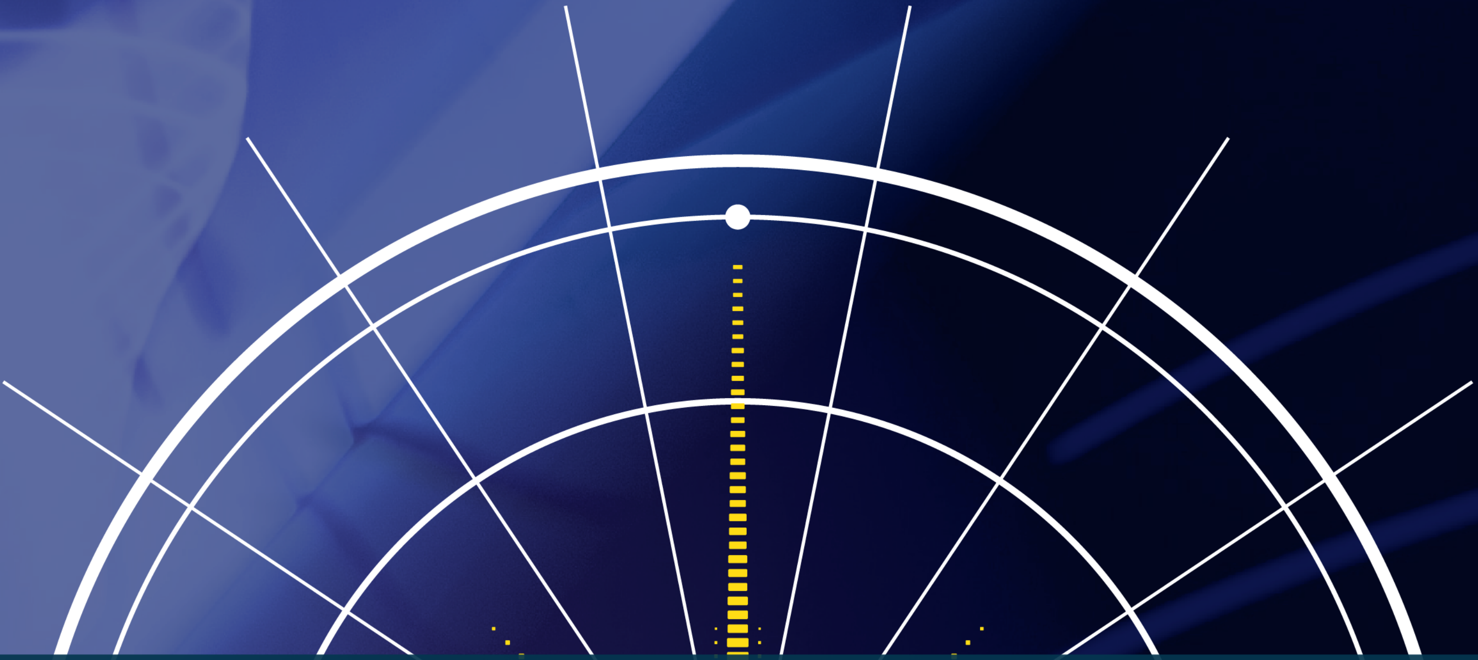
31st RAU

Annual Users Meeting LNLS | CNPEM

ABSTRACT BOOK



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Foreword

Dear participants,

On behalf of the Scientific and Local Committees, I am pleased to welcome all of you to the 31st Annual Users Meeting (RAU) of the Brazilian Synchrotron Light Laboratory of the Brazilian Center for Research in Energy and Materials (CNPEM).

In spite of the global pandemic situation, Sirius, a 4th generation machine, continues shedding light on the progress of the science.

In this context, the Sirius project has reached another milestone in commissioning its accelerators and beamlines. Five new beamlines are entering the scientific commissioning stage, completing the number of six beamlines available for the user community: MANACÁ, for macromolecule crystallography; CATERETÊ, for X-ray coherent diffracting imaging; CARNAÚBA, for X-ray spectro-nanoscopy and nano-diffraction; EMA, for samples under extreme conditions; IMBUIA, for nano and micro Fourier-Transform Infrared spectroscopy; IPÊ, for Soft X-ray Inelastic scattering and Photoemission. In addition to the beamlines, two support laboratories, LCTE, for samples under Extreme Thermodynamic Conditions and LCIS, for in situ growth of thin films and heterostructures, and the scientific computing center TEPUI, for data storage and analysis, were officially inaugurated the last month.

Due to the COVID-19 pandemic, we will host the second online edition of the RAU via Whova platform. During 4 days, around 500 participants will be able to share the scientific agenda throughout six plenary conferences given by prestigious international speakers, interactive sessions of the LNLS beamlines presentations which include live virtual tours, 25 oral communications and 62 poster presentations.

For the first time, the award to the best thesis that was carried out in the LNLS facilities will be held among the candidates who applied and were selected. Besides, at the end of the Users Group assembly, the two new Committee members who were elected will be presented.

Finally, I would like to thank the Local Committee and the CNPEM staff for their dedicated work in the organization, and also thank our sponsors whose support made this event possible.

As member of the LNLS Users Group, I hope this RAU allows the sharing of knowledge and experience, and I wish it helps all of you keep in touch with the scientific community.

María Fernanda Mera
Chair of the 31st RAU

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Invited Talks

Invited Talk

Crystallographic fragment-screening: workflow and procedures

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Fragment screening is a technique that helps to identify promising starting points for ligand design. Given that suitable crystals of the protein of interest are available and exhibit reproducibly good X-ray diffraction properties, X-ray crystallography is nowadays probably the preferred method for fragment screening, because - in addition to a simple yes/no answer with respect to binding - it provides detailed 3D information of the binding mode. In the presentation, the complete practical workflow and the included tools on how to conduct crystallographic fragment screening (CFS) at the Helmholtz-Zentrum Berlin (HZB) are presented. This includes the use of a suitable library, the use of special tools for handling many crystals easily and reliably, automated facilities for diffraction data collection and processing as well as automated structure refinement and ligand identification. Also, glimpses will be provided in how to evolve the initial fragment hits into more tightly binding compounds.

Invited Talk

Developing field-relevant synchrotron techniques to support agricultural innovation

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Synchrotron techniques have been used to investigate a range of processes in soils and plants. While these applications were initially addressing environmental issues related to pollution, recent years have seen increasing interest in using synchrotron approaches for agricultural research. However, a significant barrier to their application resides in the difficulty to extrapolate the very detailed information that can be obtained using synchrotron techniques to the field scale. This is because synchrotron techniques have in the past been considered a) generally 'low-throughput' and not particularly sensitive compared with other methods and b) only able to provide very detailed information on a few, small samples containing reasonably high elemental concentrations.

The development of new synchrotron sources, of increasing brilliance and the advances in detector technologies has now generated new opportunities. It is now possible to use synchrotron techniques as 'high-throughput' screening methods to select plant germplasm in a way that is less time consuming than laboratory methods and non-destructive. Recent advancements have also made possible the performance of experiments in tandem, at the same beamline and at the same time: this allows larger samples to be investigated without compromising throughput. Finally, the development of increasingly powerful tomographic and computational techniques are allowing probing of soil-plant samples at a scale that is agronomically-relevant. In this presentation we will provide examples of the advances we have made in these areas in a project supported by the Australian Grain Research and Development Corporation (GRDC).

Invited Talk

Momentum resolved resonant inelastic X-rays scattering on correlated quantum materials

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Resonant Inelastic X-ray Scattering (RIXS) is a powerful probe of excitations from the electronic ground state of quantum materials involving lattice, charge, orbital and spin degrees of freedom. RIXS gives direct information as a function of momentum and energy transfer, on the elementary excitations within these degrees of freedom. These excitations are sensitive to many-body and collective effects of strongly-correlated materials, e.g. low-temperature phenomena in the energy scale of magnetic exchange and lattice vibrations. Soft x-ray RIXS at the ADRESS beamline of the Swiss Light Source has successfully been utilized in scientific problems associated with superconductivity, metal-insulator transitions, charge order, magnetic order and low-dimensional magnetism, as well as in Li-ion battery materials, molecular physics and organic transition-metal complexes. Several instruments at synchrotron radiation sources world-wide have recently further boosted the scientific capabilities with soft X-ray RIXS.

In this talk, we illustrate the scientific capabilities of momentum resolved soft X-ray RIXS on correlated quantum materials in investigations on quasi-one dimensional cuprates, iron based superconductors and the metal-insulator transition mechanism of rare-earth nickelates. In addition to the two-(plus four)-spinon continuum, we observed dispersive orbital excitations, „orbitons", in the spin chain compound Sr_2CuO_3, which are related to the separation of the spin and orbital degree of freedom [1]. The spin excitation response of isolated one-unit-cell thick layers of La_2CuO_4 show that in these nearly ideal two dimensional cuprate layers already a Neel state is stabilized instead of a resonating valence bond state [2]. Furthermore, we show how RIXS at the Fe L_3 edge is sensitive to collective magnetic excitations in iron-based superconductors that are persistent for under-, nearly optimal- and over-doping across the phase diagram of iron pnictide superconductors [3]. Furthermore, we employed RIXS maps vs. incident and transferred photon energies to reveal that the metal-to-insulator transition undergoing rare-earth (Re) nickelates $ReNiO_3$ assume a Ni $3d^8$ electronic configuration with holes in the surrounding oxygen ligands and negative charge transfer energy.

References:

[1] Spin–orbital separation in the quasi-one-dimensional Mott insulator Sr2CuO3, J. Schlappa, K. Wohlfeld, K. J. Zhou, M. Mourigal, M. W. Haverkort, V. N. Strocov, L. Hozoi, C. Monney, S. Nishimoto, S. Singh, A. Revcolevschi, J.-S. Caux, L. Patthey, H. M. Rønnow, J. van den Brink, and T. Schmitt, Nature 485, 82–85 (2012). DOI:10.1038/nature10974
[2] Spin excitations in a single La2CuO4 layer, M. P. M. Dean, R. S. Springell, C. Monney, K. J. Zhou, J. Pereiro, I. Božovic, B. Dalla Piazza, H. M. Rønnow, E. Morenzoni, J. van den Brink, T. Schmitt, and J. P. Hill, Nature Materials 11, 850–854 (2012). DOI:10.1038/nmat3409
[3] Persistent high-energy spin excitations in iron pnictide superconductors, Ke-Jin Zhou, Yao-Bo Huang, Claude Monney, Xi Dai, Vladimir N. Strocov, Nan-Lin Wang, Zhi-Guo Chen, Chenglin Zhang, Pengcheng Dai, Luc Patthey, Jeroen van den Brink, Hong Ding, Thorsten Schmitt, Nature Communications 4, Article number 1470 (2013). DOI: 10.1038/ncomms2428
[4] Ground-state oxygen holes and the metal–insulator transition in the negative charge-transfer rare-earth nickelates, Valentina Bisogni, Sara Catalano, Robert J. Green, Marta Gibert, Raoul Scherwitzl, Yaobo Huang, Vladimir N. Strocov, Pavlo Zubko, Shadi Balandeh, Jean-Marc Triscone, George Sawatzky, and Thorsten Schmitt, Nature Communications 7, 13017 (2016). DOI: 10.1038/ncomms13017

Invited Talk

Shining synchrotron infrared light on microbial world

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Fourier transform Infrared (FTIR) absorption spectroscopy is routinely used to characterize materials of all kinds. Every functional group of molecules in any material has its unique infrared spectroscopic absorption signature. FTIR absorption spectroscopy provides quantitative information on the chemical composition of materials by identifying the type of functional groups that are present. De-convolving FTIR spectral features further allows the identification of these functional groups' local chemical environment. When combined with microscopy, FTIR spectromicroscopy allows one to conduct chemical analysis and to map the distribution of chemical species with a micro-scale spatial resolution. Using infrared light from a bright synchrotron radiation (SR) source, instead of standard benchtop glow-bar sources, one can increase signal-to-noise by up to a thousand-fold. A long-standing desire in biological science is to be able to probe and understand the unique microbial biochemistries amassed over eons in every niche on the planet. Although microbes are exceedingly small, only $1/8000^{th}$ the volume of a human cell and spanning about $1/100^{th}$ the diameter of a human hair, their high surface-to-volume ratio enhances their interactions and supports their adaptation. Microbes have become masters at living in almost every mild to extreme environment. They are also masters at harvesting energy in almost every form to generate organic molecules and minerals. Their unique biochemistries offer a virtually limitless resource of capabilities that we can benefit from. In this presentation, I will discuss method development at the Berkeley Synchrotron Infrared Structural Biology (BSISB) imaging program for microscale probing of the chemistries with which microbes and their communities confer their genetic properties and express their adaptability to the modern world. I will provide examples of microbes from aquatic and terrestrial ecosystems.

Invited Talk

Synchrotron radiation X-ray microscopy for health and energy materials

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X-rays are invaluable to obtain the three dimensional structure of materials in a non destructive manner. A virtually unlimited range of length scales can be covered as the X-ray energy can be increased to obtain sufficient transmission while enough contrast is preserved down to the nanoscale by exploiting phase sensitivity. Furthermore, the temporal resolution is constantly improved thanks to faster detector technology, exploration of the synchrotron time structure and new generation X-ray sources. Full field microscopy methods are of particular interest because of their speed, simplicity and stability. Complementary, scanning methods offer alternative contrast mechanisms such as X-ray fluorescence and diffraction.

X-ray nano-tomography is a practical method to zoom non-destructively into the three-dimensional structure of matter and map the electron density with improved sensitivity [1, 2], spatial [2, 3] and temporal [4] resolution. X-ray holography and near field ptychography exploit the divergent beam behind a (nanofocus) secondary source to record magnified in-line holograms and reach a spatial resolution of a few tens of nanometer. These methods are very complementary to X-ray fluorescence analysis acquired with the sample in the focus for label-free, highly efficient trace element quantification. This correlative nanoprobe approach is implemented on ESRF beamline ID16A [5]. All measurements can be performed under cryogenic conditions to preserve biological samples close to their native hydrated state and reduce radiation damage. The cutting edge capabilities of the instrument enable unprecedented studies in metallo-biology [6, 9], neurosciences [1, 10], bio-materials [11] and energy related materials [12, 13], thus opening new scientific frontiers.

The new ESRF source provides a 30-fold increase in brilliance and coherent fraction of the X-ray beams. This 'Extremely Brilliant Source' is ideally suited for fast nanoprobe and coherent imaging applications. In this context, we will present the current achievements and challenges to fully exploit the new source.

References:

[1] A. Kuan, J. Phelps, L. Thomas, et al., Nat. Neurosci., 23, 1637 (2020).
[2] J. Gussone, K. Bugelnig, P. Barriobero-Vila, et al., Appl. Mater. Today, 20 100767 (2020).
[3] M. Hubert, J. Laurencin, P. Cloetens, et al., J. Power Sources 397, 240-251 (2018).
[4] J. Villanova, R. Daudin, P. Lhuissier, et al., Materials Today 20, 354-359 (2017).
[5] J.C. da Silva, A. Pacureanu, Y. Yang et al., Optica, 4, 492 (2017).
[6] C. Gramaccioni, Y. Yang, A. Pacureanu et al., Anal. Chem., 92, 4814 (2020).
[7] A. Procopio, E. Malucelli, A. Pacureanu, et al., ACS Cent. Sci., 5, 1449 (2019).
[8] J. Conesa, A. Carrasco, V. Rodríguez-Fanjul,et al., Angew. Chem. 59, 1270 (2020).
[9] F. Domart, P. Cloetens, S. Roudeau, et al., Elife 9, e62334 (2020).
[10] M. Andersson, H.M. Kjer, J. Rafael-Patino, et al., Proc. Natl. Acad. Sci. U.S.A. 117, 33649 (2020).
[11] M. Beliaev, D. Zöllner, A. Pacureanu, et al., Nature Physics, 17, 410 (2021).
[12] Y. Yang, R. Xu, K. Zhang, S.J. Lee et al., Adv. Energy Mater., 1900674 (2019).
[13] Z. Jiang, J. Li, Y. Yang, et al., Nat. Commun., 11, 1 (2020).

Invited Talk

The consortium for operando and advanced catalyst characterization via electronic spectroscopy and structure at SSRL: lessons learned and the path forward

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The Consortium for Operando and Advanced Catalyst Characterization via Electronic Spectroscopy and Structure (Co-ACCESS) is a research program funded by the US Department of Energy, Basic Energy Sciences and is located at SSRL. Its aim is to provide resources and know-how to catalysis researchers who wish to conduct their research at SSRL and has a strong focus in in-situ/operando catalyst characterization. In this talk I will provide an overview of the goals, the capabilities, and the resulting impact that Co-ACESS has had at SSRL and on catalysis characterization. The central tenet of Co-ACCESS is that by conducting collaborative research everyone gains. Examples of the research that has been enabled will be discussed and future plans presented.

Oral Communications and Poster Presentations

Poster Presentation

Analysis of the luminescent behavior of the undoped $CdSiO_3$ produced via Sol-Gel route with pH variations

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The search for new luminescent materials for application in different areas is becoming more and more intense, as these materials are increasingly present in everyday life, such as in TVs, in the detection of diseases through images, electronic devices, lighting systems, and scintillators for radiological protection. In recent years there has been increased interest in studies with cadmium silicate as host matrix due to the easy incorporation of dopant ions into its network creating different structural defects. On the other hand, cadmium silicate with 1:1:3 stoichiometry presents intrinsic luminescence, which makes it interesting for different areas of application, but the origin of this intrinsic luminescence is not fully understood yet. This work presents the synthesis and characterization of $CdSiO_3$ prepared by the sol-gel process in which cadmium oxide and TEOS were used. Different synthesis parameters, such as agitation time, pH of the starting sol, amount of water used in hydrolysis reaction, among others, and its influence on structural and optical properties of the materials were evaluated during the study. $CdSiO_3$ was obtained for the sample prepared with pH = 1, 7, and 9, which were calcined at 1000°C for 3 h. Emission and excitation measurements were performed on the TGM beamline (proposal #20190133) using the low-temperature setting for the different pH values. It was possible to observe the influence of the synthesis parameters and the temperature on the emission intensities. Preliminary results of optical characterizations showed that there are two emission bands, the first between 275-530 nm and the second between 535-700 nm which may be ideal for application in scintillators.

Aknowledgements:

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Keywords:

Luminescence, $CdSiO_3$, Sol-Gel route

Oral Communication

Arsenic speciation in natural geological samples using synchrotron radiation-based X-ray techniques

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Along the Andes and the vast lowlands that extend towards the East, elevated concentrations of arsenic (As) in natural water reservoirs are mostly sourced from the weathering of volcanic materials, and its distribution depends on subsequent (bio)chemical reactions that are controlled by the system‘s physicochemical and biological conditions.

The Environmental Geochemistry Group in CICTERRA has been carrying out numerous studies aimed at identifying the sources of As and its dynamics in natural systems threatened by this hazardous geogenic contaminant for more than 10 years [1-4] The present review summarizes the results of our studies on As speciation (oxidation state and local chemical coordination) in amorphous and crystalline mineral phases that are responsible for the release and removal of As in natural systems affected by different environmental conditions. The solid speciation of As was determined by synchrotron XAS and µFRX, at the Brazilian Synchrotron Light Laboratory (LNLS Brazil). The analyzed samples are representative of the primary and secondary sources of As in the southern portion of South America and correspond to Patagonian volcanic ashes, metal sulfide mine wastes, volcanic glass-rich loess, and carbonates and borates collected from high altitude lakes in the Puna region.

Synchrotron analysis allowed us discriminating three oxidation states of As in the studied samples: As(V) is the dominant oxidation state in secondary sources while in the primary sources, the reduced As(-1) and As(III) species were identified. As(V) is generally present in the form of arsenate ions adsorbed onto ferric (hydr)oxides and included in salts such as calcite, jarosite and ulexite, substituting the carbonate, sulfate, and borate ions respectively. We found that the As(-1) species is only associated with arsenopyrite or arsenical pyrite in all the samples where this species was detected, while As(III) is related to arsenite ions included as impurities within the glass structure.

References:

[1] Bia G., Garcia M.G., Borgnino L. (2017) Changes in the As solid speciation during weathering of volcanic ashes: a XAS study on Patagonian ashes and Chacopampean loess. Geochim. Cosmochim. Acta 212, 119–132.
[2] Bia G., García M.G., Soto Rueda E., Mors R.A., Mlewski E.C., Gomez F.J., L. Borgnino (2021) Arsenic in natural carbonates: The role of the biogeochemical conditions in its solid speciation. Chemical Geology, 583, 120477.
[3] Nieva N.E., Bia G., Garcia M.G., Borgnino L. (2019) Synchrotron XAS study on the As transformations during the weathering of sulfide-rich mine wastes. Science of the Total Environment, 669, 798-811.
[4] Nieva N.E., Garcia M.G., Borgnino L., Borda L.G. (2021) The role of efflorescent salts associated with sulfide-rich mine wastes in the short-term cycling of arsenic: Insights from XRD, XAS, and µ-XRF studies. Journal of Hazardous Materials, 404, 124158.

Aknowledgements:

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Keywords:

Arsenic, speciation, geological samples, XAS

Poster Presentation

Automated sample-holder for liquids for SAXS experiments at SAPUCAIA beamline

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Dedicated to small-angle X-ray scattering technique, SAPUCAIA beamline will combine the high flux provided by SIRIUS machine and the low divergence of a high beta section to provide a very stable beam with one of the lowest parasitic scatterings worldwide. The beamline was designed to have high performance and reproducibility, which will increase both the quality and the number of experiments, allowing the development of new research areas in Brazil. To fulfill all the experimental demands that arose concerning the measurement speed, sample change and reproducibility itself, new sample holders are being designed and assembled by the beamline staff. Here, we present a sample-holder for liquids that will allow many essential embedded features such as the automation of the sample loading, flow control during the experiment – necessary due to high beamline flux –, with camera monitoring, temperature control and holder cleaning. It also can be coupled to a UV-Vis or HPLC equipment, always maintaining the beamline vacuum. Due to this automation, the sample cycle – loading, measurement and holder cleaning – will occur faster, decreasing human interference and optimizing the beamtime. Currently, other beamlines (such as at SSRL [1] and ESRF [2]) already have automated sample changers; some, however, are used in air environments. We believe that the combination of this automation and the capabilities of SAPUCAIA beamline can bring the national research to the state-of-the-art in the scientific scenario.

References:

[1] MARTEL, Anne et al. An integrated high-throughput data acquisition system for biological solution X-ray scattering studies. J of Synch Rad (2012) XX, 431-434.
[2] ROUND, Adam et al. BioSAXS Sample Changer: a robotic sample changer for rapid and reliable high-throughput x-ray solution scattering experiments. Acta Cryst. (2015) 71, 67-75.

Aknowledgements:

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Keywords:

Sample-holder, SAXS, automation, beamline, measurement, load, flow-control, temperature-control

Poster Presentation

Bayesian methods for error analysis in XAFS measurements

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Given the standard *formulae* of XAFS:

$$\chi_\Gamma(k) = \frac{S_0^2 N_\Gamma F_\Gamma(k)}{2kR_\Gamma R_{\Gamma^2}} e^{-2k^2\sigma_\Gamma^2} e^{-R_\Gamma/\delta_\Gamma} \sin[2kR_\Gamma + \delta_\Gamma(k)]\,, \quad \chi(k) = \sum_\Gamma \chi_\Gamma(k)$$

it is usual separate the parameters in theoretical (known) and obtained from experimental data (unknown).
Several methods are developed aiming to estimate the unknown parameters. The objective of our work is present a brief review of the standard classical procedures of these estimators,and analyze and discuss the methods with Bayesian techniques implemented.
The standard procedures focuses on least square estimation, and are based on linearization and approximation algorithms implementing Fourier or Wavelet transform.
Krappe and Rossner [1] proposed a Bayesian approach following the Bayes-Turchin model, in which the prior selected follows a Normal distribution, where the variance-covariance matrix is diagonal. Rehr *et.al*[2]. suggest a more general implementation on XAS models. Our focus is detail the advantages and drawbacks/limitations of this approach. According to the conclusions, we suggest a few modifications in order to offer more generality and flexibility to the Bayesian implementation.

References:

[1] Krappe, H. J., & Rossner, H. H. (2000). Error analysis of XAFS measurements. Physical Review B, 61(10), 6596.
[2] Rehr, J. J., Kozdon, J., Kas, J., Krappe, H. J., & Rossner, H. H. (2005). Bayes–Turchin approach to XAS analysis. Journal of synchrotron radiation, 12(1), 70-74.

