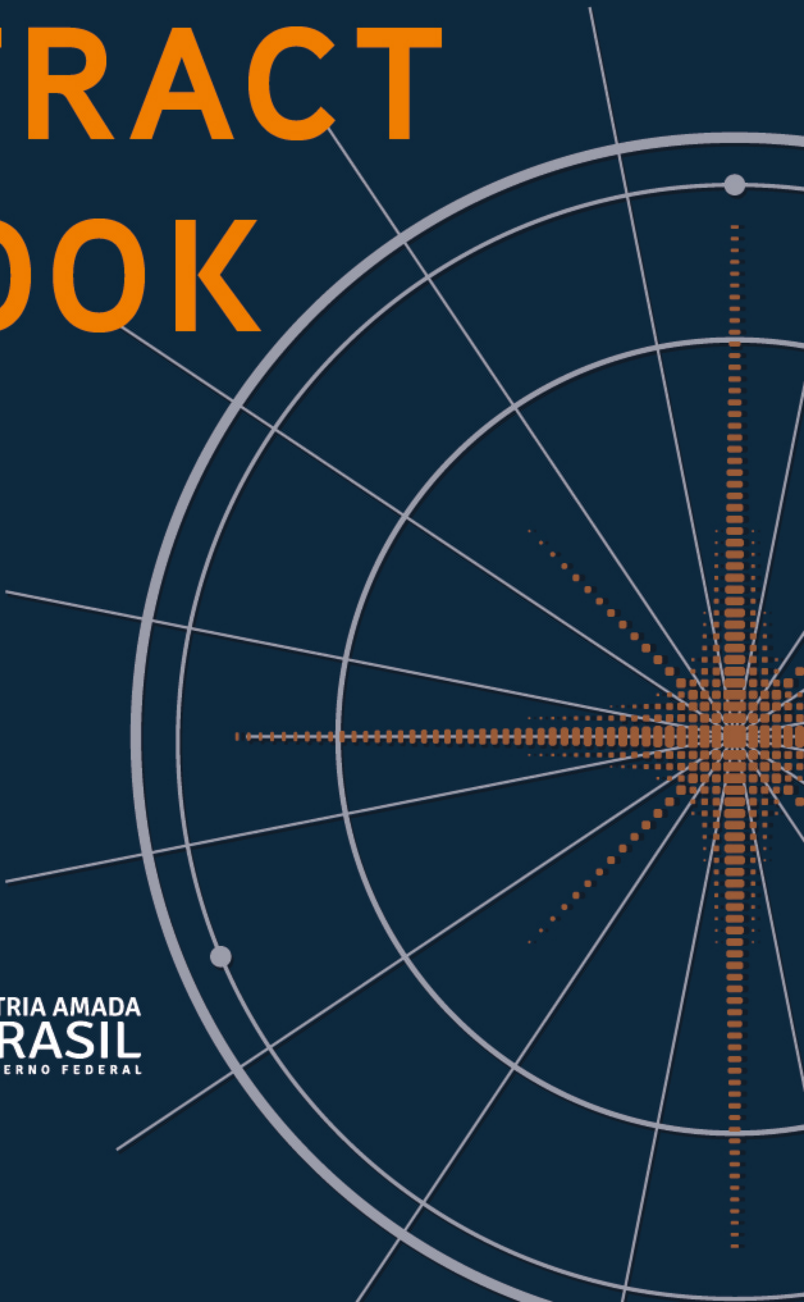
32nd RAU

Annual Users Meeting LNLS | CNPEM

November, 2022

ABSTRACT BOOK



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Foreword

Dear colleagues,

On behalf of the Scientific Organizing Committee, we would like to thank the participants of the 32nd Annual Users Meeting (RAU) of the Brazilian Synchrotron Light Laboratory (LNLS) of the Brazilian Centre Center for Research in Energy and Materials (CNPEM). Trying to reach as many people as possible, this year, the event was held in hybrid mode. The event hosted 139 participants in person and 159 online.

Due to the transition from the UVX machine to the 4th generation Sirius accelerator, most of the slots of the event were dedicated to a deep review of the facility's capabilities and operational status. Since the 31st RAU, the scientific commissioning of the Sirius beamlines has advanced and as announced by the LNLS directory, the first users through regular proposals shall be performing experiments already in the first semester of 2023. After the success of the Doctoral Thesis Award, at the 32nd RAU, the committee received applications and was awarded a prize for a Master’s Thesis.

In the past 12 months, the LNLS Users' Committee promoted nine online seminars, which contributed to keeping the community up to date on the progress of the assembly and scientific commissioning phase of Sirius, and aware of state-of-the-art developments in other synchrotrons around the world.

I also would like to thank the speakers and participants for their scientific contributions. We are also grateful to the sponsors and funding agencies that invested in the event. Finally, yet importantly, we thank the Local Committee and the CNPEM staff for their dedicated work in the organization.

Hudson W. P. Carvalho
Chair of the 32nd RAU

Summary

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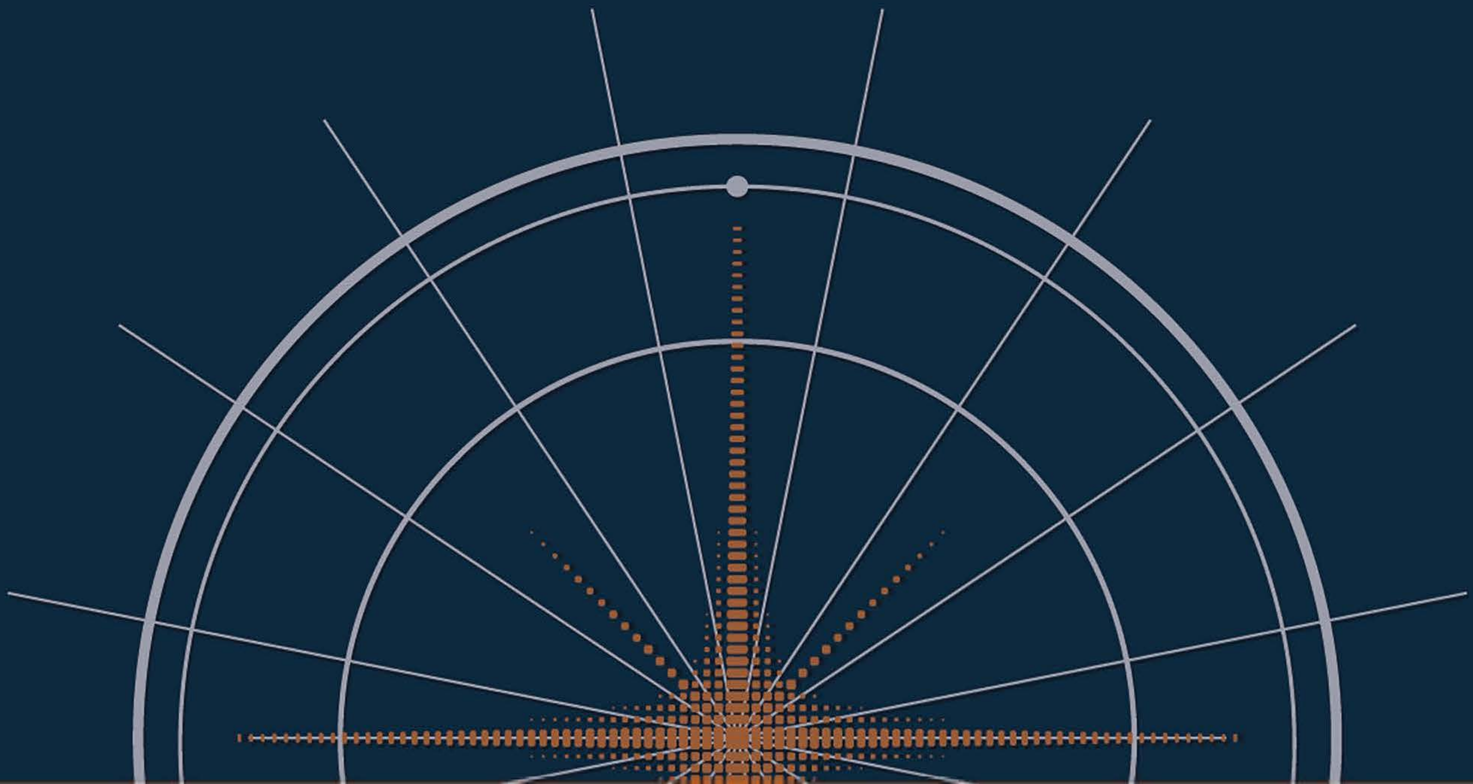
INVITED TALKS



Chemical Imaging of Heterogeneous Catalytic Systems using Hard X-ray Microscopy, Tomography, and Combined Methods

Thomas Sheppard[1]

[1]Karlsruhe Institute of Technology (Universität Karlsruhe)

e-mail: thomas.sheppard@kit.edu

Abstract

Solid catalysts play a crucial role in modern chemical and energy industries. Heterogeneous catalysis underpins the vast majority of synthetic chemical processes, as well as being essential for emissions control systems, air/water purification, and more recently in the global transition towards sustainable energy. Solid catalysts are functional materials, in which the physicochemical structure of the catalyst is strongly linked to its catalytic activity and performance. In addition, solid catalysts often possess complex hierarchical structural elements, such as individual active sites or metal nanoparticles, supported on hierarchically porous carrier materials, including composite materials and technical systems such as pellets, extrudates, and monoliths. In this context, catalyst characterisation is a broad and demanding field, requiring the interaction of many complementary analytical methods together with catalytic performance tests from model scale up to large reactor scale.[1] While no single characterisation method can give all the answers, each has a particular role to play.

Recent developments in synchrotron hard X-ray microscopy and tomography have opened a flexible and powerful toolbox for characterisation of catalysts and functional materials. Modern light sources are capable of producing focused micro- and nanoscale X-ray beams, which can perform spatially- resolved imaging together with a broad range of contrast modes such as absorption, fluorescence, and scattering. This contribution will highlight several applications which are particularly relevant for catalysis research, with a particular focus on hard X-ray ptychographic tomography (PXCT) for quantitative 3D imaging of catalysts at the nanoscale, and operando hard X-ray spectrotomography for chemical imaging of catalysts at work. The first case outlines a strategy for studying pore networks in solid catalysts, including hierarchically-structured materials with at least two distinct pore size distributions.[2] The role of PXCT is compared with complementary X-ray and electron imaging methods to visualise pore networks in 3D space from micro- to nanoscale. Further applications include the study of carbon deposition (coking) and other common deactivation mechanisms in solid catalysts,[3] along with the potential for quantitative structural analysis at <50 nm 3D spatial resolution.[1-3] The second case focuses on operando tomography combined with XANES to study technical catalyst materials under realistic reaction conditions. This includes observation of 3D structural and chemical gradients within washcoated Cu/zeolite and Pt/alumina monoliths for emissions control reactions such as NO_x reduction and NH_3 oxidation.[4] Here, development of appropriate sample environments for performing such studies will also be discussed.[5] In summary, one central aim of this

contribution (and of our group) is to improve awareness of hard X-ray tomography in the catalysis community and chemical industry, highlighting the unique capabilities of synchrotron radiation to solve complex challenges in this field.

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Integrating multiple Sirius beamline techniques to study complex hierarchical problems

Dean Louis Ralph Hesterberg[1]

[1]Laboratório Nacional de Luz Síncrotron (*DIRETORIA LNLS - DIR*)

e-mail: dean.hesterberg@lnls.br

Abstract

Natural systems generally comprise hierarchical structures that exhibit unique heterogeneities at different spatial scales of observation. I will present strategies for studying such hierarchical systems using multiple, complementary techniques at various Sirius beamlines in the context of examples from our current research. The focus will be on soils and the rhizosphere, the region of soil that is influenced by the presence of plant roots. Prior to the advent of advanced analytical techniques such as those available at synchrotrons, soil scientists often focused on synthetic model analogues of isolated soil components to gain deeper knowledge about chemical reactions such as those affecting the behavior of plant nutrients and potentially toxic soil contaminants. Highly specific information about surface reactions, for example, can be derived from measurements on single, isolated minerals. However, when only two dissimilar components are mixed, understanding non-additive behavior requires multiple analytical approaches that provide complementary viewpoints. Such multi-modal analyses are even more critical for gaining mechanistic information on soils, which comprise heterogeneous assemblages of many components including minerals and non-crystalline solids, biological residues, organic matter, living organisms, water, and air. Research on systems with such overwhelming complexity benefits from well-formulated hypotheses that can be strategically evaluated using experimental approaches and analytical techniques that match the spatial and temporal scales of the problem.

Nano-optics of atomic layered materials via synchrotron infrared ultramicroscopy

Raul O. Freitas[1]

[1]Centro Nacional de Pesquisa em Energia e Materiais (*LNLS*)

e-mail: raul.freitas@lnls.br

Abstract

Infrared (IR) spectroscopy is a standard analytical modality ready to approach multidisciplinary scientific questions. Among several advantages of this spectral tool, it is important to highlight its sensitivity to natural vibrational signatures of materials, enabling label-free access to chemical composition and coherent vibrations in materials in general. Despite the power of the technique, the advance of scientific questions at sub-micron scales has challenged IR analysis due to the intrinsic diffraction limit of light. Then, to overcome this limitation, novel techniques exploring near-field optics allowed IR to approach quantum scale phenomena in materials as they operate with few-nanometers lateral resolution and high sensitivity to the local optical properties of materials. That is the case for the scattering Scanning Near-field Optical Microscopy (s-SNOM), a technique that combine atomic force and IR microscopies to achieve nano-resolution for spectral imaging. The reach of the s-SNOM for broadband analysis is then extended with the use of synchrotron storage rings as they provide excellent spectral irradiance throughout the whole IR spectral range.

In this plenary talk, fundamentals of s-SNOM are presented in a multidisciplinary narrative in order to inspire the user's community of LNLS. Moreover, the talk brings a display of applications of synchrotron- and laser-based s-SNOM used to access nano-optics of a variety of two-dimensional materials. These applications emphasize the protagonist role of synchrotron s-SNOM in the field of nanophotonics and invite the community to explore this open-user facility to approach alike scientific questions.

Synchrotron radiation and laser light microscopy partnership for the study of biological systems: The case of soft X-ray tomography and structured illumination microscopy at cryogenic temperatures

Maria Harkiolaki[1]

[1]Diamond Light Source

e-mail: maria.harkiolaki@diamond.ac.uk

Abstract

CryoSXT offers us the opportunity to image cells and cell populations in 3D to a resolution of 25 nm (**Figure 1**). This places SXT well within capacity to deliver clear cellular imaging and, given the sizeable fields of view achieved (anywhere between 10 to 20 µm), document ultrastructure through swathes of intracellular and pericellular space in 3D. SXT imaging is done through absorption contrast in the water window of X-ray light where carbon-rich biological structures obstruct light as it passes through them as opposed to the oxygen-rich surrounding medium that does not. As a result, the impression left on a detector when an image is taken is a negative projection of the cell structure exactly like in the case of medical X-ray imaging. In fact, in concept and optical implementation this method is the cellular equivalent of a full body CT scan in a medical setting only adapted for the microworld of cells. Because imaging depends on cellular content alone, there is no requirement for contrast enhancing chemicals to be added and therefore the information captured has not been altered in any way by foreign material. An additional benefit comes from the fact that to help cells endure sustained exposure to X-ray light during imaging we snap freeze them before use, thereby perfectly preserving the exact instant of their lives that is of interest without altering any of the structures that we see.

Using cryoSXT we capture cellular ultrastructure that is faithful to the native conformation of the fully hydrated intracellular world in 3D. The next challenge we face is decorating this 3D map of life at the cellular level with chemical information pertinent to the distribution of biomolecules of interest such as the proteins within. Therefore, correlative imaging of the same sample across techniques and scales is both a necessary and rewarding proposition but also a challenging one. Collecting data on the same sample at different microscopes while preserving all its delicate structures intact and associating these data to a rich and meaningful correlated volume is a real challenge.

B24 is the correlative cryo-imaging beamline at the UK synchrotron, Diamond Light Source where two high resolution imaging systems have been developed side by side to enable the in-depth interrogation of biological systems at near physiological states in a semi-automated and user accessible platform [1]. The two imaging methods are: cryoSXT which uses the natural absorption contrast of hydrated biological material, such as cells and tissues and

cryo-fluorescence structured illumination microscopy (cryoSIM) which records localisation of tagged molecules, organelles and other cellular structures within the cellular map captured through X-ray imaging [2]. The attraction of this combination is that samples that are due to be used for X-ray imaging can be used first to generate 3D fluorescence information at high resolution on identified areas of interest before taken to the transmission X-ray microscope allowing for the accumulation of directly correlated localisation data meaning that the same sample is imaged sequentially avoiding sample to sample variations and therefore enabling the unambiguous interpretation of data.

The imaging pipeline we have described has allowed us to investigate pathogen-host interaction at the cellular level, drug-induced cellular landscape remodelling, cell-to-cell killing mechanisms, contaminant clearance and many other areas of biomedical importance [3]. A compendium of these results will be presented alongside particulars regarding the use of CLXT for their requirements.

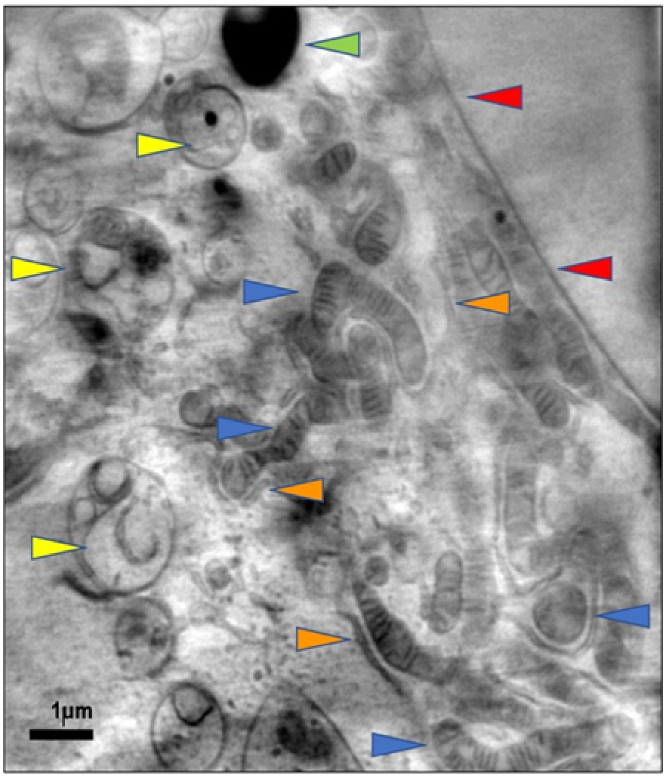

Figure 1. Projection through a human bone osteosarcoma fibroblast; field of view (10x10 microns) captures a cytoplasmic perinuclear area full of organelles and a small part of the nucleus (top right). Projection collected on B24 at 500 eV using a 25 nm objective zone plate. Arrows point to selected organelles; blue – mitochondria; green – lipid droplets; orange–endoplasmic reticulum; yellow–multivesicular bodies; red – nuclear membrane.

