROM *Saccharomyces cerevisiae*

CARLOS A. TAIRUM JR[1]; LUIS EDUARDO SOARES NETTO[2]; MARCOS ANTÔNIO DE OLIVEIRA[1].

[1] UNIVERSIDADE ESTADUAL PAULISTA – SÃO VICENTE – SP – BRAZIL

[2] UNIVERSIDADE DE SÃO PAULO – SÃO PAULO – SP – BRAZIL

Palavras-chave: Peroxiredoxin;Crystallographic structure;Saccharomyces cerevisiae

Resumo:

Typical 2-Cys Peroxiredoxins are enzymes that make use of a reactive Cys (Cys_P) to decompose peroxides culminating with an intermolecular disulfide bond formation with a second Cys (Cys_R) that is carried out by Thioredoxin. The formation of this disulfide bond is related with structural enzyme alternations between states fully folded (FF), in which the enzyme is in the reduced state, and locally unfolded (LU), which occurs the partial unfolding of Cys_P containing α-helix to form the disulfide bond. We have solved and refined the crystallographic structure of yeast Tsa1^{C47S}, which revealed that Arg^{146} appeared to stabilize Tsa1 structure in FF state, through polar interactions with residues in active site. The substitution of Arg^{146} by a Gln indicated that Arg^{146} is implicated on the interaction Tsa1-Trx, which may be explained by redox-dependent alteration in protein shape with the involvement of Arg^{146}. Aiming to a better understanding on the effects of Arg^{146} substitution over Tsa1 structure we have performed crystallization experiments to determine Tsa1^{R146Q} structure. Best crystals were obtained in a H_2O_2 treated sample with the crystallization solution: 100mM citric acid-Na_2HPO_4 pH 6.0, PEG-8000 6% and 200mM $MgCl_2$. Data were collected using synchrotron radiation at the beamline D03B-MX1 of LNLS and they were indexed as P1 space group in a 2.6Å resolution (unit cell parameters a=39.35, b=130.43, c=132.20 Å and α=89.93; β=89,95 and γ=89,99).

Financial support: FAPESP; CNPq (Redoxoma)

CLONING, EXPRESSION, PURIFICATION AND CRYSTALLOGRAPHIC STUDIES OF A SCHISTOSOMA MANSONI ANTIGEN (RP22)

MARIANA FIGUEIREDO COSTA[1]; FERNANDES GOMES RODRIGUES[1]; BRISA ALVES CHAGAS[1]; CINTIA FAGUNDES REZENDE[1]; ALFREDO MIRANDA GOES[1]; RONALDO ALVES PINTO NAGEM[1].
1.UFMG, BELOHORIZONTE - MG - BRASIL.

Palavras-chave: Schistosomiasis;rP22;crystals

Resumo:

Schistosomiasis is a major parasitic disease which remains a public health problem in several tropical countries. Protective assays were done using one recombinant protein, named rP22. This polypeptide was identified as a parasite tegumental protein and was capable to reduce the granuloma size and the worm burden in a murine model (Rezende et al, 2011). In the present work, we characterized the structural components of this immunogenic protein. The rP22 gene was cloned into the pGEM vector and sub-cloned into the pET28a(TEV) vector. The recombinant protein was purified by affinity and size exclusion chromatographies. Crystals suitable for diffraction were grown in two different conditions: (i) 200 mM ammonium sulfate, 30% (w/v) PEG monomethyl eter 2000 and 100 mM sodium acetate buffer pH 4.6; (ii) 200 mM ammonium sulfate, 30% (w/v) PEG 8000 and 100 mM sodium cacodylate pH 6.5. X-ray diffraction data were collected at the Brazilian Synchrotron Light Laboratory (LNLS). Native crystals diffracted to 2.05 Å resolution while a quick cryo-soaked NaI derivative diffracted to 1.95 Å resolution. Crystals belong to space group $p6_122$ with unit cell parameters a=b=108.483, c=55.801 Å. SIRAS-derived phases were used to generate the first electron density map enabling rP22 model building and refinement. The study of the structure of rP22 is an important step to better understand its function and to localize the epitopes responsible for its protective immune responses.

STRUCTURAL CHARACTERIZATION OF NAHB: AN ENZYME INVOLVED IN METABOLIZATION OF A TOXIC COMPOUND

RONALDO ALVES PINTO NAGEM[1]; JULIANA BARBOSA COITINHO[1]; SAMUEL LEITE GUIMARÃES[1]; DÉBORA MARIA ABRANTES COSTA[1].

1.UNIVERSIDADE FEDERAL DE MINAS GERAIS, BELO HORIZONTE - MG - BRASIL.