Aknowledgements:

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Keywords:

EXAFS, bayesian methods, errors

Poster Presentation

Bis(L-histidinate) nickel(II) monohydrate crystals under high temperature conditions

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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's 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 under high temperature conditions using X-ray diffraction with synchrotron radiation and thermal analysis. 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 $\beta = 90.11(1)$ °. At high temperatures the crystal presents an endothermic event around 410 K, absorbing energy and losing mass relative to the water molecules. Around 413 K the X-ray diffraction patterns show changes indicating the beginning of a structural phase transition. The lattice parameters exhibit discontinuities around the mentioned temperature, this result supports the phase transition hypothesis. At 491 K the phase transition is complete, however the diffraction pattern has not yet been identified.

References:

[1] M. N. Hugues, The Inorganic Chemistry of Biological Processes, John Wiley and Sons, London, 1972.
[2] P. C. Wilkins, R. G. Wilkins, Inorganic Chemistry in Biology, Oxford University Press, Kettering, 1997.
[3] A. L. Bush, Curr. Opin. Cem. Biol. 4 (2000) 184.
[4] T. Sakurai, H. Iwasaki, T. Katano, Y. Nakahashi, Acta Crystallogr., Sect. B: Struct. Sci. 34 (1978) 660.

Keywords:

Bis(L-histidinate) nickel(II) monohydrate, X-ray diffraction, synchrotron radiation, thermal analysis, phase transitions

Poster Presentation

Charcoal fine as a sustainable reinforcement alternative for biocomposites

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Several studies have sought to develop new materials that meet current technological demands, industrial sectors, with low impact on the environment. Charcoal is a highly friable material that, during its production, results in significant amounts of fines. Most of the time, charcoal fines do not have an adequate destination and it becomes a problem to be solved in countries that produce it, mostly in developing countries, such as Brazil. The first stage of the research aimed to evaluate aspects of porosity, morphology (Scanning Electron Microscopy), determination of immediate chemical composition, and surface chemical composition (X-ray photoelectron spectroscopy) of charcoal fines pyrolyzed at three different temperatures (400, 600 and 800 ℃). Where interesting results for the use of this material for use as bio-reinforcement in composites were found. The second stage of the research has the bias of studying biocomposites with incorporation with fillers in elastomers and/or thermoplastics in four different proportions of charcoal fines (0, 10, 20 and 30%), in order to analyze the physical, mechanical and chemical properties of carbonaceous biocomposites, in addition to their resistance to photodegradation. Synchroton light techniques will allow for in-depth knowledge, giving possible more specific subsidies for biocomposites. The Mahogany beamline will provide three-dimensional multiscale images providing a detailed characterization of the biocomposites interface structures. Together with the Ipê beamline (Inelastic scattering and PhotoElectron spectroscopy), it will make it possible to know the characterization of the chemical composition, electronic structure and elementary excitations, in addition to providing subsidies for new materials with specific functionalities. Thus, with the results obtained in these analyses, it will be possible to advance in knowledge and improve the properties of biocomposites, contributing to future studies and expanding the opportunities for inserting a new product in the market.

References:

[1] AKALUZIA, R. O. et al. Evaluation of the effect of reinforcement particle sizes on the impact and hardness properties of hardwood charcoal particulate-polyester resin composites. Materials Today: Proceedings, v. 38, p. 570–577, 2021.
[2] DELATORRE, F. M. et al. Insights acerca do uso de finos de carvão vegetal para geração de bioenergia. AGROPECUÁRIA CIENTÍFICA NO SEMIÁRIDO, v. 16, n. 3, p. 138, 28 dez. 2020.
[3] POLOK-RUBINIEC, M.; WŁODARCZYK-FLIGIER, A. Polypropylene matrix composite with charcoal filler. Journal of Achievements in Materials and Manufacturing Engineering, v. 2, n. 103, p. 60–66, 1 dez. 2020.

Keywords:

RIXS, XPS, X-Ray micro and nanotomography, polymeric matrices

Oral Communication

CORAL: a toolbox for XAS data analysis in Jupyter Notebook

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CORAL (Curve ResOlution foR dAta anaLysis) is a new set of chemometric tools built in Python to perform multivariate spectral decomposition of large amount of XAS data. Jupyter Notebook permits to overcome difficulties related to the huge amount of data coming from fast data acquisition during time-resolved XAS studies. On beamlines controlled by Jupyter environment, such as the XAS beamline at SIRIUS [1], it also allows the creation of a complete experimental Notebook that allows to get on track the data analysis [2].
Principal Component Analysis (PCA) and Iterative Target Transformation Factor Analysis (ITTFA) from Prestopronto [3] are implemented and optimized to deal with larger datasets. This new implementation follows the evolution of a time-resolved experiment in the same experimental Jupyter Notebook and reduces the use of Random-access memory (RAM) by a considerable amount.
Multivariate curve resolution with alternating least-squares (MCR-ALS) fitting analysis is a powerful tool for isolating pure spectra of intermediate species involved in kinetic studies [4]. This method is becoming commonly used for XAS studies, as for example in catalysis [5]. Our new implementation can be easily extended to parallel processing (using GPU or CPU) and has the advantage to be easily integrated to other applications thanks to the use of the freely usable Python language.

References:

[1] Liu, L., N. Milas, N., Mukai, A. H. C., Resende, X. R. Sá F. H., (2014) J. Synch. Rad., 21, 904.
[2] Randles, B. M., Pasquetto, I. V., Golshan, M. S., & Borgman, C. L. (2017) ACM/IEEE Joint Conference on Digital Libraries (JCDL) 1-2.
[3] Figueroa, S. J. A., & Prestipino, C. (2016) J. Phys.: Conf. Ser. 712, 012012.
[4] Jaumot, J., Juan, A., Tauler, R., (2015) Chem. and Intel. Lab. Syst., 140, 1.
[5] Rochet, A., Baubet, B., Moizan, V., Pichon, C., Briois, V., (2016) Comptes Rendus Chimie, 19, 1337.

Oral Communication

Can we understand the transient dynamics of charged carriers after X-ray and/or VUV-UV light excitation?

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Spectroscopy techniques associated to UV, vacuum ultraviolet (VUV), X-rays beams available in synchrotron sources are very useful tools for a variety of scientific problems in a broad range of areas from biomolecules, soft matters up to very hard materials. In material science, spectroscopy techniques target basically the electronic states and, depending on the energy of the photons of the excitation beam and the rate of energetic deposition in the material, various dynamic processes are triggered, from localized electronic excitation to multielectronic-multiphonic processes. The transient dynamics of the charge carriers generated just after excitation is also a crucial issue for radiation detection in a range of applications from scintillators for medical tomography to large area detectors in astrophysics and high energy physics installations. The dynamics defines the response time of the detector that normally operated converting the incident radiation into UV, visible or near IR light. The transient processes after the absorption of energetic photons have characteristic times that can range from picoseconds up to years, depending on the material, the energy of the photons, on the rate of energy deposition and a number of other factors. It is a very common praxis to describe a specific dynamic process using simple exponential behaviour, or the so-called, first order kinetics. Very often the light response of a material used in a detector or a potential candidate to be used in one of such detectors did not follow the simple exponential decay curve and is extremely frequent that the authors just add up as many exponential terms as needed to describe the decay curve. Such approach was usually done without considering other possibilities and a number of possible processes that cannot be described as a simple exponential decay due to the relative complex nature of the dynamics. The present work presents an attempt to face the transient dynamics of the generated charge carriers form the point of view of the possible mechanisms that may be trigged after the absorption of the incident photons. Applications to a range of materials that were already studied by our research group were used as a benchtop tests. All systems were synthesised in our laboratory under controlled conditions and structurally characterized. EXAFS, XANES, XEOL, VUV spectroscopy and time resolved XEOL and luminescence were investigated using the facilities installed in the XAFS2, SXS and TGM beamline of the UVX storage ring at LNLS. The potential use of time-resolved and variety of types of pump-and-probe experiments to unveils the details of the dynamics of the charged carriers were discussed in view of the future potential uses in the new beamlines of the Sirius storage ring. (Work partially supported by CNPQ, CAPES, FINEP and FAPITEC/SE Brazilian funding agencies).

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Poster Presentation

Challenges in determining protein-ligand complexes in Schistosoma mansoni dihydroorotate dehydrogenase

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Schistosomiasis is the second most devastating parasitic disease worldwide, for which the only available treatment is Praziquantel, an old drug where resistance, failures to prevent reinfection, and low efficacy against the young stages of the parasite have been reported. The flavoenzyme dihydroorotate dehydrogenase (DHODH) of *Schistosoma mansoni* emerges as an interesting target to be explored for drug development. DHODH participates in the pyrimidine de novo pathway and structural studies of protein-ligand complexes is a crucial step to understand the binding mechanisms of the identified inhibitors. The low reproducibility during crystallization process was explained by molecular dynamics that revealed high flexibility in the N-terminal region of the protein. To overcome this caveat in our drug discovery pipeline, a multivariable approach was used where different precipitant concentrations, pHs, salts, cryogenic solution, temperature, and even new crystallization conditions were tested therefore allowing co-crystallization of DHODH-inhibitor and determining the molecular basis of inhibition.

References:

[1] Hotez PJ, Alvarado M, Basáñez M-G, Bolliger I, Bourne R, Boussinesq M, et al. The Global Burden of Disease Study 2010: Interpretation and Implications for the Neglected Tropical Diseases. PLOS Neglected Tropical Diseases. 2014.
[2] Nonato MC, de Pádua RAP, David JS, Reis RAG, Tomaleri GP, D'Muniz Pereira H, et al. Structural basis for the design of selective inhibitors for Schistosoma mansoni dihydroorotate dehydrogenase. Biochimie. 2019;158:180-90.
[3] de Mori RM, Aleixo MAA, Zapata LCC, Calil FA, Emery FS, Nonato MC. Structural basis for the function and inhibition of dihydroorotate dehydrogenase from Schistosoma mansoni. FEBS J. 2020.

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Poster Presentation

Challenges on characterizing the layer formed on nitrided austenitic stainless steel

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The nitrided layer formed on austenitic stainless steel can improve hardness, wear and also corrosion resistance. This improvement varies with the nitriding conditions, however the characterization of the formed layer is still an open field for many reasons, for instance: i) there are many nitriding processes and the layer is sensitive to even small changes in the parameters of the same process. So a myriad of different layer can be formed, hampering the intercomparison with other results in literature; ii) the crystallographic structure of the expanded austenite, which is the main structure formed, is not yet established; iii) techniques that can analyze the nitride layer often are not easily intercompared, which leads to difficulties in the results interpretation, and even, misinterpretations; iv) recent results show not only that the characterization of the submicrometric region of the surface is critical, but also that characterizing this specific region is a great challenge.

Against this background, the use of synchrotron-based techniques can be a game changer. Nanodiffraction and synchrotron Mössbauer source (SMS) can probe much smaller volumes. It is important to keep in mind that nitriding is an anisotropic process, the sample is polycrystalline, the nitrided layer has a nitrogen gradient profile and, finally, the main formed phase is non-stoichiometric. Therefore, the simultaneous characterization of different grains, leads to a superposition of results from different crystallographic structures. This may partly explain the difficulty in establishing the crystallographic structure of expanded austenite. Thus, the use of nanodiffraction and SMS can allow a step further on characterizing the layer formed on nitrided austenitic stainless steel.

References:

[1] D. Olzon-Dionysio, J.D. Fabris, M.D. Martins, M.A.B. Tavares, J.D. Ardisson, Magnetic and 57Fe hyperfine structural features of nitrided austenitic stainless steel, Surf. Coatings Technol. (2020) 125544. DOI:10.1016/j.surfcoat.2020.125544.

Poster Presentation

Clinochlore as a natural promising layered material to 2D applications

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The research on layered materials (LMs) was motivated by the exfoliation of naturally occurring graphite minerals to isolate single graphene layers [1]. Most of the attempts in finding alternative LMs that are also capable of being reduced to mono layers and present quantum effects that can change its properties in an interesting way to contribute to technological applications have been made in synthesized materials such as hexagonal boron nitride [2] and transition metal dichalcogenides [3]. In an effort to increase the list of naturally occurring LMs that are abundant in nature and could become a better cost-effective 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 [4,5].

Within the phyllosilicate chlorite group, we can identify clinochlore as a promising LM with applications already explored in biological and catalytic systems [6,7]. A few works on its bulk form have been done regarding its optical, mechanical and electrical properties [8]. However, further investigations into its 2D form for applications in electronic devices and heterostructures remain unexplored. In this sense, we present here a systematic characterization of clinochlore samples performed by several techniques, including synchrotron radiation facilities, to extent the material applicability potential to 2D technologies. As preliminary results, we identified by X-ray Fluorescence the impurities present in the sample that play a fundamental role in determining its macroscopic properties and we demonstrated by Synchrotron Infrared Nanospectroscopy that few layers of clinochlore maintain their bulk vibrational properties in addition to having a good surface with low roughness. We also identify band-to-band transitions by X-ray Reflectivity that can be interesting for applications in optical devices.

References:

[1] Novoselov K et al 2004 Electric field effect in atomically thin carbon films Science 306 666–669.
[2] Zhang K, Feng Y, Wang F, Yang Z and Wang J 2017 Two dimensional hexagonal boron nitride (2D-hBN): synthesis, properties and applications J. Mater. Chem. C 5(46) 11992-12022.
[3] Wang Q, Kalantar-Zadeh K, Kis A, Coleman J and Strano M 2012 Electronics and optoelectronics of two-dimensional transition metal dichalcogenides Nat. Nanotechnol. 7 699–712.
[4] Frisenda R et al 2020 Naturally occurring van der Waals materials npj 2D Mater. Appl. 4 38.
[5] Alencar A, Barboza A, Archanjo B, Chacham H and Neves B 2015 Experimental and theoretical investigations of monolayer and few-layer talc 2D Mater. 2 15004.
[6] Valdrè G 2007 Natural nanoscale surface potential of clinochlore and its ability to align nucleotides and drive DNA conformational change Eur. J. Mineral. 19(3) 309-319.
[7] Quaranta E et al 2021 Using a natural chlorite as catalyst in chemical recycling of waste plastics: Hydrolytic depolymerization of poly-[bisphenol A carbonate] promoted by clinochlore Waste Manage. 120 642-649.
[8] Gopal N, Narasimhulu K and Lakshmana Rao J 2004 Optical absorption, EPR, infrared and Raman spectral studies of clinochlore mineral J. Phys. Chem. Solids 65 1887–93.

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Keywords:

Layered materials, clinochlore, 2D applications.

Poster Presentation

$CoFe_2O_4$ nanoparticles studied by synchrotron techniques

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The magnetic properties of CoFe2O4 nanoparticles (CFO NPs) are usually dominated by their size. For example, the NPs with 8 nm diameter have almost single-domain behavior occupying approximately the whole NP, while in those with 6 nm diameter the surface anisotropy is large enough to alter the ferrimagnetic order in the NP shell. Larger particles (d> 8 nm) showed some reduction of saturation magnetization with respect to the bulk, pointing to the existence of partial inversion.

In this work we present an investigation of the structural and electronic properties of CFO NPs with different sizes and also the bulk material. We explore their structure employing Atomic Pair Distribution Function (PDF) analysis, their local bonds and electronic properties by Extended X-Ray Absorption Fine Structure (EXAFS) and X-ray Emission Spectroscopy (XES). These experiments were performed at UVX-LNLS with the objective of correlating the magnetic properties of the NPs with their size, local structure and electronic properties.

PDF data were collected at XDS beamline (LNLS) [1]. This technique is an attractive characterization tool in material science, alternative to conventional X-ray diffraction (XRD). Contrary to XRD that only reflects information about the average structure, PDF analysis allows the detection of small local distortions and brings information of the local and medium-range order. Our PDF investigations of these NPs focus on determining the structural arrangement of the smallest NPs, which cannot be performed properly by conventional Rietveld analysis.

The CoKβ1,3 XES spectra of the NPs were acquired at XDS beamline (von Hamos geometry) [2], to study their electronic structure and compare it with bulk material and other Co oxides. The Kβ mainline of XES spectra is often used as an experimental fingerprint of the oxidation and spin states of the absorber metal, thus we will exploit this fact to get insight into the local Co spin state in the different CFO NPs.

References:

[1] M.E. Saleta, et al., "Atomic pair distribution function at the Brazilian Synchrotron Light Laboratory: application to the Pb1−xLaxZr0.40Ti0.60O3 ferroelectric system", J. Synch. Rad. 24 (2017), 1098–1104.
[2] F.A. Lima, M.E. Saleta, et al. "XDS: A flexible beamline for X-ray diffraction and spectroscopy at the Brazilian", J. Synch. Rad. 23 (2016), 1538–1549.

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Keywords:

PDF, XANES, XES, CoFe2O4 nanoparticles

Poster Presentation

Comparative study of magnetic nanoparticles with potential applications in biomedical applications

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This work presents a comparative study between magnetic nanoparticles (NPM) of iron oxide (FeOx) and iron core/shell and iron oxide (Fe/FeOx). These NPM were characterized by SAXS, VSM, TGA, DSC, SAR and finally cell viability studies were performed by MTT.
FeOx NPs were synthesized by chemical coprecipitation, which is a procedure sufficiently contrasted in the literature, while Fe/FeOx type NPs were obtained by a mixed route, where initially the iron core was obtained by mechanosynthesis and the FeOx shell was made by ultrasound-assisted coprecipitation. The saturation magnetizations are 65 emu/g and 130 emu/gFe, respectively. While the sizes are in the range of 13 - 20 nm which were obtained by SAXS by fitting with the Beaucage model, it is worth noting that these sizes are desirable for this type of applications.

Keywords:

SAXS, TEM, nanoparticles, biomedical applications

Oral Communication

Copper-aluminum MOF type materials as precursors of catalysts for NOx removal

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MOFs (Metal-organic Frameworks) are a promising class of materials with a variety of applications, versatility, and good catalytic properties [1]. This work aimed to evaluate the presence of aluminum in the performance of catalysts obtained from CuAl-MOFs as alternatives for NOx reduction. In this work, two precursors, one bimetallic (Cu, Al) and another monometallic (Cu) have been prepared by the coprecipitation method. Their derived catalysts (calcined at 600 ℃ – 4 h and thermally aged at 900 ℃- 12 h) have been applied in the reduction of NO and N2O by CO (conventional catalytic unit). The precursors were characterized by EXAFS at Cu K-edge. The crystalline phases evolution of the catalysts during the reduction in H2 was accompanied by in situ XRD. EXAFS spectra of the catalyst with aluminum (calcined at 600 ℃) were taken before and after its reduction in H2 at 300 ℃. There are no significant differences in the EXAFS spectra of both precursors indicating that neighboring atoms and interatomic distances are not much different. Very small differences may come from the presence of aluminum. The interatomic distance for the first shell is related to Cu-O. By in situ reduction (XRD) it was seen that the thermally aged catalyst with aluminum showed better reducibility than the one without it. This result agrees with the conventional H2-TPR. Moreover, metallic copper crystallites are more stable in the catalysts with aluminum, and crystallites of CuAl2O4 reduce their size probably due to a rearrangement of Cu and Al in the spinel phase. Catalysts without aluminum showed catalytic deactivation above 400 ℃ in both reactions probably due to sintering of metallic copper crystallites which are active sites for N2O reduction [2]. The catalysts with aluminum showed the best catalytic activities and thermal stability during the reactions, thus they are promising catalysts for NOx removal in vehicle emission control.

References:

[1] Y.S. Kang, Y. Lu, K. Chen, Y. Zhao, P. Wang, W.Y. Sun, Metal–organic frameworks with catalytic centers: From synthesis to catalytic application, Coord. Chem. Rev. 378 (2019) 262–280. DOI:10.1016/j.ccr.2018.02.009
[2] Y. Okamoto, T. Kubota, H. Gotoh, Y. Ohto, H. Aritani, T. Tanaka, S. Yoshida, XAFS study of zirconia-supported copper catalysts for the NO–CO reaction: Deactivation, rejuvenation and stabilization of Cu species, J. Chem. Soc. Faraday Trans. 94 (1998) 3743–3752. DOI:10.1039/a807152g

Keywords:

MOFs, copper, aluminum, XRD, in situ

Poster Presentation

Cryogenic strain in silver using in-situ synchrotron radiation

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In face-centered cubic (FCC) metals such as silver alloys, cryogenic deformation processes increase the mechanical resistance and promotes the formation of a finer microstructure [1,2]. Therefore, processing at cryogenic temperature (around 77 K) is an alternative to traditional manufacturing processes at room temperature (around 293 K). In this work, the correlations between the microstructural evolution and the mechanical properties of commercially pure silver were studied, using the X-ray Scattering and Thermo-Mechanical Simulation (XTMS), which is located at Brazilian Center for Research in Energy and Materials (CNPEM). Specimens were tested at room and cryogenic temperatures (298 and 78 K, respectively) and at strain rates of 10-3, 5 x 10-4 and 2 x 10-4 s-1. The results obtained indicated that the tests at cryogenic temperature induced changes in the microstructure and mechanical properties of the metal, simultaneously increasing its mechanical strength and ductility. This is related to the lattice deformation kinetics, which indicates the partial suppression of dynamic recovery during the deformation process and the formation of twins as deformation mechanism. A refinement in the microstructure was also observed by the size of the crystallite and dimples, which is associated to the Hall-Petch effect. On the other hand, the increase in the straining rate has a greater effect at room temperature, suggesting a higher influence of the dynamic recovery.

References:

[1] Izumi MT, Quintero JJH, Crivoi MR, Maeda MY, Namur RS, de Aguiar DJM, Cintho OM. In situ X-ray diffraction analysis of face-centered cubic metals deformed at room and cryogenic temperatures. J. Mater. Eng. Perform. 2019;28:4658-66. DOI:10.1007/s11665-019-04226-5
[2] Crivoi MR, Hoyos JJ, Izumi MT, Aguiar DJM, Namur RS, Terasawa AL, Cintho OM. In situ analysis of cryogenic strain of AISI 316L stainless steel using synchrotron radiation. Cryogenics 2020;105:103020. DOI:10.1016/j.cryogenics.2019.103020

Keywords:

Cryogenic deformation, dynamic recovery, twinning, stacking fault energy, X-ray powder diffraction

Oral Communication

Development of polymeric screens containing scintillator nanoparticles for application in X-ray imaging

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In this work, the $CdWO_4$ scintillator was synthesized using the microwave-assisted hydrothermal method. The methodology developed employs metal oxides (CdO and WO_3) as precursors and the reaction occurs successfully through the pH control of the final solution. The single crystalline phase was obtained after hydrothermal treatment at 120 °C for 60 min. These samples were then used in the preparation of polystyrene-based composite films of different thicknesses and scintillator/polymer mass ratio. In the films production, in order to improve the chemical affinity of the scintillator with polystyrene, a strategy of surface modification of particles with stearic acid was used. The study of the optical properties of the scintillating composites showed which composites scintillators display a broad band emission, centered at 400 nm when excited by UV or ionizing radiation. Microstructural characterization of the composites was performed trough microtomography images at IMX beam line of the Brazilian Synchrotron Light Laboratory (LNLS). The results showed that the scintillator distribution into polymer matrix becomes more uniform for superficial modification nanoparticles and for the increases of concentration of the PS solution. In addition, to investigate the performance of composites as a detector for x-ray imaging, microtomography experiments were carried out at the IMX beam line of LNLS. The results showed that composite films made are able to forming radiographic images with resolution comparable to the commercial detector, having advantages in cost and ease of handling of the detector.

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Keywords:

Scintillator, CdWO4, polystyrene, composites

Poster Presentation

Development of tools to enable a structure-based drug discovery program targeting leishmania glycogen synthase kinase 3

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New treatments are urgently needed against leishmaniasis, a group of neglected tropical diseases caused by parasites from the genus Leishmania, which claims over 20,000 lives and affects more than 1 million people every year. Protein kinases represent promising candidates for drug development against parasitic diseases. Glycogen synthase kinase 3 (GSK3) is a multifunctional Ser/Thr kinase found in all eukaryotes. Leishmania GSK3a and GSK3b (long and short isoforms, respectively) have been identified as genetically-essential for parasite viability, and GSK3b has also been pharmacologically validated. Here we started a target-based drug discovery program to develop potent and selective inhibitors of L. infantum GSK3a and GSK3b. Recombinant protein kinases were produced and screened against a set of ~1,400 compounds by thermal-shift assay. Hit validation employed enzymatic assays and the most potent compounds were further evaluated in phenotypic assays. To better guide chemistry efforts, we obtained co-crystal structures of LinGSK3b bound to two of the most promising compounds (AZD-5438 and CGP60474). To ascertain that the observed phenotype is due to the on-target activity of selected compounds, we also developed a novel BRET-based target engagement assay using live Leishmania (promastigotes and intracellular amastigotes). We are currently evaluating the selectivity of the most promising compounds in a large panel of human host protein kinases. We expect our efforts to lead to development of new anti-leishmanial drugs based on the inhibition of parasite kinases GSK3a and GSK3b.