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ORAL COMMUNICATION

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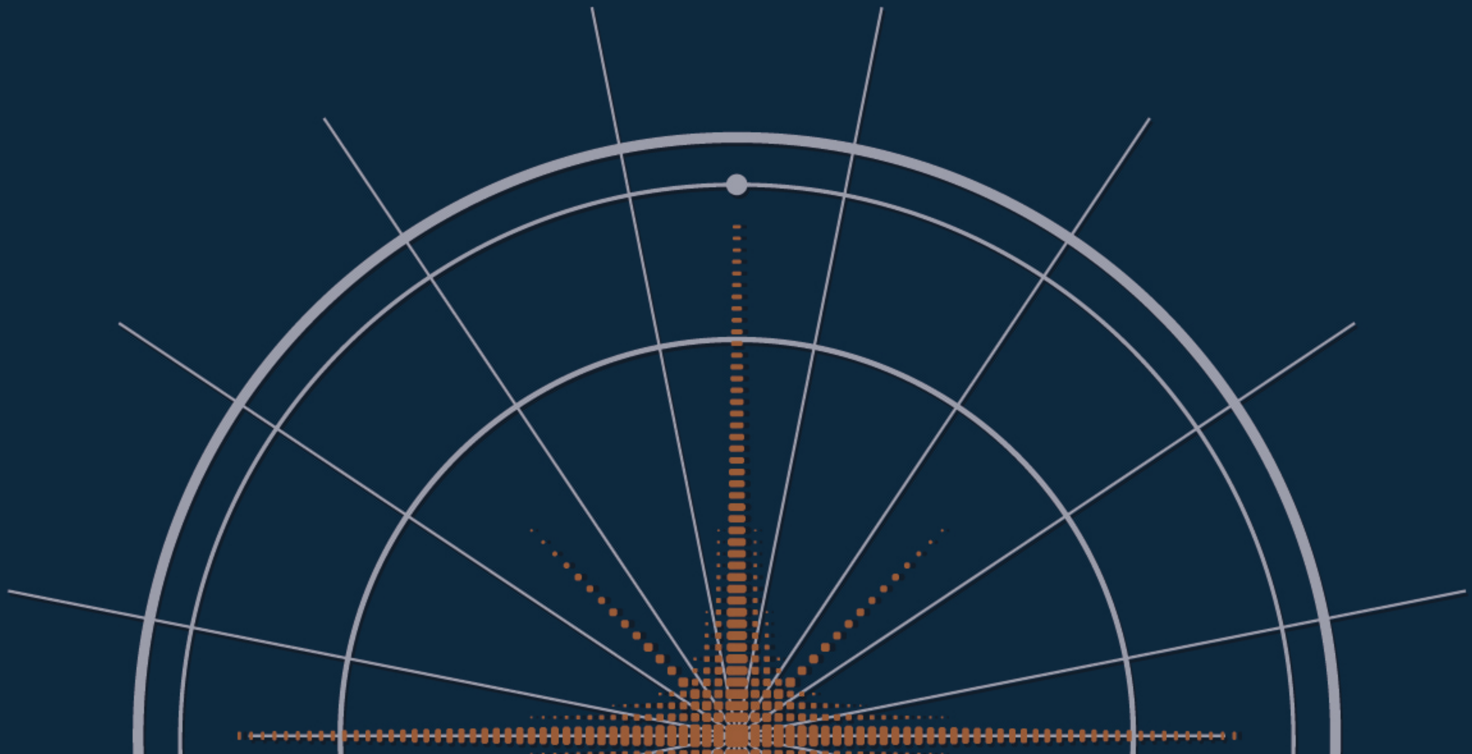

Cavity effect of phonon-polaritons on two-dimensional heterostructures of hBN and G-hBN

FLÁVIO HENRIQUE FERES[1]

[1]Brazilian Synchrotron Light Laboratory (*IMBUIA*)

e-mail: flavioferrs@gmail.com

Abstract

Optical phenomena of polar van der Waals crystals, on the nanoscale, occur primarily via polaritons, which are quasi-particles originated from the coupling between photons and fundamental resonances of matter. There are different Tipos of polaritons, named according to the presented light-matter interaction: plasmon-polaritons, exciton-polaritons, magnon-polaritons and phonon-polaritons. In this work, we study phonons-polaritons confined in two-dimensional crystals of hexagonal boron nitride (hBN). This crystal pertains to the class of hyperbolic materials, thus, supporting hyperbolic phonon-polaritons (HP^2) of subdiffractional wavelength. Hyperbolic polaritons are evanescent modes meaning they are confined to the crystal volume and do not propagate in the free space. Therefore, only near field techniques are able to detect the HP2 waves as the Synchrotron Infrared Nano Spectroscopy (SINS) utilized in this work. By means of SINS, we investigate first the hBN polaritonic response on gold (Au) flat substrates by proposing the Hertzian dipole antenna (HDA) modelling to characterize the HP2 waves. We have recently published this novel approach in journal Nanoscale. Additionally, we study the influence of different type of substrates on HP^2 waves propagation: (i) in-plane anisotropic substrate composed by Au stripes spaced by Air gaps (Au-Air) and (ii) out-of-plane anisotropic substrate composed by silicon dioxide thin films deposited via sputtering on Au (Au/SiO2). In the first case, we demonstrate the formation of HP^2 microcavities due to the momentum mismatch at the Au-Air substrate transitions. In the second case, we show modulation of wavelength and group velocity of HP^2 modes as function of the SiO2 thickness. This work presents pioneer results for the polaritonic area in mid-infrared of two-dimensional crystals.

Magnetic structures and transitions of $GdNiSi_3$ and $TbNiSi_3$

Rodolfo Tartaglia Souza[1]

[1]Universidade Estadual de Campinas (*IFGW*)

e-mail: rodolfotartaglia.s@gmail.com

Abstract

In this work, we solved the magnetic structures of GdNiSi3 and TbNiSi3 by means of resonant magnetic x-ray diffraction experiments. These compounds are members of the family RNiSi3 (R = Y, Gd-Lu), that presents an interesting antiferromagnetic ground state at low temperatures (TN = 2-32 K) evolving with R and metamagnetic transitions under applied magnetic field for some of the compounds. In our measurements on both Gd and Tb based-compounds, we found that the primitive magnetic unit cell matches the chemical cell below the N´eel temperatures TN = 22.2 and 33.2 K, respectively. The magnetic structure features ferromagnetic layers of Gd/Tb magnetic moments in the ac plane stacked in an antiferromagnetic + - + - sequence along the ~b axis, with magnetic moments along the ~a direction (magnetic space group Cmmm’), which contrasts with the + - - + stacking sequence and magnetic moments towards the ~b direction previously reported for YbNiSi3. This indicates a change in the coupling between second-neighbor as we move from Gd and Tb to Yb. We also observed that GdNiSi3 and TbNiSi3 shows a magnetoelastic expansion of the b lattice parameter upon cooling below TN , indicating that the + - + - coupling stabilizes the magnetic structure under this expansion.

Spin Orientation Manipulation of Antiferromagnetic CoO Thin Films Through Structural Deformations

Marina Raboni Ferreira[1]

[1]Centro Nacional de Pesquisa em Energia e Materiais (*LNLS*)

e-mail: marina.ferreira@lnls.br

Abstract

Spintronics is the research branch that uses the electron spin as the degree of freedom for transporting, processing, and storing information. In recent years, many studies have been focusing on applying antiferromagnetic (AFM) thin films as active layers for spintronic devices. Although AFM materials present many interesting properties, such as robustness against magnetic fields perturbations and ultrafast spin dynamics, the magnetic moment manipulation in such materials is very challenging. One approach to overcome that is through the application of controlled structural deformations to the film crystalline structure, which promote alterations to its magnetocrystalline anisotropy energy. Therefore, the goal of this Master‘s work is to study the possibility of manipulating the spin orientation in AFM Cobalt Oxide (CoO) thin films through the application of a controlled macroscopic strain. For this purpose, polycrystalline CoO thin films were deposited onto flexible cruciform Kapton substrates using reactive Magnetron Sputtering. To controllably perform in-plane extensive and compressive bi-axial deformations to such films, we developed a Bi-axial Multi Analysis Strain Instrument (2D-MASI). A device compatible with multiple synchrotron radiation techniques (e.g. X-ray Diffraction and X-ray Absorption Spectroscopy) and sample environments (e.g. low temperatures and high vacuum). The sample crystalline structure deformation was characterized by in-situ X-ray Stress Analysis (XSA) measurements. As a result, while performing an in-plane biaxial extension, we observed an increase of the in-plane Bragg distances (dhkl) along with a decrease of the out-of-plane dhkl values. Moreover, by performing in-plane contraction experiments along a single direction, we observed an opposite behavior than the described above (interplanar distances' in-plane contraction and out-of-plane extension). Finally, to connect the results obtained by XSA with the sample magnetic behavior, we performed X-ray Magnetic Linear Dichroism (XMLD) experiments. During these measurements, we acquired multiple absorption spectra for different strain states. By analyzing the intensity changes within the spectrum peaks, we deduced that the sample mechanical deformation was indeed causing the film spin axis to tilt. More specifically, the analysis of the XMLD data acquired at low temperatures suggests a tendency of spin axis orientation parallel to the film direction which is contracted the most.

Vibrational and Structural Properties of the Fe$_4$Sb$_{12}$ (R = Na, K, Ca, Sr, Ba) Filled Skutterudites

JULIANA GONÇALVES DE ABRANTES[1]

[1]Universidade de São Paulo

e-mail: juliana.abrantes@usp.br

Abstract

Skutterudites form a large family of intermetallic solid state functional materials presenting a high potential for thermoelectric applications. They are known to present a wide range of physical properties related to quantum many-body effects, such as superconductivity and magnetism, and in some instances strong electronic correlations giving rise to unexpected physical phenomena, that are sensitive to tuning parameters such as pressure, magnetic fields and chemical substitution. The resulting phase diagrams are rich and diverse. Accordingly, this type of material is in the spotlight of studies in many fields of research, given the vast number of phenomenological possibilities that remain unexplored. In fact, our group has a longstanding interest in the properties of skutterudite materials and in particular in the subject of this dissertation: the RFe4Sb12 (R = Na, K, Ca, Sr and Ba) filled skutterudites. This particular series is an example of one of the most challenging problems in condensed matter physics, which is the description of magnetic properties of the itinerant magnets. In this type of magnetism, the magnetic moment per magnetic atom site (in this case, the Fe site) is much smaller than expected for localized spins, suggesting their delocalization. Thence, itinerant magnets are also called small moment magnets. We addressed their electronic properties in order to investigate the nature of their magnetism and XANES (X-ray Absorption Near Edge Structure) experiments were performed, probing the local electronic structure of the FeSb3 coordination. It was noteworthy to find that this local structure could be connected to their magnetic behaviour, despite the character of their magnetism being itinerant. Nevertheless, what seems the main subject triggering most of the skutterudite oriented research is indeed their large potential for thermoelectric applications. Hence, in this dissertation we turn our attention to other properties of the RFe4Sb12 (R = Na, K, Ca, Sr and Ba) series, namely their vibrational and structural properties, all of which intimately relate to their thermoelectric properties. This way, we are able to present an integral picture of this series of skutterudites, so as to unravel the effect of the R filler atom substitution among them. In a first approximation, the good thermoelectric properties of R filled skutterudites are assigned to specific phonon modes inserted in the system through the presence of the R filler cations, that are believed to be weakly coupled to the rest of the structure. In this dissertation, we show that this scenario is not outright, and does not comprise all the R filled materials. This is exposed in the first set of results, that examined the vibrational dynamics of the materials by means of X-Ray Absorption Spectroscopy (XAS) experiments. Additionally, a systematic structural analysis of the materials is conducted via X-Ray Diffraction (XRD) as function of pressure, where the elastic properties of the materials are probed. These lead to theoretical calculations about the bonding properties, aiming to unwind some unexpected features of our experimental

fidings. Altogether, with the aid of EXAFS and XRD experiments, we hope to deliver a comprehensive study of the thermoelectric RFe4Sb12 (R = Na, K, Ca, Sr and Ba) filled skutterudites, providing a complete overview of their vibrational, elastic and bonding properties.

X-ray spectroscopy unfolding the effects of glyphosate on soybean (Glycine max L.) manganese foliar uptake

Bianca de Almeida Machado[1]

[1]Universidade de São Paulo (*CENA*)

e-mail: bianca.almeidamachado@gmail.com

Abstract

The spraying of tank mixtures with manganese (Mn) and glyphosate allows the nutrition of soybean crops resistant to glyphosate, while controlling weeds. However, complexation reactions can occur between these species, which has the potential to significantly decrease the efficiency of this operation. Thus, this study aimed to investigate the chemical reactions and the absorption of Mn by soybean supplied as MnSO4, MnCO3, Mn-ethylenediaminotetraacetic (Mn-EDTA), Mn-phosphite and Mn-glycine. In tank mixtures, approximately 30% of the Mn supplied via MnSO4 and Mn-glycine precipitated together with glyphosate molecules, in ca. 2:1 Mn:glyphosate molar ratio. X-ray absorption spectra (XAS) of the precipitates indicated that they presented the same chemical environment regardless of the employed source, this technique did not show evidence of soluble complexes. The use of Mn-EDTA, as well as maintaining the pH of the mixture below 2.5 prevents precipitation, while pH above 7 resulted in MnO(OH). MnSO4, MnCO3, Mn-EDTA and Mn-phosphite solutions/dispersions, with and without glyphosate, applied to soybean leaflets damaged the leaf cuticle, regardless of the glyphosate mixture. Except for MnCO3, all sources increased the Mn content in the treated leaf petioles. The glyphosate mixture reduced the absorption and transport of Mn when supplied via MnSO4 and Mn-phosphite, but XAS analysis showed no evidence of complexation of Mn by glyphosate inside the plants. The absorbed manganese is transported in a similar chemical environment when supplied as MnSO4 and Mn-phosphite, but Mn-EDTA was found in its pristine form in the treated petioles. The foliar absorption of droplets of MnSO4 and Mn-EDTA, with and without glyphosate, was monitored for 72 hours, following a sigmoid tendency of absorption. The glyphosate mixture decreased the leaf absorption of MnSO4 due to the precipitation of complexes on the leaf surface, but no effect on the absorption of Mn-EDTA was observed. The absorption of MnCO3 followed linear behavior, being absorbed very slowly. The application of glyphosate in conjunction with MnSO4 increased the activity of the superoxide dismutase enzyme (SOD), probably due to the unavailability of Mn for leaf absorption. The results presented in this study show that the efficiency of foliar fertilization with Mn is reduced due to interactions that occur in solutions where free Mn2+ ions are available for complexation at pH above 2.5. No evidence of intracellular complexation was found. In this sense, the employment of chelated sources, such as Mn-EDTA, is an alternative to enable the application of tank mixtures in glyphosateresistant soybean crops without losing the efficiency of the operation.

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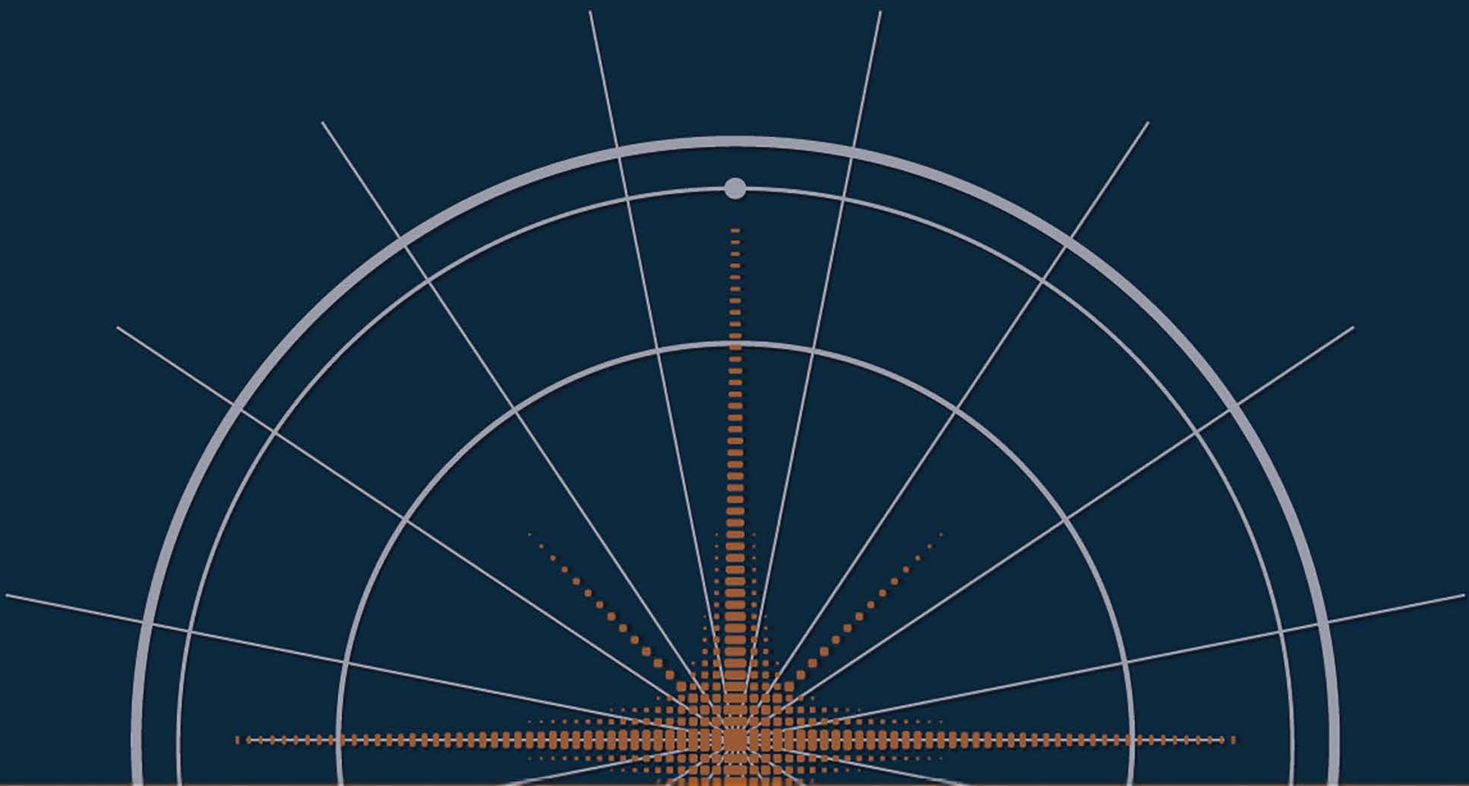
POSTER PRESENTATIONS



Accelerating phonon-polaritons in two-dimensional crystals by engineering dielectric-metallic substrates

FLÁVIO HENRIQUE FERES[1], Rafael Alves Mayer[2], Ingrid David Barcelos[3], Raul O. Freitas[3], Francisco Carlos Barbosa Maia[3]

[1]Brazilian Synchrotron Light Laboratory (*IMBUIA*) , [2]Universidade Estadual de Campinas (*IFGW*) , [3]Centro Nacional de Pesquisa em Energia e Materiais (*LNLS*)

e-mail: flavioferrs@gmail.com

Abstract

Control light-matter interactions at the nanoscale, like polaritons in two-dimensional (2D) crystals [1], is a prime goal in nanophotonics. Here we use synchrotron infrared nanospectroscopy (SINS) to demonstrate group velocity modulation [2] of subwavelength hyperbolic phonon-polariton waves, propagating in a 2D hexagonal boron nitride (hBN) crystal lying on a SiO_2/Au substrate, as a function of the SiO_2 film thickness, **d**. In quantitative agreement with our theoretical predictions, we observe that the polariton group velocity value notably increases **d** varies from 0 to 300 nm . Underpinned on such insightful observation, we simulate the polaritonic pulse dynamics for a layered heterostructure with a SiO_2 thickness gradient consisting of a hBN crystal lying on a SiO_2 wedge etched in Au . For the same timeframe, we note that the pulse propagates faster in the hBN/SiO_2-wedge/Au compared to that in hBN/Au. In contrast to the linear temporal displacement of the pulse on hBN/Au (crosses), we see a non-linear behavior (circles) for the wedge case. Using a semi-classical approach considering polaritonic pulse as a free particle possessing effective mass depending on the group velocity, we derive an equation of motion that not only explains the pulse dynamics either on the wedge and on Au but also allows for predicting its acceleration . Our work, therefore, reveals fundamental details on the semi-classic behavior of the polaritons in 2D crystals. Moreover, we show that metallic-dielectric functional substrates can be designed to control the dynamics of subwavelength polaritons which is highly desirable for polaritonic devices.