Palavras-chave: nahB;Pseudomonas putida G7;bioremediation

Resumo:

The oil is a natural resource composed of a mixture of compounds including polycyclic aromatic hydrocarbons (PAHs), some of which are mutagenic and carcinogenic. The use and production of oil and its derivatives result in contamination of various ecosystems. Bioremediation is a strategy for elimination of hazardous compounds from the environment, which uses enzymes or microorganisms displaying the capacity to metabolize these compounds into inert substances. Pseudomonas putida G7 has the NAH7 plasmid, which possesses catabolic genes involved in metabolism of naphthalene, a PAH. The nahB gene is responsible for codification of the protein cis-1,2-dihydro-1,2-dihydroxynaphthalene-1,2-dehydrogenase, which converts cis-1,2-dihydronaphthalene-1,2-diol to naphthalene-1,2-diol in the presence of NAD^+. We present the cloning, optimization of expression and purification, crystallization assays and X-ray analysis of recombinant 6xHis-NahB. Purified 6xHis-NahB was used in circular dichroism and dynamic light scattering experiments for secondary structure and oligomerization state characterization, before crystallization assays. We have identified conditions for the crystallization of the enzyme. A crystal of 6xHis-NahB diffracted to 1.64 Å resolution belonging to space group I222, with unit-cell parameters a = 62.96, b = 69.33, c = 117.56 Å. The structure was solved by the Molecular Replacement method and refinement is currently underway.

Financial support: CAPES, FAPEMIG, Vale S.A.

CRYSTALLIZATION AND PRELIMINARY THREE-DIMENSIONAL STRUCTURE OF THE NAHK/NAHL: A PROTEIN COMPLEX INVOLVED IN NAPHTHALENE METABOLISM

SAMUEL LEITE GUIMARÃES[1]; JULIANA BARBOSA COITINHO[1]; DÉBORA MARIA ABRANTES COSTA[1]; RONALDO ALVES PINTO NAGEM[1].

1.UNIVERSIDADE FEDERAL DE MINAS GERAIS, BELO HORIZONTE - MG - BRASIL.

Palavras-chave: NahK / NahL;Pseudomonas putida;bioremediation

Resumo:

Many types of pollutants are released to the environment by anthropic activities related to the use of oil and its derivatives. Polycyclic aromatic hydrocarbons (PAHs) are an important family of such pollutants, some of which are mutagenic and carcinogenic. Several microorganisms were identified with the capability to metabolize these molecules, turning the bioremediation an interesting strategy for the reduction of PAHs from the environment. Naphthalene is a common and hazardous PAH, and the use of Pseudomonas putida for its degradation has been the focus of numerous studies. In P. putida G7, the enzymes NahK (4-oxalocrotonate decarboxylase) and NahL (vinylpyruvate hydratase) perform two sequential steps along the naphthalene degradation pathway. We present the cloning, expression, purification, crystallization assays and X-ray analysis of the NahK/NahL complex. The complex was also subjected to Circular Dichroism for secondary structure analysis; Dynamic Light Scattering and Small-Angle X-ray Scattering for oligomeric state characterization. These results were ambiguous about the oligomeric state of the complex, suggesting a hexamer or an octamer assembly. This doubt was solved by the crystal structure of the complex at 2.5 Å resolution, with unit-cell parameters a=100.41, b=219.96, c=310.36 and space group p212121, where two heterodecamers were identified. The structure was solved by the Molecular Replacement method and further structural refinement is currently underway.

CRYSTALLOGRAPHIC STUDIES OF NAHI AND ITS MUTANTS, AN ALDEHYDE DEHYDROGENASE FROM NAPHTHALENE DEGRADATION PATHWAY OF PSEUDOMONAS PUTIDA G7

SIMARA SEMÍRAMIS DE ARAÚJO[1]; CÍNTIA MARA LEAL NEVES[1]; RONALDO ALVES PINTO NAGEM[1].
1.UFMG, BELO HORIZONTE - MG - BRASIL.

Palavras-chave: Pseudomonas putida;Naphthalene;Bioremediation

Resumo:

Pseudomonas putida G7 is one of the most studied naphthalene-degrading species. Catabolic genes of NAH7 plasmid encodes for enzymes involved in the conversion of naphthalene to pyruvate and acetaldehyde. The NahI enzyme (2-hydroxymuconic semialdehyde dehydrogenase) is an aliphatic-metabolizing aldehyde dehydrogenase required for conversion of 2-hydroxymuconic semialdehyde to 2-hydroxymuconic acid. Crystals of recombinant NahI diffracted to 1.85 Å resolution and belong to the hexagonal space group $P6_422$, with unit-cell parameters a = b =189.47 c = 79.28 Å. It is noteworthy that NahF (salicylaldehyde dehydrogenase), other enzyme of the same degradation pathway, is an aromatic-metabolizing ALDH but shares a common scaffold with NahI despite their overall low sequence identity and different substrate specificity. Since slight differences on catalytic site of these enzymes may be suggested to be responsible for their diverse kinetic properties within a variety of aldehyde substrates, three NahI mutants forms were proposed. Diffraction data were collected and the structure determination is still in progress by Molecular Replacement method. Kinetic characterization will be conducted in order to allow determination of kinetics parameters for a wide range of substrates and conditions. These data may give evidences for NahI reaction mechanism and substrate specificity and are particularly useful for enzyme engineering aiming enzyme-assisted degradation processes of pollutants compounds

Index

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