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Keywords:

Target-based drug discovery; therapeutic targets; leishmaniasis

Poster Presentation

Determination of metal concentration of silica-based materials modified with Zr or Ti and PMODS by energy dispersive X-ray spectroscopy coupled to scanning electron microscopy

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Silica-based sorbents for solid phase extraction (SPE) tend to present chemical instability in the basic liquid eluents (pH > 9), since silanols present at the structure interact with alkaline mobile phases, causing silica hydrolysis and, consequently, loss of material content. In order to modifying the chemical activity of the silanols groups, one interresting alternative is incorporate zirconia and titania into the sorbent materials by the chemical reaction with metal alkoxides [1]. In this work, labmade sorbent materials were prepared modifying commercial silica structure (100 µm) with Zr and Ti alkoxides and poly(methyloctadecylsiloxane) (PMODS) (C-18). The metal concentration incorporated at the supports was determined using energy dispersive X-ray spectroscopy coupled to scanning electron microscopy. The results obtained for the analysis of the coupled tecniques (SEM-EDS) have demonstrated the presence of elements already expected such as Si and O, and also indicated that the metals (Zr or Ti) have been incorporated at the materials, with a certain degree of homogeneity presenting concentrations of 1.9% (w/w) Ti for titanized materials and 5.9% (w/w) of Zr for zirconized materials. The presence of PMODS, coating the materials surface structure also could be observed in both Silica-Zr(PMODS) and Silica-Ti(PMODS) sorbents, by the detection of carbon content, showing a suitable hydrophobic layer coating for extracting pollutants, as the pesticides, from aqueous environmental samples, using the reversed phase separation mechanism [2], and the results were compared with those obtained by Fourier transform infrared (FTIR) spectroscopy .

References:

[1] Faria, A.M.; Magalhães, D.R.; Collins, K.E.; Collins, C.H. Anal. Chim. Acta v. 550, p. 137-143 (2005).
[2] Andrade-Eiroa, A.; Canle, M.; Leroy-Cancellier, V.; Cerdà, V. Trends Anal. Chem. v. 80, p. 641-654 (2015).

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Keywords:

Solid phase extraction, energy dispersive X-ray spectroscopy, scanning electron microscopy, metallized silica based materials.

Oral Communication

Development of an automatic data processing pipeline for serial crystallography on Manacá (Sirius)

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Manacá (MAcromolecular micro and NAno CrystAllography), first beamline in commissioning at Sirius (LNLS/CNPEM), is dedicated to a range of crystallography experiments applied to small and macro molecules, including the most recent technique of serial crystallography (SX). SX takes advantage of microfocus beam and higher flux from advanced light sources, such as Sirius, to acquire unique diffraction patterns from several tens of thousands of microcrystals per experiment, possibly, at room temperature.

One of the biggest challenges for SX is to merge partial datasets, randomly oriented in the reciprocal space, as if they had been obtained from a single crystal rotation. Regarding the final data, the main goal is to extract the best results from a range of all possible subdataset combination. To solve this, it has been applied different algorithms, each with their respective parameters that should be adjusted to every data collection. The aim of this dissertation is to provide an automated data processing pipeline for SX experiments on Manacá. We have built a script, in Python, that will act as an interface between users and new softwares being developed for SX (*CrystFEL[1], nXDS, cctbx.xfel, ccCluster[2], BLEND[3], xscale_isocluster*, among others). Users will be able to, with minimal effort, call different data processing programs, adjust parameters that best fit their data, visually explore the figures of merit and choose the best data processing options.

In order to test our data processing pipelines, we have performed three experiments during the Manacá's scienctific commisioning. Firstly, it was measured 21 crystals of AmeGH128, in oscillation mode (9.15 keV, beam size varying from 20 to 60 μm), at 77K. From that experiment, we obtained a total of around 64800 diffraction patterns. Afterwards, we collected 64 cryocooled lysozyme crystals, in grid-scan mode [4] (12.69 keV, beam size 25 μm, flux at sample ~10 ^{12} ph/s). In this experiment, it was collected 2910 images in total. Finally, the same grid-scan experiment was done on 20 lysozyme crystals at room-temperature, using an in-house build sample device, sealed with Kapton. In this condition, we obtained a total of 601 images.

The diffraction patterns were used as an input for the two main branches of SX data processing: Hierarchical Cluster Analysis HCA (*ccCluster*) and snapshot images routine (*CrystFEL*). Our script could successfully index the diffraction patterns, according to the already known unit cell parameters. Our SX automatic data processing pipeline is versatile for immediate data quality verification and software parameters adjustments. In the snapshot routine, better final data quality might be achieved by tuning the indexing rate and/or increasing the number of crystals measured. Nevertheless, the SX data processing tool is functional and customizable for Manacá future users.

Serial Crystallography is a huge promise for the study of time-resolved protein dynamics and in the revealing of proteins structures that are extremely difficult to crystallize, as membrane protein structures. Enabling this new technique on Manacá will have a great impact in a variety of fields, from drug discovery for effective treatment of diseases to the optimization of renewable biofuels production.

References:

[1] White, T. A. P. Acta Crystallographica Section D, 75, 219–233 (2019).
[2] G. Santoni, et. al. Journal of Applied Crystallography, 50, 1844–1851 (2017).
[3] J. Foadi et. al. Acta Crystallographica Section D, 69(8): 1617–1632 (2013).
[4] Halsted, T. P. et. al. IUCrJ, 5, 22-31 (2018).

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Keywords:

Serial crystallography, macromolecular crystallography, protein dynamics, python

Oral Communication

Development of efficacious NTM-DHFR inhibitors based on in-clinic Plasmodium DHFR inhibitor P218

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Non-tuberculous Mycobacteria (NTM) consists of a large (>200) number of environmental bacteria that can cause opportunistic infections in humans. Amongst NTMs, *M. abscessus* and *M. avium* are emerging human pathogens causing severe respiratory, skin and mucosal infections, which are particularly difficult to treat, as these bacteria are resistant to most classes of antibiotics. Antibiotic resistance in *M. abscessus* and *M. avium* is attributed to a combination of factors, including the presence of a cell wall rich in mycolic acids, which makes it a virtually impregnable to hydrophilic compounds, and a large number of drug efflux pumps and drug-inactivating enzymes. The dihydrofolate reductase enzyme (DHFR) is a validated antimicrobial target and employs a co-factor, NADPH, to catalyze the reduction of 7,8-dihydrofolate (diHF) to 5,6,7,8-tetrahydrofolate (THF), which is an essential component in the synthesis of purines, pyrimidines, and several amino acids in bacteria. Inhibition of bacterial DHFR blocks DNA synthesis and causes cell death. Nevertheless, the use of DHFR inhibitors has not been explored as a therapeutic strategy to treat Mycobacterial infections. Here we report our progress in developing novel DHFR inhibitors that are effective against the enzymes from *M. avium* and *M. abscessus*, but are much less active against the human enzyme. Compound development was guided by co-crystal structures of Mycobacterial enzyme bound to some of the most active compounds. We expect our results to facilitate the exploration of antifolates as a therapeutic strategy to treat Mycobacterial infections caused by emergining NTM.

Aknowledgements:

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Keywords:

nontuberculous mycobacteria, target-based drug discovery; therapeutic targets

Oral Communication

Development of methodologies for the visualization and treatment of X-ray fluorescence microscopy data in geological samples collected at the Carnaúba beamline

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The pre-salt is among the most important discovery within Brazilian territory in recent decades. Due to the immense quantity of light oil, of excellent quality, and with high commercial value, it places Brazil in a strategic position in front of the great global demand for energy. Among the regions with the greatest oil-producing capacity is the Libra region. This region is characterized having carbonate reservoirs from the Early Cretaceous, containing hydrocarbons with a high gas/oil ratio and a high concentration of CO2. Understanding the geological processes that have happened in the Libra region is essential to explain the characteristics of this oil reservoir. For this, a geochemical approach for carbonate rocks must be pursued. However, due to their heterogeneity and complexity, the description of the chemical composition of these rocks is a complicated task. The use of the Carnaúba beamline looks very promising to shed some light on this issue. Its high spatial resolution, combined with high elemental sensitivity and the ability to perform a multi-elemental analysis simultaneously makes the Carnaúba beamline a powerful tool for the geochemical characterization of carbonate rocks. For this purpose, initial developments were related to data visualization and processing strategies to handle large datasets coming from the measurements. This involves tools developed in the Jupyter Notebook environment as well as several artificial neural network codes written in Python. On the other hand, since samples are composed of different regions of interest over a large area, fiducials are also needed for precisely identifying the region to be measured. In this sense, a mesh composed of pure metals sputtered on a thin film was designed. In this work, detailed information about the above-mentioned developments will be presented and future activities will be sketched.

Poster Presentation

Discovery of pteridine-based inhibitors for the human CDC42 binding protein kinase gamma (MRCKγ)

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The human CDC42 binding protein kinase gamma (MRCKγ), a serine/threonine kinase remains mostly unexplored in comparison to its related isoforms MRCKα and MRCKβ. The α and β MRCKs are involved in the regulation of actomyosin cytoskeleton, in tumorigenesis (invasiveness and metastasis) and in developmental processes (morphogenetic signaling and tissue remodeling). Meanwhile, evidence suggests that MRCKγ can modulate the maturation of dendritic spines in cortical neurons in culture and can be related to glioblastoma, in agreement with its higher expression in the peripheral nervous system. To allow better understanding of the biology of MRCKγ, and in search for selective compounds, here we report the docking studies, synthesis, selectivity profile and preliminary cellular data of pteridine scaffolds as a novel class of potent MRCKγ inhibitors. Our analysis of the Published Kinase Inhibitor Set (PKIS2) revealed a pteridine core molecule, SD208, as a potent and slight selective MRCKs inhibitor with score S(35) of 0.013, and greater affinity for MRCKγ. Supported by in-silico docking studies, a series of derivative compounds were designed and synthesized, initially ranked based on thermal stability in a differential scanning fluorimetry (DSF) assay and later by FRET-based enzymatic assay. Our chemical series was used to compose a SAR (structure-activity) analyses. The original hit SD208 still represents the most potent molecule among the series, with IC50 in nanomolar range in the enzymatic assay. Our derivative SV42 is also selective, cell-permeable and, together with SD208, show inhibition effects on cellular invasion in A172 glioblastoma cells. We are currently following up with co-crystallization attempts to guide better inhibitor design, and intend to use Sirius Beamlines for collection of the X-ray diffraction data. Also, Cryo-EM is being considered for structural determination of the full-length MRCKγ. Access to Sirius beamlines will represent a great opportunity to accelerate this and other projects from our lab with structural-activity base for inhibitors development.

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Keywords:

Kinase inhibitor, MRCK, pteridine, CDC42BP, molecular docking

Poster Presentation

EDIXS: A versatile spectroscopic tool for chemical state characterizations

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In X-ray fluorescence analysis, spectra present singular characteristics produced by the different atomic and molecular processes. When atoms are irradiated with incident energy lower but close to an absorption edge, scattering peaks appear due to an inelastic process known as Resonant Inelastic X-ray Scattering (RIXS), or X-ray Resonant Raman Scattering (RRS) [1]. In general, RIXS studies are carried out in third or fourth generation synchrotron facilities using high-resolution systems for detection. The RIXS peaks present a variety of particular features; between them, a characteristic long-tail spreading to the region of lower energies. In the past decade it has been observed that, hidden in this tail, there is valuable information about the local environment of the atom under study. In addition, it has been demonstrated that RIXS spectroscopy can be attained using low-resolution systems, i.e., solid state detectors. This gave place to a new technique named EDIXS (Energy-dispersive Inelastic X-ray Scattering)[2].

One of the most important features of the EDIXS methodology is the possibility of combining it with the experimental methods and geometries associated with usual XRF spectroscopy and all its non-conventional associated techniques. Combinations of EDIXS spectroscopy with total reflection, depth-profiling analysis using grazing incidence geometries and even confocal arrangements have been reported during the last decade [3-13]. Among the distinctive features of the EDIXS technique reported in these works, the use of an energy dispersive spectrometer for measuring the RIXS spectra and the application of Multivariate Methods for an objective data analysis should be remarked. As result, a variety of samples of interest have been successfully analyzed and characterized, from contaminated waters to lithium-ion battery materials.

In this presentation, the basis, advantages, potentiality and the state-of-the-art of this versatile tool for chemical state determinations will be presented and discussed.

References:

[1] A.G. Karydas and T. Paradellis, J. Phys. B: At., Mol. Opt. Phys. 30, 1893 (1997).
[2] J.J. Leani, J.I. Robledo, H.J. Sánchez, Spectrochim. Acta Part B 154, 10 (2019).
[3] J.I. Robledo, J.J. Leani, A.G. Karydas, A. Migliori, C.A. Pérez, H.J. Sánchez, Anal. Chem. 90, 3886 (2018).
[4] J.J. Leani, H.J. Sánchez, M. Valentinuzzi, C. Pérez, J. Anal. Spectrom. 26, 378 (2011).
[5] J.J. Leani, H. Sánchez, M. Valentinuzzi, C. Pérez, X-Ray Spectrom. 40, 254 (2011).
[6] J.J. Leani, J.I. Robledo, H.J. Sánchez, X-Ray Spectrom. 46, 507 (2017).
[7] J.J. Leani, H.J. Sanchez, M.C. Valentinuzzi, C. Pérez, M. Grenón, J. Microsc. 250, 111 (2013).
[8] H.J. Sanchez, J.J. Leani, C. Pérez, R.D. Perez, J. Appl. Spectrosc. 80, 912 (2014).
[9] J.I. Robledo, H.J. Sánchez, J.J. Leani, C.A. Pérez, Anal. Chem. 87, 3639 (2015).
[10] J.J. Leani, H.J. Sánchez, C.A. Pérez, J. Spectrosc. 2015 (2015).
[11] J.J. Leani, H.J. Sánchez, R.D. Pérez, C. Pérez, Anal. Chem. 85, 7069 (2013).
[12] J.J. Leani, R.D. Perez, J.I. Robledo, H.J. Sanchez, J Anal Spectrom. 32, 402 (2017).
[13] J.I. Robledo, J.J. Leani, S. Chauque, O. Cámara, F.Y. Oliva, H.J. Sánchez, J. Anal. At. Spectrom. 35, 2948 (2020).

Poster Presentation

Effect of stress-induced martensitic transformation on mechanical properties of Co-28Cr-6Mo alloy fabricated by laser-powder bed fusion

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The development of biomaterials fabricated by additive manufacturing techniques is essential for medical, technological, and scientific reasons. In particular, Co-based alloys are suitable for implants that undergo compression and friction stress, such as knee and hip joints because of their high wear resistance combined with superior mechanical strength. In this work, the effect of the stress-induced martensitic transformation on the mechanical properties of the Co-based alloy was evaluated. Specimens of the Co-28Cr-6Mo alloy were fabricated by laser-powder bed fusion and divided into two groups. In the first one, the samples were maintained in the as-built condition. In the second one, the samples were solution heat-treated at 1150 ℃ for 1 h followed by water quenching. For both groups, in-situ synchrotron radiation trials during tensile tests at room temperature were performed [1,2]. The tests were conducted using the X-ray Scattering and Thermo-Mechanical Simulation (XTMS) located at Brazilian Center for Research in Energy and Materials. In both groups, the X-ray diffraction analysis evidenced the stress-induced martensitic transformation. Results revealed that solution heat treatment reduces microstrain while increases the ductility [1]. The higher microstrain found in the as-built specimen favored the onset of the stress induced γ-ε phase transformation [1]. Furthermore, the accumulation rate of the ε-phase is higher on the surface compared to that in the bulk [2].

References:

[1] L.H.M. Antunes, J.J. Hoyos, E.B. Fonseca, M. Béreš, P.F. da Silva Farina, E.S.N. Lopes, A.L. Jardini, R.M. Filho. Mater. Sci. Eng. A 764 (2019), 138262. DOI:10.1016/j.msea.2019.138262

[2] L.H.M. Antunes, J.J. Hoyos, T.C. Andrade, P.W.C. Sarvezuk, L. Wu, J.A. Ávila, J.P. Oliveira, N. Schell, A.L. Jardini, J. Zilkov, P.F. da Silva Farina, H.F.G. Abreu, M. Béreš. Deformation-induced martensitic transformation in Co-28Cr-6Mo alloy produced by laser powder bed fusion: Comparison surface vs. bulk. Additive Manufacturing 46 (2021) 102100. DOI:10.1016/j.addma.2021.102100

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Keywords:

CoCrMo alloy, martensitic transformation, selective laser melting

Poster Presentation

Electronic and magnetic properties of $La_{0.67}Sr_{0.33}MnO_3$ ultrathin films

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One of the most studied ferromagnetic oxides is the $La_{0.67}Sr_{0.33}MnO_3$ (LSMO). It has a perovskite structure, high electric conductivity and is a half metal with almost 100 % spin polarization at room temperature [1]. These characteristics make LSMO thin films very interesting for applications in spintronics and oxide-based devices. However, the formation of layers that exhibit no magnetism at the interfaces of LSMO epitaxial films, called magnetic dead layers (MDL), is an obstacle for the development of new devices [2]. Although previous studies have linked the formation of MDL to strain, oxygen vacancies and cation non-stoichiometry, its microscopic origin is still not entirely clear [3]. In this work, we grew, by pulsed laser deposition, epitaxial ultrathin films of LSMO (thicknesses between 1.2 and 8.4 nm) on $SrTiO_3$ (001) single crystals in order to verify whether the oxidation state of manganese (Mn) and/or an orbital reconstruction at the LSMO interfaces could be related to the formation of the MDL. The samples' electronic structure was investigated by Mn $L_{2,3}$-edge X-ray absorption spectroscopy (XAS) and X-ray linear dichroism (XLD). The magnetic properties were investigated by Mn $L_{2,3}$-edge X-ray magnetic circular dichroism (XMCD) and vibrating sampling magnetometer. Our results suggest a reduction in the Mn valence and a consequent decrease in the magnetic moment as the LSMO thickness decreases. We also observe a breakdown in the e_g orbitals degeneracy at the LSMO surface, leading to an orbital reconstruction. Our results corroborate the formation of MDL at the surfaces of the ultrathin films of LSMO.

References:

[1] TRAPPEN, Robbyn et al. Electrostatic potential and valence modulation in $La_{0.67}Sr_{0.33}MnO_3$ thin films. Scientific reports, v. 8, n. 1, p. 1-7, 2018.
[2] PORTER, S. B. et al. Magnetic dead layers in $La_{0.67}Sr_{0.33}MnO_3$ revisited. IEEE Transactions on Magnetics, v. 53, n. 11, p. 1-4, 2017.
[3] PESQUERA, D. et al. Surface symmetry-breaking and strain effects on orbital occupancy in transition metal perovskite epitaxial films. Nature communications, Nature Publishing Group, v. 3, n. 1, p. 1–7, 2012.

Keywords:

Oxidation states, orbital reconstruction, magnetic dead layers

Oral Communication

Elemental distribution in Rhodnius prolixus head structures after Azadirachtin treatment by low energy X-ray fluorescence

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In this work, phase-contrast microtomography and X-ray microfluorescence synchrotron techniques were used to study *Rhodnius prolixus*, a potential vector of *Trypanossoma cruzi*, the etiologic agent of Chagas disease, which is a serious parasitic disease in Latin America, affecting approximately 8 million people in this region. Vector control is the most powerful method against this disease [1].

Fifth stage specimens of the *Rhodnius prolixus* were taken from the colony of the Laboratory of Biochemistry and Physiology of Insects (FIOCRUZ, Brazil) and the insects were divided into two groups. The first group was treated with azadirachtin, which is a triterpene that prevents metamorphosis from the insect to the adult stage, and the other was the control group. After sample preparation, microtomography measurements were performed in the SYRMEP beamline, and X-ray microfluorescence measurements in the TwinMic beamline, both in the ELETTRA synchrotron, Trieste, Italy.

The main objective of this work was to compare the two groups, in order to find morphological and multielementary changes between them, using microtomography and microfluorescence synchrotron techniques. The results showed that azadirachtin is a powerful natural pesticide, directly affecting the internal structures of this insect, preventing metamorphosis and, consequently, preventing the proliferation of Chagas disease [2].

References:

[1] Azambuja, P., et al. "Rhodnius prolixus: from physiology by Wigglesworth to recent studies of immune system modulation by Trypanosoma cruzi and Trypanosoma rangeli." Journal of insect physiology 97 (2017): 45-65.

[2] Sena, G., et al. "Evaluation of the effects of Azadirachtin on internal structures of Rhodnius prolixus head using low-energy X-ray microfluorescence." Spectrochimica Acta Part B: Atomic Spectroscopy 177 (2021): 106064.

Keywords:

Low-energy X-ray microfluorescence, Microtomography, Rhodnius prolixus

Oral Communication

Evaluation of chemical elements distribution and their inter-elemental correlations in tumor progression

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Cancer is considered one of the most complex and fatal diseases worldwide. New approaches to study tumor progression and growth are relevant subjects of research. In this context, the particular role of chemical elements in cancer progression is a subject still not fully explored that presents opportunities for investigation. The main goal of our study is to assess the distribution of chemical elements in cancer progression as well as to discover correlations between elements, observing both the primary tumor and the distant tissues that the tumor cells may affect. For simulating tumor progression *in vivo*, murine Lewis lung carcinoma cells were injected in C57BL/6 mice and data indicating the presence, concentration, and location of different elements in distinct tissues, in both control and experimental groups, were obtained in a time frame of 5 weeks of tumor progression. The data were collected via Synchrotron Radiation X-Ray Fluorescence in the Brazilian Synchrotron Light Laboratory (LNLS). In order to extract relevant information inherent to the voluminous available data, we adopt statistical analysis. With this work, it was possible to observe the elements' relevance for biological processes of normal, as well as tumor cells, during its tumor progression. Thus, it was possible to notice indications of tumor influence on distant tissues as well as highlight the importance of elements and their correlations for the tissues, including for processes of tumor progression, such as growth and cellular migration, angiogenesis, among others. This work also confirmed information found in the literature and featured results apparently not yet observed. Moreover, elements and correlations of relevance for more investigation, regarding their role in the processes described, were highlighted to bring to light explanations for such observations not yet noted.

Aknowledgements:

CNPq, CAPES, FAPERJ, UFRJ, IFRJ and LNLS

Keywords:

tumor progression, elemental distribution, X-ray fluorescence

Poster Presentation

Evaluation of the protective effect of losartan in coronary arteries of rats submitted to thoracic radiotherapy

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Cardiac regeneration and developments in the diagnosis and treatment techniques for the breast cancer, which include radiotherapy, have been studied to understand more about the destruction of some structures and elemental changes that can occur. One possible complication is the cardiotoxic side effects, which includes arrhythmia, blood pressure alterations, myocardial ischemia, thrombosis or congestive heart failure.

The aim of this work is to verify the possibility of using antihypertensive drugs to minimize and/or prevent damage to arteries caused by irradiation. For this study, eighteen Wistar rats were divided into either a control group, a group that received irradiation (IR) or a group that received irradiation and were treated with losartan (IR+L). Using the LEXRF technique, the effects of irradiation and the protective effects of losartan were evaluated through the maps of O, Na, Mg, Fe, and Cu in the coronary arteries of the rats.

CARNAÚBA (Coherent X-Ray Nanoprobe Beamline) is the tender-to-hard X-ray nanoprobe under construction at the new Brazilian synchrotron light source SIRIUS. The beamline provides two separated experimental stations, one with sub-micrometer resolution and another with nanometer resolution, to cover various analysis techniques, including X-ray fluorescence (XRF). The all achromatic CARNAÚBA optics will covers continuously the energy range from 2 to 15 keV. With this energy range, it will be possible to analyze K-lines of light elements, like phosphorus and sulfur, and also heavier elements, like calcium and zinc. The use of CARNAÚBA beamline will provide both submicrometer spatial resolution and elemental mapping of important elements in coronary artery of rats allowing analyze the tissue in a cellular level.