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Advanced Modelling of Lyotropic Liquid Crystals by Small Angle X-Ray Scattering

Cristiano Luis Pinto de Oliveira[1], Oscar Rodrigues dos Santos[2], Dennys Reis[1], Arnaldo Gomes de Oliveira Filho[1], Antonio Figueiredo Neto[1]

[1]Universidade de São Paulo (*Instituto de Física*) , [2]Universidade Tecnológica Federal do Paraná (*Departamento de Física*)

e-mail: crislpo@usp.br

Abstract

The micelles of a lyotropic liquid crystal present long-distance orientational order sensitive to concentrations of amphiphilic molecules, alcohols, ions and to the temperature of the sample. Under specific combination of these parameters, a biaxial nematic phase may emerge between calamitic and discotic phases. Also, by the inclusion of small fractions of ferrofluids, the use of external magnetic fields can promote the orientation of the groups of micelles in the system [1,2]. Small-Angle X-ray scattering experiments is a very useful probe to investigate structural features on this system since it can be used directly in the solution system. However, since one has the micelles combined in different types of supramolecular arrangements, the analysis of the scattering data is not trivial, and demands the development of advanced modelling tools. In this work we present a recent model [3] very useful to investigate the micellar structure by the use of SAXS experiments. As will be shown, the micelles are modelled as core-shell ellipsoidal particles forming planar layers, which pills up as lamellar structures. From the fitting of the full scattering curve one can obtains detailed structural parameters. This model was successfully applied for the investigation of the effect of chiral molecules in lyotropic cholesteric calamitic phases [3] but it is a very versatile approach and can be used in a number of systems composed by liquid crystals.

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Advances towards performing in situ Bragg coherent diffraction imaging in electrochemical systems

Rafael Alcides Vicente[1], Itamar Tomio Neckel[2], Pablo Sebastián Fernández[1]

[1]Universidade Estadual de Campinas (*Físico-química*) , [2]Centro Nacional de Pesquisa em Energia e Materiais (*SIRIUS*)

e-mail: rafael_ph1@hotmail.com

Abstract

Bragg coherent diffraction imaging (BCDI) is a lensless imaging technique which uses x-rays to recover the tridimensional shape and strain from single nanoparticles. Both these parameters are extremely important for electrochemical systems [1]. The shape can be used for tracking particle stability, or it can be correlated to other experimental data to elucidate the reaction mechanism. The strain is directly connected to the binding energy, one if not the most important for catalysis. Although strain is that important in the field, studying it *in situ* is not straightforward. In this context, BCDI represents a potentially powerful tool for electrochemists.

The Carnaúba beamline in SIRIUS is a nanofocus beamline which allows performing BCDI [2]. However, being a nanofocus beamline implies that the sample must meet several important physical requirements related to size and mechanical stability. Thus, in order to perform *in situ* BCDI, we developed, along with the Carnaúba research team, a spectroelectrochemical cell that fits the beamline. The cell electrochemical response has already been extensively characterized. In addition, it has already been successfully employed in *in situ* analyses using other techniques such as nanoXAS and nanoXRF.

In this work, we will show our recent advancements towards *in situ* BCDI. We will show the sample preparation of the shape-controlled nanocrystals. Besides, we will show the nanodiffraction results, which is an important step towards the final image reconstruction. At last, we will conclude with some important perspectives, and also show the challenges we are facing during the development stages.

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An integrative structural biology pipeline for the discovery of novel human kynurenine 3-monooxygenase inhibitors

Amanda Araujo Souza[1,2], Andrew Albert de Oliveira[1,2], Artur Torres Cordeiro[2], Jessica do Nascimento Faria[2], Renata Rocha de Oliveira[2], Joane Kathelen Rustiguel Bonalumi[2], Alexandre Cassago[3], Rodrigo Villares Portugal[3], José Carlos Alves-Filho[1], Fernando de Queiroz Cunha[1], Thiago Mattar Cunha[1], Daniela Barretto Barbosa Trivella[2]

[1]Universidade de São Paulo (*FMRP*) , [2]Centro Nacional de Pesquisa em Energia e Materiais (*LNBio*) , [3]Centro Nacional de Pesquisa em Energia e Materiais (*LNNano*)

e-mail: amanda.araujo@lnbio.cnpem.br

Abstract

The kynurenine 3-monooxygenase (KMO) is an important protein branching of the kynurenine pathway, catalyzing the hydroxylation of L-kynurenine to form 3-hydroxykynurenine (3-HK), a neurotoxic compound. The 3-HK induces apoptosis and injurious to different cell types. This enzyme is an attractive therapeutical target for neuroinflammatory diseases and is the target of our project which intends to discover and develop novel KMO inhibitors in the context of neuropathic pain[1]. We aim to find new inhibitors for KMO coupling screening of innovative chemical libraries (from both synthetic and natural origins) with integrative structural biology. The first step was to purify the KMO for both inhibition and structural biology assays. A robust high-throughput screening (HTS) assay (Z’>0.8, I/noisy> 6) was developed for screening hKMO inhibitors. About 15 thousand compounds were tested, and the hits found were further validated using orthogonal assays. For structural studies, the complexity of full-length hKMO, a membrane protein, and the crystallization is challenging, being so far unsuccessful. In our project, hKMO-FL was produced for HTS campaigns, as well as for cryo-EM data collection and structural elucidation. We produced a truncated version of the hKMO and homologous pfKMO and scKMO, for high-throughput crystallography approaches[2]. These KMO variants were crystallized and diffracted at the MANACA beamline (Sirius, Brazil), with structures determined to up to 1.8 Å. The next step will be the soak of the hits found in our HTS, for structure determination of protein-ligand complexes, using XDS and PanDDA pipelines. In parallel, electron microscopy routines are being established to determine the hKMO-FL structure and its complexes with the hits found by HTS. It is expected that strategy of the different structural approaches and orthogonal assays will help us to obtain KMO complexes with hits that will be used to guide lead molecules for neuropathic pain targeting KMO.

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A two-step GISAXS characterization of $NiSi_2$ nanoplates buried in a Si(001) wafer and Ni nanocrystals embedded in a deposited Ni-doped SiO_2 thin film

Daniel da Silva Costa[1], Guinther Kellermann[2], Aldo Felix Craievich[3]

[1]Universidade Federal do Paraná (*Física*) , [2]Universidade Federal do Paraná (*Departamento de Física*) , [3]Universidade de São Paulo

e-mail: daniel.costa@ufpr.br

Abstract

We present here a 2D-GISAXS study of the nanostructural features of a Si(001) wafer - in which a Ni-doped SiO_2 thin film was deposited - after submitting it to a isothermal treatment at 700 °C. During this thermal treatment two types of nanocrystals are formed: (i) thin hexagonal $NiSi_2$ nanoplates located near the external surface of the S(001) wafer with their {111} crystallographic planes parallel to the Si{111} planes, and (ii) spherical Ni nanocrystals embedded in the Ni-doped SiO_2 thin film. The formation and the growth of these nanocrystals take place because of the thermal diffusion of Ni atoms during the isothermal treatment. A preliminary study indicated that the 2D-GISAXS intensity associated to the whole sample is essentially isotropic and produced by spherical Ni nanocrystals. Additionally, a very weak anisotropic contribution from $NiSi_2$ nanoplates was observed. Thus, the analysis of this pattern only allowed us the structural characterization of the Ni nanocrystals. For characterizing the $NiSi_2$ nanoplates we have recorded another GISAXS pattern corresponding to the same sample after removal of the SiO_2 thin film by chemical etching. The GISAXS measurements were performed at the Department of Physics, UFPR. As expected, the anisotropic GISAXS pattern recorded after removal of the SiO_2 thin film was almost totally produced by the scattering intensity from the $NiSi_2$ nanoplates. By applying the best-fitting procedure of a modeled isotropic 1D-GISAXS function to the experimental scattering intensity from the whole sample, we were able to precisely determine the average radius and radius dispersion of the polydisperse set of the spherical Ni nanocrystals. By also applying the fitting procedure to the anisotropic experimental scattering intensity recorded after thin film removal, we could precisely determine the lateral sizes and average thickness of the hexagonal $NiSi_2$ nanoplates.

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Characterization of pillared-layered bimetallic MOFs using synchrotron radiation

Christian Wittee Lopes[1], Tatiana Zanette[2], Katia Bernardo-Gusmão[2], Giovanni Agostini[3]

[1]Universidade Federal do Rio Grande do Sul (*Instituto de Química*) , [2]Universidade Federal do Rio Grande do Sul, [3]ALBA synchrotron

e-mail: chriswittee@gmail.com

Abstract

Ni2(BDC)2(DABCO) is a highly active catalyst in the ethylene oligomerization into alpha olefins, although the reaction results in the breaking of M-L bonds when a Ni coordination site is taken by ethylene. This could be avoided by preparing bimetallic MOFs containing Zn, which is inert to the reaction. Although, the metals might adopt a heterogeneous distribution throughout the MOFs, deviating from the desired molar ratio. The goals of this study are to evaluate the influence of synthesis approaches on the properties of bimetallic MOFs. During the synthesis, the metals were added using two approaches: both metals were simultaneously added (1 step), or the first metal was added along with the organic linkers, and the second metal was added 24 h later (2 steps). The reflux and autoclave syntheses occurred at 110 °C for 48h, using DMF as the solvent. The materials Ni/Zn-R and Ni/Zn-A were obtained through 1 step approach. As for the 2-step materials, Ni-Zn-R and Ni-Zn-A, Ni was added first, then Zn was added 24h later. For the materials Zn-Ni-R and Zn-Ni-A, Zn was added first, while Ni was added 24h later (where R= reflux and A= autoclave). The metal locations were determined through Micro-XRF at Carnaúba Beamline at Sirius. The results indicated that the synthesis approach influences the crystal size, morphology, and metal distribution across the materials. Ni-Zn-R showed spherical particles with Zn agglomerates on the surface while Zn-Ni-R showed cylindrical particles with Ni agglomerates on the surface. Autoclave samples presented irregular morphology and crystal sizes, with Ni and Zn isolated agglomerates. In addition, Ni/Zn-R was analyzed by XAS at ALBA synchrotron (Spain). The obtained data indicated the absence of Zn and Ni in the oxidic and metallic forms, indicating the presence of Ni2+, which is the main catalytic active precursor species in heterogeneous systems, suggesting the suitability of the bimetallic MOF for ethylene oligomerization.

Characterization of the flexibility of proteins in solution

Julia Caroline Porfirio[1], Mario de Oliveira Neto[2]

[1]Universidade Estadual Paulista (*Biofísica e Farmacologia*) , [2]Universidade Estadual Paulista (*Biofísica e Farmacologia*)

e-mail: jporfirio1@hotmail.com

Abstract

Knowledge about the structure and function of proteins is extremely important for understanding their functioning. The structural flexibility of proteins is presented as a characteristic without which few of them could perform their biological functions. The flexibility present in certain regions of proteins can often be related to evolutionary events, allowing the expansion of the understanding of the system under study. Small angle X-ray scattering (SAXS) can be used to obtain structural information under conditions close to the native state in a wide variety of biological systems, where physiological conditions such as pH, ionic strength and temperature can be simulated. The validation of macromolecular flexibility in solution through the Small angle X-ray scattering (SAXS) has become a central tool in the characterization of systems that have multistates. SAXS provides critical technology for evaluating macromolecular flexibility as well as shape. Rambo et al. He described the use of Kratky and Porod-Debye law as a powerful tool to distinguish between rigid and flexible particles. As an objective, the work characterizes the flexibility of different proteins as Glycoside hydrolase, Bovine Serum Albumin, Glucose Isomerase e Chitanase, available on Small Angle Scattering Biological Data Bank (SASBDB), from the use of Kratky (I(q).q2 vs q) and Porod-Debye (I(q).q4 vs q4) analyses.

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CORRELATION BETWEEN CHROMIUM OXIDATION STATE AND PHOTOCATALYTIC PROPERTIES IN STRONTIUM TITANATE

Alejandro Fernández[1], Manuela Leticia Kim[2], Eugenio Hernan Otal[3], Ismael Oscar Fábregas[1]

[1]Instituto de Investigaciones Científicas y Técnicas para la Defensa (*Departamento de Materiales Avanzados y Procesos Estratégicos*) , [2]Shinshu University (*Department of Chemistry and Materials*) , [3]Shinshu University (*Department of Materials Chemistry*)

e-mail: afernandez@citedef.gob.ar

Abstract

Strontium titanate (STO) has a perovskite structure whose atoms can easily be substituted by transition metal dopants (usually abundant and low-cost elements). This modulates the STO physicochemical properties (magnetic, electrical, catalytic, etc.). A feature that is advantageous vs. TiO_2, where Cr transforms anatase into rutile, thus losing the desired properties[1].

STO has an ideal band-gap (BG = 3.2 eV)[2] for photocatalytic decomposition, but a low absorption in the visible light range that limits its use to the ultraviolet region (UV). The UV is a small part of the solar energy that reaches the earth surface. (4% UV vs. 41% visible light)[3].

Pure STO and Cr-doped STO (Cr:STO) samples were synthesized and characterized by diffuse reflectance spectroscopy (DRS), photocatalytic activity (PCA), X-ray diffraction (XRD) and absorption (XANES).

All samples showed the same crystalline phase (Space group *Pm3m*), without impurities.

All Cr:STO samples showed a decrease in BG from 3.2 eV to 2.5 eV, an optimal value for efficient absorption of visible light.

XANES data showed that Cr in all Cr:STO samples is in an octahedral ($\mathbf{O}_h$) environment, replacing Ti[4], in a +3 oxidation state. The exception was STO:0.5 mol% Cr (Cr0.5:STO), with an unusual +4 state. To confirm this state, the peaks preceding the Cr *K*-edge were carefully analyzed, this sample presented a peak at 5991.8 eV (assigned to Cr^{4+}) and absence of the peak at 5989.5 eV (assigned to Cr^{3+})[5]. The $(\text{Cr6:STO})_{\text{Ox}}$ sample exhibited, in addition to the Cr^{3+} peak, a signal at 5993.4 eV, assigned to Cr^{6+} or a distorted $\mathbf{O}_h$ environment[5]. The peak disappeared after a reducing thermal treatment.

To conclude, Cr was introduced into the STO crystal lattice in all samples, hosted in an $\mathbf{O}_h$ environment, replacing Ti. Regardless of the Cr oxidation state, its presence decreases the PCA despite the successful shift of BG.

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Crystal structure of L-threonine dehydrogenase from T. cruzi and its allosteric activation by potassium ion

Jessica do Nascimento Faria[1], Michelle Fagundes[1], Gustavo Fernando Mercaldi[1], Artur Torres Cordeiro[1]

[1]Centro Nacional de Pesquisa em Energia e Materiais (*LNBio*)

e-mail: jessica.faria@lnbio.cnpem.br

Abstract

Here, we report for the first time the potassium allosteric activation of the enzyme L-threonine dehydrogenase from Trypanosoma cruzi (TcTDH) based on new crystallography structures diffracted in MANACA beamline (SIRIUS-CNPEM). TcTDH activity is increased 20-fold in the presence of 50 mM KCl and at this concentration the potassium causes an increase in the enzyme velocity with a concomitant reduction in the affinity for the substrate and cofactor. Furthermore, direct site mutagenesis at a potassium coordination residue abolishes TcTDH activity. These kinetics studies corroborate that potassium allosteric activity and its binding site in TcTDH crystallography structure.

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Development of Spectroelectrochemical Cells for In *situ* FTIR Imaging and *Ex situ* XRF Mapping:*A* Multi-Technique Approach

Swathi Patchaiammal Raju[1], Rafael Alcides Vicente[2], Pablo Sebastián Fernández[2], Itamar Tomio Neckel[3]

[1]Universidade Estadual de Campinas (*Physical chemistry*) , [2]Universidade Estadual de Campinas (*Físico-química*) , [3]Centro Nacional de Pesquisa em Energia e Materiais (*SIRIUS*)

e-mail: s264616@dac.unicamp.br

Abstract

We have developed two spectroelectrochemical cells, which allows Fourier Transform Infrared (FTIR) imaging and X-ray Fluorescence (XRF) mapping analysis for the same working electrode. This combination was chosen to take advantage of each technique, in a way that the results from both techniques complement each other. The combination of elemental mapping with the molecular spectroscopy provides an in-depth characterization of catalyst participating in the electrochemical reactions. In order to locate the same region in the catalyst using different techniques, we mark the region of interest with focused ion beam milling using FIB-SEM technique. XRF mapping of FIB electrodes were performed in the Carnaúba nanofocus beamline[1], at SIRIUS synchrotron facility. The XRF mapping technique offers elemental and structural analysis in the range of nanoscopic scale. On the other hand, FTIR imaging provides the chemical sensitivity that XRF lacks. Using this set up, the analysis of multicomponent systems with both structural and chemical sensitivity is attainable which are necessary for better understanding of intricate electrochemical mechanisms. Besides these advantages, all of the FTIR measurements are performed*in situ* , allowing more accurate determination of phenomena occurring at the electrochemical interface. Although the cells were made for a specific purpose, they allow experiments using other techniques.

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Effect of adding TiO_2 nanoparticles to systems stabilized by surfactant containing different vegetable oils

Renata C. K. Kaminski[1]

[1]Universidade Federal de Sergipe (*Quimica*)

e-mail: re_kaminski@hotmail.com

Abstract

Cosmetic creams are examples of surfactant stabilized systems. Such systems are good alternatives for a possible controlled release of assets. Within this perspective, some vegetable oils, such as coconut oil (*Cocos nucifera L.)* and Pracaxi oil (*Pentaclethra macroloba*) can be used due to their anti-inflammatory, antibacterial and repellent/insecticide properties, respectively. Can also be added to multifunctional cosmetics TiO_2 (titanium dioxide) nanoparticles, an inorganic filter widely used in industry[1]. Thus, the aim of this work is to develop nanosystems stabilized by surfactants containing TiO_2 nanoparticles to photoprotection and study the influence of contends (oil/water/surfactant) in nanostructure of systems.

The formulations were obtained from a ternary surfactant/oil/water mixture, keeping a constant ratio of oil, in which the surfactant used was Polysorbate 80. In formulations with TiO_2 nanoparticles, the same was added in the amount of 15% (w/w).

The results of the analysis of the formulations containing 30, 40 and 50% surfactant, both with Pracaxi oil and coconut oil, indicated that the increase in the amount of surfactant in the system, causes a tendency to increase the structuring and viscosity of the formulations. This behavior is due to the tendency that the surfactante presents to form a mixture of cubic phases[2]. Was observed that only the formulation with 30% surfactant shows a pseudoplastic behavior, which is satisfactory for use in sunscreens. From the results obtained formulations with the presence of TiO_2, it was observed that the interaction between the components of the formulation containing Pracaxi oil is stronger than in those containing Coconut oil. The SAXS curves obtained for the formulations showed a single broad peak, thus, it is suggested that the TiO_2 associated with the surfactant may have imposed a new structure on the system, which may occur with the insertion of the nanoparticle in the middle of a micelle of the core- shell.

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Effect of high pressure on the structure of lithium disilicate glass-ceramic

Gisele de Lima Hippler[1], Leonardo de Lima Evaristo[1], RAFAEL ABEL DA SILVEIRA[1], Ricardo Donizeth dos Reis[2], Ulisses Ferreira Kaneko[2], Silvio Buchner[3]

[1]Universidade Federal do Rio Grande do Sul (*Programa de Pós-Graduação em Ciência dos Materiais*) , [2]Brazilian Synchrotron Light Laboratory, [3]Universidade Federal do Rio Grande do Sul (*Laboratório de Altas Pressões e Materiais Avançados - Instituto de Física*)

e-mail: gl.hippler@gmail.com

Abstract

Glasses are defined as amorphous solids obtained from melting-quenching, resulting in isotropic solid materials. When glasses are heated to the glass transition (Tg) region, the atomic mobility increases, leading to the formation of crystalline nuclei embedded in the amorphous matrix. Depending on the thermal treatment, these nuclei can grow and give rise to a glass-ceramic materials above the crystallization temperature (Tc). With extremely high loads in the GPa region, static pressures can exert an actual catalyst effect on the crystallization of glass at room temperature [1]. The lithium disilicate glass and glass ceramic have been widely studied at high pressure, presenting interesting results such as formation of polyamorphism due to the induced densification, and this structure has been found to be compatible with presence lithium metasilicate [2]. In this work we discuss the in situ analyses of Raman spectroscopy and x-ray diffraction (XRD) of both amorphous and crystalline lithium disilicate, at pressures up to 75 GPa performed at EMA beamline (proposal #20210168). Preliminary results suggested pressure induced phase transformation on a crystalline sample, followed by amorphization observed through XRD, where it presents a Raman spectrum similar to the pristine glass.

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Effect of Pressure on L-asparagine Monohydrate Fe(III) Crystal: An synchrotron radiation X-ray diffraction study

Cláudio Remedios[1], Raul Costa de Oliveira[1], Guilherme Calligaris de Andrade[2]

[1]Universidade Federal do Pará (*Física*) , [2]Centro Nacional de Pesquisa em Energia e Materiais (*LNLS*)

e-mail: rocha@fisica.ufc.br

Abstract

Controlling polymorphism as well as predicting new polymorphs are important problems in solid state science. Modifications in the crystalline environment, variations in pressure, for example, can induce distortions in the crystal structure and consequently generate new polymorphs. In this work Crystals of L-asparagine monohydrate doped with Fe(III) were studied by X-ray diffraction. The measurements were performed at the Brazilian Synchrotron Light Laboratory (LNLS-Sirius) at the EMA (Extreme Methods of Analysis) beamline [1]. these results are part of recently published studies with this material. [2, 3]. The selected energy was 25 keV (λ = 0.48594 Å), calibrated by Ag K-edge absorption. Pressure cells (DAC) used a stainless-steel gasket charged with Ne gas at 0.67 GPa. Measurements were performed in the range of 1.0 to 9.3 GPa The diffraction patterns were adjusted by Le Bail refinement at different pressures. All diffraction patterns were fitted with the same orthorhombic symmetry and P212121 (D4 2) space group. The lattice parameters contract up to 9.3 GPa, with the exception of parameter b, which exhibits expansion from 7.2 GPa. The lattice parameters exhibit discontinuities between 3.0 and 4.0 GPa. All these observations are compatible with conformational changes.

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Electronic band structure of the CDW candidate material Ni_xZrTe_2 (x = 0.0 and 0.05) probed by ARPES

Pedro Henrique Arantes Moya[1], FERNANDO ASSIS GARCIA[2], Marli dos Reis Cantarino[2], Rodrigo Calle Rodrigo Mário Calle Huamani[2], Hanna Martins Morilhas[2], Wagner Ribeiro[2]

[1]Universidade de São Paulo (*Física Aplicada*) , [2]Universidade de São Paulo

e-mail: pedro.moya@usp.br

Abstract

Transition Metals Dichalcogenides (TMDs) constitute an important family of 2D materials suitable for a number of device applications as well as an important platform to explore the effects of lattice commensurability and competing, or cooperating, ordered phases. The $ZrTe_2$ crystal structure features stacked layers of hexagonal lattices, making $ZrTe_2$ a quasi 2D hexagonal material[1,2].

Transition metal intercalation in $ZrTe_2$ fills the material van de Waals gap and contributes with a few d states to the Fermi level, with a significant impact on the material electronic properties. Indeed, it was recently demonstrated[1] that Ni intercalation promotes the emergence of a CDW transition at about 285 K, which is followed by a SC transition at about 4 K. Therefore, Ni_xZrTe_2 is a novel material platform to explore the coexistence between CDW and SC as well as the relation between the lattice symmetries and the mechanism of CDW formation.

In this work, we present results from angle-resolved photoemission spectroscopy (ARPES) experiments of Ni_xZrTe_2 (x = 0.0 and 0.05). ARPES is the standard technique to characterize the band electronic structure and Fermi surface of metals. Experiments were performed above and below the CDW transition temperature in a synchrotron ARPES setup on the BLOCH beamline, at MAX IV, adopting a different range of incident photon energy. In this energy range, it was possible to probe the electronic structure at the material G and A points. The bands were probed in the G-X (A-H) and G-M (A-L) directions of the hexagonal Ni_xZrTe_2 Brillouin Zones (BZ) as well as Fermi maps.

We find well dispersive bands across the material BZ that compares quite well with electronic band structure calculations. The band folding due to the CDW transition, however, was not clearly observed. A preliminary dependence of the folding on the incident photon energy is presented.

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Electronic characterization of the Mn_3O_4 thin film on metal substrates: resonant photoemission study

Emilia Annese[1], Astrid Alí[2], Jade Barreto[2], Guilherme De Lima Felix[2], Fernando Stavale[2]

[1]Centro Brasileiro de Pesquisas Físicas (*COMAN*) , [2]Centro Brasileiro de Pesquisas Físicas

e-mail: emiliaannese@gmail.com

Abstract

Manganese oxides have been extensively employed in applications related to battery devices, non-volatile memories, and water-splitting photocatalytic processes. These applications are generally related to its surface properties connected to their wide variety of valence states and structural forms [1,2].

In this study, we are interested in disentangling the role of the substrates (i. e.: Ag(001), Cu (111) and Au (111)) in the resonant photoemission valence band spectra of Mn_3O_4 thin film. The substrate surfaces differ in plane lattice parameter (4.07 Å (Ag); 2.56 Å (Cu); 2.84 Å (Au)) and surface work function (4.64 eV(Ag); 4.7 eV(Cu); 5.31 eV (Au)). Our preliminary characterization of Mn oxides film on these substrates, using low energy electron diffraction (LEED) and X-ray photoelectron spectroscopy (XPS) evidences different stability and structural phase diagram. The LEED analysis have shown that Mn_3O_4 thin film grows as (110) orientation on Cu (111) and (001) on Au (111) and Ag (001). In our previous analysis, X-ray linear dichroism experiments revealed the sensitivity of the 3d orbital occupancy and their intensity ratio (d 2− 2 /d3 2− 2) to the surface orientation. The variation of relative 3d occupation as a function of strain was quantified by using the XLD sum rules [3].

In this work we are trying to identify the contributions to the valence band originated from the Mn_3O_4 thin film by analysing the resonant photoemitted (RPES) electron excited at Mn $L_{2,3}$ and O K edges. RPES gives pieces of information about the hybridization among Mn, O ligand and substrate and allow us monitoring the dynamics associated to Mn and O elements within the core-hole life time.

These results may reveal important aspects for the identification and further engineering of well-defined crystallographic surfaces in several fields of applications.

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Establishment of a cellular model for the study of the biological bases of conventional and flash radiotherapy

Isabella Nascimento dos Santos Bernardo[1], Déborah Assis de Almeida Carneiro[2], Mariana Paranhos Stelling[1], SIMONE COUTINHO CARDOSO[3], Cristiano Gonçalves Ponte[1], juliana do carmo godinho[4]

[1]Instituto Federal de Educação, Ciência e Tecnologia do Rio de Janeiro (*Campus Rio de Janeiro*) , [2]Instituto Federal de Educação, Ciência e Tecnologia do Rio de Janeiro (*Campus Rio de Janeiro*) , [3]Universidade Federal do Rio de Janeiro (*Instituto de física*) , [4]Instituto Federal de Educação, Ciência e Tecnologia do Rio de Janeiro (*ESTUDANTE*)

e-mail: isabellabernardo8@gmail.com

Abstract

Flash radiotherapy (RT) is a new modality in preclinical studies and its differential and promising potential lies in the application of a very high dose rate in a short time. In conventional RT, the patient receives the full dose in several sessions of approximately 5 to 10 minutes, while RT Flash proposes to deliver the same total dose in a single session with an average duration of milliseconds. This protocol leads to the Flash effect, in which the tumor tissue suffers and is eliminated with high efficiency, while the adjacent healthy tissue is protected. The biological basis for this has not yet been revealed and the safety of using RT Flash in patients has not been established, although current data is promising. Therefore, this project, which is part of a collaboration with the Physics Institute, UFRJ, aims to validate an experimental cell model for the systematic analysis of different radiotherapy conditions, mainly conventional and RT Flash. From the establishment of the cell bank of glioblastoma lineages, irradiation at different dose rates by conventional RT and the subsequent analysis of cell viability by the MTT assay, it was possible to evaluate dose rates that present greater or lesser mortality efficiency. Our data shows that the T98G cell line is affected at the dose rate of 400 cGy/min while the U87MG cell line did not present statistically relevant changes. Such results are consistent with the literature. Our main perspectives include performing the clonogenic assay, as it is the gold standard for cell viability analysis in RT. We intend to use the new Sirius synchrotron light source (CNPEM, SP) as a tool to work on the dose rate necessary to reach the Flash range and as a research line, we aim at the possibility of using the Mogno line of X-Ray tomography as a possible source for high dose rate irradiation, and carry out experiments that will bring to light the differences between the conventional and Flash from the point of view of Cell Biology.

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Feasibility of using low-cost optical monitors for PM2.5 and PM10

Martin de Oliveira Kotsis[1], João Basso Marques[2], RAYANNA DE OLIVEIRA COSTA[3], Amanda Crystina Araujo da Silva[4], Thais Costa Brunelli[5], Lucas Cardoso Ramos[4]

[1]Universidade Federal de Mato Grosso (*Programa de Pós-Graduação em Física Ambiental*) , [2]Universidade Federal de Mato Grosso (*Inst. Física*) , [3]Universidade Federal de Mato Grosso (*Instituto de Fisica - PGFA*) , [4]Universidade Federal de Mato Grosso (*Instituto de Física*) ,

[5]Universidade Federal de Mato Grosso (*Instituto de Física - PPGFA*)

e-mail: martinkotsis@fisica.ufmt.br

Abstract

Air pollution affects the entire planet, especially developing countries, at an accentuated rate, as a result of human action. Pollutants are any particles present in the air, with a concentration capable of rendering it unfit, harmful, or offensive to health, causing damage to property, fauna, flora, and health. Numerous studies relate polluted air as the main risk factor for respiratory, cardiovascular, and autoimmune diseases, cancer, and damage to cognitive functions. The damage caused affects natural and anthropogenic ecosystems, the climate, the economy, and the entire society. Based on the guidelines established by the World Health Organization (WHO), a group of pollutants was adopted worldwide as indicators of air quality, due to their frequency of occurrence, and their adverse effects. Among them are particulate materials: PM2.5 and PM10. Using as reference publicly available data such as AERONET (Aerosol Robotic Network), as well as other databases established as reference methods, this work aims to investigate the feasibility of integrating optical sensors of particulate matter, PM2.5 and PM10, in microcontrolled platforms. These sensors, are relatively inexpensive and have compact sizes, working in conjunction with the ESP32, can perform size and concentration measurements in real time, and send them over wireless networks, which enables communication with mobile devices. The monitors described in this paper use the PMS7003 and SPS30 sensors, both low-cost sensors that are based on the principle of optical scattering. The sensor has a LASER light source, which emits light focused on the point where the particles pass; and a photodiode, which receives the light scattered by the particles, and through signal conversion and processing, one can estimate the amount of particles present in the air per cubic meter, as well as differentiate particle sizes.

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Green Synthesis of BioC-dots

Ana Carolina Cunha Serafim[1], Isabela Marques Ramos[1], Mario Rodrigo dos Santos Soares[1], Ailton José Terezo[1], Adriano Buzutti Siqueira[1], Eralci Moreira Therézio[2], João Basso Marques[3]

[1]Universidade Federal de Mato Grosso (*Depto de Química*) , [2]Universidade Federal de Mato Grosso (*Instituto de Física*) , [3]Universidade Federal de Mato Grosso (*Inst. Física*)

e-mail: anacarolinaserafim2@gmail.com

Abstract

The expansion of agriculture and productivity improvement is linked to innovations in agricultural practices, requiring the use of different agrochemicals, such as herbicides, fungicides, and fertilizers, which are crucial for the control of pests, insects, weeds, and diseases, as well as for the development of cultivated plants. However, managing these agrochemical residues has taken place in crucial concerns to its destination without impacting the environment and human health. Another concern is the effluents from swine farms. Therefore, a viable alternative to an ecologically correct destination in favor of the Principles of Green Chemistry is proposed to use these residues in synthesizing carbon quantum dots (CQDs). The CQDs are highlighted as carbon nanoparticles with different properties, especially luminescence. The characterization evaluated the preparation efficiency of the CQDs by spectroscopic techniques of UV-vis, photoluminescence, FTIR, and ICP-OES. These techniques allow us to evaluate the quantum yield of their luminescence, around 6.68% (agrochemicals) and 27,12% (effluent). Also, to evaluate the presence of existing functional groups in the chemical structure of the CQDs, in addition to making it possible to assess whether the presence of the metallic ions present could suppress the luminescence of the CQDs. The addition of ethylenediaminetetraacetic acid (EDTA) sodium salt shows that the presence of metal ions did not change with the luminescence of the CQDs when exposed to UV. So, it is viable to use the residues of agrochemical mixtures as raw materials for producing CQDs to be a promising and sustainable destination from the socio-economic and environmental point of view. We noticed that forming a carbon core with the surface formation of functional groups is more efficient for the luminescence of CQDs. We thus justify the importance of using synchrotron Infrared, AFM-IR, and perhaps XPS techniques to characterize the functional groups.

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High-resolution XRF probing of elemental distribution in crops species: outputs from the commissioning Tarumã endstation of the Carnaúba beamline

Gabriel Sgarbiero Montanha[1,2], Lucas Coan Perez[3], João Paulo Rodrigues Marques[3], Eduardo Santos[4], HUDSON WALLACE Pereira de Carvalho[5]

[1]Universidade de São Paulo (*Centro de Energia Nuclear na Agricultura*) , [2]Università degli Studi di Roma La Sapienza (*Biology and Biotechnology Department “Charles Darwin\"*) ,

[3]Universidade de São Paulo, [4]Universidade de São Paulo (*Centro de Energia Nuclear na Agricultura- Lab. Instrumentação Nuclear*) , [5]Universidade de São Paulo (*CENA*)

e-mail: gabriel.montanha@usp.br

Abstract

A proper understanding of the elemental composition of plants is essential for promoting enhanced agricultural outputs and environmental preservation. In this scenario, X-ray fluorescence spectroscopy (XRF) outstands as a major technique to interrogate the ionome of botanical materials under fresh conditions with high lateral-resolution[1,2]. Herein, we have explored the XRF facility of the commissioning Tarumã endstation of the Carnaúba beamline (150 x 150 nm beamsize; 10^8 photons s^{-1} 100 mA^{-1} photon flux) at the Brazilian Synchrotron Light Laboratory operating in fly scan mode at Zn Kα excitation energy (9,750 eV) to assess: i) the composition of soybean (*Glycine max* (L.) Merrill) seed’s cotyledonary tissues; ii) the uptake of Zn and Mn complexes applied at 2.5 g L^{-1} (I:I Zn and Mn atomic ratio) to coffee (*Coffea arabica*) leaves. In this regard, both soybean and coffee tissues were cryofixed through rapid-plunging in supercooled isopentane[3] and then cut using a cryostat at -25 ºC to yield 30-µm thick cross sections. For the soybean seeds' cotyledonary tissues, the resulting XRF maps revealed that Zn is not homogeneously distributed across the cotyledonary tissues of soybean seeds cross-sections. Besides, Zn distribution was found to be moderately correlated with other detected elements, such as potassium (K), and manganese (Mn), thereby suggesting their biological functions in the metabolism of the seed. Furthermore, the high-resolution XRF maps recorded for the coffee leaves showed that Zn and Mn signals were mostly found surrounding the cells through the whole leaf-cross sections exposed to the treatments, whereas it is less noticeable in the control groups thereby suggesting that it was absorbed through the apoplastic pathway, i.e., between the cell wall and the cell plasmalemma, which might foster new strategies for improved generations of foliar-based fertilisers for this crop.

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High-throughput screening to discover a new Indoleamine2,3-Dioxygenase-1 (IDO1) inhibitor.