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Oral Communication

First SAXS/XPCS results obtained at the CATERETÊ beamline

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The Cateretê beamline, under commissioning at the Brazilian Synchrotron Light Laboratory (LNLS), is optimized for coherent diffraction imaging (CDI), x-ray photon correlation spectroscopy (XPCS); small and wide angle x-ray scattering techniques (WAXS, SAXS and USAXS). These techniques provide a powerful set of methods for the investigation of nanostructured materials in diverse fields such as catalysis, biology, petroleum and pharmacy, among others. In this presentation we will show the first USAXS/SAXS/XPCS results obtained at the beamline. Ongoing data analysis from time-resolved in situ experiments with nanozeolites will be addressed. The description of the experimental data by a Monte Carlo theoretical SAXS model allowed to unveil the temporal evolution of structural features from different populations of nanoparticles during the formation process. The correlation of information on the dynamics of the growing nanoparticles retrieved from the XPCS data with structural parameters obtained from the SAXS data may supply valuable knowledge about the formation mechanisms of the nanoparticle system.

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Keywords:

Cateretê, beam line, in situ, zeolites, time-resolved, SAXS, XPCS, nanoparticles, autocorrelation

Poster Presentation

Gold nanorods: synthesis and structural characterization

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Gold has unique properties in the macro scale, namely, low electrical resistance, protection against oxidation among many other characteristics. However, when going to nanoscale, particles made of gold, and many other noble materials, also present striking properties which opens a wide range of applications [1]. Gold nanorods (GN) with well-defined sizes can be used as sensors due to its high biocompatibility and unique plasmon resonant properties. In recent applications, GN has been used to enhance chiral recognition of enantiomers, drug carriers for photothermotherapy and promote optical information storage. The efficiency of these applications depends on the fine-tuning of the rods radius and aspect ratios [2]. Therefore, optimized synthesis control and detailed structural characterization of the GN on different synthesis times are crucial for the selection and application of the synthetized nanorods. In this work a small change in the traditional synthesis procedure [3] led to a synthesis of GN with slower reaction speed and nanorods with larger radius and smaller aspect ratios when compared to the original synthesis [4]. The structural characterization of the GN was performed using Small-Angle X-Ray scattering, X-Ray Diffraction, Dynamic light scattering, Transmission Electron microscopy and Ultraviolet-visible spectroscopy. As a result, the time evolution of the rods dimensions could be followed and described. As will be shown, the structural characterization enabled the description of the parameters as a function of synthesis time as well as reliable quantification of molar concentrations.

References:

[1] Shnoudeh AJ, Hamad I, Abdo RW, Qadumii L, Jaber AY, Surchi HS, et al. Chapter 15 - Synthesis, Characterization, and Applications of Metal Nanoparticles. In: Tekade RK, editor. Biomaterials and Bionanotechnology: Academic Press; 2019. p. 527-612.
[2] Cobley CM, Chen JY, Cho EC, Wang LV, Xia YN. Gold nanostructures: a class of multifunctional materials for biomedical applications. Chemical Society Reviews. 2011;40(1):44-56.
[3] Morasso, C.; Picciolini, S.; Domitilla, S.; Mehn, D.; Ojea-Jimenez, I.; Zanchetta, G.; Vanna, R.; Bedoni, M.; Prosperi, D.; Gramatica, F., Control of size and aspect ratio in hydroquinone-based synthesis of gold nanorods. Journal of Nanoparticle Research 2015, 17 (8).
[4] Garcia, P. R. A. F.; Araujo, W. W. R.; Teobaldo, G. B. M.; de Menezes, A. S.; Otubo, L.; Oliveira, C. L. P., Synthesis and structural characterization of gold nanorods. International Nano Letters 202, 11 (1), 59-68.

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Keywords:

gold nanorods, small-angle X-ray scattering, synthesis

Poster Presentation

HRSTEM of spinodal decomposition of β Ti-13Mo-2Fe alloy during continuous heating and aging heat treatment

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This paper describes the correlation between thermomechanical routes and the resulting microstructure of Ti-13Mo-2Fe alloy. The phase transformation mechanisms in these systems were studied using advanced characterization techniques such as scanning transmission electron microscopy using high-angle annular dark field detector (STEM-HAADF) with EDS elemental mapping (ChemiStem system) and high-resolution scanning transmission electron microscopy (HRSTEM), combined with electron diffraction and scanning electron microscopy. The addition of Fe to the Ti-13Mo system significantly reduces the formation of athermal ω phase after solution heat treatment followed by rapid cooling, although its high diffusivity favored isothermal ω phase formation and growth during isothermal heat treatment at 400 °C. Applying a slow heating rate to reach the aging temperature resulted in refined α-phase precipitates in both alloys due to ω-assisted α phase precipitation. The thermal analysis indicated that α phase precipitates transformed into β phase in two stages, beginning with intragranular precipitates, whose dissolution started before that of grain boundary precipitates. The Ti-13Mo-2Fe alloy showed spinodal decomposition, which was detected through HRSTEM-HAADF image using TEM TITAN Themis, after heat treatment at 400 °C for 24 h along with the expected isothermal ω phase, suggesting that the interfaces between β and β' structures may act as nucleation sites for the isothermal ω phase. Advanced characterization techniques such as STEM-HAADF combined with EDS elemental mapping and HRSTEM demonstrated to be a powerful techniques to probe the solute rejection in the ω phase precipitates and the phase separation (β and β' phases) in Ti-13Mo-2Fe alloy.

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Keywords:

β Ti alloy, HRSTEM analysis, EDS Mapping, atomic resolution, X-ray imaging, implant biomaterials

Oral Communication

Human fumarase-metabolites binding sites revealed by cocrystallization

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Fumarases are enzymes that catalyze the estereospecific and reversible hydratation of fumarate to L-malate. Human fumarase (HsFH) belongs to class II and in mitochondria participates in the tricarboxylic acid (TCA) cycle, and in the cytosol can act in the metabolism of amino acids and also play a key role in DNA damage response to DNA double strand breaks. HsFH gene mutations have been mainly associated with heritable diseases: fumarate hydratase deficiency (FHD), multiple cutaneous and uterine leiomyomatosis (MCUL) and hereditary leiomyomatosis and renal cell cancer (HLRCC). There are few inhibitors and activators reported for fumarases, and its regulation mechanisms remains unclear. This present work aimed the evaluation of different metabolites interactions in the human fumarase structure. A mass spectrometry integrated with equilibrium dialysis for the discovery of allostery systematically (MIDAS) was perfomed to evaluate protein-metabolite interactions and the preliminary analysis identified the maleic acid and D-2-amino-3-phosphono- propionic acid as potential ligands. Cocrystallization experiments were carried out in order to obtain the complex structure, and datasets (at 1.8 Å and 2.15 Å resolution for maleic acid and D-2-amino-3-phosphono-propionic acid, respectively) were collected. The solved structures revealed the presence of maleic acid in a pocket formed by different chains, far away from the active site, while the D-2-amino-3-phosphono-propionic acid was found bound at the active site. MIDAS was proved to be a reliable method to identify enzyme- metabolite interactions, and the cocrytallization experiments allowed the identification of maleic acid and D-2-amino-3-phosphono-propionic acid binding sites. The results obtained so far are promising and revealed a new site of interaction in the HsFH structure.

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Keywords:

Fumarase, enzyme-metabolite interactions, cocrystallization

Oral Communication

In situ GIWAXS during spin coating: Perovskite formation by gas quenching method

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The modern lifestyle, together with the increase of population, has dramatically increased the energy demand year after year, encouraging the development of energy sources. Perovskite solar cells (PSCs) emerged in the last decade and have become the most promising emerging third-generation photovoltaic technology. The optoelectronic property of perovskite depends strongly on the crystallization process that starts at film deposition by spin coating. The solvents and composition impact intermediates and, consequently, device performance. Here, we used in situ grazing incidence wide angle X-ray scattering (GIWAXS) to follow the perovskite formation during spin coating. The effect of solvents (DMSO vs. NMP) and perovskite composition ($\mathrm{Cs}_{X}\mathrm{FA}_{1-X}\mathrm{Pb}(\mathrm{I}_{0.83}\mathrm{Br}_{0.17})_{3}$, x =0.10 and 0.40) were investigated. The results reveal that using DMSO; the intermediates formed depend on the perovskite composition. For $\mathrm{Cs}_{0.10}\mathrm{FA}_{0.90}\mathrm{Pb}(\mathrm{I}_{0.83}\mathrm{Br}_{0.17})_{3}$, hexagonal phases (2H and 4H) are formed after solvent drying and partially consumed to perovskite growing even without thermal annealing during spin coating. Regarding composition, increasing the amount of Cs inhibited the formation of hexagonal phases. On the other hand, for NMP, the same intermediate is formed independently of the composition. The intermediate PbI_{2}.NMP forms quickly and is consumed in the process of formation of an amorphous ($\mathrm{Cs}_{0.10}\mathrm{FA}_{0.90}\mathrm{Pb}(\mathrm{I}_{0.83}\mathrm{Br}_{0.17})_{3}$) or crystalline ($\mathrm{Cs}_{0.40}\mathrm{FA}_{0.60}\mathrm{Pb}(\mathrm{I}_{0.83}\mathrm{Br}_{0.17})_{3}$) perovskite phase. All these intermediates were converted to perovskite by post thermal annealing and test in solar cells devices. The performance of devices suggested that synergic inhibition of hexagonal phases formation by NMP and Cs improves the PSCs' efficiency.[1-2]

References:

[1] Szostak, R.; Marchezi, P. E.; Marques, A. D. S.; Da Silva, J. C.; De Holanda, M. S.; Soares, M. M.; Tolentino, H. C. N.; Nogueira, A. F. Exploring the Formation of Formamidinium-Based Hybrid Perovskites by Antisolvent Methods: In Situ GIWAXS Measurements during Spin Coating. Sustain. Energy Fuels 2019, 3 (9).
[2] Szostak, R.; Sanchez, S.; Marchezi, P. E.; Marques, A. S.; Silva, J. C.; Holanda, M. S.; Hagfeldt, A.; Tolentino, H. C. N.; Nogueira, A. F. Revealing the Perovskite Film Formation Using the Gas Quenching Method by In Situ GIWAXS: Morphology, Properties, and Device Performance. Adv. Funct. Mater. 2021, 31 (4), 2007473.

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Keywords:

Perovskite solar cells

Oral Communication

In situ study of growth of NiSi2 nanoplates in Si(001) wafer

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Composite thin films formed by NiSi2 silicide nanocrystals embedded in single-crystalline Si have attracted a renewed interest due to their potential applications in electronic devices. We describe here an in situ study of the formation and growth of NiSi2 nanoplates in Si(001) wafer near the surface using Grazing Incidence Small Angle X-ray Scattering (GISAXS). A new preparation method was used to obtain well separated NiSi2 nanoplates embedded in Si. The sample was prepared using two precursor wet solutions deposited on the Si wafers through spin-coating method. The first solution is composed of 0.150 g of Ni(NO3)2.6H2O salt diluted in isopropyl alcohol. The second solution is composed of a mixture of 0.050 g of TEOS (tetraethyl orthosilicate) and 0.30 of HNO3 diluted in isopropyl alcohol. Both solutions were deposited on the Si(001) in the same order present here. The sample was dried in air and then heated at 300 ℃ in 5% H2+He flow to promote the reduction of Ni oxide and evaporation of the volatiles. As result we obtained a Ni-doped SiO2 thin film (thickness ~100 nm) covering one of the surfaces of the Si wafer. This sample was placed in a specially designed high temperature furnace installed at the XRD2 beam line of the Brazilian Synchrotron Radiation Laboratory (LNLS). The GISAXS intensity produced by the thin film and by the thin Si layer close to its external surface was measured several times during annealing at 405 ℃ in He flow. 2D GISAXS intensity patterns were recorded each 60 seconds of the thermal treatment. Previous Scanning Transmission Electron Microscopy (STEM) results of a sample prepared using the same method but annealed at 500 ℃ during 50 min indicated the formation of NiSi2 nanoplates in Si is a consequence of the diffusion of the Ni atoms from the Ni-doped SiO2 thin film into Si followed by the reaction with the Si atoms [1]. This previous study showed the NiSi2 nanoplates have the shape of nearly regular hexagons with their larger surface parallel to the planes of the Si{111} crystalline form. In the here reported in situ study a lower temperature was preferred to avoid nanoplates growing too fast. From the analysis of the GISAXS intensity patterns we determined the average value of the largest diameter of the hexagonal surface, thickness, number and total volume of the nanoplates as a function of the treatment time [2]. The results showed the nanoplates reach their final size after 10 minutes of annealing while the number of the nanoplates increases until 50 minutes. This behavior indicates the final size of the nanoplates is not limited by the concentration of Ni atoms in the thin film. The dependence on time of the total volume of the NiSi2 nanoplates, V(t), was compared to the function predicted by the Jhonson-Mehl-Avrami theory. The parameters determined from the best fit of this function to the experimental V(t) function are consistent with the growth of planar shaped nanoparticles formed by an heterogeneous nucleation process.

References:

[1] D. S. Costa et al. Highly oriented NiSi2@Si thin-nanocomposite produced by solid state diffusion: morphological and crystallographic characterization. Submitted (2021).
[2] D. S. Costa et al. In situ study of the process of formation of hexagonal NiSi2 nanoplates and spherical Ni nanoparticles embedded in a Si(001) wafer covered by a Ni-doped SiO2 thin film. Journal of Alloys and Compounds, 879 (2021).

Aknowledgements:

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Keywords:

GISAXS, NiSi2, nanoplates

Poster Presentation

Influence of PEO content on nanoscopic structure and properties of a new PLA-Siloxane-PEO organic-inorganic hybrid prepared by Sol-Gel process

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This work presents the synthesis, structural investigation and some interesting properties of a new PLA-Siloxane-PEO hybrid prepared by Sol-Gel process featuring covalent bonds between polymers chains and siloxane nodes 1. The structural features, thermal properties and chemical stability of this biocompatible system have been studied by Fourier-Transform Infrared Spectroscopy (FTIR), Raman Spectroscopy, 29Si Nuclear Magnetic Resonance (NMR), Scanning Electron Microscopy (MEV), X-Ray Diffraction (XRD), Small-Angle X-ray Scattering (SAXS), Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC). A systematic study has been done as a function of PEO content by changing the PLA:PEO weight ratio (30-70, 50-50 and 70-30). SEM and SAXS measurements showed that the siloxane nodes act as crosslinks between the polymer chains promoting high miscibility between PLA and PEO. FTIR, Raman XRD, DSC and TGA showed that the presence of the siloxane nodes diminishes the crystallinity of both polymers and increases their thermal resistance. Lorentz-corrected Small-Angle X-ray Scattering (SAXS) patterns of PLA-Siloxane-PEO hybrids showed the presence of two convoluted peaks. The peak centered at lower q-values (0.2, 0.17 and 0.13 Å-1 for 30-70, 50-50 and 70-30 respectively) has already been observed at similar position for siloxane-PEO hybrids (0.15 Å-1) prepared with a polymer of same molar mass as used in this study and originates from the spatial correlation between the siloxane nodes located at polymer chains extremities 2. From comparison with the SAXS curve of neat PLA it is possible to attribute the peak centered at larger q-values (0.2 Å-1 for PLA and 0.33, 0.3 and 0.26 Å-1 for 30-70, 50-50 and 70-30 respectively) to the long period of lamellae located inside PLA crystallites. In order to extract information associated to the long period of PLA crystalline phase, we have used the classical method of investigation of crystalline polymers which consists of determining, from the Fourier-transform of the Lorentz-corrected SAXS peak, the structural parameters such the thicknesses of crystalline lamellae (Lc) and amorphous layers (La) and the values of the most probable long period Lp. This SAXS study allowed to understand at a nanometer scale how the presence of PEO chains affects the spherulites-based structure associated to the semi-crystalline PLA polymer and consequently affects the hybrid properties. It is important to emphasize that in addition to the absence of brittleness due to the low crystalline character of PLA, this new material exhibits a fantastic resistance to PLA degradation in aqueous medium, attributed both to the presence of the siloxane particles acting as a barrier towards water diffusion and to the hydrophilic PEO segments which may attract water molecules, preventing PLA hydrolysis. All of these characteristics offer an amazing perspective for the use of this hybrid material in biological, medical and pharmaceutical applications.

References:

[1] Silva, R. de O.; Silvino, A. C.; Ribeiro, J. M.; Dahmouche, K. J. Sol-Gel Sci. Technol. 2021, 99, 512.
[2] Dahmouche, K.; Santilli, C. V.; Pulcinelli, S. H.; Craievich, A. F. J. Phys. Chem. B 1999, 103, 4937.

Poster Presentation

Influence of heating rate and tempering time on reversed austenite kinetics of a supermartensitic stainless steel weld deposit

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In recent years, supermartensitic stainless steels have been used in pipes because they displays a better combination of weldability, toughness and corrosion resistance than conventional martensitic and duplex stainless steels [1]. Nevertheless, several post weld heat treatments (PWHT) are usually required to control the microstructure, and consequently mechanical properties such as toughness, ductility, and resistance to localized corrosion. Thus, the intercritical tempering of martensite induces the formation of austenite reversed, improving the properties of weld deposits [2]. In this work, the influence of the heating rate on the transformation kinetics of martensite into austenite in supermartensitic stainless steel weld deposit was studied, using the X-ray Scattering and Thermo-Mechanical Simulation, which is located at National Laboratory Synchrotron Light. In first place, dilatometry measurements were recorded at 1, 10, and 100 °C/s. In second place, in situ synchrotron X-ray measurements were carried out during a post weld heat treatment cycle, in which the steel weld deposit were subjected to intercritial tempering at 665 °C for 15 min, with heating and cooling rates of 1 and 2 °C/s, respectively. This techniques allows to detect the critical transformation temperatures, phase transformations and their kinetics, monitoring particularly the kinetics of austenite reversed during the post weld heat treatments cycle. It was found that the increase of the heating rate increases critical temperatures and reduces the range of the reverse transformation of martensite to austenite. However, the increase of the heating rate increased the average transformation rate, reducing the range of the transformation. Furthermore, the maximum transformation rate was reached for the slowest heating rate. On the other hand, the kinetics of the austenite reversed followed an exponential trend as a function of time during the intercritical tempering.

References:

[1] S. Zappa, E. Surian and H. Svoboda, Effects of Welding Procedure on Corrosion Resistance and Hydrogen Embrittlement of Supermartensitic Stainless Steel Deposits, J. Iron Steel Res. Int., 2013, 20(12), p 124-132, in English.
[2] D. Zou, X. Liu, Y. Han, W. Zhang, J. Li and K. Wu, Influence of Heat Treatment Temperature on Microstructure and Property of Cr 13 Ni 5 Mo 2 Supermartensitic Stainless Steel, J. Iron Steel Res. Int., 2014, 21(3), p 364-368, in English.

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Keywords:

Dilatometry, post-welding heat treatments, X-ray powder diffraction, critical temperatures, transformation rate

Oral Communication

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

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Perovskite solar cells have received significant attention due to the excellent photovoltaic performance obtained through low-cost and straightforward techniques.[1] The perovskites showing the best efficiencies are FAPbI3 (FA = NH2CHNH2)-related compounds, with small amounts of Cs and Br for stabilizing the photoactive phase. Increasing the amount of Br increases the perovskite bandgap, allowing the adjustment to tandem solar cells, but halide segregation becomes stronger.[2] MACl (MA = CH3NH3+) is often added to the perovskite precursor solution to increase grain size, improve optoelectronic properties, and, consequently, improve performance. However, the relationship between the Br amount and incorporation of the Cl- into the lattice, affecting sample homogeneity and properties, is poorly known.[3] For this, we characterized films of perovskites with different amounts of Br and MACl deposited by the gas quenching method.[4] Photoluminescence (PL) and ultraviolet-visible (UV-VIS) spectroscopies on Cs0.05FA0.95Pb(BrxI1-x)3 ($0 \leq x \leq 0.5$) films revealed a bandgap between 1.50 and 1.87 eV, with a slight reduction in bandgap with the addition of MACl for the same amount of Br. X-ray diffraction (XRD) showed a decrease in the unit cell lattice parameters with the Br increment compared to the perovskite phase. We have also detected that with the addition of MACl, the perovskite film has a preferential orientation in the direction [001]. In addition, for the same percentage of Br, there is a slight decrease in the lattice parameter, which indicates the possible incorporation of Cl in the perovskite lattice. 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. In summary, the addition of MACl is also beneficial to Br-rich perovskites.

References:

[1] ROMÁN-VÁZQUEZ, M. et al. Recent advances on synthesis and applications of lead- and tin-free perovskites. Journal of Alloys and Compounds, 2020.
[2] ROY, P. et al. A review on perovskite solar cells: Evolution of architecture,fabrication techniques, commercialization issues, and status. Solar Energy, 2020.
[3] XU, J. et al. Triple-halide wide-bandgap perovskites with suppressed phase segregation for efficient tandems. Science, 2020.
[4] SZOSTAK, R. et al. Revealing the perovskite film formation using the gas quenching method by in situ GIWAXS: morphology, properties, and device performance. Advanced Functional Materials, 2021.

Poster Presentation

Interrogating sedimentary silica-rich rocks using a multi-technique approach: first insights on preservation of organic molecules in heterogeneous geological systems.

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In recent years, experimental silicification of microorganisms proved organic molecules (OMs) preservation under its early entombment and subsequential induration of silica [1]. Thus, sedimentary silica-rich rocks (chert) are considered a record of life in past geological times. The occurrence of OMs has been advocated as evidence of biogenic origin for microfossils founded on Archean chert [2]. Contrarily, such OMs could have also been sourced by abiotic processes [3].

During its precipitation, silica interacts with OMs via adsorption controlled by electrostatic interactions [4]. Such OM-silica composites undergo low-temperature processes (diagenesis), leading to both porosity reduction as the crystallization of more stable SiO2 polymorphs [5] to become sedimentary rock. Reduction of permeability occurs as the pore throat closes, isolating the porosity network from exogenous fluids [6] and precluding mobility of OMs [7].

However, studies dealing with chert do not address the structural control of silica – porosity system as a potential preservation mechanism for OMs. Thus, we have characterized chert using (U)SAXS, WAXS, Raman, mass spectrometry, TGA, SEM and XRD. Samples were collected from Pacific Ocean´s locations.

Samples are composed of microcrystalline quartz spheres supporting a network of sub-micrometrical pores, which have a fractal geometry as SAXS data exhibit a power-law behaviour. GC-MS shows aliphatic carbons suggesting veritable preserved OMs [3]. Raman and MALDI-TOF suggest amide, lipids, and peptide occurrences. OMs are adsorbed onto quartz spheres [TGA data].

Geochemical homogeneity points to the microspheres-pore network as the source of X-ray scattering. (U)SAXS data show spatial heterogeneities suggesting dissimilar diagenetic effects. Accordingly, shifts in I(q) shown by sample 27c could reveal a nanopore control on mineral precipitation. A similar shift was reported for OMs-mediated carbonate precipitation on amorphous silica substrates [8].

References:

[1] Alleon, J. et al. 2016. Chemical Geology, DOI: 10.1016/j.chemgeo.2016.05.034 0009-2541
[2] Schopf, J.W. and Kudryavtsev, A.B. 2012. Gondwana Research, DOI: 10.1016/j.gr.2012.07.003
[3] Brasier, M. et al. 2002. Nature 416, 76-81.
[4] van den Heuvel, D.B. et al., 2018. Frontiers in Materials. DOI: 10.3389/fmats.2018.00019
[5] Williams, L. A., Parks, G., Crerar, D.A. 1985. J. Sedimentary Petrology, 55(3), 301-311.
[6] Ledevin, M. et al. 2014. Precambrian Research. DOI: 10.1016/j.precamres.2014.10.009
[7] Stack, A. 2015. Reviews in Mineralogy and Geochemistry. DOI: 10.2138/rmg.2015.80.05
[8] Stack, A., et al. 2014. Environ. Sci. Technol. DOI:10.1021/es405574a

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Keywords:

Silica-rich sedimentary rocks, SAXS, WAXS, Raman, GCMS, MALDI-TOF, TGA, XRD, SEM, porosity, fractal geometry, hierarchical materials

Poster Presentation

Investigation of Mn-rich niches formation during tumor progression

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Manganese acts as a cofactor to central molecules responsible for cell survival and invasion. Our group has described Mn as a relevant aspect of tumor progression [1]. Our study revealed that tumor-bearing mice present altered Mn distribution in the form of Mn-rich niches found in primary tumors and distant organs. X-ray fluorescence (LNLS, CNPEM) was applied to detect and quantify Mn, among other elements, in our samples. Our in vivo data revealed that primary tumors and distant tissues present Mn-rich niches and our in vitro data showed that tumor cells accumulate Mn in culture and secrete this element in exosomes. Interestingly, when analyzing Mn-rich niches in primary tumors, we were able to observe additional elemental changes related to these niches. The element P presented a negative correlation as its concentration decreased at week 5, while Mn was increased compared to weeks 1 and 3 of tumor progression. The elements K, Fe and Cu all presented a positive correlation, increasing alongside Mn in Mn-rich niches. Ca concentration decreased specifically at week 3, but levels at weeks 1 and 5 were similar. Interestingly, Mn-rich niches found in distant organs only presented alterations in Mn levels, all other detected elements presented similar levels between experimental groups. Analysis of extracellular vesicles derived from LLC cells after Mn exposure revealed that these structures do not present any elemental differences when compared to control cells-derived extracellular vesicles, Mn was found to be the only significantly altered element in the vesicles. In conclusion, our data highlight exosomes as a possible route for Mn distribution in cancer. Our perspectives involve the study of Mn transport in tumor cells, specifically, we aim to investigate Mn route from internalization to secretion in exosomes by high-resolution multi-elemental imaging at the new light source, Sirius.