Paulo Jardim[1], Amanda Araujo Souza[2], Andrew Albert de Oliveira[3], Thiago Mattar Cunha[1], Daniela Barretto Barbosa Trivella[4]

[1]Universidade de São Paulo (*Farmacologia*) , [2]Centro Nacional de Pesquisa em Energia e Materiais (*LNBio*) , [3]Universidade de São Paulo (*FMRP*) , [4]Centro Nacional de Pesquisa em Energia e Materiais

e-mail: paulo.jardim@lnbio.cnpem.br

Abstract

Indoleamine-2,3-dioxygenase 1 (IDO1) is the first enzyme in the kynurenines pathway (kynpath), considered a key enzyme for compromising tryptophan into the path. Preliminary results obtained by Prof. Dr. Thiago Cunha's research group demonstrated that neuropathic pain could be ablated or reduced by tryptophan catabolic pathway inhibition, particularly kynpath, indicating this pathway as a potential pharmacological target. Therefore, IDO1 was elected as a molecular target to discover and characterize new inhibitors. Firstly, hIDO1 expression and purification procedures were implemented and validated to obtain the required quantities of the enzyme with high purity. Biophysical assays were performed to evaluate the secondary structure profile, structural stability, oligomeric profile and the oxidation state of the iron group. Biochemical characterization using colorimetric and fluorescence assays evidenced hIDO1 activity. To define the high throughput screening (HTS) standard protocol we evaluated different fluorescent probes, the enzyme's DMSO tolerance and concentration, the stability of the fluorescence read-out, reaction temperature and time, and the compatibility of the developed assays with automation. The developed hIDO-1 HTS protocol was validated using reference hIDO inhibitors, showed low-cost using piperidine analog as probe, low enzyme concentration (20-40 nM) and was robust (Z-factor >0.75, S/B >120. The next steps will be to screen >10,000 small molecules availablable at LNBio-CNPEM and the HTS protocol developed for hIDO1. In parallel, we are working to implement crystallization and structure characterization of IDO1 and its complexes with inhibitors by X-ray crystallography.

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Influence of methylammonium chloride on wide-bandgap hybrid perovskites for solar cells

Maria Gabriella Denote Guaita[1,2], Rodrigo Szostak[3], Francisco Mateus Cirilo da Silva[2], Veronica de Carvalho Teixeira[2,4], Helio Cesar Nogueira Tolentino[2,5], Ana Flávia Nogueira[6]

[1]Universidade Estadual de Campinas (*Instituto de Química*) , [2]Centro Nacional de Pesquisa em Energia e Materiais (*LNLS*) , [3]Brazilian Synchrotron Light Laboratory (*Carnaúba beamline*) , [4]Laboratório Nacional de Luz Síncrotron, [5]Brazilian Synchrotron Light Laboratory, [6]Universidade Estadual de Campinas (*IQ*)

e-mail: maria.guaita@lnls.br

Abstract

Perovskites have been receiving great attention because they have excellent photovoltaic performance, are obtained through simple and low-cost techniques. For tandem cell applications, Br-rich perovskites with a wide-bandgap are required, however these compositions have greater compositional heterogeneity. [1] MACl (MA = $CH_3NH_3^+$) is often added to the perovskite precursor solution to increase grain size, improve optoelectronic properties, and, consequently, improve performance. However, the effect of MACl additive on Br-rich perovskites is poorly known.[2] For this, we characterized thin films of perovskites with different amounts of Br and MACl. In situ grazing-incidence wide-angle X-ray scattering (GIWAXS) performed in the Advanced Light Source synchrotron (ALS - Berkeley) showed that the formation of $Cs_{0.05}FA_{0.9}5Pb(Br_xI_{1-x})_3$ ($0 \leq x \leq 0.5$) perovskites produced with MACl occurs without the formation of intermediate phases even for the richest Br compositions, favoring their greater crystallization. Photoluminescence (PL) and ultraviolet-visible (UV-VIS) spectroscopies on films revealed greater compositional homogenization for samples with MACl by reducing photoinduced halide segregation and a bandgap between 1.50 and 1.87 eV. X-ray diffraction (XRD) showed a decrease in the unit cell lattice parameters with the Br increment compared to the perovskite phase and an increase in the crystallinity of the films produced with MACl. We have also detected that with the addition of MACl, the perovskite film has a preferential orientation in the direction [001]. The increase in grain size of perovskite was observed by scanning electron microscopy (SEM). X-ray fluorescence (XRF) mapping at the Carnaúba beamline identifies changes in the morphology and distribution of elements, indicating that MACl homogenized the Br distribution in the samples by reducing the size of domains richer or poorer in Br. In summary, the addition of MACl is also beneficial to Br-rich perovskites.

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Investigation of divalent metal transporters in cancer associated metallomics

juliana do carmo godinho[1], Mariana Paranhos Stelling[2], Isabella Nascimento dos Santos Bernardo[2], Ananda de Araujo Bento[3], Simone Coutinho Cardoso[4], Luiz Dione Barbosa de Melo[3]

[1]Instituto Federal de Educação, Ciência e Tecnologia do Rio de Janeiro (*ESTUDANTE*) , [2]Instituto Federal de Educação, Ciência e Tecnologia do Rio de Janeiro (*Campus Rio de Janeiro*) , [3]Instituto Federal de Educação, Ciência e Tecnologia do Rio de Janeiro,

[4]Universidade Federal do Rio de Janeiro (*Instituto de física*)

e-mail: julianacarmog15@gmail.com

Abstract

Changes in metal distribution and concentration can lead to cell cycle disorder, cell death resistance and malignancy. In our previous work, it has been demonstrated that tumor cells that accumulate manganese show changes in its metallomic profile when compared to tumor cells that were continuously cultured in manganese standard concentrations. Additionally, manganese exposed cells also presented alterations in other elements, such as iron and copper. Considering several metal transport and distribution paths involved in this process, DMT1 has been shown as a promising candidate in the investigation of metallomic imbalance that is observed as tumor cells accumulate manganese. Our objective is to map the distribution of metals transported by DMT1 in subcellular resolution by X-ray fluorescence at Carnaúba beamline. LLC tumor cell line (Murine Lewis lung cancer) were cultured in a culture medium supplemented with 5 µM manganese chloride for 24 h, and through real-time PCR of these samples, a possible increase of 17% in DMT1 expression was observed. Finally, we expect to describe the regulation of this transporter in the face of its different ligands in search of a better understanding of tumor microenvironment metallomics. We hope that the understanding of these processes contributes to the development of cancer metallomics.

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Ionic-radii - Power relation in $REBa_2Cu_3O_{6+\delta}$ (RE = La, Nd, Sm, Gd and Y) IT-SOFC cathodes.

Joaquín Grassi[1], Natasha Di Benedetto[1], Juan Basbus[2], Alejandra Montenegro Hernández[2], Adriana Cristina Serquis[2], Leopoldo Suescun[3]

[1]Universidad de la República, [2]Instituto Balseiro, [3]Universidad de la República (*Facultad de Química*)

e-mail: joaquingrassi@fq.edu.uy

Abstract

Solid Oxide Fuel Cells (SOFCs) are considered an excellent alternative among the different sources of clean energy, due to its demonstrated efficiency, fuel flexibility and long term stability [1]. Currently, the interest in those devices is focused especially in the intermediate temperature IT-SOFC that operate between 600 and 800 °C, increasing cell durability and reducing materials costs. These features, however, require materials with higher electrochemical activity in this temperature range besides chemical and thermomechanical stability. In the search for new cathodes we have found promising activity in some Cu-containig perovskites such as $Ba_{0.5}Sr_{0.5}Fe_{0.8}Cu_{0.2}O_{3-\delta}$ [2] and $La_{0.6}Sr_{0.4}Fe_{0.8}Cu_{0.2}O_{3-\delta}$ [3] and $La_4BaCu_5O_{13+\delta}$ [4]. Following this idea, we initially studied the traditional high-temperature superconductor oxide $YBa_2Cu_3O_{6+\delta}$ as potential cathode for IT-SOFCs with promising results [5]. The YBCO structure exibits mobile oxo anions (O^{2-}) at low temperatures and depending on δ it is metallic or semiconducting allowing for MIEC activity. Replacement of Y by lanthanoids gives REBCO materials where the oxygen vacancy concentration and it´s mobility is strongly depended on the A size cation radii (RE or Y in this case) and the oxidation state of Cu.

The REBCO cathodes (RE = La, Nd, Gd and Sm) were prepared via an autocombustion modified route. Ceramic powders where successfully spin coated on electrolyte pellets and the electrochemical performance in symmetrical and full cells were investigated as cathodes for IT –SOFCs. The ORR activity of the REBCO cathodes decreased as the Ln^{3+} ionic radius increases which may be attributed to the oxygen vacancy concentration and it´s mobility. The best electrochemical performance was observed on the YBCO cathode, 425 $mW \cdot cm^{-2}$ at 800 ºC corresponding to the smallest RE cation. These results indicated that triple perovskite cuprates such as REBCO may have promising applications as IT-SOFC cathodes.

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In vivo investigation of biotransformation of metallic nanoparticles in soybean plants using synchrotron-based techniques

Susilaine Maira Savassa[1], Dean Hesterberg[1], Renata de Lima[2], Leonardo F Fraceto[3], Carlos Alberto Pérez[1]

[1]Centro Nacional de Pesquisa em Energia e Materiais (*LNLS*) , [2]Universidade de Sorocaba, [3]Universidade Estadual Paulista (*ICTS*)

e-mail: susilaine.savassa@lnls.br

Abstract

Soybean is one of the most important crops in the world, it is one of the most efficient leguminous species in the use of nitrogen from the symbiotic associations between roots and rhizobia [1]. Some nutrients like nickel, cobalt, and iron are extremely important for root nodulation of soybean and in the nanoparticle form, these elements are poorly studied for this crop. Few studies are reporting possible interaction mechanisms of nanoparticles (NPs) and soybean rhizosphere (root nodules and soil). Currently, with the fourth-generation synchrotron, Sirius, there is a great opportunity to further contribute to this issue. It will be possible to understand the mechanisms of absorption and distribution, as well as the biotransformation of nanoparticles in soybean roots. The main objective of this work is to understand the biotransformation and accumulation of metallic NPs (obtained by chemistry and biogenic ways), in the rhizosphere of soybean plants, including their chemical and structural changes due to exposure to planta to these NPs and how these changes can impact biological nitrogen fixation (BNF) and plant development. For this study, synchrotron techniques (X-ray fluorescence microanalysis (µXRF), X-ray absorption microanalysis (µXANES), ptychography, and tomography) will be used to obtain submicron chemical and morphological information at the structural level. There are few studies exploring micronutrients absorbed and transported in plants using *in vivo* analysis or fresh conditions [2,3]. Carrying out localization, chemical speciation, quantification, and imaging of NPs *in vivo* can provide new information on the biodistribution and fate of NPs in living systems [4]. These results will open perspectives for a better understanding of the properties of nanomaterials that manage important interactions with plants to promote the development of alternatives for using in agriculture.

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Micro-FTIR as a characterization tool for a new platform based on calixarene derivative and a metal-organic framework: A fluorescent probe for Fe^{3+} detection

José Daniel Da Silva Fonseca[1], Ohanna Maria Menezes Madeiro da Costa[2], Bráulio Silva Barros[3], JOANNA ELZBIETA KULESZA[3]

[1]Universidade Federal de Pernambuco (*Instituto Nacional de Tecnologia em União e Revestimento de Materiais-INTM*) , [2]Brazilian Synchrotron Light Laboratory, [3]Universidade Federal de Pernambuco

e-mail: josedaniel.fonseca@ufpe.br

Abstract

Calixarenes are a class of macrocyclic compounds with an intrinsic cavity that enables the formation of host-guest complexes [1]. Calixarenes can be easily functionalized and used in the construction for new hybrid materials. Metal-Organic Frameworks (MOFs) are a class of crystalline materials with outstanding properties like high surface area, adjustable pore size, and chemical functionalization [2]. The combination of materials from different classes can give new properties to the hybrid material, opening possibilities for new applications [3]. In this work, we report a new hybrid material grounded on a calixarene derivative based on calix[4]arene-carboxylate and the MOF UiO-66-NH_2 and its use as a fluorescent probe for cation detection in water. The calixarene derivative was synthesized through the condensation of *p*-*tert*-butylphenol and further introduction of the carboxylate groups. ^1H NMR and FTIR techniques were used to confirm the cone conformation of the calixarene and the introduction of the carboxylate groups, respectively. The UiO-66-NH_2 was synthesized by a solvothermal method followed by chemical activation. The coordination of the carboxylic groups, from the organic linker to the inorganic unit was evidenced by FTIR, indicating the formation of the MOF, which was further confirmed by the XRD technique. SEM showed characteristic octahedral shape-like particles of the MOF. The calixarene derivative was linked to the MOF through an amide bond. The amide bond formation was investigated by MICRO-FTIR and the results evidenced the functionalization of the MOF with calixarene. The fluorescent properties of all materials were investigated. The emission for the new platform was higher than for the precursor materials. The new fluorescent probe showed a great response to Fe^{3+} in water characterized by fluorescence suppression.

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MINERAL INCLUSIONS IN SUPER DEEP DIAMOND REVEALS THE UNUSUAL ASPECT OF THE TRANSITION METALS Fe, Cu, Ni AND Ti

Carolina Michelon Camarda[1], Francisco Mateus Cirilo da Silva[1], Paola Rosa[2], Nathaly Lopes Archilha[1], Eduardo X. Miqueles[3], Daniel Grings Cedeño[4], Tiago Luis Reis Jalowitzki[5], Fernanda Gervasoni[6], Helio Cesar Nogueira Tolentino[1,7]

[1]Centro Nacional de Pesquisa em Energia e Materiais (*LNLS*) , [2]Centro Nacional de Pesquisa em Energia e Materiais (*Mogno*) , [3]Centro Nacional de Pesquisa em Energia e Materiais (*LNLS-GCC*) , [4]Universidade Federal do Rio Grande do Sul (*IG*) , [5]Universidade de Brasília (*IG*) , [6]Universidade Federal de Pelotas (*CEng*) , [7]Brazilian Synchrotron Light Laboratory

e-mail: carolina.camarda@lnls.br

Abstract

Diamonds are time-capsules that record the history of Earth`s mantle processes through mineral inclusions. Some diamonds might form in the super deep mantle regions, from 300 to 1000 km in depth. In this study, our main aim is to investigate mineral inclusions in super deep diamonds (SDD) to get information about the behavior and the distribution of some elements and uncover unusual mineral structures. We employ sub-micrometer analysis synchrotron light tools at the newly available 4th generation source of LNLS. The sample used in this study is from Juína-MT, Brazil, where is known for the occurrence of SDD hosted by kimberlites. Our first step was to perform microtomography at the Mogno beamline to distinguish and get the inclusion's location. Based on electron density contrast, it was possible to identify 98 mineral inclusions with different shapes and sizes. Then, we chose four mineral inclusions to analyze at the Tarumã station of the Carnaúba beamline. We performed compositional maps using X-ray fluorescence (XRF) and found Fe, Ni, Cu, and Ti as the main metal elements. We reconstructed the volume of two inclusions from scanning transmission X-ray microscopy (STXM) projections and got the 3D volume and elemental composition. In addition, Raman spectroscopy identified these minerals as a possible solid solution of Armalcolite ($(Mg,Fe^{2+})Ti_2O_5$) and Pseudobrookite/ Ferropseudobrookite ($FeTi_2O_5$/ $Fe^{3+}{}_2TiO_5$). Our analysis reveals that Fe and Ti are evenly distributed throughout the inclusion, with Fe being the most abundant element. However, Cu and Ni are also present and show a robust spatial negative correlation; surprisingly, Cu covers the mineral crystal faces. XANES spectroscopy at the Fe and Cu K-edge gave insights into the local chemical order, showing that they have a disordered structure with a possible amorphization state, probably owing to the high stress on the crystals inside the diamond.

Modeling the thermal conductivity of soil between layers for a region north of the Matogrossense Pantanal

Rayanna de Oliveira Costa[1], João Basso Marques[2], Martin de Oliveira Kotsis[3], Amanda Crystina Araujo da Silva[4], Lucas Cardoso Ramos[4], Thais Costa Brunelli[5], Nicolas Neves de Oliveira[4]

[1]Universidade Federal de Mato Grosso (*Instituto de Fisica - PGFA*) , [2]Universidade Federal de Mato Grosso (*Inst. Física*) , [3]Universidade Federal de Mato Grosso (*Programa de Pós-Graduação em Física Ambiental*) , [4]Universidade Federal de Mato Grosso (*Instituto de Física*) , [5]Universidade Federal de Mato Grosso (*Instituto de Física - PPGFA*)

e-mail: rayanna.oli.costa@gmail.com

Abstract

Thermal conductivity is one of the most important thermophysical properties of soils, as it is directly linked to the heat transfer mechanism by conduction in materials (WANG et al. 2022). However, it is not easy to determine the thermal conductivity of soils because some factors such as high cost, hard work are the main obstacles to experimentally obtain thermal conductivity. Therefore, many calculation models have been proposed to determine it. Conductivity can be estimated or measured by experiments, empirical or semi-empirical models and numerical simulations, in short, they are commonly done using empirical relationship models, theoretical calculation models and artificial neural network models (ZHANG et al, 2018, WANG et al. al. 2022). Currently, soil thermal conductivity is generally obtained by direct measurements or by means of predictive models. While there has been significant progress in thermal conductivity measurement technology, with methods such as pulse heat, line source, and heat plate, these techniques have other complex problems in the measurement process due to being limited by experimental conditions. Since the use of synchrotron light has increased and has helped in a better understanding of areas such as geosciences, this advance is extremely important to improve the deepening of knowledge about the soil in processes that occur on microscopic scales. A possibility of study using synchrotron light would be to analyze the thermal conductivity of each chemical element in the soil, at its most fundamental level and compare it with what is observed in the field, showing how accurate the storage of heat in the soil is when compared to field equipment. The objective of this work is to analyze a simple model of soil thermal conductivity estimated for two different areas of the same ecosystem in order to discuss how the presence of water in the system directly affects this physical property of the soil over a Pantanal region.

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Modulators of PKM2 tetramerization: an x-ray crystallographic assessment

Andrew Albert de Oliveira[1], José Carlos Alves-Filho[1], Daniela Barretto Barbosa Trivella[2]

[1]Universidade de São Paulo (*FMRP*) , [2]Centro Nacional de Pesquisa em Energia e Materiais

e-mail: andrew.oliveira@lnbio.cnpem.br

Abstract

Traditional medical thought holds that inflammation is a helpful reaction to infection or tissue damage. Inflammatory disorders pose significant challenges to public health as a large and varied group of diseases. In this setting, LNBio/CNPEM and the Center for Research in Inflammatory Diseases (CEPID/FAPESP/CRID/USP) collaborate to conduct translational research throughout the spectrum of inflammatory disorders by integrating fundamental and clinical research methodologies. The purpose of this study is to locate potential therapeutic modulators for the treatment of psoriasis. Glycolysis rates are tightly regulated by a group of enzymes called pyruvate kinases (pkm). Dissociation to lower oligomeric states of PKM2 enhances the IL-23/Th17 pathway,[1] which is crucial to the pathogenesis of psoriasis but may be affected by various allosteric modulators. Glycolytic enzyme PKM2 is migrated to the nucleus by the help of post-translational modifications (PTMs), which play a vital role in regulating PKM2's noncanonical activity and are typically related to its pro-inflammatory effects.[2] Here, we present findings from our intensive tetramerization modulator investigation at the MANACA beam line. The thermal stability assay (DSF)[3] has helped in selecting a large number of compounds and focusing on a smaller group of outstanding hits. Secondly, tetramerization and protein activity have been shown by several biochemical and biophysical assays. Data sets matching wild-type and mutant structures, as well as data sets collected in the presence of enzyme inhibitors and activators, have been collected and resolved, which has contributed to the advancement of the study. When doing structure-based drug research, using a state-of- the-art synchrotron like Sirius and the Manacá beamline greatly improves the quality of the data and the evaluation of hits binding mode.

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Multi-techniques methodological study on radiation effect in hybrid organic-inorganic perovskites and strategies to mitigate interferences after high brilliance x-ray photon source measurements

Francisco Mateus Cirilo da Silva[1,2], Maria Gabriella Denote Guaita[1,3], Rodrigo Szostak[1], Veronica de Carvalho Teixeira[1], Ana Flávia Nogueira[3], Helio Cesar Nogueira Tolentino[1]

[1]Centro Nacional de Pesquisa em Energia e Materiais (*LNLS*) , [2]Universidade Estadual de Campinas (*IFGW*) , [3]Universidade Estadual de Campinas (*IQ*)

e-mail: francisco.mc.silva@outlook.com

Abstract

The modern lifestyle, together with the increase in population, has dramatically increased the energy demand year after year, encouraging the development of new energy sources. Among the new photovoltaic materials studied in the last decades, the hybrid organic-inorganic perovskite (HOIP) (ABX_3, where $A = CH_3NH_3^+$, $CH(NH_2)_2^+$ or Cs, $B = Pb^{2+}$ and $X= I^-$ or Br^-) used in solar cells and radiation detectors is one of the most promising due to its low processing cost, easy fabrication, high-power conversion efficiency and high scintillation yield.[1] Despite that, several aspects related to chemical composition, structural and optical properties need to be better understood from the micro to the nanoscale such as environment and the probe effects on the sample. X-ray nanoscopy techniques such as those available in CARNAUBA beamline (SIRIUS/LNLS) are very promising to investigate HOIP.[2] However, the radiation damage caused to these samples is a great challenge yet. Then, the x-ray beam damage has been investigated revealing that the environment plays an important role in the resilience of the signals like x-ray fluorescence (XRF). Nano-XRF maps have successfully revealed the ionic migration in some compositions of HOIP, while X-ray ptychography shows the ejection of matter by the x-ray beam under open air environment. We also have observed that the high photon flux of the beamline leads to irreversible chemical damage in the HOIPs at the energy of 10 keV, but not at 14 keV. XRF maps of iodide at 5x5 and 10x10 um^2 areas, with different exposure times (10 – 1000 ms), reveal that the iodide moves far from the scanned region proportionally to the deposited doses. To mitigate beam damage two environments (RT and cryogenic N_2) were used and strongly reduce or completely inhibit the iodide migration. Correlative characterization of the organic part (FTIR) and opto-electronic properties (XEOL) will also be presented to completely track of beam effect and environmental influence.

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New binding-site search of the 20S proteasome: crystallographic fishing, PanDDa analysis and cryo-EM validation

Joane Kathelen Rustiguel Bonalumi[1], Raphael Meneghello[2], Daniela Barretto Barbosa Trivella[3]

[1]Centro Nacional de Pesquisa em Energia e Materiais (*Farmacologia*) , [2]Centro Nacional de Pesquisa em Energia e Materiais (*LNBio*) , [3]Centro Nacional de Pesquisa em Energia e Materiais

e-mail: joane.bonalumi@lnbio.cnpem.br

Abstract

The proteasome is a well-known multi catalytic and highly regulated complex responsible for degradation of intracellular proteins in ubiquitin-proteasome system[1]. It is involved in a wide range of cell process, such as cell cycle control, apoptosis, and stress response[2] and it is a validated target for cancer treatment[3]. Proteasome inhibitors, designed to modulate its degradation capacity, show undesired characteristic as toxicity and resistance[4]. One of the strategies is to find new non-canonical binding-sites to lead structure-based drug design. A proprietary library of compounds was soaked into yeast core particle proteasome crystals. Such molecules worked as probes for scanning protein pockets and cavities that could act as novel binding sites and modulate proteasome activity. Soaked crystals were submitted to data collection, processed with XDS program, and prepared with dimple for PanDDa protocol and analysis. Difference density maps were highlighted and evaluated by visual inspection. The probed and most promising binding-sites were validated with isolated natural products, synthetic and commercial molecules. Cryo-EM is being applied to validate this new binding-sites in human core particle proteasome samples. The results of soaking methodology, data processing, adaptation for PanDDa protocol and cryo-EM data collection and processing will be presented.

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Novel method for determination of the radius dependences of the melting and freezing temperatures of nanoparticles by exclusively using the SAXS technique

Guinther Kellermann[1], Felipe Leonardo C. Pereira[2], Aldo Craievich[3]

[1]Universidade Federal do Paraná (*Departamento de Física*) , [2]Universidade Federal do Paraná, [3]Universidade de São Paulo

e-mail: keller@fisica.ufpr.br

Abstract

Previous studies have shown that the melting and freezing temperatures of many nanoparticles of different materials strongly depend on their size and shape. In addition, the melting and freezing temperatures of confined nanoparticles also depend on the particle/matrix interface energy. On the other hand, the properties of nanoparticles that make them useful for several applications to nanotechnology strongly depend on their physical (solid or liquid) state. For this reason, the knowledge of the thermal behavior of nanocomposite materials is a research subject of growing interest. We here propose a novel method for determining the radius dependences of the melting and freezing temperatures of polydisperse sets of nanoparticles embedded in solid matrices; this method being exclusively based on the temperature dependence of SAXS intensity for different *q*-values. The melting and freezing temperatures are determined from the observed small - but not negligible - jumps in SAXS intensity *versus* temperature curves as a consequence of sudden changes in electron density and radius of nanoparticles at the melting and freezing transitions. We applied this experimental procedure to the determination of the radius dependence of the melting and freezing temperatures of spherical Bi and Pb nanoparticles embedded in glass matrices. The SAXS intensity at different *q*-values from these nanoparticle-glass composites was recorded *in situ* during the heating and during the subsequent cooling of the samples. The radius dependences of the melting and freezing temperatures that we have determined for Bi and Pb nanoparticles - using exclusively the SAXS technique - agree well with the results previously obtained by using other experimental methods.

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NP3 Blob Label: A Deep Learning Application for Unknown Ligands Segmentation to Ligand Building in X-ray Protein Crystallography

Cristina Freitas Bazzano[1], Guilherme Pimentel Telles[2], Daniela Barretto Barbosa Trivella[3]

[1]Centro Nacional de Pesquisa em Energia e Materiais (*LPN*) , [2]Universidade Estadual de Campinas, [3]Centro Nacional de Pesquisa em Energia e Materiais

e-mail: cristina.bazzano@lnbio.cnpem.br

Abstract

The NP^3 Blob Label is an automated application to help solve the problem of reconstructing the molecular structure of unknown protein ligands (e.g.: enzyme inhibitors and other types of bioactive molecules) from modeling with deep learning (DL) for automatic labeling of the 3D electron density image of protein crystallography data with a given vocabulary. Existing solutions solve the problem of interpreting the electron density of protein ligands already known and commonly found in protein crystallography databases, which does not cover the universe of unknown molecules, some of which may have an unusual complex structure.

Several modeling approaches, based on chemical substructures of ligands, were evaluated to create vocabularies and labeled 3D image databases of the electron density of ligands in point clouds. Semantic segmentation models were trained with these databases and showed good performance, with mIoU accuracies in the test between 50.5% and 77.4%. Contributions of this work include: the first 3D DL application for electron density image of ligands; the created databases; the trained models; and the NP^3 Blob Label application - that uses the obtained models to label the images of possible ligands and help in their interpretation.

NP^3 Blob Label is capable of refining entries (.mtz + .pdb), finding blobs (possible ligand sites), creating the blobs images, labeling these images with a model prediction and converting the prediction result to CCP4 maps that can be opened by protein crystallography visualization tools. This solution can be of great help to large scale crystallography facilities

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Operando setup for perovskite solar cells characterization at the CARNAÚBA beamline at Sirius/LNLS

Rodrigo Szostak[1], Michel Bernardino Machado[2], Natália Aparecida Ferreira[2], Francisco Mateus Cirilo da Silva[3], Francesco Rossi Lena[2], Renan Ramalho Geraldes[2], Helio Cesar Nogueira Tolentino[2]

[1]Brazilian Synchrotron Light Laboratory (*Carnaúba beamline*) , [2]Brazilian Synchrotron Light Laboratory, [3]Centro Nacional de Pesquisa em Energia e Materiais (*LNLS*)

e-mail: rodrigo.szostak@lnls.br

Abstract

Perovskite solar cells (PSCs) have received great attention recently due to their optoelectronic properties being appropriate for use in high-efficiency solar cells, LEDs, and X-ray detectors.[1,2] In solar cells, in just one decade, the performance reached the levels of silicon. Despite the high performance achieved, many aspects still need to be better understood, especially the chemical and structural properties under operando conditions when the device is submitted to heating, light, bias, and environmental changes. To investigate the properties of the PSCs in conditions closer to real-life use, we have developed a setup for PSCs compatible with the TARUMÃ station at the CARNAÚBA beamline. A heating chip coupled with a resistance temperature detector (RTD) was developed to reduce thermal drifts in heating experiments. This chip allows localized heating, homogenous temperature distribution, and precise temperature control on the area of interest (3 x 3 mm^2). The heating chip is held in a special holder that allows reflective and transmission X-ray-based techniques with white light illumination and environmental control (e.g., different gases or humidity levels). In situ characterization with half devices (e.g., glass/perovskite sample) also be possible. The preliminary setup commissioning results, status, perspectives, and challenges will be presented.

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Oxidative desulfurization of S molecules using Cu and Ag atomic quantum clusters: A XANES study

Khalil Jori[1], Martin Mizrahi[1], José Martín Ramallo López[2,3,4]

[1]Universidad Nacional de la Plata (*INIFTA*) , [2]Universidad Nacional de la Plata, [3]Instituto de Investigaciones Fisicoquímicas Teóricas y Aplicadas, [4]Consejo Nacional de Investigaciones Científicas y Técnicas

e-mail: khaliljori10@gmail.com

Abstract

Oxidative desulfurization of Sulphur molecules is applicable to different petroleum products, including natural gas liquids, gasoline, kerosene and diesel, as part of the S content reduction process, which makes it a process of paramount practical importance. Vanadium, platinum and iron oxides were commonly used to catalyze the oxidation; however, its use is currently declining. [1] A new alternative is provided using arrangements of few atoms (less than 50), which can fulfill the requirements for a good catalyze, i.e., high activity, selectivity and stability. In this sense, the atomic quantum clusters (AQCs) represent a novel state of matter, with properties completely different from nanoparticles (NP), and strictly dependent on the number of atoms. Contrary to what would be expected, AQCs possess a surprising high chemical and thermal stability, superior to the bulk material. Recent results obtained shows that Ag and Cu AQCs display high catalytic activities for the fully aerobic oxidation of different types of sulfur species to sulfates at room temperature. This occurs even for the most complicated aromatic thiols to be oxidized in the industrial field, such as asphaltenes.[2] In this work, the catalytic oxidation of different sulfur compounds, commonly present in liquid fuel, was studied over the use Ag and Cu clusters. An oxidation kinetics study was also investigated when dibenzothiophene solution was exposed to minimal amounts of clusters. For these purposes, XANES measurements at the S K-edge, were performed on the SXS beamline of the LNLS. In all cases, it was observed that the various starting thiolate compounds were oxidized to an S^{+6} state after interacting with the atomic clusters.

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Perspectives of the Biaxial Multi-Analysis Strain Instrument (2D-MASI) at SIRIUS

Márcio Medeiros Soares[1], Marina Raboni Ferreira[2], José Claudio Corsaletti[2], Guilherme Calligaris de Andrade[2], Thiago J. A. Mori[3]

[1]Universidade Federal da Paraíba (*Departamento de Física*) , [2]Centro Nacional de Pesquisa em Energia e Materiais (*LNLS*) , [3]Centro Nacional de Pesquisa em Energia e Materiais (*Laboratório Nacional de Luz Síncrotron*)

e-mail: marcio.soares@fisica.ufpb.br

Abstract

Understanding how thin films react to mechanical stress is of key importance for fields like flexible electronics, micro-electro-mechanical systems (MEMS) and for applications such as electronic textiles, paperlike displays, roll-to-roll flexible solar cells, wearable or imperceptible sensors and high precision actuators [1]. A device named 2D-MASI, the Biaxial Multi-Analysis Strain Instrument, has been developed at LNLS and tested at the last year of operation of UVX machine. This device is designed for in-situ study of strained thin films grown at flexible and stretchable substrates by using advanced synchrotron techniques. Capable of applying moderate loads (<400N) on two independent orthogonal axes, it is adapted by construction to several experimental stations (beamlines) and different sample environments (high-vacuum and low temperatures), allowing in-situ study of the effect of strain on thin films through x-ray diffraction, absorption, imaging and scattering. A unique feature is that one can keep the sample/substrate in a stretched condition at an independent low-profile transfer frame. By doing so, it is also possible to realize ex-situ measurements (like scanning probe microscopies) or making deposition (ex. sputtering) with the film/substrate already stretched. The instrumentation has been used to study the effect of strain on antiferromagnetic Cobalt Oxide films, aiming to manipulate the spin axis of such material. We were able to test and validate the instrument for in-situ measurements of X-ray Stress Analysis at XRD2 and angular dependent XMLD at PGM beamlines at UVX, however insufficient flux, spot size and beamline stability prevented a systematic and conclusive study of the strain effect in both micro-structure and spin axis. This poster highlights the main features of the 2D-MASI and discuss its status and perspectives of use at SIRIUS beamlines.

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Phase transition in the crystal of bis(L-histidinate)nickel(II) monohydrate in high temperatures

Raul Costa Oliveira[1], Cláudio M.R. Remédios[1]

[1]Universidade Federal do Pará (*Instituto de Ciências Exatas e Naturais*)

e-mail: raulmashida@gmail.com

Abstract

Transition metals perform some functions associated with biological processes [1]. In living organisms metals interact with proteins [2], these interactions could help in the study of diseases such as Alzheimer and Parkinson [3]. The structural behavior of these crystals under different thermodynamic conditions is important and serves as a model to study metal-protein interactions. In this work we investigate bis(L-histidinate)nickel(II) monohydrate crystals in high temperatures using X-ray diffraction with synchrotron radiation. At room temperature this crystal presents monoclinic symmetry, space group C2, with four molecules per unit cell (Z = 4) [4] and lattice parameters a = 29.467(2), b = 8.2845(6), c = 6.3262(5) Å and β = 90.11(1) °. At high temperatures (around 413 K) this organic crystalline system undergoes a phase transition to an anhydrous phase. This new phase was analyzed and its unit cell was indexed with monoclinic symmetry, space group P2/m and lattice parameters a = 12.125(4), b = 13.235(2), c = 5.5961(9) Å and β = 117.29(2) °.

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Plant metallomics: are metal distribution patterns a cause or consequence of plant tissue fate?

Gabriel Sgarbiero Montanha[1,2], João Paulo Rodrigues Marques[3], Eduardo Santos[4], HUDSON WALLACE Pereira de Carvalho[5]

[1]Universidade de São Paulo (*Centro de Energia Nuclear na Agricultura*) , [2]Università degli Studi di Roma La Sapienza (*) Biology and Biotechnology Department “Charles Darwin”*) ,
[3]Universidade de São Paulo, [4]Universidade de São Paulo (*Centro de Energia Nuclear na Agricultura- Lab. Instrumentação Nuclear*) , [5]Universidade de São Paulo (*CENA*)

e-mail: gabriel.montanha@usp.br

Abstract

The ionome might play crucial roles in the development of plants. In this study, the commissioning Tarumã endstation of the Carnaúba beamline (150 x 150 nm beamsize; 10^8 photons s^{-1} 100 mA^{-1} photon flux) at the Brazilian Synchrotron Light Laboratory was employed for characterizing the unusual Mn and Fe distribution patterns previously observed in the embryo of soybean seeds in order to assess (i) the concentration of Fe and Mn in the "spot cells" compared to "regular cells" and (ii) which cell compartments are responsible for storing Fe and Mn in "spot cells" and "regular cells". In this regard, the radicle tissue of mature soybean seeds was manually excised, mounted on paraffin wax film, and cross-sectioned using a stainless-steel razor blade at 0.5 or 5 mm far from the radicle tip region, then fixed in a proper XRF sample holder using an adhesive cellophane film. The cross-sectioned radicle tissue samples were measured in flyscan mode at Zn K excitation energy (9750 eV) through 250 x 250 µm panoramic images. The resulting XRF maps revealed that at 0.5 mm from the radicle tip, both Mn and Fe were concentrated in stripe-like structures where Mn are outermost from Fe. However, Fe signals were mostly found forming a quadrupole structure surrounded by an Mn stripe at 5 mm from the root tip. Furthermore, Zn was found homogeneously distributed in both regions, reinforcing that the observed Fe and Mn patterns are not artefacts induced by different cell densities. As the radicle tissues on the seed’s embryo encompass several provascular cells that will give origin to root tissues on the germinated plant [1], the found Mn and Fe ring-shaped spots herein observed might be associated with the VACUOLAR IRON TRANSPORTER1 (VIT1) gene activity[2]. Nevertheless, it remains unclear whether such Mn and Fe spots act as building blocks of processes that will take place during germination, or as triggers to processes that will define the fate of these groups of cells.

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Preparation of fresh plant tissue samples for XRF analysis in Tarumã endstation of the Carnaúba beamline at the Brazilian Synchrotron Light Laboratory

Eduardo Santos[1], Gabriel Sgarbiero Montanha[2], João Paulo Rodrigues Marques[3], HUDSON WALLACE Pereira de Carvalho[4]

[1]Universidade de São Paulo (*Centro de Energia Nuclear na Agricultura- Lab. Instrumentação Nuclear*) , [2]Universidade de São Paulo (*Centro de Energia Nuclear na Agricultura*) ,

[3]Universidade de São Paulo, [4]Universidade de São Paulo (*CENA*)

e-mail: eduardosr07@usp.br

Abstract

Synchrotron-based X-ray fluorescence spectroscopy techniques are suitable for properly understanding the ionome of fresh biological materials, including plants, at tissue or cellular levels. Nevertheless, as both tissue structure and elemental composition need to be preserved, the sample preparation is crucial, yet challenging. Herein, the Tarumã endstation of the Carnaúba beamline facility at the Brazilian Synchrotron Laboratory was explored to establish suitable cryofixation methods for high-resolution XRF analysis of plant tissues. In this regard, leaves of coffee (*Coffea arabica*), soybean (*Glycine max* (L.) Merrill), and tomato (*Solanum lycopersicum*) plants were detached, and *ca*. 5 x 5 mm pieces were imbibed into optimal cutting temperature (OCT) medium and frozen through rapid-plunging in supercooled isopentane. The resulting blocks were fixed on an adhesive cellophane film (Fitar, Brazil) and then cut using a cryostat at -25 ºC to yield 30-µm thick cross sections that were subjected to the 250 µm or 80 x 80 µm panoramic XRF mappings at Zn Kα absorption energy (9750 eV). The results revealed that the structure of the coffee, maize, and tomato leaves were preserved during the cryofixation process, thereby indicating that the procedures employed are suitable for the leaf tissues of different species. Besides, no evidence of radiation damage, sample dehydration or structural collapse within the measurement timeframe was observed, suggesting that these analyses might be accomplished without the use of a cryojet.