References:

[1] STELLING, M. P. et al. Manganese systemic distribution is modulated in vivo during tumor progression and affects tumor cell migration and invasion in vitro. Scientific Reports, v. 11, n. 1, p. 15833, 4 ago. 2021.

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Keywords:

Manganese, cancer, exosomes, multi-elemental imaging, X-ray fluorescence

Poster Presentation

Investigation of cerium influence on luminescent properties of LiLaP$_4$O$_{12}$:Bi

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One of the important characteristics of a scintillator, material used to detect ionizing radiation, is that the light intensity be high enough for the type of desired application. One kind of scintillators studied are those with red emission, which coincides with the maximum detection efficiency of silicon-based photodetectors (Si-PDs). Si-PDs have some advantages over photomultipliers tubes (conventionally used detectors) such as low cost and greater quantum efficiency [1]. The bismuth ion at the 2+ valence (Bi $^{2+}$) is one of the ions that, in general, gives red emission in the electromagnetic spectrum. It has already been observed that some bismuth-doped phosphates at the 3+ valence (Bi $^{3+}$) exhibit Bi $^{2+}$ emission induced by interaction with X-rays [2]. However, this effect has not yet been observed in the LiLaP$_4$O$_{12}$ structure. Furthermore, there are reports in the literature that, in co-doped matrices with cerium and bismuth, electron transfer from cerium to bismuth can occur, improving the Bi $^{2+}$ emission [3]. This suggests a way to increase bismuth-related emission using the co-doping method with cerium and bismuth ions. Therefore, to study whether there is X-ray induced Bi $^{2+}$ emission and, if so, it can be potentiated by electron transfer from cerium, into the phosphate structure, we performed photoluminescence measurements on the TGM line at Brazilian Synchrotron Light Laboratory (LNLS). In addition, radioluminescence (RL) and thermoluminescence (TL) analysis were also performed. The results indicate that cerium influences bismuth-related emission. Furthermore, the red emission, characteristic of Bi $^{2+}$, was observed in the RL spectrum. The red emission grew when the concentration of cerium increases in the structure.

References:

[1] YANAGIDA, T. Study of rare-earth-doped scintillators. Optical Materials, v. 35, n. 11.
[2] AWATER, R.H.P.; DORENBOS, P. X-Ray Induced Valence Change and Vacuum Referred Binding Energies of Bi3+ and Bi2+ in Li2BaP2O7. The Journal of Physical Chemistry C, v. 120.
[3] AWATER, R. H. P. The Bi3+ 6s and 6p electron binding energies in relation to the chemical environment of inorganic compounds. Journal of luminescence, v 184.

Poster Presentation

Investigation of initial hydration of type-III Portland cement using the in situ XRD technique by synchrotron light

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Partial replacement of clinker in Portland cements (PC) by supplementary cementitious materials, such as blast furnace slag, is beneficial in order to reduce the environmental impact of CO2 emissions in cement production [1]. However, initial slag hydration is very slow compared to traditional PC, and phase transformation analyses are usually carried out with benchtop equipment [2] that collects diffractograms in approximately one hour. Therefore, the first moments are lost and also require the use of Kapton, which reduces the intensity of peak counting, compromising phase identification. This study aimed at monitoring the hydration of type-III Portland cement in water through in situ DRX using the XRD1/LNLS Line [3]. The diffractograms (Fig. 1) showed the presence of alite, belite, calcite, quartz, periclase and dolomite. Portlandite and hydrotalcite were also identified in the pre-hydrated anhydrous cement. It is possible to see the consumption of gypsum, aluminate and brownmillerite in the first ten minutes and the evolution of ettringite hydration after three hours. The peak of alite had a greater reduction after 11 hours; gypsum, in 18 hours; and brownmillerite, in 20 hours.

References:

[1] R. Baldusco, T.R.S. Nobre, S.C. Angulo, V.A. Quarcioni, M.A. Cincotto. Dehydration and rehydration of blast furnace slag cement. J Mater Civil Eng., 2019.
[2] Scrivener, K. L. et al., Quantitative study of Portland cement hydration by X-ray diffraction/Rietveld analysis and independent methods. Cement and Concrete Research 34, 2004.
[3] Carvalho et al., X-ray powder diffraction at the XRD1 beamline at LNLS, Journal of Synchrotron Radiation 23, 2016.

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Keywords:

Portland cement, hydration, in situ X-ray diffraction, synchrotron

Poster Presentation

Lithium batteries characterization with 4th generation syncrotron: in operando studies with phase contrast and spatial resolution

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Recents Lithium-ion batteries (LIBs) studies are devoted to understand the interface processes that are crucial in the reversible Li ion uptake. Some of the most promising cathodes for LIBs are based on LiFePO4 (LFP), Mn and Ni spinels (LMNO) and LMNO modified with the incorporation of transition metals. Those materials arise as candidates because they are safer and cheaper to produce and possess higher energy densities compared with the state-of-the art LiCoO2(LCO)[1]. Previously using DXAS beamline at the recently closed LNLS, we were able to follow changes in the electronic structure, in operando conditions, by X-ray absorption Near Edge Structure for different types of LMNO mixtured with lithium rich phase materials at Ni and Mn K edges (see poster presented by Silveira & Jori et al. in this congress). The possibility to combine those characterizations with spatial resolution or taking advantage of the phase contrast capability will be available in the new 4th generation machine like Sirius. An example of these future improvements is the spatially correlated X-ray pictographic tomography, known as X-ray ptychography[2,3] that is a lensless imaging technique that provides quantitative electron density tomograms at levels of spatial resolution hardly achievable by common X-ray microscopic techniques. By the combination of this phase contrast based techniques and, for example, scanning X-ray diffraction microscopy[4], it is possible to directly visualize morphological and crystalline changes during the Li intercalation. The access to that type of combined information would enable observe the stresses in crystals, within individual secondary particles, that is only possible with a few nm resolutions.
In this work we describe the state of the art of these novel experimental methodologies that could be implemented in Sirius giving the the possibility to perform the characterization, for example, of cathode materials used in Li+ ion batteries in operando conditions.

References:

[1] Aderemi B. Haruna, Kenneth I. Ozoemena, Effects of microwave irradiation on the electrochemical performance of manganese-based cathode materials for lithium-ion batteries, Current Opinion in Electrochemistry, 2019.
[2] M. Dierolf, A. Menzel, P. Thibault et al., "Ptychographic X-ray computed tomography at the nanoscale", Nature, vol 467, pp. 436-439, 2010.
[3] M. Holler, A. Diaz, M. Guizar-Sicairos, P. Karvinen et al., "X-ray ptychographic computed tomography at 16 nm isotropic 3D resolution", Sci. Rep., vol 4, p. 3857, 2014 .
[4] S.J. Leake et al., "The Nanodiffraction beamline ID01/ESRF: a microscope for imaging strain and structure", J. Synchrotron Rad., vol 26, no. 2, pp. 571-584, 2019.

Aknowledgements:

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Keywords:

X-ray absoption, energy, Li-ion batteries

Poster Presentation

Low-temperature luminescence of inorganic hybrid system (BaTiO3-CaF2) under VUV spectroscopy

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The synergic between two inorganic hosts was investigated for potential application in photo absorbers of solar panels outside the atmosphere, such as satellites. The proposed type of absorber can improve the absorption in the UV region of solar cells. The system developed consists of a combination of $BaTiO_3$ and CaF_2 undoped and doped with Europium. The samples were synthesized by microwave-assisted hydrothermal method, employing low temperature (140 ℃) and short synthesis times (1 minute of the plateau). The structural, morphologic, and optical properties have already been explored in previous works[1]. Therefore, this work was explored the defects that were measured at low temperatures. The luminescent measurements at 60 K were performed in the TGM beamline of LNLS/CNPEM. Comparing the samples undoped, it is possible to see differences between the system and the isolated CaF_2. The emission band reported as center F, predominant in fluorides, is more accentuated in the system. Possibly, this result is due to the synthesis method, which can promote the interaction of free oxygen ions from $BaTiO_3$ with fluorine vacancies. For the doped-samples, the CaF_2:Eu emission and excitation spectra reveal the appearance of a characteristic band of the divalent Eu. This band is more intense when measured at room temperature and decreases when analyzed at the temperature of 60 K. However, compared to the doped-system, the band has greater intensity when measured at low temperatures. This behavior can be due to the association of two defects: the F center emission located at 430 nm and the emission coming from the typical 5d-4f transitions of Eu^{2+}. Another difference in relation to the doped-CaF_2 is the presence of the 4f-4f transitions that are typical of the trivalent Eu. Emission spectrum analysis of these transitions can indicate structural changes in the system. The differences seen in the spectroscopic analysis indicate that both hosts interact with europium ions, evidenced by the formation of intrinsic and extrinsic defects.

References:

[1] LILGE, T. S. et al. Influence of Eu valence on the optical activity of BaTiO3 decorated with CaF2 synthesized by microwave-assisted hydrothermal method. Dalton Transactions, The Royal Society of Chemistry, v. 49, p. 8540–8548, 2020.

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Poster Presentation

Microstructural study of air-drying kinetics of Ca(II)-alginate beads to preserve cowpea extracts

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The great potential of Ca(II)-alginate beads in preserving biomolecules and their use as a carrier of bioactive compounds has been demonstrated. However, several food applications require long-term storage and thus, numerous preservation techniques such as drying have been applied. Still, research of stability of bioactive compounds in these treatments focus on the morphology of the beads and the microstructure of the network but do not consider the microstructural changes that occur during the drying process.

Ca(II)-alginate beads were prepared to preserve phenolic compounds extracted from cowpea (Vigna unguiculata) by-products by using high-intensity ultrasound (VCX500, Sonics, US). Also, the influence of the addition of cowpea isolated proteins as an excipient of the beads has been analysed. The microstructural changes of the network during air-drying treatment have been studied by SAXS at the LNLS SAXS1 beamline in Campinas, Brazil at $\lambda = 0.1488$ nm. The wave vector (q) was selected in the range $0.142\ \text{nm}^{-1} < q < 5.035\ \text{nm}^{-1}$. All the Ca(II)-alginate beads analysed showed isotropic scattering and were modelled as a fractal system composed of rod-like structures.

Significant differences were observed between the alginate beads containing the whole extract with respect to those containing cowpea isolate protein, revealing that cowpea protein is embedded within the rods, obtaining thicker but less dense rods disposed in a more disordered structure. These differences remained constant until 60 min of the air-drying treatment at 25 ℃ (even with moisture losses up to 30%). From this time, the microstructure of the dried beads at the final stage if drying ($x_w = 0.5$ kgw/kgT) showed the loss of the typical scattering of rod-like structures and even displayed new signals at high q in the presence of cowpea proteins.

Keywords:

Microstructure, Ca(II)-alginate, cowpea by-products

Poster Presentation

Mechanochemical synthesis of nanocrystalline Tellurides applied as electrochemical sensors

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Electroanalytical methods have been developed to simplify the quantification of many different analytes as an alternative to those based on optical properties and chromatography. Recently, we report on a novel electrochemical sensor based on carbon paste electrodes (CPE)/Ni3-xTe2 for the simultaneous detection of the neurotransmitters dopamine (DA) and adrenaline (AD) in phosphate buffer solution (pH 7.0) [1]. It represents a promising electrochemical platform for DA and AD quantification in various kinds of matrices, with preparation and operation routes totally based on green chemistry principles. Another proposed sensor CPE/NiTe2 was successfully applied to morin determination in high, medium, and low polyphenols content red wines such as Tannat, Cabernet Sauvignon, and Pinot Noir [2]. All the Nickel Telluride composites were produced by ball milling in just a few hours and carefully characterized by X-ray diffraction, transmission electron microscopy, Raman spectroscopy, and magnetometry techniques. The nanometric character of the crystals was confirmed by XRD-Rietveld and TEM analysis. The average volume-weighted crystallite sizes found for Ni3-xTe2 was 10 nm and 4 nm for Ni, in the sensor CPE/Ni3-xTe2, and 18 nm for trigonal NiTe2 present in the CPE/NiTe2. Our aim with this presentation is to expose our recent multidisciplinary work and to have some feedback from the audience to better understand how to usufruct some incredible scientific opportunities offered by the X-ray nanoprobes at Sirius-CNPEM. By the time, we are thinking to overpass the experimental challenges to describe more precisely our nanocrystalline alloys and, who knows, in the future, to perform in-operando X-ray computed tomography of our electrochemical sensors.

References:

[1] Ulbrich, K. F. ; Winiarski, João Paulo ; Jost, Cristiane Luisa ; Campos, C.E.M. . Mechanochemical synthesis of a Ni3-xTe2 nanocrystalline composite and its application for simultaneous electrochemical detection of dopamine and adrenaline. Composites Part B-Engineering, v. 183, p. 107649, 2020. DOI:10.1016/j.compositesb.2019.107649
[2] Ulbrich, K. F. ; Winiarski, João Paulo ; Jost, Cristiane Luisa ; Campos, C.E.M. . Green and facile solvent-free synthesis of NiTe2 nanocrystalline material applied to voltammetric determination of antioxidant morin. Materials Today Communications, v. 1, p. 101251, 2020. DOI:10.1016/j.mtcomm.2020.101251

Aknowledgements:

CNPq

Keywords:

Mechanochemistry, tellurides, X-ray, Rietveld, electrochemistry

Poster Presentation

Melting and freezing temperatures, mass densities and coefficients of thermal expansion of solid and liquid Pb nanoparticles embedded in a lead-borate glass determined by SAXS

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We here present a novel method for the evaluation and validation of a proposed theoretical model for the determinations of the radius dependences of the melting $T_m(R)$ and freezing $T_f(R)$ temperatures of spherical nanoparticles, through the analysis of the temperature dependences of the experimental small-angle X-ray scattering (SAXS) intensities at several scattering vectors q_i. This procedure was applied to determine the radius dependence of the melting and freezing temperatures of spherical Pb nanoparticles embedded in a lead-borate glass and also the ratio of solid/liquid specific mass and coefficient of thermal expansion of solid and liquid Pb nanoparticles. Modelled SAXS intensity functions for several q_i values, $I(q_i, T)$, were fitted to the experimental SAXS intensities during the heating and cooling of samples over the 298-638 K range. The modelled $I(q_i, T)$ curves calculated by the best fit procedure for both heating and cooling processes agreed well with the experimental SAXS intensity versus temperature curves, $I_{exp}(q_i, T)$. This best fitting procedure provided several a priori unknown parameters of previously proposed theoretical $T_m(R)$ and $T_f(R)$ functions, from which the radius dependences of the melting temperatures of Pb nanocrystals and the freezing temperatures of Pb nanodroplets were determined. The value of the coefficient of thermal expansion of solid Pb nanoparticles - derived from the fitting procedure - is close to the coefficient of bulk solid Pb while the coefficient of thermal expansion of liquid Pb nanoparticles was found to be significantly lower than that of bulk liquid Pb.

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Keywords:

SAXS, phase transition, nanoparticles, melting, freezing

Poster Presentation

Method for analysis of non-stoichiometric phases using X-ray diffraction and computational thermodynamics

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Phase quantification using X-ray diffraction is a widely used procedure in materials science. The Rietveld method is used for this purpose and the implementation of fundamental parameters through Topas Academic is a reliable and accessible way. The difficulty of the method lies in the use of CIF (crystallographic information file), which in most cases is composed of stoichiometric phases. The work motivation was due to the difficulty of quantifying δ and α ferrites in Al alloyed steels. These phases are characterized through their morphology, where δ ferrite has large grains due to its formation in solidification dendrites and small grains α ferrite due to formation by austenite decomposition. Phase composition measurements indicate that they have different compositions, but the ordinary method leads to quantification imprecision. Quantification through x-ray diffraction is not simple either, since both phases have BCC (cubic-centered body) structures and, in crystallographic datas both are only differentiated by the lattice parameter. Analyzes in the UVX XPD line were acquired around the diffraction peaks of the ferrites. To apply the Rietveld method, CIF datas adjusted from those available on the Crystal Toolkit on materialsproject.org website were modified according to the occupation of the given sublattice through thermodynamic calculations. The Calphad method was used through the Thermo-Calc software in 4 aluminum alloys ranging between 3.5%wt and 5.6%wt. The occupancy of the sublattice was evaluated between 1500°C and 25°C and the occupancy fractions used for δ ferrite were given between 1200°C and 1400°C and for α ferrite below 700°C. The differentiation and consequent quantification of ferrites was obtained and the method proved to be efficient, opening the possibility of quantification of non-stoichiometric phases through conventional diffraction.

Keywords:

Crystallographic information file, calphad, Rietveld method

Poster Presentation

Mössbauer and crystallographic studies of sintered Nd-Fe-B magnets machining sludge

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Rare earth permanent magnets are of great importance for cutting-edge technologies, such as: energy generation, electronic information, home appliances, medical treatment, aerospace, among others [1]. The magnets based on Nd-Fe-B stand out, mainly due to their high value of energy product (BH)max, which grants to the miniaturization of technologies in which as higher (BH)max value is, smaller the magnet volume required [2]. In recent years, there has been a growing demand and, consequently, an increase in magnets production and waste generation [3,4]. One of the challenges in the production of rare earth-based permanent magnets is the recycling of their waste, due to the various challenges inherent to reprocessing techniques[1].

Among all residues, machining sludge residue stands out for being obtained in the mandatory machining step in the production process of sintered magnets based on Nd-Fe-B [5]. The recycling and reuse of machining sludge residues is still a challenge for the magnet industry, due to the lack of knowledge about the characteristics of the residues, such as their structural properties, the level of degradation, which makes it difficult to develop efficient recycling processes.

In order to contribute to this research gap, this work aimed to determine the structural characteristics of the machining residue of sintered Nd-Fe-B magnets to enable the evaluation of its use in different recycling technologies. For this purpose, machining sludge residues of sintered Nd-Fe-B magnets and the magnet used for the generation of residues were characterized by Mössbauer spectroscopy, X-ray diffraction and Rietveld refinement method.

Mössbauer spectroscopy enabled alpha-iron phases quantification and diffraction patterns contributed to phase quantification analyses, lattice parameters and crystallite size evaluation. By analyzing the Mössbauer spectrum it was possible to determine that the cutting process without the use of a cutting fluid was more aggressive and resulted in higher phase degradation. In another hand, the diffraction patterns analysis showed that the cutting fluid did not affect the parameters of the Nd-Fe-B phase in the machining residue, but it causes a reduction in the crystallite size.

References:

[1] NLEBEDIM, I. C.; KING, A. H. Addressing Criticality in Rare Earth Elements via Permanent Magnets Recycling. Jom, v. 70, n. 2, p. 115–123, 2018.
[2] Constantinides, S. (2016). Market Outlook for Ferrite, Rare Earth and other Permanent Magnets. The International Forum on Magnetic Applications, Technologies & Materials, 1–43.
[3] BINNEMANS, K. Rare Earths and the Balance Problem: How to Deal with Changing Markets. v. 8, 2018.
[4] YUE, M. et al. SHORT-PROCESS METHOD FOR PREPARING SNTERED NIDFEBMAGNETS WITH HIGH MAGNETIC PROPERTIES RECYCLING FROMNDFEB SLUDGEUnited States, 2016.
[5] AMATO, A. et al. Sustainability analysis of innovative technologies for the rare earth elements recovery. Renewable and Sustainable Energy Reviews, v. 106, n. February, p. 41–53, 2019.

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Keywords:

Magnets recycling, Mossbauer spectroscopy, X-ray diffraction

Poster Presentation

Nb-bioactive glass nanoparticles through Sol-Gel chemistry

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Bone tumours, periodontal diseases, and degenerative cartilage disorders disrupt the daily activities of people. Therapeutic approaches to these pathologic conditions prompted the development of materials that could replace bone and joint tissues. Several materials have been developed for this purpose. In this context, vitreous compositions containing niobium have been investigated to obtain glasses with improved biological properties, and chemical reactivity. Studies incorporating Nb5+ ions have revealed a reduction in cytotoxicity and induction of significant calcification in normal human osteoblasts. Furthermore, Nb species promote the activity of alkaline phosphatase (ALP), an important factor in the generation of new bone. In the present work, the chemical composition of 58S bioactive glass was slightly modified using Nb2O5. For this purpose, a glassy series was prepared by a simple substitution of P2O5 for Nb2O5, i.e., 60SiO2-36-CaO- (4-x)P2O5-xNb2O5 in mol% with x=0, 1, 2, 3 and 4%, giving rise to five bioactive glass compositions: 58SN0, 58SN1, 58SN2, 58SN3, and 58SN4. All materials were synthesized by a sol-gel method coupled with a self-propagating combustion method for preparing bioactive glass nanoparticles with high structural homogeneity developed in our research group. The morphology and chemical composition were investigated by SEM-EDS while the textural properties and surface area were investigated via BET analysis. The microstructure of 58S was investigated using some physical properties, infrared and Raman spectroscopies. The results show the presence of glassy nanoparticles with high porosity, chemical composition similar to nominal and a microstructure with high homogeneity, characterized by the presence of NbO6 octahedrons replacing the SiO4 tetrahedra in the glass backbone. Complementary analyzes by XAFS spectroscopy may be carried out in the future in order to obtain more information about the short range order of these bioactive glasses.

References:

[1] O. M. V. M. Bueno, C. L. Herrera, C. A. Bertran, M. A. San-Miguel and J. H. Lopes, Materials Science and Engineering: C, 2021, 120, 111759.
[2] L. P. L. de Souza, J. H. Lopes, F. V. Ferreira, R. A. Martin, C. A. Bertran and J. A. Camilli, J Biomed Mater Res A, 2020, 108, 446-457.
[3] L. Souza, J. H. Lopes, D. Encarnacao, I. O. Mazali, R. A. Martin, J. A. Camilli and C. A. Bertran, Sci Rep, 2018, 8, 12808.

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Keywords:

Nb-bioactive glass manoparticles, bioactive glass, sol-gel, nanoparticles, Nb-bioactive glass, bioactive glass nanoparticles

Poster Presentation

Nematic anisotropy and magnetic fluctuations in iron arsenides using RIXS

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Resonant Inelastic X-ray Scattering (RIXS) is a technique that probes both the energy and momentum dependency of the sample's low energy excitations. With the RIXS end station at the IPE beamline, a good energy resolution will be achieved by the designed spectrometer and the beam spot size. With this, the lowest energy excitations, such as magnons and orbital excitations, can be probed with much more detail in comparison with some years ago.

The iron-based superconductors (FeSC) are a family of materials where unconventional superconductivity appears in a complex phase diagram. In proximity to an itinerant magnetic phase preceded by a structural nematic transition, the high-temperature superconductivity (SC) emerges in some phase diagrams as a function of atomic substitution or applied pressure.

However, when doping the Fe site in $BaFe_2As_2$ with Cr and Mn, the SC does not emerge [1]. Instead, these systems present a more correlated scenario with a different phase diagram: the proximity to a $3d^5$ state pushes to a more localized phase, where the magnetic order has a much higher transition temperature and there is no structural transition [2-4].

In this research project, we intend to use RIXS to characterize the magnetic excitations as a function of reciprocal space direction, temperature, and doping for the Cr sample. Some results were already published for the Mn sample [5], however, the possibility to apply strains and observe the evolution of magnetic excitations anisotropy in the nematic phase [6] permits to elaborate a more complete phase diagram for the non-SC samples in terms of electronic correlation and magnetic excitation.

We expect that such experiments will shed some light on the mechanism of the emergence of high-temperature SC by explaining the conditions where it does not emerge.

References:

[1] A. S. Sefat et al. Physical Review B 79, 224524 (2009).
[2] K. Marty et al. Physical Review B 83, 060509(R) (2011).
[3] A. Thaler et al., Physical Review B 84, 144528 (2011).
[4] S. Lafuerza et al. Physical Review B 96, 045133 (2017).
[5] F. A. Garcia et al. Physical Review B 99, 115118 (2019).
[6] X. Lu et al., arXiv:2108.04484 [cond-mat] (2021).

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Fapesp, IFUSP, IPE group, CNPEM.