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SAXS And XAFS Characterization Of ZrO2-Based Catalysts Prepared By Sol-Gel Techniques

Federico Piovano[1,2,3], Fernando Pschunder[4,5,3], Alicia Boix[1,2,3], Lisandro J. Giovanetti[4,5,3], José Martín Ramallo López[4,5,3], Soledad Aspromonte[1,2,3]

[1]Universidad Nacional del Litoral, [2]Instituto de Investigaciones en Catálisis y Petroquímica, [3]Consejo Nacional de Investigaciones Científicas y Técnicas, [4]Universidad Nacional de la Plata, [5]Instituto de Investigaciones Fisicoquímicas Teóricas y Aplicadas

e-mail: fpiovano@fiq.unl.edu.ar

Abstract

Lately, lactic acid has emerged as a renewable platform molecule in modern industry for the production of new generation biodegradable plastics, bio-solvents and other bio-chemicals like acrylic acid and polyethylene glycol. Zirconia-based materials are widely known for their catalytic activity, particularly for biomass-derived sugars conversion into lactic acid. In recent years, numerous efforts have been applied to develop new synthesis approaches to obtain more stable and active materials, as well as improving textural properties such as specific surface area, pore size distribution and pore volume. Sol-gel method has become one of the most studied due to its versatility.

In a typical sol-gel procedure, a surfactant is used as structure director and a zirconium alkoxide as metal precursor dissolved in an alcoholic media. Subsequently, the surfactant is removed by means of solvent extraction processes or thermal treatments. The different synthesis methods and their parameters strongly affect the final textural properties of the catalysts and as a consequence the catalytic performance in reaction. To achieve a global understanding of the synthesis procedure and the local environment of Zr, diverse morphological and structural characterizations are needed, such as SAXS and XAFS.

In this work ZrO_2-based catalysts were synthesized by sol-gel method assisted by non-ionic copolymer Pluronic P123 as structure director and $Zr(OPr)_4$ as Zr precursor in ethanol or isopropanol. Synthesis progress, from initial sol to resultant gel, was followed by SAXS measurements in situ. First, micellar structures of Pluronic P123 in alcohol were characterized with and without Zr precursor at different concentration. Then, hydrolysis and condensation reactions leading to the gelation process were induced by the addition of hydrochloric acid. Finally, obtained gels were treated by reflux extraction or calcined for surfactant removal. The resultant solid catalysts were also analyzed by XANES.

Acknowledgments

SAXS measurements were performed at INIFTA Small Angle X-ray Scattering Laboratories using a Xeuss 1.0 SAXS setup, by Xenocs, provided with a Cu source and a Pilatus 100K detector. XAS measurements were also performed in our laboratories at INIFTA with an x-ray absorption spectrometer from Rigaku.

Size dispersion evaluated by X-ray diffraction and scattering in crystalline nanoparticles of CeO_2

ADRIANA VALERIO[1], Fabiane J. Trindade, RAFAELA FELIX DA SILVA PENACCHIO, MAURÍCIO BASTOS ESTRADIOTE, Cristiane Barbieri Rodella[2], Andre S Ferlauto, Stefan Kycia, SERGIO LUIZ MORELHAO

[1]Universidade de São Paulo (*Instituto de Física*) , [2]Centro Nacional de Pesquisa em Energia e Materiais (*LNLS*)

e-mail: adrivalerio@gmail.com

Abstract

Accessing size distributions in nanocrystalline particle systems is important for understanding its physical and chemical properties. Nanoparticles systems performance is dependent of structural variables, such as morphology, size distribution, surface area, among other properties. To ensure a nanocrystalline system perform as expected is essencial to characterize it properly. X-ray diffraction and scattering methods are widely used as analytical tools to control nanomaterials synthesizing processes. However, the physical meaning of size values determined by X-ray methods is still controversial. In order to investigate this question in detail, whole X-ray diffraction and scattering patterns were calculated via pair distance distribution function for monodisperse nanostructured cubes and spheres, ranging from 1 to 70 nm. Each X-ray method interpret the size distribution with different weight. This work shows that the Scherrer equation applied to diffraction peaks provides as measure of size the median value of the fourth-moment integral of the size distribution. Also, the Scherrer equation applies to the scattering peak. Combined analysis of small-angle scattering and diffraction techniques lead to accurate estimates of particle size, size dispersion, and crystallinity. In order to validate the procedure, powder samples of CeO2 nanocubes were measured by X-ray diffraction (XRD) and small angle X-ray scattering (SAXS) and its results were correlated with synthesis parameters.

Spacial distribution of LiYF$_4$:Ce,Tb scintillator in polystyrene matrix using X-ray mapping

RAYSSA LIMA COSTA COURA[1], Adriano Borges Andrade[2], Zelia Soares Macedo[3], Veronica de Carvalho Teixeira[4,5], Mario Ernesto Giroldo Valerio[3]

[1]Universidade Federal de Sergipe (*Departamento de Ciência e Engenharia de Materiais*) , [2]Universidade Federal de Sergipe, [3]Universidade Federal de Sergipe (*Depto de Física*) , [4]Centro Nacional de Pesquisa em Energia e Materiais (*LNLS*) , [5]Laboratório Nacional de Luz Síncrotron

e-mail: rayssacouraeng@hotmail.com

Abstract

In this work, composite films based on lithium yttrium fluoride (LiYF$_4$) particles co-doped with Ln^{3+} (Ln = Ce, Tb) and polystyrene (PS) have been investigated as possible candidates for X-ray detection with high efficiency. The luminescent properties of the films were analyzed by photoluminescence (PL) with excitation at ultraviolet and visible (UV-VIS) range. X-ray fluorescence (XRF) and X-ray excited optical luminescence (XEOL) 2D mapping were performed at Coherent X-ray Nanoprbe Beamline (Carnaúba) to investigate the dispersion of the constituent elements in the polymer matrix. The results showed that the PS precursor solution concentration directly affects the particles distribution on the film body influencing, consequently, the efficiency of emission process. In addition, the images reveal that the powder is mainly deposited at the bottom of the films leading to different radio and photoluminescent response obtained from each side of the film. The films show visible emission in the green region of the spectrum, that is suitable to the spectral sensitivity of charge coupled device (CCD) image sensor. The results obtained so far indicates that the LiYF$_4$:Ln^{3+} – PS composites are potential candidates for use in scintillator devices.

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Spectroscopic Comparisons of the Color of Emeralds from MG, BA, GO and TO (Brazil).

Carlos Magno de Lima e Silva[1], Rúbia Ribeiro Viana[1], José Maria Leal[1], Ricardo Santana[2], Douglas Galante[3], Veronica de Carvalho Teixeira[4]

[1]Universidade Federal dos Vales do Jequitinhonha E Mucuri (*PPGGEO*) , [2]Universidade Federal de Goiás, [3]Laboratório Nacional de Luz Síncrotron (*Linha de Luz Carnaúba*) ,

[4]Laboratório Nacional de Luz Síncrotron

e-mail: magnodelimaesilva@gmail.com

Abstract

In classical theory, Chromium (Cr^{3+}) and Vanadium (V^{3+}) ions are impurities that act on the color centers of emerald crystals. In this study, samples of emeralds from 4 deposits in Brazil (MG, GO BA and TO) were analyzed by spectroscopic techniques at UFVJM/MG, UFG/GO and LNLS-CNPEM/SP. Initially, the EDXRF analysis (UFVJM) identified a higher content of Fe ions in relation to Cr and V. The measurements of optical absorption of emerald crystals in a P-EL/B1050 spectrophotometer (UFG), in the spectral region from 1800 to 250 nm showed Cr^{3+} ions with a lower energy state described by the irreducible representation of $^4A_2$ and, in NIR, the bands centered at 1149, 1410 and 1785 nm also attribute to the vibrational processes of H_2O molecules associated with alkaline ions in the structural channels of emeralds. On the Carnaúba Line (LNLS), in the variable sampling environment of the TARUMÃ station, analyzes were carried out with correlations between different elements, in the energy range from 2.05 to 15 keV and XRF characterization techniques (XANES) demonstrated the presence of Cr, V, Fe, Ca, Ti, Ni, Cu, Zn with a predominance of Fe and Cr. XANES data in the F and K region show Fe^{2+} and Fe^{3+}, with a greater influence of Fe^{3+}. There is a predominance of Fe, with Cr in second place. In other cases, Cr is not localized together with Fe or the distribution of both is correlated. These data were compared with synthetic standards of metallic Fe (Fe 0), FeO (Fe^{2+}), Fe_2O_3 (Fe^{3+}) and Fe_3O_4 (magnetite with mixture of Fe^{2+} and Fe^{3+}). Through X-ray absorption spectroscopy was possible to evaluate Cr, V, Fe ions and the results of spectroscopic comparisons by synchroton light analysis demonstrate presence of $Fe^{2+/3+}$ oxidation occupying crystallographic sites and indicate that the presence of these Fe ions influences the variation of shades in the color centers of the crystallines structures and are integral part of the composition and geochemical fingerprint of Brazilian emeralds.

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LNLS - Laboratório Nacional de Luz Síncrotron

CNPEM - Centro Nacional de Pesquisas em Energia e Materiais - SP

Spectroscopic investigation of polythiophene/gold nanoparticles/carbon nanotubes nanocomposites thin films

Thauany Hellmann[1], Camila Suemi Inagaki[2], Matheus F. F. das Neves[2], Marcela Mohallem Oliveira[3], Lucimara S. Roman[2], Aldo J. G. Zarbin[2], Maria Luiza Miranda Rocco[4]

[1]Universidade Federal do Rio de Janeiro (*Instituto de Química*) , [2]Universidade Federal do Paraná, [3]Universidade Tecnológica Federal do Paraná, [4]Universidade Federal do Rio de Janeiro (*Departamento de Físico-Química*)

e-mail: thauany@pos.iq.ufrj.br

Abstract

It is well known that the development of polymer-based hybrid nanocomposite materials are very interesting due to the synergistic effect when there is an intimate contact between them, thus allowing a wide range of applications for such materials [1]. Hybrid nanocomposite films containing polythiophene/gold nanoparticles (PT/Au) and polythiophene/gold nanoparticles/carbon nanotubes (PT/Au/CNT), synthesized through a liquid-liquid interfacial polymerization route at different reaction times and amounts of carbon nanotubes, were investigated through near-edge X-ray absorption fine structure (NEXAFS), X-ray photoelectron spectroscopy (XPS), reflection electron energy loss spectroscopy (REELS), and Resonant Auger spectroscopy (RAS). Synchrotron measurements were carried out at the SXS beamline of the LNLS UVX machine. XPS showed the presence of large gold particles and formation of polythiophene aggregates caused by the introduction of carbon nanotubes (CNT). This may also explain the surface- and bulk-sensitive NEXAFS results, which pointed to the formation of amorphous films. By employing the core-hole clock (CHC) method [2] from RAS results, ultrafast charge transfer times were estimated for each film. The results obtained by XPS and NEXAFS are also reflected in the values calculated for the charge transfer times, which are faster for samples with less content of CNT. The experimental conditions reported here led to the formation of clusters of the nanotubes, thus making the interaction with the polymer difficult. With the increase in the reaction times forming consequently larger polymer chains, the energy of the bandgap obtained by REELS is reduced as well as with the decrease in the amount of CNT. These films were heat-treated and further analyzed by NEXAFS and RAS. Faster charge transfer times were calculated, although no preferential order of the polymeric chains was observed after annealing.

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Structural analyses of alamosite phase (PbSiO3) derived from lead glass metasilicate via Synchrotron X-ray diffraction measurements under extreme conditions

Thiago Rodrigues da Cunha[1], Rafaella Bartz Pena[2], David Vieira Sampaio[3], Ariano Rodrigues[2], Paulo Sergio Pizani[2]

[1]Universidade Federal De São Carlos (*Departamento de Física*) , [2]Univerdade Federal de São Carlos (*Física*) , [3]Universidade Federal de Alagoas (*Departamento de Física*)

e-mail: trcunhafisico@gmail.com

Abstract

Within this work we propose to investigate the stable crystalline phase of lead metasilicate glass with the alamosite structure. By analyzing the diffraction patterns taken in *in situ* Synchrotron X-ray diffraction measurements (SXRD) under extreme conditions of high temperature (HT) and high pressure (HP) using Rietveld refinement, we estimated the evolution of structural parameters, such as atomic positions and lattice parameters, through which was possible derivate thermodynamic constants of state, such as thermal expansion coefficients, compressibility of the structure, bulk modulus (from Birch-Murnaghan Equation of State) and stability of this structure submitted to HT and HP. The interest in these glass-ceramic materials is millenary, due to this transformative characteristic [1], and the control of nucleation–growth–crystallization process, such as the knowledge of these properties is fundamental to achieve a good control in the production of glass-ceramics, widely used from domestic to high technology applications. Recently reported works point to a growing interest in these analyses, from which is possible to provide the thermodynamic variables and envisage applications based on elastic properties and the structural stability limit [2,3].

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Study of carbonaceous aerosols through synchrotron radiation

Lucas Cardoso Ramos[1], João Basso Marques[2], Flavio C Vicentin[3], Amanda Crystina Araujo da Silva[1], Rayanna de Oliveira Costa[4], Nicolas Neves de Oliveira[1], Martin de Oliveira Kotsis[5], Thais Costa Brunelli[6]

[1]Universidade Federal de Mato Grosso (*Instituto de Física*) , [2]Universidade Federal de Mato Grosso (*Inst. Física*) , [3]Laboratório Nacional de Luz Síncrotron, [4]Universidade Federal de Mato Grosso (*Instituto de Fisica - PGFA*) , [5]Universidade Federal de Mato Grosso (*Programa de Pós-Graduação em Física Ambiental*) , [6]Universidade Federal de Mato Grosso (*Instituto de Física - PPGFA*)

e-mail: lucasc.ramos1@gmail.com

Abstract

The study of atmospheric aerosols is getting even more important to understand the atmosphere and consequently the dynamics of Environment. There is great gaps about atmospheric aerosols, small solid or liquid particles with a diameter around 0.1 and 100 nm that being suspended, mainly, at the troposphere and that have notables characteristics like substance transporte, hygroscopic, thermodynamics and optical properties, besides to act like condensation nucleus that assist the formation of clouds, something fundamental to climate dynamics of Amazon and Midwest Region of Brazil. Recently, a new study have shown that Primary Organic Aerosols (POA), Secondary Organic Aerosols (SOA) and Secondary Inorganic Aerosols (SIA) can coexist in three different liquid phases inside the same particle, it change our comprehension between atmosphere and atmospheric aerosols. We are surrounded by increasingly intense climate changes and a large amount of annual emissions of particles and gasses. Carbonaceous Aerosols (CA) are an important study object once they are involved in many reactions and processes. It's possible to find the carbon in different forms in the atmosphere, which is known as Black Carbon (BC) is the elementary form of carbon, furthermore, the incomplete combustion of organic matter can produce another type of CA, called Brown Carbon (BrC), there is evidences in the literature that organic carbon is linked with the formation of organic acids in the city of São Paulo atmosphere [1]. The use of techniques based on synchrotron radiation is a single source of information, the consistency between the dimensions of radiation beam and the size of particles, turn adequate its use to extract information from samples. The combined use of Small Angle X-ray Scattering (SAXS) with others like X-ray Absorption Spectroscopy (XAS) and Scanning Electron Microscopy (SEM) can help solve fundamental gaps around aging and reactivity of CA.

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Surface characterization of atmospheric aerosol by X-ray photoelectron spectroscopy: a scientific interest

Thais Costa Brunelli[1], João Basso Marques[2], Flavio C Vicentin[3], Amanda Crystina Araujo da Silva[4], Rayanna de Oliveira Costa[5], Lucas Cardoso Ramos[4], Martin de Oliveira Kotsis[6], Nicolas Neves de Oliveira[4]

[1]Universidade Federal de Mato Grosso (*Instituto de Física - PPGFA*) , [2]Universidade Federal de Mato Grosso (*Inst. Física*) , [3]Laboratório Nacional de Luz Síncrotron, [4]Universidade Federal de Mato Grosso (*Instituto de Física*) , [5]Universidade Federal de Mato Grosso (*Instituto de Fisica - PGFA*) , [6]Universidade Federal de Mato Grosso (*Programa de Pós-Graduação em Física Ambiental*)

e-mail: thais12@fisica.ufmt.br

Abstract

Atmospheric aerosol is the second largest climate-modifying agent with indirect impacts on human health, after carbon dioxide, and causes several health problems, including cardiovascular and pulmonary diseases, accounting for about 7.6% of total global deaths [1]. Atmospheric aerosols are identified as surfaces of aggregation and viral transmission of SARS-COV 2 reinforcing the COVID-19 pandemic. The level of understanding of atmospheric aerosols is still low in view of the great impact these particles have on climate and health. The Carbonaceous Aerosol (AC) is one of the agents that carries the greatest uncertainty in its knowledge, the AC represents from 20% to up to 50% of the total mass of the atmospheric aerosol. Characterization at nanometer scales can provide a set of information to describe the chemical properties of AC and its role in atmospheric chemistry and physics. Under conditions of a saturated atmosphere, the AC act as condensation nuclei of clouds, in this process the water molecules in the gas phase condense on the surface of the atmospheric particles. Some issues are not yet described in the process of cloud formation and subsequent precipitation, such as what elemental interactions and oxidation states of the elements affect the ability of the aerosol to form rain clouds in the atmosphere [2]. X-ray photoelectron spectroscopy (XPS) is a powerful technique to elucidate the surface electronic structure of AC such as its elemental composition and the oxidation states of the outer layers. A great scientific interest arises in exploring chemical interactions and as well as interfacial processes of condensation nuclei by the XPS technique, for its ability to measure the surface properties of atmospheric aerosol with little sampling time and provide information for future research.