Keywords:

RIXS, superconductivity, FeAs

Oral Communication

NiO/CeO2-Sm2O3 nanocomposites for partial oxidation of methane: In-situ experiments by dispersive X-ray absorption spectroscopy

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CeO_2-based materials are being extensively used for catalytic and electrocatalytic applications due to their redox properties. In particular, the addition of a metallic phase such as Ni to CeO_2-based catalysts for methane oxidation has been widely recognized to increase Ce reducibility by the presence of a strong metal-support interaction. However, it remains unclear if boosting Ce reducibility promotes a direct increase in catalytic activity for partial oxidation of methane. In this context, the role of sample nanostructure in the redox behavior of NiO/CeO_2-Sm_2O_3 (NiO/SDC) samples is of key interest to understand CH_4 activation, particularly, in terms of (i) the interaction between metallic and ceramic phases, (ii) the effect of the average crystallite sizes of both phases in catalytic activity, and (iii) the concentration of reduced species in the surface of the catalyst. In order to study samples with different average crystallite sizes and specific surface areas, and potentially different redox behavior, SDC and NiO/SDC nanocomposites submitted to different calcination temperatures, from 400 ℃ up to 1100 ℃, were prepared. In this work, we analyze the sample reducibility and catalytic activity for partial oxidation of methane. We assess the role of the average crystallite size and specific surface area in Ni and Ce reduction kinetics by studying diluted H_2 and CH_4/O_2 mixtures by in-situ dispersive X-ray absorption spectroscopy experiments with synchrotron radiation. Our results indicate that the average crystallite size and surface area play a key role in CH_4 activation through modification of the sample redox behavior [1]. The oxidation of the metallic phase is the main cause of sample deactivation, revealing a clear relationship between the temperature of maximum Ni oxidation rate and grain size. An interplay between Ce atoms from the support and Ni from the active phase was observed during the experiments, evidencing that a high Ce^{3+} content in catalyst support is detrimental to catalytic activity.

References:

[1] L.M. Toscani, M. Bellora, C. Huck-Iriart, A. Soldati, J. Sacanell, T. Martins, A.F. Craievich, M.C.A. Fantini, S. Larrondo, D. Lamas, Applied Catalysis A 626 (2021) 118357.

Aknowledgements:

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Keywords:

CeO2, methane oxidation, in-situ, XANES, oxygen vacancies

Oral Communication

Operando studies of toxic gas sensors using Near Ambient Pressure (NAP) XPS

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Semiconductors (SMO) Gas sensors materials for NO, NO_2, NH_3, CO, CO_2, SO_2, H_2S, etc., are receiving significant attention because of their important applications in numerous areas such as environmental monitoring in industry and residential areas, disease diagnosis, agriculture, industrial wastes, food quality monitoring, security at home or the workplace. The overall conductivity of SMO gas sensors depends on the charge transfer mechanism between adsorbed gaseous species and semiconductor metal oxides and the gas-surface reaction. This study aims to better understand the gas sensing mechanisms of semiconducting metal oxides materials such as WO3 and ZnO using the NAP-XPS technique under operando conditions. To thoroughly understand the mechanism of gas detection, it is crucial to characterize the surface composition and the material electronic structure during the exposure of the material to target gases.

Aknowledgements:

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Keywords:

Gas sensors mechanism, electronic structure, NAP-XPS

Poster Presentation

Optimizing data collection and processing to improve native anomalous diffraction phasing in macromolecular crystallography

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Macromolecular crystallography is inextricable from major advances in structural biology as it provides conclusive information at atomic level. Unsurprisingly, crystallography has contributed ~90% of the protein structures at the PDB. However, the elucidation of a macromolecular crystallographic structure can be very laborious. Besides the difficulties observed in sample preparation, the main intrinsic problem of crystallography is the phase problem, which prevents the direct solution of the structure. In the diffraction experiment, only the diffracted intensities and not the phases are recorded, whereas the phases are essential to compute the electron density map underlying the structural model. Classically to overcome this problem, techniques involving heavy-atoms or similar structures can be used, but the difficulty in obtaining properly diffracting derivatized crystals and/or the availability of known similar structure often prevents the structure solution[1].

Native single-wavelength anomalous diffraction (SAD) phasing is an excellent method to solve phase problem, since it does not require any derivatization process. This method uses the protein native heaviest atoms (sulfur) anomalous signal to solve the phase problem. However, this native anomalous signal is usually very weak and depends on the relative sulfur content of the protein.

Here, we have developed optimized data collection and processing protocols to enhance the power of native SAD. Using single and multiple-crystal datasets collected from lysozyme, trypsin and catalase crystals at MANACA-Sirius and SHELX specific parameters we could find some parameters that lead to a better solutions. So far, our results indicate an important role of multiplicity and resolution on SAD. Currently, we are performing clustering analysis on the solutions dataset to shed light on how parameter combination can improve the quality of obtained solutions and using mixed methods[2] to deal with difficult cases.

References:

[1] Taylor, G. Acta Cryst D 59, 1881–1890 (2003).
[2] Rodríguez, D. et al. Acta Cryst D 68, 336–343 (2012).

Aknowledgements:

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Keywords:

Native SAD, ab initio phasing, MANACA, low energy data collection

Poster Presentation

Pearls colors study by synchrotron light techniques

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This proposal aims to analyze through synchroton light techniques the colors of pearls and the biogenic distribution of chromophores in the structure of aragonite crystals to create a 2D map of the color centers and verify through biochemical studies the processes of their formation and biomineralization enabling a 3D dimensional simulation.

Pearls are considered mineraloids arising from biological activities or organic processes. They are complex biogenetic structures, with mineralization mediated by an inorganic calcium carbonate matrix in aragonite phases, carried out by living tissues, with a wide variety of colors - white, cream, black, gray, silver and gold, with overtones - pink, green , purple or blue and other iridescent colors. It is a mixture of proteins, glycoproteins and polysaccharides and calcifying matrix (CaCO3). However, the complexity of these structures is also proven by the fact that not all biochemical reactions involved during the genesis of pearls are yet known.

Synchroton light, as a differentiated technique, will allow the study of colors and analysis of biomineralization and crystalline structures of aragonite (CaCO3) and micrometric layers of nacre, enabling the creation of 2D XRF and XRD maps with simulation of color center variations and verification 3D of the distribution of chromophores of biogenic origin in pearls.

To visualize the growth of the crystalline layers of the nacre growth plates and the internal structures that form the pearls, it is necessary to obtain 3D X-ray images. Synchroton radiation and imaging techniques can be used and incorporated to improve and benefit the quality of pearls and change colors and hues with differentiation and greater value in the international market.

The prospection of technologies involving Syncroton radiation and its use in pearl processing is a potential for the use and application of innovative databases related to pearl processing with market value and differentiation.

Aknowledgements:

Douglas Galante and his team.

Keywords:

Pearls colors, crystalline structures of aragonite, biomineralization, synchroton radiation

Poster Presentation

Phase-contrast synchrotron microtomography applied to the morphometric analysis of Thoropa miliaris notochord in larval stages

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Amphibians are used extensively in physiological studies aimed at generating new insights in evolutionary biology, especially in the investigation of the evolution of air-breathing and terrestriality [1]. Anurans present a variety of reproductive modes, most species are direct developers and lay eggs on water, and a tadpole hatches and swims in bodies of water till completion of metamorphosis, with a small froglet that abandons the aquatic life [2]. The species *Thoropa miliaris* presents morphological conditions that differentiate it from other species. Tadpoles live in the film of water on rock surfaces at the wet borders of waterfalls in rainforest areas, and in rock fields of mountain ranges of southeastern Brazil [2].

Although most species in the genus are common and well sampled in collections of the natural history museums, little is known of the group's morphology. The application of microtomography (microCT) for the study of frogs is quite recent [3,4]. The first work of our group was to show the virtual dissection of this species [5] and, the second, the morphometric quantification of tissues that undergo major morphological changes during the animal's development [6]. Here, we present the results of the high-resolution non-invasive morphometric analysis of notochord of the *Thoropa miliaris* tadpoles. The notochord is a cartilaginous tissue and it was possible to observe using phase-contrast technique without staining. Microtomographic images were obtained at the imaging beamline SYRMEP at Elettra synchrotron (Trieste - Italy).

Detailed knowledge of the interior of biological structures and organisms is crucial for a better understanding of their function and evolution. In this work, whole-specimens of *Thoropa miliaris* in different larval stages of development were imaged. The phase-retrieval algorithm was implemented together with the conventional filtered backprojection reconstruction algorithm using the SYRMEP Tomo Project (STP) software developed by the SYRMEP team. The resulting voxel data sets were visualized with Avizo. The contrast between the different tissues in the microCT images was sufficient to be able to distinguish internal structures like soft and hard tissues.

References:

[1] W.W. Burggren, S. Warburton, ILAR J 48(3), 2007, 260-269.
[2] R.B Cocroft, W.R. Heyer, Proc. Biol. Soc. of Washington 101, 1988, 209–220.
[3] A. Haas et al, Zoomorphology, 133, 2014, 321–342.
[4] E. Descamps et al., Belg. J. Zool. 144(1), 2014, 20-40.
[5] G. Fidalgo et al., J. Inst., 13(C05012), 2018.
[6] G. Fidalgo et al., Scientific Reports, 10(18934), 2020.

Keywords:

Thoropa miliaris, micro-CT, phase-constrast

Oral Communication

Probing the atomic structure of CVD graphene on Ir(111) via photoelectron diffraction

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CVD graphene grown on metallic substrates presents, in several cases, a long-range periodic structure due to a lattice mismatch between the graphene and the substrate. For instance, graphene grown on Ir(111), displays a corrugated supercell with distinct adsorption sites due to a variation of its local electronic structure. This type of surface reconstruction represents a challenging problem for a detailed atomic surface structure determination for experimental and theoretical techniques. In this work, we revisited the surface structure determination of graphene on Ir(111) by using the unique advantage of surface and chemical selectivity of synchrotron-based photoelectron diffraction. We take advantage of the Ir 4f photoemission surface state and use its diffraction signal as a probe to investigate the atomic arrangement of the graphene topping layer. We determine the average height and the overall corrugation of the graphene layer, which are respectively equal to 3.40 ± 0.11 {\AA} and 0.45 ± 0.03 {\AA}. Furthermore, we explore the graphene topography in the vicinity of its high-symmetry adsorption sites and show that the experimental data can be described by three reduced systems simplifying the moir\'{e} supercell multiple scattering analysis [1].

References:

[1] Lucas Barreto et al 2021 J. Phys.: Condens. Matter 33 105001.

Keywords:

Graphene, photoelectron diffraction, atomic structure

Poster Presentation

Producing blue persistent luminesce translucent thin-films

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Persistent luminescent materials present several recent studies on new applications and novel properties. The design of translucent thin-films with persistent luminescent could bring new perspectives for this group of compounds like the application for better solar energy harvest and storage. Here we present a a fast and green method to produce unprecedented translucent blue persistent luminescence films based on $Sr_2MgSi_2O_7$:Eu^{2+},Dy^{3+} nanoparticles (250 nm) in hydroxypropyl methylcellulose (HPMC). These HPMC/SMSO composites were designed and optimized in function of their transparency achieving more than 1 h of blue (~475 nm) emission with high translucency (>50%). Since the particles and element distribution is essential to both emission and translucency, the nanofocused X-ray fluorescence mapping was studied at Carnauba beamline under 9656 eV irradiation, detecting Eu (5845 eV) and Dy (6495 eV) L_1 fluorescence lines. The X-ray images showed a highly homogeneous distribution of ~5 μm agglomerates without lixiviation of Eu and Dy from the nanoparticles to the polymer. The results indicate that the methodology applied can be expanded to other systems allowing the development of new efficient translucent materials.

Aknowledgements:

FAPESP, CAPES, CNPq

Keywords:

Persistent luminescence, nanoparticles, thin-films

Poster Presentation

Prospecting new opportunities for characterization of Perovskite-based Ca-Ni-Fe oxides for azo pollutants fast abatement through dark catalysis

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Dark heterogeneous catalysis dismisses the need for both light and additional chemicals, and it also complements or even replaces more traditional pollutant abatement processes. Although recently reported, dark catalysts take several hours to bring the pollutant concentration to under 50 %, tested just with low weight pollutants, and their structural-mechanism relations have remained uncharacterized. Therefore, calcium nickel-iron mixed oxides (CNF) based catalysts, synthesized targeting CaNixFe(1-x)O3-δ, were recently introduced by our group [1]. The oxides mixture demonstrated (under 50 % after 5 min) to be effective and fast on the degradation of several pollutants under dark conditions, without the addition of reagents or energy/light irradiation, degradation attributed mainly to Ni dopedCa2Fe2O5. The active species analysis revealed a reaction scheme initiated by the contact pollutant catalyst, followed by the pollutant molecule's breakdown, following the generation of hydroxyl radicals, electrons, singlet oxygen, and electrons/holes hopping within the material. It is anticipated that this work will inspire the future design of this sort of catalyst and prospecting new opportunities using Synchrotron radiation is very interesting and can be a chance for new cutting-edge scientific work. This presentation aims to structure some questions to be answered for further research on catalysts, such as reaction mechanisms; understand mechanisms of the effectiveness of the presence of certain metals in the combined oxides as a function of the structural organization and reception and transfer of charges; nature of functional groups and effectiveness of the catalytic reaction, among others.

References:

[1] Stefane V. Besegatto, Adriano da Silva, Carlos E.M. Campos, Selene M. A. Guelli Ulson de Souza, Antônio A. Ulson de Souza, Sergio Yesid Gomez Gonzalez, Perovskite-based Ca-Ni-Fe oxides for azo pollutants fast abatement through dark catalysis, Applied Catalysis B: Environmental 284 (2021) 119747. DOI:10.1016/j.apcatb.2020.119747

Aknowledgements:

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Keywords:

Perovskite, heterogeneous catalysis, calcium-nickel-iron oxides, dark catalysis, X-ray diffraction, rietveld

Poster Presentation

Quantitative phase analysis and ceramic/graphene composite performance

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Refractory materials require a high melting point. This is usually engineered in ceramics combining not only high hardness, but chemical inertia and high Young modulus. Thus, they are frequently used in industry as a component of fabrication tools or raw materials for the final product. The challenge in this class of material is to decrease their high fragility, due to its low fracture toughness, keeping (or even increasing) its hardness. To perform that, manufacturing composites is a conventional way. In this work, the composites were synthesized by mixing two different ceramic materials as matrix and nanoparticles aimed at increasing their mechanical properties. The matrix here is alumina and yttria-stabilized zirconia (YSZ) and the nanoparticle is multilayered graphene (MLG). The MLG weight concentrations were 0%, 0.5%, 0.75%, 1% and 1.25%. Vickers hardness and X ray diffraction were carried out at the bulk material. As expected, the increase of MLG concentration increased the mechanical properties. Despite being observed by scanning electron microscopy, the graphene phase could not be detected by conventional X ray diffraction measurement and higher flux and resolution XRD measurements are required. As a result, two non-intuitive results were observed. First, the increase of mechanical properties stops at 0.75% and then the fracture toughness decreases. And secondly, an exponential increase in the cubic phase proportion of YSZ is observed when the MLG concentration increases. Searching for the structure-microstructure-property relationship on this system, here is discussed this result and how it can influence the final mechanical properties, such as fracture toughness and hardness.

Aknowledgements:

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Keywords:

Graphene, XRD, ceramics, composites

Poster Presentation

SAPUCAIA: the small-angle scattering beamline of SIRIUS

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SAPUCAIA is a second-phase beamline of SIRIUS aimed to reach the large Brazilian SAXS user community. It was conceived and designed to have a high performance and high reproducibility, taking full advantage of the great increase in brilliance of SIRIUS, in addition to its easy use and change of experimental setups. Its source is planned to be two KYMA undulators placed at a high beta straight section, providing a beam with small intrinsic divergence and, consequently, making unnecessary the optimization of the experimental setups. The primary optics will contain an HD-DCM monochromator followed by a toroidal mirror for beam focalization and harmonic rejection. The beam will be approximately rounded at sample position – 200 μm of diameter, 48 meters from source – reaching 5 x 10^{13} ph/s at 10 KeV. It will host a 15 m long x 2 m diameter tunnel kept under low pressure where the detector system will be placed. This system can move along rails allowing to change automatically the sample to detector distance from 0.5 to 10.5 m in few minutes, covering a range in the reciprocal space from 10^{-3} to 30 nm^{-1} – sizes from the order of few Angstroms to about 4 μm. Due to the high flux and detection system, it will be possible to perform time-resolved measurements in the millisecond time-scales. The optics was designed to have no vacuum windows through the beam path, allowing very low parasitic scattering.

The beamline will be equipped with an automatic liquid sample changer that will reduce the time of the experiments and data collection, also allowing to change temperature and reducing the minimum volume required to only a few dozens of μl. For the user community that works with solid or viscous samples, the beamline will open the possibility to perform remote experiments using a mail-in system. WAXS technique will also be measured in SAPUCAIA beamline, allowing to obtain information also on the molecular conformation of studied structures.

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Poster Presentation

SAXS and XAFS In-Situ temperature dependent study of gold nanostructures synthesis and stability

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Ultrathin gold nanowires (AuNWs) have attracted great interest due to their unique conductivity properties making them suitable candidates for a myriad of applications. Many relatively simple syntheses protocols have been reported using gold salts and surfactants in organic media, in general $HAuCl4{\cdot}3H2O$ and oleylamine (OAm) in hexane, resulting in micrometer long wires with sub 5 nm diameters. Comparing similar reported procedures, the OAm/Au molar ratio appears to be of crucial importance to lead the synthesis toward thin wires with high efficiency or spherical nanoparticles, although the effect of the synthesis temperature is still a factor to address systematically [1, 2, 3]. Moreover, temperature stability studies of AuNWs are fundamental for future developments and applications.

Here we present a small angle x-ray scattering (SAXS) and extended X-ray absorption fine structure (EXAFS) in situ temperature dependent study of an already reported AuNWs synthesis [4]. We also studied the stability of the final nanostructures in solution in the range of 20 − 90°C. SAXS and EXAFS measurements were complemented with transmission electron microscopy (TEM) images. OAm/Au molar ratio was kept at 40, well within the nanowires high yield range, and the synthesis temperatures varied from 20 to 80°C without stirring. It was found that the synthesis evolves toward the formation of nanowires when the temperature is kept below 40℃, and ununiform nanoparticles started to be produced above this temperature. In addition, the AuNW were found to be stable up to 70°C, when the correlation between AuNWs began to decrease and above 80℃ the nanowires were disassembled to generate correlated nanoparticles. In situ XAFS measurement at Au L3 edge showed an acceleration in the gold reduction rate from Au(3) to Au(1) with higher temperatures, and the Fourier transformed of EXAFS spectra showed how the gold coordination transitions from Au-N to Au-Au at earlier times.

References:

[1] Loubat, A.; Impéror-Clerc, M.; Pansu, B.; Meneau, F.; Raquet, B.; Viau, G.; Lacroix, L.-M. Langmuir 2014, 30 (14), 4005–4012. DOI:10.1021/la500549z

[2] Loubat, A.; Lacroix, L.-M.; Robert, A.; Impéror-Clerc, M.; Poteau, R.; Maron, L.; Arenal, R.; Pansu, B.; Viau, G. J. Phys. Chem. C 2015, 119 (8), 4422–4430. DOI:10.1021/acs.jpcc.5b00242

[3] Kirichkov, M. V.; Guda, A. A.; Budnyk, A. P.; Bugaev, A. L.; Lastovina, T. A.; Shapovalov, V. V.; Guda, S. A.; Trigub, A. L.; Rusalev, Y. V.; Chernyshev, A. V.; Lamberti, C.; Soldatov, A. V. Radiat. Phys. Chem. 2020, 175. DOI:10.1016/j.radphyschem.2018.11.021

[4] Pschunder, F.; Puig, J.; Giovanetti, L. J.; Huck-Iriart, C.; Requejo, F. G.; Buceta, D.; Hoppe, C. E.; Ramallo-López, J. M. J. Phys. Chem. C 2018, 122 (50), 29051–29061. DOI:10.1021/acs.jpcc.8b10449

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Keywords:

SAXS, XAFS, gold, nanowires, in situ, temperature

Poster Presentation

Study of electronic structure of carbonaceous aerosols using synchrotron techniques

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To study atmospheric aerosols has been shown every time more essential to grow our understanding about the dynamic of Environment. Beyond its act to transport substances between ground and atmosphere, the aerosols have some optical properties and hygroscopic properties that directly affect the water vapor column present in the atmosphere and the cloud condensation nuclei that promote rain. Nonetheless, there are important gaps in the comprehension of this atmospheric element [1]. Recent studies have shown that aerosols can coexist in 3 different liquid phases [2], this discovery can provide a better comprehension about aerosol formation and its dynamics in the atmosphere. This study looks to utilize the techniques of spectroscopic based on synchrotron light as the X-ray absorption (XANES) in carbon K-edge and the photoemission (XPS) of level 1s of C and O to probe the electronic structure of carbonaceous aerosols [3]. To realize this experiment the samples of aerosols must be kept in a monitored cell and isolated from the experimental chamber in ultra-vacuum conditions. Furthermore, the synchrotron beam from Sirius, with high intensity and micrometers dimensions it's adequate for this experiment, because it reduces the volume and the time of interactions with the sample. This experimental results together with the elaborations of a theoretical model, must contribute to current comprehension of atmospheric aerosols, mostly the carbonaceous. The viability of this proposal depends on the development of one sample environment that allows the realization of measures in ambient pressure coupled with the experimental station. The surrounding of the sample must be controlled and monitored by the cell during the experiment, to parameters such as pressure, temperature, relative humidity and aerosols formation. Certainly, the implementation of this instrumentation can help as in the execution of this experiment as future searches in the area of Environmental Science.

References:

[1] RABHA, Shahadev; SAIKIA, Binoy K. Advanced micro- and nanoscale characterization techniques for carbonaceous aerosols. [S. l.]: Elsevier Inc., 2019. DOI 10.1016/B978-0-12-816699-4.00018-9
[2] HUANG, Yuanzhou; MAHRT, Fabian; XU, Shaun; SHIRAIWA, Manabu; ZUEND, Andreas; BERTRAM, Allan K. Coexistence of three liquid phases in individual atmospheric aerosol particles. Proceedings of the National Academy of Sciences of the United States of America, vol. 118, no. 16, 20 Apr. 2021. DOI:10.1073/pnas.2102512118
[3] OUF, F. X.; PARENT, P.; LAFFON, C.; MARHABA, I.; FERRY, D.; MARCILLAUD, B.; ANTONSSON, E.; BENKOULA, S.; LIU, X. J.; NICOLAS, C.; ROBERT, E.; PATANEN, M.; BARREDA, F. A.; SUBLEMONTIER, O.; COPPALLE, A.; YON, J.; MISERQUE, F.; MOSTEFAOUI, T.; REGIER, T. Z.; ... MIRON, C. First in-flight synchrotron X-ray absorption and photoemission study of carbon soot nanoparticles. Scientific Reports, vol. 6, no. October, p. 1–12, 2016. DOI:10.1038/srep36495

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Keywords:

Carbonaceous aerosols, XANES, XPS, instrumentation

Poster Presentation

Study of the formation of aqueous clusters on atmospheric aerosols using synchrotron techniques

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The water in the atmosphere exists in the gas phase as water vapor and as droplets in the aqueous phase and wet aerosols. Due to their hygroscopic characteristics, aerosols act as condensation nuclei (NC), regulating the process of water vapor condensation on the aerosol surface, interfering with the processes of cloud and dew formation [1]. Through the dynamic interaction with water, the aerosol can act in the energy balance of the earth system, as a source or sink of heat, regulating the thermodynamics of the air. Environmental analyzes based on net radiation measurements applied to the turbulent covariance method point to the non-closure of the energy balance in ecosystems, resulting in an energy deficit of up to 20% that has not yet been justified by current models [2]. The impact and interaction of aerosols on the atmospheric energy balance is a mechanism that can be quite relevant and still completely unexplored. It is assumed that during the night cycle, the saturation condition occurs in the atmosphere close to the surface of trees and the water vapor condenses on the aerosols forming small clusters of aqueous solutions coexisting in distinct liquid phases [3]. It is intended to associate thermodynamic and kinetic modeling with X-ray spectroscopy, to analyze and monitor the dynamics of water molecules between the gaseous and aqueous phases on the surface of aerosols. To carry out the experiment, a sample environment with control and reproducibility of atmospheric parameters, such as relative humidity, temperature and ambient pressure, in addition to the type and concentration of the aerosol, is required. We expect use the synchrotron light spectroscopic techniques, such as photoemission (XPS) of the 1s level of the O and absorption (XANES) of the K edge of the O, to explore the binding and oxidation states, as well as the elemental chemical composition and relative concentrations of clusters of aqueous solutions under varied experimental conditions.

References:

[1] J. H. Seinfeld e S. N. Pandis, ATMOSPHERIC From Air Pollution to Climate Change SECOND EDITION. 2006.
[2] T. Foken, "The energy balance closure problem: An overview", Ecol. Appl., vol. 18, no 6, 2008. DOI: 10.1890/06-0922.1.
[3] Y. Huang, F. Mahrt, S. Xu, M. Shiraiwa, A. Zuend, e A. K. Bertram, "Coexistence of three liquid phases in individual atmospheric aerosol particles", Proc. Natl. Acad. Sci. U. S. A., vol. 118, no 16, 2021. DOI: 10.1073/pnas.210251211

Aknowledgements:

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Keywords:

Atmospheric aerosols, water, hygroscopy, XPS, XANES

Poster Presentation

Screening of fragments as a strategy to develop Leishmania braziliensis dihydroorotate dehydrogenase inhibitors

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Cutaneous leishmaniasis (CL) is a neglected tropical disease spread over 85 countries and responsible for up to 119,600 deaths/year, only in Brazil [1]. The available drugs display high toxicity and low efficacy, highlighting the need for novel therapeutic alternatives to fight CL [2]. Aiming at identifying compounds that bind outside orotate-binding site, fragments that shift *Leishmania braziliensis* dihydroorotate dehydrogenase Tm (melting temperature) in Thermofluor assays (DTm ≥ 1.0 °C), but not in ThermoFMN, were selected, as thermal stabilization in ThermoFMN assays is highly correlated to competitive inhibitors. Among 102 fragments were assayed at a single concentration (0.5 mM) and 16 hits that show concentration-response behavior were identified. Currently, kinetic and co-crystallization assays are being conducted to exclude false-positives, confirm their non-competitive mechanism of action and select the most promising fragment for hit-to-lead optimization.

References:

[1] Cohen JP, Silva L, Cohen A, Awatin J, Sturgeon R. Progress Report on Neglected Tropical Disease Drug Donation Programs. Clin Ther. 2016;1–12.

[2] Castro M, Cossio A, Velasco C, Osorio L. Risk factors for therapeutic failure to meglumine antimoniate and miltefosine in adults and children with cutaneous leishmaniasis in Colombia : A cohort study. 2017;1–14.

Aknowledgements:

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Keywords:

Leishmania brazilienses, dihydroorotate dehydrogenase, fragment screening

Oral Communication

Simultaneous X-ray fluorescence and ptychography experiments performed in hybrid organic-organic perovskites (HOIPs) thin films at the Tarumã station of the Carnaúba beamline

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This work presents the preliminary results of simultaneous X-ray fluorescence and ptychography experiments performed in hybrid organic-inorganic perovskites (HOIPs) thin films at the Taruma station of the Carnaúba beamline from a methodological point of view. The compositions studied here are $\mathrm{Cs}_{y}\mathrm{FA}_{1-y}\mathrm{Pb}(\mathrm{Br}_{x}\mathrm{I}_{1-x})_{3}$, y:x=20:38, 30:38, and 40:38. Close to the nominal beamline performance allows X-ray fluorescence maps with about 200nm x 500 nm spatial resolution. Preliminary X-ray ptychography reconstructions ensure pixel sizes between 12 to 18 nm, which allowed to visualize micro and nanometer features in the HOIPs. The micrometer-scale exhibits the well-known wrinkle structures[1,2,3] within which different regions show up, correlating with different Br/Pb and I/Pb chemical ratios. The nanometer-scale, from X-ray ptychography, exhibits grain boundaries of the order of a few nanometers, as previously observed by AFM topography. We will present here compositional trends concerning the correlation between morphology and chemical segregation. The ptychography experiments were performed in two different beam energies: 9750 eV and 13657 eV. These energies values were chosen to optimize the fluorescence maps from the different elements present in the sample, acquired simultaneously. Beam damage was not observed in these samples during the experiment. However, compositions more sensitive to beam damage were systematically tested to verify the possible influence of the nanoprobe flux on the sample. A characteristic I^{-} migration, seen by the X-ray fluorescence data, occurs from the center to the peripheral contour in the irradiated region. Correlated to that, the beam damage signature shows up in the ptychography reconstruction as a region with a higher phase value, consistent with observing a material scape from the irradiated region, as observed by the fluorescence. The same beam-induced segregation does not appear in the Pb^{2+}, and only a slight variation occurs in the Br^{-} content.

References:

[1] Kim, Seul-Gi, et al. "How antisolvent miscibility affects perovskite film wrinkling and photovoltaic properties." Nature communications 12.1 (2021): 1-10.
[2] Bush, Kevin A., et al. "Controlling thin-film stress and wrinkling during perovskite film formation." ACS Energy Letters 3.6 (2018): 1225-1232.
[3] Nasti, G., et al. "Patterning of perovskite–polymer films by wrinkling instabilities." Soft matter 13.8 (2017): 1654-1659.

Aknowledgements:

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Keywords:

Ptychography, coherent imaging, fluorescence, hybrid perovskite, radiation damage

Poster Presentation

Strong Co-Mo interaction behind unexpected physicochemical properties in $SrMo_{0.9}Co_{0.1}O_{3-\delta}$ perovskite

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A novel combined chemical procedure was employed to synthesize homogeneous $SrMo_{0.9}Co_{0.1}O_{3-\delta}$ (SMC) perovskite at lower temperatures (900 °C). The physicochemical properties of SMC were analyzed by means of in situ X-ray diffraction (XRD) and X-ray Absorption Spectroscopy (XAS) experiments under reducing and oxidizing conditions from 20 to 700 °C. The study reveals a strong interaction between Mo and Co cations in SMC perovskite, which leads to an unexpected oxidation number speciation of them and a critical modification of their first coordination shell. Perovskite-like unit cells containing Co in their center can drastically increase the occupation number of oxygen anions, enhancing SMC oxygen storage capability. Under reducing conditions, these loosely bonded anions are easily released from the material to chemically react with H_2 in the gas phase. These findings bring novel insights into the physicochemical processes that take place in SMC materials, which give rise to the catalytic and electrochemical activity that spot this material as candidate for IT-SOFC anode application.

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Keywords:

Perovskites, SOFC, XAS, XRD

Oral Communication

Structural characterization of the co-chaperone SGT of Aedes aegypti: a small-angle X-ray scattering approach

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Protein function is directly related to molecular structure and environment, so issues related to protein folding, such as misfolding, unfolding and aggregation, are not only of special fundamental research interest, but also related to diverse pathologies, such as neurodegenerative diseases and certain types of cancer. Molecular chaperones are proteins that comprise the Protein Quality Control (PQC) along with the proteasome system to maintain proteostasis, being central for cell survival. Co-chaperones are auxiliary elements of the PQC, and the Small Glutamine-rich TPR-containing protein (SGT) is a co-chaperone that interacts with Hsp70 and Hsp90, mediating the action between these chaperones and stabilizes the ADP/Hsp70/client protein complex, among other functions. SGT are dimeric proteins, and each monomer has a dimerization domain in the N-terminal, a TPR domain that interacts with chaperones, and a glutamin-rich unstructured C-terminus that binds to hydrophobic regions of client proteins. The objective of this study was to elucidate the structural features from SGT of Aedes aegypti (AaSGT), an important mosquito in disease proliferation. To do so, we employed Small Angle X-Ray Scattering (SAXS), which brings information regarding protein size, shape and dynamics of proteins in solution. This analysis is part of a wider work that sought to study the structure and function of the C-terminal region of AaSGT in an effort of collecting more information on the Aedes aegypti chaperone network. Two AaSGT constructs were expressed and purified: a wild type and a truncated state that didn't contain the C-terminal region. Along with other techniques, such as CD and SEC-MALS, SAXS has shown that both constructs are elongated dimers in solution, with a more disordered profile in the wild type construct. This highlights SGT's overall shape, the role of the N-terminal region in dimerization and also the highly disordered state of the C-terminal region of AaSGT.

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Keywords:

Protein folding, chaperones, SAXS

Oral Communication

Study of vapors sensing materials employing rapid acquisition of total scattering experiments analyzed by the atomic pair distribution function method at Jatobá beamline

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Atomic pair distribution function (PDF) is an attractive technique to analyze X-ray total scattering data. PDF is a powerful characterization tool in material science, and it is an alternative /or complement to conventional X-ray diffraction (XRD) and X-ray absorption spectroscopy. Contrary to XRD that only reflects information about the average structure, PDF analysis allows the detection of small local distortions [1], bringing information of the local and medium-range order. This method has also been used to study amorphous phases of materials, i.e., those presenting XRD patterns containing broad and low-intensity Bragg peaks. Additionally, it has been useful in structural studies of nanomaterials in which their characteristic sizes limit the proper study by conventional XRD [1]. PDF helps to answer a series of questions regarding local structure, nano-phase detection and quantification [2], and elucidate anion redox or sensing reactions [3]. The first PDF experiment performed at LNLS was measured at the XDS beamline studying ferroelectic materials with perovskite structure [4].

The following characteristics are mandatory to perform total scattering experiments to be interpreted by PDF: (i) reach high momentum transfer (Q), preferably higher than 20 Å-1; (ii) obtain high resolution in Q and good statistics (high signal-to-noise ratio) for high Q-values; and finally, (iii) use instruments with low background noise, since the data need to have a better signal-to-noise ratio than for Rietveld refinement [1]. The projected beamline, Jatobá, will satisfy all these characteristics. It would reach energy values up to 71 keV, that it is reflected in a Qmax of 37 Å-1 at the 2D detector.

We propose to analyze by PDF nanostructures of (Cr,Ti)2O3 as a function of temperature and at different atmospheres. With this experiment we expect to elucidate if the surface if affected with the external parameters (temperature and atmosphere) producing nanocluster with distorted structure.

References:

[1] T. Egami & S. Billinge, "Underneath the Bragg peaks: structural analysis of complex materials. Pergamon, 2003.
[2] M.E. Saleta et al., "Local structure on BaFe2As2: formation of nanotwins studied by atomic pair distribution function", 27th Annual Users' Meeting LNLS (RAU), Campinas – Brazil, November 2017.
[3] Zhu H. et al., "A New Insight into Cross-Sensitivity to Humidity of SnO2 Sensor" Small 14 (2018), 1703974.
[4] M.E. Saleta, et al., "Atomic pair distribution function at the Brazilian Synchrotron Light Laboratory: application to the Pb1−xLaxZr0.40Ti0.60O3 ferroelectric system", J. Synch. Rad. 24 (2017), 1098–1104.

Keywords:

Rapid acquisition PDF

Poster Presentation

Studying ferroelastic domain dynamics in CsPbBr3 nanowires using synchrotron X-ray diffraction techniques

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Metal halide perovskites (MHPs) has shown impressive results in solar cells, light emitting devices, and scintillator applications, but questions regarding its complex structure are still open [1]. Image dynamics of ferroelastic domains in MHPs requires a challenging combination of high spatial resolution, strain sensitivity and long penetration depth. With recent developments in X-ray optics and the advance of synchrotron sources, including the new fourth generation facilities [2,3], it is now possible to study the structural properties of MHPs nanoscale domains.
We studied the dynamics of domains in CsPbBr3 nanowires across the orthorhombic to tetragonal crystal phase transition using in situ temperature-dependent nanofocused scanning X-ray diffraction with a 60 nm beam at the NanoMAX beamline (MAX IV) [4]. The formation of highly organized domain pattern near 80 ℃ revealed the ferroelastic nature of the domains. A different approach using the same technique also indicated the formation of ferroelastic domains at room temperature on CsPbBr3 nanowires when applying stress with an Atomic Force Microscope tip [5]. Orthorhombic domains with orthogonal lattice orientation and terminating on {112}-type domain walls were noted near manipulated areas. More recently, making use of the newly developed Full-Field Diffraction X-ray Microscopy technique, at the ID01 beamline (ESRF), we probe the domain evolution near the critical temperature with high temporal resolution [6]. Studying the formation of ferroelastic domains within single-crystal perovskites is crucial to better understand their fundamental properties, helping on the development of perovskite-based devices.

References:

[1] Zhang, W.; Eperon, G. E.; Snaith, H. J. (2016). Nature Energy 1 (6), 16048. DOI: 10.1038/NENERGY.2016.48
[2] Bjorling, A.; Kalbfleisch, S.; Kahnt, M.; Sala, S.; Parfeniukas, K.; Vogt, U.; Carbone, G.; Johansson, U. (2020). Opt. Express 28 (4), 5069. DOI: 10.1364/OE.386068
[3] Leake, S. J.; Chahine, G. A.; Djazouli, H.; Zhou, T.; Richter, C.; Hilhorst, J.; Petit, L.; Richard, M-I; Morawe, C; Barrett, R; Zhang, L; Homs-Regojo, R. A.; Favre-Nicolin, V.; Boesecke, P; Schulli, T. U. (2019). J. Synchrotron Rad. 26, 571. DOI: 10.1107/S160057751900078X
[4] Marçal, L. A. B.; Oksenberg, E.; Dzhigaev, D.; Hammarberg, S.; Rothman, A.; Björling, A.; Unger, E.; Mikkelsen, A; Joselevich, E; Wallentin, J. (2020). ACS Nano 14, 15973. DOI: 10.1021/acsnano.0c07426
[5] Marçal, L. A. B.; Benter, S.; Irish, A.; Dzhigaev, D.; Oksenberg, E.; Rothman, A.; Sanders, E.; Hammarberg, S.; Zhang, Z.; Sala, S.; Björling, A.; Unger, E.; Mikkelsen, A; Joselevich, E; Timm, R.; Wallentin, J. (2021). Phys. Rev. Mat. 5, L063001. DOI: 10.1103/PhysRevMaterials.5.L063001
[6] Marçal, L. A. B.; Dzhigaev, D.; Zhang, Z.; Sanders, E.; Rothman, A.; Zattering, E.; Bellec, E.; Schulli, T.; Mikkelsen, A; Joselevich, Wallentin, J. In preparation.

Poster Presentation

Synchrotron PXRD as tool to study the influence minor constituents have in crystal structure of clinker phases

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Alternative fuels has been widely adopted by cement industry as an unavoidable strategy to reduce the amount of CO2 emissions by the clinker manufacturing. However, the incorporation of foreign elements by clinker phases, coming from the use of alternative fuels, e.g. biomass, coke, can be a source of concern [1], possibly influencing mechanical properties [2] and durability of concrete mixed with this material [3]. There is evidence that Mg and S, which can be found in raw materials and alternative fuels composition, respectively, together influence the stabilisation of the M3 and M1 alite polymorphs, respectively [4]. To date, mostly alite crystal structure models do not give information about the presence of minor constituents. Models obtained from single crystal cannot properly represent the phases produced inside large scale kilns, some metastable high temperature polymorphs for instance, which migth be the case of alite phase. More realistic structural models of clinker phases are needed, suplying relevant information for quality control of cement manufacturing through the use of Rietveld refinement of PXRD data. In a recent study, a revision of M1 alite crystal structure model using synchrotron high resolution PXRD data collected from an industrial clinker sample was performed, representing, for the first time, the position minor constituents migth occupy inside the crystal structure of a real industrial clinker phase [5]. The study observed that foreign ions would probably occupy preferential sites, in disagreement with previous expectations, leading to distortions in Si-O and Ca-O bond lengths. The use of synchrotron powder X-ray diffraction over conventional lab XRD allows much higher resolution data to be obtained due to the high flux and collimated X-ray beam, improving the signal:noise ratio as well as the sharpening of peaks. In a complex multi-phase system, which is the case of real industrial clinkers, the high quality data allows multiphase refinements. This technique also provides greater confidence in deconvolution of overlapping peaks without using selective dissolution techniques, which capacity to remove minor constituents within crystal structure of phases could be an issue. Substitutional and interstitial sites for minor constituents can be investigated using the Bond Valence Sum (BVS) technique [6], allowing the amount of incorporated foreign ions estimation, which is important for waste processing inside cement kilns.

References:

[1] F. Sorrentino, Cem. Concr. Res., vol. 41, no. 7, pp. 616–623, 2011.
[2] T. Staněk and P. Sulovský, Cem. Concr. Res., vol. 32, no. 7, pp. 1169–1175, 2002.
[3] S. M. Torres, C. A. Kirk, C. J. Lynsdale, R. N. Swamy, and J. H. Sharp, Cem. Concr. Res., vol. 34, no. 8, pp. 1297–1305, 2004.
[4] X. Li, W. Xu, S. Wang, M. Tang, and X. Shen, Constr. Build. Mater., vol. 58, pp. 182–192, 2014.
[5] W.V. Fernandes, S. M. Torres, C. A. Kirk, A. F. Leal, M. R. Lima Filho, D. Diniz, Cem. Concr. Res. (accepted) 2020 .
[6] I. D. Brown, The Chemical Bond in Inorganic Chemistry: The Bond Valence Model. 2010.

Keywords:

Clinker, polymorphism, bond valence

Poster Presentation

Synchrotron radiation micro-CT experimental setup on biological sample

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Microcomputed tomography (micro-CT) technique has been highly used for studying the structural and morphological properties of biological specimens mainly due to the advantage of being a non-destructive technique. With the advent of synchrotron laboratories, such as Sirius (Campinas, Brazil), micro-CT technique has become highly sophisticated, as it is able to obtain high spatial and contrast resolution about a specimen, among other advantages of a synchrotron laboratory [1][2][3]. In this work, in order to optimize micro-CT imaging protocols for small animals, different acquisition setups and reconstruction of the scanned dataset were tested. The biological model used was the tadpole *Thoropa miliaris*, in which 5 developmental stages were selected (according to the Gosner table) [4] and scanned on the SYRMEP beamline of the Elettra synchrotron laboratory (Trieste, Italy). *T. miliaris* tadpole was scanned using a white X-ray beam filtered using 0.5 mm of Silicon resulting in a spectrum with a mean energy of 20 keV. The exposure time per projection was 100 ms by taking 1800 and 3600 projections over 180° and 360°, respectively, with different configurations of sample-detector distance (50 mm, 150 mm and 250 mm). The experiment was conducted with 2 μm of isotropic voxel size, corresponding to a field of view of about 4 mm^2. Some samples stained with 1% metallic iodine were also tested in the phase-contrast regime. The optimization of the experimental setup on the SYRMEP beamline allowed few details to be adjusted during the reconstruction process of the scanned dataset. As a consequence, the detailed study of the structures of the specimen by means of semiautomatic and automatic segmentation using Deep Learning showed a significant improvement. Many discussions remain open about other ways to optimize from the experimental setup of the micro-CT technique, the reconstruction process, and even the post-processing using Machine Learning for structure segmentation.

References:

[1] Broeckhoven C., et al (2017). Methods Ecol Evol, 8: 358-369.
[2] Fidalgo G., et al. Scientific Reports (2020), 10:18934.
[3] Clark D.P., et al (2021). Physica Medica, 88: 175-192.
[4] Gosner, K.L. (1960). Herpetologica, 16: 183.

Keywords:

Synchrotron radiation, microtomography, biological imaging, deep learning, image segmentation

Poster Presentation

Synchrotron-based XRF applied to the paleohistological study of giant sloths' osteoderms

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The Santa Elina archaeological site (MT, Brazil) has a paradigmatic importance due to the possibility of one of the oldest human/fauna interactions. The shelter features an expressive rock art panel and a rich archaeological record containing lithic tools, bonfire structures, materials worked with plant fibers, and faunal remains attributed to human's culture. Among the most important records are the Pleistocene giant sloth (*Glossotherium* sp.) osteoderms (~7,000), displaying distinct shapes and sizes, and including some with surface modifications and fusions. Here, we investigate the chemical and histological features of two fossil osteoderms by synchrotron-based X-Ray Fluorescence (XRF) that resulted in unprecedented elemental imaging maps for this mylodontid species. Besides the detailed microstructure revealed by the cross-sections, we were able to observe a compact histological structure, composed predominantly by Zn-rich phases which we interpreted as collagen fiber bundles and growth lines parallel to the external surface. Our results also show conspicuous vascular channels filled by diagenetic traits corroborated by Sr, Ba, Ni and Eu enrichment and Ca and K depletion. Another sample analyzed represents two fused elements. Its imaging maps show distinct directions of the growth lines along the two centers of ossification, highlighted by Zn. Our team is still performing other synchrotron-based analyses in order to investigate if some of the distinct shape and fused osteoderms are related to a bone disease in this animal, as well as the taphonomic history of these fossils.

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Keywords:

XRF, paleontology, osteoderms, giant sloth, pleistocene, histology, taphonomy

Poster Presentation

Synthesis and characterization of silicate bioactive glass doped with Nb and Ga: a promisor material in the treatment of osteosarcomas

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According to the American Câncer Society, osteosarcomas are responsible for 2% of all childhood cancers, and 8,9% of all deaths caused by cancer during this age are accounted for by bone and joint cancers. Currently, the treatment involves the removal of the affected part, followed by an aggressive therapy which leads to several collateral effects. In the present project, the development and characterization of a multifunctional system of mesoporous bioactive glasses (MBG) doped with Nb and Ga was proposed. In this approach, MBG could act as potential drug carriers for controlled and local drug delivery, while the ionic product from glasses dissolution plays a decisive role in ion therapy. The bioactive glass was synthesized via the sol-gel route, which helps to achieve greater structural homogeneity. The MBG thermal properties were studied via TGA and DTA, its microstructure and morphology was analyzed via FTIR and SEM, carried out at the LNNano, and its leaching behavior was studied through pH variation studies, while the surface area and textural properties were studied via BET. The presence of Nb in the glassy matrix greatly decreased the network connectivity, improving the solubility, whereas Ga has shown to have an opposite effect. The MBGs exhibit a stacking of nanometric plates, generating a material with a high surface area and high porosity. Complementary analyzes by X-Ray Absorption Fine Structure (XAFS) spectroscopy may be carried out at the LNNano in the future in order to obtain more information about the short range order of these bioactive glasses, which is extremely important for bioactivity.

References:

[1] Souza, Lucas et al. Comprehensive in vitro and in vivo studies of novel melt-derived Nb-substituted 45S5 bioglass reveal its enhanced bioactive properties for bone healing. Sci. Rep. (2018).
[2] Hart, M. M. & Adamson, R. H. Antitumor activity and toxicity of salts of inorganic group 3a metals: aluminum, gallium, indium, and thallium. Proc. Natl. Acad. Sci. U. S. A. (1971).
[3] Lopes, João et al. Investigation of citric acid-assisted sol-gel synthesis coupled to the self-propagating combustion method for preparing bioactive glass with high structural homogeneity. Mater. Sci. Eng. (2019).

Aknowledgements:

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Keywords:

Bioactive glass, niobium, gallium, osteosarcoma

Poster Presentation

Synthesis and physicochemical characterization of aluminium-based hydrogels through the Epoxide Route

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Aluminium hydrogels (AlHG) represent a key material owning catalytic properties for a large variety of industries, specially due to their transparency in a wide range of energies and their high stability.[1,2] However, the chemical nature of the phases, shape and size distribution are important aspect that need to be addressed. For instance, precise laboratory-based methods[3] would permit the identification of AlHGs growth, the effect over the chemical reactivity, as well as the physicochemical properties of the material.1 Furthermore, in recent years, the interest in eco-friendly synthetic procedures has been increased, mainly in obtaining of compounds under mild conditions and aqueous or biocompatible solvents.[4]

In line with this, the Epoxide Route[5] has shown a high versatility for leading the homogeneous precipitation at room temperature of several inorganic and hybrid materials,[6,7] including metal oxides/hydroxides,[7] in a highly controllable scenario.[5] In addition, due to this method can be performed in one step approach and at room temperature (desirable characteristics for synchrotron experiments) several in situ experiments can be carried out from kinetic to thermodynamic information.[8]

In this work, the synthesis of AlHGs through the Epoxide Route was characterized via time-resolved Small Angle X-Ray Scattering (SAXS) experiments, performed using synchrotron light sources, which has allowed the thorough characterization of key features related to the nucleation and growth processes. Interestingly, the results indicate that the AlHG nanoparticles have a relatively slow growth kinetic, from an initial quasi-spherical morphology which evolves to a lamellar symmetry (1D to 2D growth process). It is worth mentioning that this growth process and the features of the obtained phases are conserved even with a high concentration precursor, a fundamental aspect from the industrial point of view. Additionally, by tuning the nature of the solvent mixture the size of the AlGH nanoparticles can be enlarged by simply increasing the ethanol-water ratio. Therefore, this work highlights the use of the Epoxide Route as a versatile synthetic tool for in situ understanding of growth mechanism in the design of new composites with unexplored properties.[9]

References:

[1] S. Shen, P. S. Chow, F. Chen, S. Feng and R. B. H. Tan, J. Cryst. Growth, 2006, 292, 136–142.
[2] A. D. V. Souza, C. C. Arruda, L. Fernandes, M. L. P. Antunes, P. K. Kiyohara and R. Salomão, J. Eur. Ceram. Soc., 2015, 35, 803–812.
[3] X. Zhang, W. Cui, K. L. Page, C. I. Pearce, M. E. Bowden, T. R. Graham, Z. Shen, P. Li, Z. Wang, S. Kerisit, A. T. N'Diaye, S. B. Clark and K. M. Rosso, Cryst. Growth Des., 2018, 18, 3596–3606.
[4] P. Kwolek and M. Wojnicki, J. Photochem. Photobiol. A Chem., 2014, 286, 47–54.
[5] V. Oestreicher and M. Jobbágy, Langmuir, 2013, 29, 12104–12109.
[6] N. Tarutani, Y. Tokudome, M. Jobbágy, F. A. Viva, G. J. A. A. Soler-Illia and M. Takahashi, Chem. Mater., 2016, 28, 5606–5610.
[7] V. Oestreicher, D. Hunt, C. Dolle, P. Borovik, M. Jobbágy, G. Abellán and E. Coronado, Chem. - A Eur. J., 2021, 27, 921–927.
[8] V. Oestreicher and M. Jobbágy, Chem. - A Eur. J., 2019, 25, 12611–12619.
[9] V. Oestreicher, C. Huck-Iriart, G. Soler-Illia, P. C. Angelomé and M. Jobbágy, Chem. - A Eur. J., 2020, 26, 3157–3165.