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Synchrotron-based X-ray spectroscopy (XPS and XAS) for probing the nature of electrochemical formed vacancies a Prussian Blue based catalyst

Rafael Lavagnolli Germscheidt[1], Túlio C. R. Rocha[2], Juliano Alves Bonacin[1]

[1]Universidade Estadual de Campinas (*Inorganic Chemistry*) , [2]Centro Nacional de Pesquisa em Energia e Materiais (*LNLS*)

e-mail: r226597@dac.unicamp.br

Abstract

Prussian Blue (PB) is an inorganic material of mixed valence in a tridimensional framework formed by Fe(II) bound to Fe(III) through a cyanide bridge. Furthermore, do its outstanding electrochemical properties it represents a great alternative as a catalyst for the water oxidation reaction, producing green H_2 from H_2O.[1,2] However, the low number of active sites is the main drawback, thus, the creation of vacancies is the best strategy to increase active sites and improve the catalyst activity. Synchrotron-based X-ray photoelectron spectroscopy (XPS) and soft X-ray absorption spectroscopy (XAS) can be used to probe the surface composition, transition metal oxidation states speciation, and give information about orbitals energies.[3] Herein, we report a methodology to synthesize the PB and promote the improvement of its properties on water oxidation by electrochemically formed vacancies (APB). Moreover, synchrotron-based spectroscopy, XPS and XAS, performed at IPÊ beamline of the synchrotron light source Sirius, at LNLS, were used to probe the surface composition and Fe speciation of the films to probe the nature of these defects. Quantitative XPS analysis shows that the films have similar surface elementary compositions. However, the drastic differences in the lineshape of the Fe 2p peaks between the traditional PB (TPB) and the APB indicate that oxidation state and local chemical environment of Fe are different for the films. XAS analysis shows that the spectrum for APB is shifted in 0.3 eV toward lower energies when compared to the TPB spectra, indicating some CN^- left the structure and was replaced by aquo ligand, providing spectroscopy evidence of the creation of CN^- vacancies in the structure. We believe the unique sensitivity to element and valence of soft x-ray spectroscopy might break the complexity of defect chemistry in PBAs and other compounds with mixed valence and multiple transition metal centers recently exploited for catalysis and energy conversion.

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The influence of atmospheric particles on photovoltaic energy production

Amanda Crystina Araujo da Silva[1], João Basso Marques[1], Ian Maxime Cordeiro Barros da Silva[1], Rayanna de Oliveira Costa[1], Lucas Cardoso Ramos[1], Thais Costa Brunelli[2], Martin de Oliveira Kotsis[3], Nicolas Neves de Oliveira[1], Flavio C Vicentin[4]

[1]Universidade Federal de Mato Grosso (*Instituto de Física*) , [2]Universidade Federal de Mato Grosso (*Instituto de Física - PPGFA*) , [3]Universidade Federal de Mato Grosso (*Programa de Pós-Graduação em Física Ambiental*) , [4]Laboratório Nacional de Luz Síncrotron

e-mail: amanda.araujo@fisica.ufmt.br

Abstract

In recent years, there has been a high expansion in the field of solar energy in Brazil. It is believed that this increase is due to both the concern with the environmental impacts generated by conventional sources, as well as the high Brazilian energy inflation. Despite being a desirable alternative, the use of solar energy has disadvantages when compared to conventional sources. This is due to the high dependence on climatic factors such as temperature, cloudiness, and availability of solar radiation. Another factor that also influences the production of solar energy is the presence of particles suspended in the atmosphere, the so-called aerosols (KHALIL, 2016). Aerosols are particles in solid or liquid state and their sizes vary between the range of micrometers to nanometers, they can be of natural or anthropogenic origin, as main sources of emission are soil dust, sea salt, the burning of biomass, industrial processes, vehicular and so forth. However, studies indicate a loss of more than 20% of the efficiency of solar energy generation in an environment polluted by aerosols (CALINOIU et al., 2013). This becomes a worrying factor, due to the substantial increase in the number of fires in recent years, which consequently also increases the number of particles suspended in the atmosphere. In this work we intend to investigate the chemical composition of aerosols through techniques such as XPS and X-ray fluorescence to identify the processes involved in the formation of aerosols, in addition to understanding how these particles absorb and scatter sunlight. Taking these aspects into account, the fundamental characterization of aerosols can bring new perspectives on which sources of pollution are predominant in the attenuation of solar radiation, making it possible to understand how the decrease in the efficiency of energy production through solar panels occurs.

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The Pressure-Induced structural phase transition of $CsCuCl_3$ like-perovskite compound

Juan Simon Rodriguez Hernandez[1], Mayra Alexandra Padron Gomez[2], Ricardo Donizeth dos Reis[3], Alejandro Pedro Ayala[4], Carlos William Araújo Paschoal[2]

[1]Universidade Federal do Ceará (*Fisica*) , [2]Universidade Federal do Ceará, [3]Centro Nacional de Pesquisa em Energia e Materiais (*Laboratório Nacional de Luz Síncrotron*) , [4]Universidade Federal do Ceará (*Física*)

e-mail: juan.hernandez@fisica.ufc.br

Abstract

Halide perovskites are widely studied for several physical properties. In fact, it has been described as widespread interest research for revealing astonishing stability in extreme conditions. The like-perovskite halide $CsCuCl_3$ belongs to the ABX_3 materials described as (A=Rb, Cs; B=Mn, Fe, Co, Ni, Cu; X= Cl, Br). It is composed of $CuCl_6$ octahedra chains along the c-axis and separated by the isolated Cs^+ ions [1]. Below T_N = 10.7 K the compound displayed an antiferromagnetic phase[2], in which it was found that the pressure-induced generates quantum magnetic phases that could be quantified by the $CuCl_6$ distortion [3,4]. In this context, we deepen further on the high-pressure measurements with the SXRPD (Synchrotron X-ray Powder Diffraction) and Raman spectroscopy on the $CsCuCl_3$ compound in order to quantify the CuCl6 distortion. We noticed an abrupt SXRPD pattern changes consistent with the Raman spectroscopy measurements. Over the Raman experiment, three phases could be extrapolated: a) ***I-Phase:*** (0 - 2.51) GPa, which is related to the room-temperature crystal structure; b) ***I-II Phase:*** (2.79 - 3.57) GPa, a mixture of both low- and high-pressure phases; and c) ***II-Phase:*** (4.01 - 6.94) GPa, the new crystal structure phase determined with the synchrotron radiation. The observed phonons correspond to the internal vibrations of the $CuCl_6$. The pressure-induced shifts of the vibrational mode frequencies increase linearly with the pressure of all peaks until the ***I-II Phase***, where the number of Raman bands increases, describing a re-orientation of the crystal. The analysis indicated a structural phase transition under pressure at 2.51 GPa from the hexagonal ($P6_522$) to a monoclinic P2.

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Time of characterization of atmospheric aerosols using Synchroton radiation.

Nicolas Neves de Oliveira[1], Thais Costa Brunelli[2], Amanda Crystina Araujo da Silva[1], Rayanna de Oliveira Costa[3], Martin de Oliveira Kotsis[4], Lucas Cardoso Ramos[1], João Basso Marques[5]

[1]Universidade Federal de Mato Grosso (*Instituto de Física*) , [2]Universidade Federal de Mato Grosso (*Instituto de Física - PPGFA*) , [3]Universidade Federal de Mato Grosso (*Instituto de Fisica - PGFA*) , [4]Universidade Federal de Mato Grosso (*Programa de Pós-Graduação em Física Ambiental*) , [5]Universidade Federal de Mato Grosso (*Inst. Física*)

e-mail: nicolas.oliveira@fisica.ufmt.br

Abstract

In this study, we intend to use the procedure performed by (Fittschen, et al. - 2008) using synchrotron X-ray fluorescence to characterize elemental quantities in atmospheric aerosols up to particle sizes of 0.015um. Also obtain speciation of some elements in the same way as was performed for Fe2+ and Fe3+. This method requires sample collection of only 20 min per low pressure impactor. Normally, atmospheric aerosol collections take at least 25 to 48 hours and the minimum amount of particles to sensitize the techniques used are high with a detection limit of conventional fluorescence is 5 ug/m^3. This is a very high time and cost for field research. This work aims to minimize this difficulty of atmospheric research for the characterization of particulate matter.

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Unveiling the Depolymerization of Densified Lead Metasilicate Glass: an Optical Raman and O K-edge X-Ray Raman Spectroscopic Study

Rafaella Bartz Pena[1,2], Ulisses Ferreira Kaneko[3], Ricardo Donizeth dos Reis[3], Thiago Rodrigues da Cunha[1], Thierry Deschamps[2], Sylvie Le Floch[2], Christine Martinet[2], Ariano De Giovanni Rodrigues[1], Paulo Sergio Pizani[1]

[1]Univerdade Federal de São Carlos (*Física*) , [2]Université Claude Bernard Lyon 1 (*Institut Lumière Matière*) , [3]Brazilian Synchrotron Light Laboratory

e-mail: rafaellabartz@gmail.com

Abstract

The effect of densification on glass materials can drive different structural modifications, whether performed at room temperature (cold-densified) or higher temperatures (hot-densified). Cold-densified lead metasilicate glass is described to present unusual depolymerization to the uncompressed glass [1]. In this work, these glasses were hot-densified to 5 GPa under comparable rates and times in a Belt press. The simultaneous effect of pressure and temperature was investigated *ex-situ* by optical Raman and O K-edge X-ray Raman scattering (XRS) spectroscopies, providing a combinatory probe to evaluate the modifications on the network connectivity. Regarding the optical Raman spectroscopy, its low-wavenumber region displays changes to the Pb-O vibrations, possibly linked to the formation of highly coordinated PbO_n polyhedra at higher compression temperatures [2]. In its turn, the high-wavenumber region, comprising the Si-O stretching modes, reveals network depolymerization as depicted by the evolution of the barycenter and Q^n population, with an increase in the non-bridging oxygen (NBO) proportion. For the most extreme compression conditions, this last trend was confirmed by the element-specific O K-edge XRS, which indicates modifications in the spectral region attributed to the NBOs [3]. The structural role of free-oxygens in the densification mechanisms of lead metasilicate glass is discussed.

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Use of high-throughput PanDDA analysis to unveil new bioactive molecules based on the Brazillian natural products biodiversity

Raphael Meneghello[1], Joane Kathelen Rustiguel Bonalumi[2], Ana Carolina de Mattos Zeri[3], Andrey Fabricio Ziem Nascimento[4], Daniela Barretto Barbosa Trivella[5]

[1]Centro Nacional de Pesquisa em Energia e Materiais (*LNBio*) , [2]Centro Nacional de Pesquisa em Energia e Materiais (*Farmacologia*) , [3]Centro Nacional de Pesquisa em Energia e Materiais (*SIRIUS*) , [4]Centro Nacional de Pesquisa em Energia e Materiais (*Laboratório Nacional de Biociências*) , [5]Centro Nacional de Pesquisa em Energia e Materiais

e-mail: raphael.meneghello@lnbio.cnpem.br

Abstract

The variability of natural products at the six Brazilian biomes and its coast-marine system provides a great pharmacological potential hidden in the huge biodiversity and is a great source of inspiration of novel drugs. To unveil it, the use of cutting-edge technologies and integrative approaches are essential given the chemical complexity and innovative of those natural molecules. In addition, especially the use of high throughput technologies reduces cost and time of the discovery of natural products-based new bioactive molecules. In this context, the Drug Discovery platform at CNPEM uses a multidisciplinary approach (NP^3 approach) in which crystallography plays a fundamental role. After the high throughput screening of the natural extracts and its enriched fractions, the bioactive samples are soaked with the target protein crystal, and then subjected to X-ray diffraction at the MANACA beamline (SIRIUS-CNPEM). Its state-of-the-art technology provides a large-scale data collection, processing, and structure resolution, in which it is possible an almost real-time observation of the bioactive ligand electron density. However, the bioactive molecule could interact with the protein crystal in a low occupancy manner, especially complex natural ligands. This leads to poor electron density, making difficult its visualization. To circumvent that, we implemented the Pan-Dataset Density Analysis (PanDDA) algorithm developed by the Diamond light source group in our drug discovery pipeline. This algorithm revels the ligand electron density of the bound-state by subtracting a fraction of a calculated mean electron density of ground-state (apo crystals), even for low occupancy ligands. Therefore, the implementation of PanDDA analyses, aligned to the multidisciplinary NP^3 approach, allows a rapid and robust approach for discovery of new scaffolds and interaction modes of natural products bound to the target of interest in a broader way.

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Using synchrotron techniques to investigate an emerging class of naturally abundant layered materials: phyllosilicates

RAPHAELA DE OLIVEIRA[1,2], Ingrid David Barcelos[2], Klaus Wilhelm Heinrich Krambrock[1], Angelo Malachias de Souza[1]

[1]Universidade Federal de Minas Gerais (*Physics Department*) , [2]Centro Nacional de Pesquisa em Energia e Materiais (*LNLS*)

e-mail: raphaeladeog@ufmg.br

Abstract

Beyond graphene, most of the attempts in finding interesting layered materials (LMs) that are capable of being reduced to mono and few-layers have been made in synthesized materials such as hexagonal boron nitride and transition metal dichalcogenides. In an effort to increase the list of naturally occurring LMs that are abundant in nature and could become an alternative low-cost source of two dimensional (2D) materials over its synthetic counterparts, recent research has been carried out in the group of phyllosilicate minerals which are wide band gap insulators that can be mechanically exfoliated to monolayers [1].
We present here this emerging class of naturally abundant LMs, focusing on the description of the 2D structure and fundamental properties starting from the 3D bulk form of two barely explored phyllosilicate specimens – clinochlore and phlogopite [2,3]. We point out several synchrotron techniques that can be used as powerful tools in the characterization of these minerals. We observed by X-Ray Fluorescence the spatial distribution of impurities that play a fundamental role in determining the macroscopic properties of phyllosilicates, establishing the oxidation states of these impurities by X-Ray Absorption Near the Edge Structure. Through Synchrotron Infrared Nanospectroscopy, we can investigate how phyllosilicates confine water in nanoscale and we demonstrated that ultrathin layers with an atomically flat surface can be obtained for both materials maintaining their bulk vibrational properties. In addition, we analyzed the arrangement of iterlamellar water in phyllosilicates by Crystal Truncation Rod Scattering using synchrotron X-ray sources.

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X-ray photoelectron diffraction study of the approximant Al_5Co_2(001) quasicrystal

Lhonidas de Senna Junior[1], Guilherme Jean Pereira de Abreu[1]

[1]Universidade Federal do Paraná (*Física*)

e-mail: lhonidas@gmail.com

Abstract

The intermetallic Al_5Co_2 is defined as a structurally complex material and is considered a low-order quasicrystalline approximant. Its unit cell contains 28 atoms, thus relatively small compared to other Al–TM (*TM* = Transition Metal = Co, Fe or Ru) approximants, like the well-known $Al_{13}TM_4$ with 102 atoms per unit cell[1,2]. A single crystal of Al_5Co_2(001) was obtained by the Czochralski method. The experiments were carried out on the Planar Grating Monochromator (PGM) beamline of the Brazilian Synchrotron Light Laboratory (LNLS), using an Ultra High Vacuum (UHV) station[3]. The sample was characterized by X-ray photoelectron diffraction (PED). In the current research, the structure study was performed applying the standard software Multiple Scattering Calculation Diffraction (MSCD) and show a (1×1) pattern. In addition, four different termination models for this reconstruction were tested. The MSCD simulations indicate the model that presented the best agreement between the experimental and theoretical data and a good visual comparison between the patterns was the reconstruction model (1×1), which consists of layers two puckered layers alternating, and both are related by a rotation of 180°. The non-structural parameters, such as: Debye temperature and surface potential, were optimized and applied in relation to the structure of the model corresponding to the linear combination of the terminations of two models, corresponding to the values of $\theta_D = 575$ K and $V_0 = 4.6$ eV, for which we found a reliability factor of 0.182, belongs to the Al-rich surface layer.

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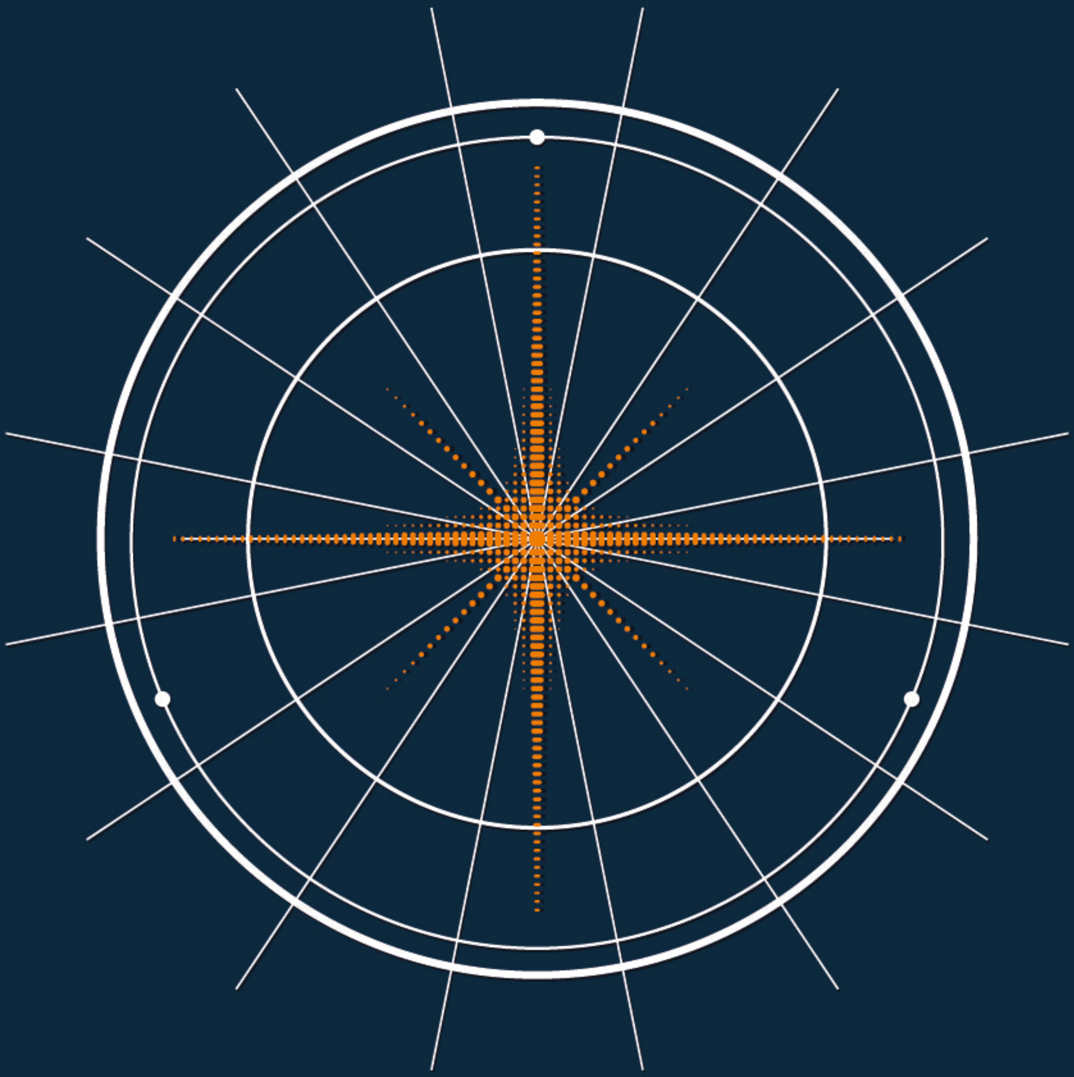

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