Keywords:

Aluminium, hydrogel, epoxide route, SAXS

Oral Communication

The use of sparse projection acquisition to scan complex biological specimens for low-dose synchrotron micro-CT imaging

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The principle of image reconstruction for computerized microtomography (micro-CT) technique consists in transform a set of 2D images acquired with regular angular steps, and through a computational process obtain a 3D image. The quality of reconstructed micro-CT images is dependent on the number of projections (NoP) acquired during the material scanning process [1]. And in cases where the main goal is to obtain micro-CT scans with a low NoP to reduce the dose of radiation in the analyzed sample, the quality of the images is impaired. When these are associated with biological materials, perform a scan using sparse data acquisition reduces the absorbed radiation dose by the sample [2]. And, this is something of relevance as the radiation can cause irreversible damage to the studied material. Thus, the main goal of this work is to investigate whether it is possible to reduce the NoP during the material scanning process using a low dose setup (synchrotron radiation and phase contrast) without losing information on the structures of interest in biological materials, thus reducing the absorbed dose and minimizing the risk of damage by radiation to the analyzed material. Thoropa miliaris tadpole was used as a biological model. The projections were obtained on the SYRMEP beamline in the synchrotron laboratory ELETTRA. Five different reconstructions were simulated varying the NoP (n=1800, n/2, n/4, n/8 and n/16, n/32 and n/64) and using two different types of reconstruction algorithms, the FBP and the FISTA-TV. To assess the quality of the reconstructed images, structures of interest were segmented and analyzed to perceive losses associated with the sparse data acquisition. Provisional results showed that it is possible to reduce up to four times the number of projections during the acquisition process without considerable loss of information for the analyzed structure of interest.

References:

[1] Kak, Avinash C., Malcolm Slaney, and Ge Wang. "Principles of computerized tomographic imaging."MedicalPhysics29.1 (2002): 107-107.
[2] Vandeghinste B, Vandenberghe S, Vanhove C, Staelens S, Van Holen R (2013) Low-Dose Micro-CT Imaging for Vascular Segmentation and Analysis Using Sparse-View Acquisitions. PLOS ONE 8(7): e68449.

Poster Presentation

Tunable emission in BaF2 scintillator-polystyrene composite films

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This work reports the observation of tunable luminescent emission of barium fluoride (BaF2) scintillator-polystyrene composite films. Optical absorption (OA) measurement in the ultraviolet and visible (UV-VIS) range was performed to investigated the influence of nanoparticles in the opacity of the films. The luminescent properties of the films were analyzed by photoluminescence (PL) with excitation at a vacuum ultraviolet (VUV) region. The PL results showed that when BaF2 nanoparticles were incorporated into the polymeric matrix, the emission of the BaF2 self-trapped exciton emission (STE) can be excited at 5.6 eV, being 3.4 eV lower than observed for nanoparticles only. It was proposed an interaction mechanism between polystyrene and BaF2 due to a non-radiative transfer of energy. In addition, it was observed that the color of light emission can be tuned for different BaF2 content present in the polymer matrix due the changes in the relative emission intensities referent to the polystyrene and BaF2 bands. From chromatic coordinates for all samples was possible to observed that light emission could be tuned at different shades of color between blue and green.

Oral Communication

Understanding complex polymorphism in Ln-M-oda metal-organic frameworks

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Polymorphism in metal-organic frameworks (MOFs) is a common occurrence. Plenty of effort has been dedicated to control such structural variations. However, full rationalization remains a privilege of simple systems. Consequently, no generalized guidance for MOFs polymorphism has been proposed so far.[1]

We have studied a family of MOFs bearing the formula [Ln2M3(oda)6]·nH2O, with Ln, M and oda being a +3 lanthanide, +2 metal cation and the ligand oxydiacetate respectively.[2,3] This system exhibits cubic/hexagonal polymorphism, depending on the identity of Ln and M and on the synthesis method. The hexagonal form contains one M site with 2/m symmetry with M(oda)4(H2O)2 composition while the cubic contains two, with site symmetry 32 and 23 and compositions M(oda)6 and M(H2O)6, respectively. Trends on the preferred phase as a function of M have not been explained so far: MOFs of Cu and Ni showing Jahn-Teller distorted octahedra crystallize mostly in the hexagonal form, Ca and Mg showing no distortion in the cubic one, while Co and Zn in both.[2] We have recently demonstrated that substitution of Co for Ni can force the appearance of cubic phases in Ni rich MOFs, which is not observed when the pure Ni compound is synthesized.[3] We have formulated the hypothesis that the stabilization of the cubic phase can be explained just in geometrical terms associated to ionic radii of M cations. To validate the hypothesis, it is imperative to locate the distributions of Co and Ni within the two sites. The closeness of Ni and Co ions in the periodic table prevents this determination based on conventional X-ray diffraction.

We will show preliminary results and propose employing anomalous diffraction of doped single crystals and powders to elucidate the Ni/Co distribution in the sites of the cubic phase. Given the intrinsic averaging of the diffraction technique, we further propose to couple the experiment with XAS spectroscopies to study the local environments of both cations.

References:

[1] Aulakh, et al. (2015). Inorg Chem., 54, 8679.
[2] Igoa, et al. (2018). CrystEngComm, 20, 4942.
[3] Igoa, et al. (2020). CrystEngComm, 22, 5638.

Keywords:

MOFs, polymorphism, anomalous diffractions, X-ray absorption spectroscopy

Poster Presentation

Understanding the interface of nanostructured lipid carriers by advanced physicochemical characterization techniques

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Some cancer cells such as melanoma show low response and resistance to chemotherapy. Encapsulation of anticancer drugs in Drug Delivery Systems such as Nanostructured lipid carriers (NLC) may overcome such limitations. Here we describe the characterization of NLC for the sustained release of docetaxel. Design of Experiments were used in the optimization of a formulation composed of Myristyl Myristate (MM 65% w/w), Miglyol® 812 (MG 35% w/w) and Pluronic-F68 (P68 3% w/w). NLCDTX showed excellent physicochemical properties (size = 214.0 ± 10.9 nm; polydispersity = 0/09 ± 0.01; zeta potential = -24.2 ± 0.30 mV; concentration = 4.4 ± 0.4 x 10^{13} nanoparticles/mL, pH = 6.12 ± 0.24 and 12 months of shelf stability) and high DTX upload capacity (%EE = 97.3 ± 2.6, %DL = 7.5 ± 0.3). From nanotracking analyses we could picture NLCDTX composition, by the estimated number of excipient molecules (204 MM; 164 MG; 4 P68 and 16 DTX - x10^5 molecules/particle). CryoEM revealed the spherical morphology of the nanoparticles. In vitro kinetic experiments in Franz diffusion cells were conducted for DTX (free and encapsulated); the release curve of NLCDTX was described by the Weibull model, revealing DTX sustained release (>150 h). Small Angle Neutron Scattering (SANS) data revealed that DTX influenced the structural organization of NLC: by increasing its gyration radius, making the surface of the particles rough and inducing appearance of two distinct hydrophobic clusters. Raman imaging showed evidence of interaction between DTX and the surfactant (P68), what could explain the clusters revealed by SANS. Therefore, a novel Drug Delivery System was developed and robustly characterized. Structural analysis reinforced the good shelf stability of the optimized NLCDTX, supporting the testing of its therapeutic effect, *in vitro* and *in vivo*.

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Keywords:

Nanostructured lipid carriers, docetaxel, melanoma

Poster Presentation

Understanding the mixture stability synergy effect in Li-rich cathode materials by in operando XAFS measurements

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Li-ion batteries (LIBs) have an unmatchable combination of affordable cost, high energy storage capabilities and power density, making it the technology of choice for portable electronics, power tools, and hybrid/full electric vehicles [1]. In particular, Mn oxide and Mn oxide doped with different transition metals (Ni, Co, Ti, etc) have aroused great interest in recent years due to their higher loading tension and a relatively easy synthesis mechanism (for example, ball milling). Layered cathode materials as Lithium-rich manganese (LirMO) and Lithium nickel-manganese-cobalt with spinel-like structure (LMNCO) have received lots of attention due to its potential usage as cathodes materials for LIBs. However, LirMO layered materials presents capacity fading and low stability due the oxygen release during extended cycling [2] in contrast LMNCO materials shows better life cycle but a lower capacity than layered materials. It was demonstrated than a mixture of LMNCO and LirMO used as cathode improve the stability of LirMO and the energy storage density of LMNCO, but there is no detailed explanation of which is the mechanism that generate this synergic effect.

In order to shed some light on this problem in this work we present an in operando XAFS characterization during Li intercalation of different mixtures of materials with layered and/or spiels-like structure. These in operando measurements were made at the Mn and Ni K-edge at the DXAS beamline of Laboratorio Nacional de Luz Sincrotron (LNLS). In particular we present LIBs cathodes containing LMNO, LirMO, LMNCO-LirMO and a LMNO-LirMO combinations. Our results show different trend of changes at the Mn and Ni oxidation states as a function of the potential during the charge-discharge cycle that strongly depends on the type of mixture used.

References:

[1] J.M. Tarascon, M. Armand, Nature 414, 359–367 (2001).
[2] Peter M. Csernica, Samanbir S. Kalirai, Nature Energy volume 6, 642–652 (2021).

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Oral Communication

Understanding the plasmon enhanced upconversion in translucent films through nanofocused X-ray fluorescence

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Upconverting nanoparticles (UNPs) have gained more attention for their wide applications in photovoltaics and bioimaging. However, their intrinsic low efficiency is challenging for further developments. In this study, YF_3: Yb^{3+}, Er^{3+} 100 nm nanoparticles (UNPs) along with ~15 nm Spheric Gold Nanoparticles (AuNPs) were synthesized and incorporated into Hydroxy-Propyl-Methyl Cellulose (HPMC) thin, translucent films. These films were prepared by the addition of an homogeneous dispersion of the UNPs in HPMC aqueous solution which received the posterior addition of the AuNps previously prepared via Turkevich method. The presence of the gold nanoparticles induced an enhancement of 3 orders of magnitude in the upconversion efficiency. This huge plasmon induced increase indicated that the UNPs and AuNPs are very close.

These composites were mapped with nanofocused X-Ray fluorescence in the Carnauba beamline using 13657 eV irradiation and detecting Er (6950 eV), Yb(7415 eV) and Au (9713 eV) L_1 fluorescence. Serendipitously, despite Au having higher affinity to softer Lewis bases, like those present in the polymer chain, the majority of the AuNPs were found around the agglomerates of UNPs. It is not clear why Au bonds with the fluoride particles, but it is evident that this proximity is responsible for the enhancement of up-conversion luminescence. These remarkable results provide a gateway to design more efficient upconverting materials, opening the way to its application on a plethora of fields.

Aknowledgements:

FAPESP, CAPES, CNPq and CNPEM

Keywords:

Upconversion, plasmonic, nanoparticle

Poster Presentation

Unraveling hausmannite (Mn3O4) thin films surface structure by X-ray linear dichroism

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There is an urgent need to understand the relationship between oxide thin-film surface plane and its electronic properties because of its key role in molecular adsorption and surface reactivity as requested in optimal applications of magnetism to catalysis. The present work intends to resolve this open issue by investigating the surface structure and electronic properties of Mn3O4 thin films. To this end, well-defined Mn3O4 (110) and (001) surfaces were prepared and their electronic properties were explored by X-ray linear dichroism, XLD (the search light effect). The Mn3O4 thin films were extensively prepared on distinct noble metal substrates (Au(111), Cu (111), Ag (001)) with the aim of disentangling the film's electronic structure and their corresponding film strain from their free surface, bulk, and interface contribution. Our experiments revealed the sensitivity of the 3d orbital occupancy and their intensity ratio (dx2−y2/d3z2−r2) to the surface orientation. The variation of relative 3d occupation as a function of strain was quantified by using the XLD sum rules. These results reveal important aspects for the identification and further engineering of well-defined crystallographic surfaces in several fields of applications.

Keywords:

XLD, hausmannite

Poster Presentation

Usage of Scherrer's formula for polidisperse powder samples

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Line profile powder X-ray diffraction (XRD) patterns are the prints left by the coherence length scale of the scattered waves by electron distribution present in the powder samples. Diffraction peaks in the XRDs are the convolutions resulted from effects of the morphologies in the nanocrystallites. NP size, lattice strain and structural deffects, like stacking faults or twinning, collectively causes the line profile shape. Advanced X-Ray sources, like synchrotron facilities, endorse in situ experiments and allow to explore in details mechanisms of nucleation and growth of NP, and controlled formation.

Cubic and spherical silicon (Si) NPs were generated computationally, varying in size at each 1 nm, ranging from 1 to 70 nm. Making use of pair distance distribution functions (PDDF), derived from the Debye Scattering Equation (DSE), simulated XRD patterns from the individual NPs were obtained. Taking advantage of the inherently parallel structure of the DSE, PDDF calculations were approached via parallel computing using the application OpenMP for C++.

Real powder samples are polidisperse systems and there is a particle size distribution (PSD) associated to each sample. Assuming lognormal PSDs it becomes possible to investigate the effect of size distributions in the line profiles. Since there is a distribution of sizes, the total scattered intensity in the XRD patterns is the sum of the intensities scattered individually by each particle of size L, weighted by the number of particles L.

The Scherrer Equation (SE) is known for giving the crystallite size from experimental peak widths. In this work it is demonstrated that the SE actually provides the median from the intensity distribution weigthed by the size to the fourth power. It is also demonstrated that for broad distributions of sizes, the Lorentzian aspect of the Pseudo-Voigt function used for line profile fitting is increased.

Poster Presentation

Use of spectral techniques in the study of color: comparisons between emeralds from Minas Gerais, Bahia, Goiás and Tocantins - Brazil

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This proposal intends to use synchroton light techniques in emerald samples from MG, BA, GO and TO (Brazil) to analyze the behavior of chromophore ions and the distribution of metals in the crystal structure in order to create a 3D map that allows a dimensional simulation of Colors. centers and verify through geochemical studies of fingerprint the processes of its regional geological formation.

The analysis of emerald colors in synchroton light spectroscopy will allow a more complete and comprehensive research, with the perspective of observing crystallographic and structural particularities of the samples and filling the existing scientific gaps and the difficulties of less capable equipment.

These studies will allow us to understand its fundamental geochemical characteristics and, in the future, we will be able to apply the knowledge acquired in processing projects and, consequently, greater value in the international market for Brazilian gemstones.

The understanding of colors is related to the crystalline and chemical structure of minerals, so this project aims to compare spectroscopic characteristics of emeralds from the states of MG, BA, GO and TO - Brazil, to answer the following questions: 1) Which processes and mechanisms are they important for the wide color gamut of emeralds? 2) Are these variations related to the types of deposits? 3) Is it possible with synchroton light studies to determine the origin of samples from each region and acquire the geochemical fingerprint? The expectation is that through studies in X-ray absorption spectroscopy (LNLS) it will be possible to identify and evaluate the oxidation states of the emerald and the interactions of the elements Cr, V, Fe, and the parameters of the metallomic profile of the 3D structure, and carry out 2D mapping structural of emeralds and high pressure studies.

These spectroscopic techniques of Synchrotron Light will be used for studies that could provide the geochemical fingerprint of Brazilian emeralds.

Aknowledgements:

The experimental conditions of the analyzes should take place in the Carnaúba Line through the co-supervision of the researcher Douglas Galante and his team, to help with the planning, testing, carrying out the experiment and treating the data.

Keywords:

Emeralds colors, crystal structure, synchroton light spectroscopy

Oral Communication

Using Fourier transform IR spectroscopy and principal component analysis for detection and identification of pathogenic bacteria and fungi

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It is critical to detect and identify pathogenic bacteria and fungus as soon as possible in order to avert disastrous effects for human life if they are exposed to them. IR spectroscopy is a new technology for extracting nonperturbative, label-free biochemical information from bacteria and fungus, as well as rich intrinsic molecular information on biomolecules and molecular structures, for diagnostic purposes, however, more study on sample preparation, spectral pre-processing, and data analysis is needed. We used the national synchrotron light source (LNLS)-FTIR to analyze four pathogenic fungal strains, A Flavus, F. Verticilliodes, A. Alternata, and A. Parasiticus, and four bacteria strains, Salmonella, Escherichia coli, Staphylococcus aureus, and Bacillus subtilis, in this investigation. Our findings reveal that the FTIR approach efficiently distinguishes between a number of common fungal diseases, allowing for direct taxonomic affiliation of fungus as well as bacterial categorization into Gram-positive and Gram-negative bacteria. Furthermore, the findings show that the characteristics determined in fungal FTIR spectra came from filamentous, spores, and hyphae molecular species, and that the characteristics determined in bacteria FTIR spectra came from the bacteria cell wall and other molecular species detached from the biochemical structures on the cell surface, and that in both cases the fingerprint region was identified with high reproducibility. Additionally, the principal component analysis (PCA) enables statistical classification of the fungal and bacterial infections under investigation. The findings of this study provide an alternative to traditional fungal and bacterium diagnoses and open the way for the creation of a new rapid, reliable, and cost-effective microorganism diagnostic tool.

Keywords:

Fourier transform infrared spectroscopy, identification, pathogen, fungi, bacteria, PCA

Poster Presentation

X-ray reflectivity applied to cobalt oxide (CoO) antiferromagnetic thin films

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This work aimed to implement in the Python programing language, using the xrayutilities package, simulations and X-ray reflectivity data analysis, being possible to determine structural properties of magnetic thin films. The X-ray reflectivity technique, widely used to characterize thin films, makes it possible to determine properties such as thickness, roughness and density. This technique, whether using conventional X-ray sources or synchrotron sources, is of great interest to the research group on Magnetism and Nanostructured Magnetic Materials at the Federal University of Paraíba (UFPB), as it allows the characterization of structural properties with direct implications for the magnetic properties of systems of interest, this work being the first implementation of XRR analysis within the group. Materials manufactured in the form of thin films are of central importance in engineering and materials science and have special relevance in spintronic materials, such as the ones we are interested in in this work. CoO is an antiferromagnetic oxide with high magnetocrystalline anisotropy, arousing interest for spintronic studies using antiferromagnetic materials as active layer (antiferromagnetic spintronics), which although difficult to manipulate, bring the advantage of great magnetic robustness and ultra-fast magnetization dynamics [1]. We used XRR to investigate thickness, roughness and electron density of cobalt oxide films, deposited using the magnetron sputtering technique, on silicon substrates, in which a platinum layer is deposited before (buffer) and after (caplayer) the antiferromagnetic film. Here, we will show curve fitting to reflectivity data obtained in the XRD2 line of the UVX source of the Brazilian Synchrotron Light Laboratory (LNLS), improving results obtained in preliminary analyses. Our results estimate a discrepancy around 10% between the nominal thickness values and the thicknesses adjusted from the XRR, while the CoO layer roughness is dominant (~ 9.95 ± 0.35 Å). We also developed a documentation that allows us to guide new XRR studies within the group.

References:

[1] FERREIRA, Marina Raboni. Spin Orientation Manipulation of Antiferromagnetic CoO Thin Films Through Structural Deformations: Manipulação da Orientação de Spins em Filmes Finos Antiferromagnéticos de CoO por Deformações Estruturais. Campinas: [s. n.], 2020.

Keywords:

Computational model, data analysis, X-ray reflectivity

Poster Presentation

XPD and in situ XANES on Ce-Zr-Sm nanomaterials synthesized by hydrothermal method

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60%NiO/Ce0.9Zr0.1O2 showed a good performance as an anode in Intermediate Temperature-Solid Oxide Fuel Cells, however, it is necessary to increase its mixed conductivity (ionic and electronic) to increase the power density of the cell [1]. The partial substitution of Zr4+ by Sm3+ is proposed to incorporate oxygen vacancies into the crystalline structure thus improving the conductivity. Ce0.9Zr0.1-xSmxO2-x/2 (x= 0.1, 0.08, 0.06, 0.04, 0.02, 0) oxides were synthesized by the urea-hydrothermal method and calcined at 550 °C. X-ray diffraction with synchrotron radiation shows that all samples, have a single phase corresponding to a fluorite structure. Average crystallite sizes (< 11 nm) and lattice parameters increase with Sm content. In-situ Dispersive X-ray Absorption Spectroscopy experiments were performed at the Ce LIII absorption edge in a 5 vol.% H2 gas-flow, from room temperature to 800 °C. Three reduction steps are observed during the process, two of which can be related to the reduction of surface Ce4+ species. The incorporation of Sm3+ decreased the superficial reduction capacity of samples whereas it increased the reduction kinetics of bulk species. The effect of reduction atmosphere and calcination temperature was studied for samples with x= 0.04 and 0.06. A decrease in the reduction kinetics in a diluted atmosphere of CH4 was observed. The oxidation of CH4 is activated at temperatures lower than 600 °C. Samples calcined at 1100 °C showed a decrease in the reduction kinetics of superficial Ce, while the reduction still occurs in three steps. The composition of the exit gas was analyzed by online mass spectrometry. Since only H2 is fed, carbonaceous species detected in the exhaust can only be ascribed to adsorbed species on the high specific surface area (83-115 m2.g-1) of samples calcined at 550 °C. This is still observed for samples calcined at 1100 °C. In CH4 atmosphere, at first, products related to the total oxidation are observed and then CO2, H2O, H2 and CO are detected.

References:

[1] M.G. Zimicz, P. Nuñez, J.C. Ruiz-Morales, D.G. Lamas, S. A. Larrondo, Journal of Power Sources, 2013, 238, 87-94.

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Keywords:

Ce-Zr-Sm, nanomaterial, DXAS, XPD

Poster Presentation

XPD on Fe(III)-doped L-asparagine monohydrate crystals under low- temperature conditions

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L-asparagine is a very important amino acid because it is one of the protein-forming amino acids, playing a fundamental role in several biological mechanisms including the formation on the hemoglobin and metabolic control of some cell functions in nerve and brain tissues, itself being used in a variety of treatment of allergic diseases and anemia, as well. Single crystal of L-asparagine monohydrate (LAM), whose molecular formula is $C4H8N2O3.H2O$, has important physical properties, such as piezoelectricity and nonlinear optical (NLO) properties. In this work, Fe (III)-doped L-asparagine monohydrate crystals were grown by using a slow solvent evaporation method. To order, the effect of Fe doping on the crystal structure of LAM was evaluated through X-ray powder diffraction. Synchrotron radiation based X-ray data acquisition was carried out at diffraction station XRD1 of the Brazilian Synchrotron Light Laboratory (LNLS) using the multi-detector powder diffractometer and cryojet flow for collect X-ray data at 8 distinct temperatures, e.g., 300K, 250K, 220K, 160K, 150K, 140K, 120K and 92 K. Monochromatic X-ray radiation of 8.351 keV was used, with exact wavelength λ = 1.4845 Å. The sample was placed inside a glass capillary with a diameter of 0.3 mm and an acquisition time of 38 s was spent for each diffraction pattern obtained in the 3–120o (2θ) angular range. The effect Fe (III) ion on stability of the crystal in changing temperature was discussed. It was verified that under low temperature conditions the crystal undergoes a conformational transition

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