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ALBA Synchrotron

Book of Abstracts

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Insights in the CO2 photo-activation over Titania-Based Photocatalysts for Artificial Photosynthesis

Authors: Carlos Escudero[1]; Consuelo Alvarez[2]; David Serrano[3]; Fernando Fresno[3]; Juan M. Coronado[3]; Laura Collado[3]; Patricia Reñones[3]; Virginia Perez Dieste[4]; Víctor Antonio de la Peña O'Shea[5]

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The development of CO2 valorisation strategies has become a crucial issue and represents a priority for the European Union, which is actively promoting international agreements to control climate change and different programmes for CO2 conversion. Currently, less than 1% of the total anthropogenic CO2 emissions (31.2 Gt/y) are recycled into chemicals or used in industrial applications. One of the most promising strategies is the photocatalytic reduction of CO2 to produce fuels and chemicals by using sunlight as a sustainable energy source (Artificial Photosynthesis, AP). The main drawback arises from the fact that the CO2 molecule is highly stable, which makes very difficult its activation1.

This work focuses on the study of the gas phase CO2 photoreduction with water using TiO2-based catalysts. Coupling of TiO2 semiconductor with plasmonic noble metal nanoparticles was studied as a pathway to retard the recombination processes and improve the photocatalytic performance in AP process.

Catalysts were fully characterized by XRD, ICP, BET, TGA, SEM, TEM, Raman. Further, in-situ synchrotron-based spectroscopy techniques were performed in ALBA NAP endstation (CIRCE) to get a better understanding of the CO2 photoreduction mechanism. Photocatalytic activity was tested in a continuous-flow gas phase reactor under UV illumination.

Photocatalytic experiments in combination with in-situ spectroscopy studies revealed the influence of surface-adsorbed carbon species in the CO2 reduction mechanism. These studies showed the activation of CO2 molecules under UV illumination to obtain CH3OH and CO. Moreover, these measurements confirmed that the photoreduction mechanism occurs via carbonate/bicarbonate intermediates. The exposure to CO2 + H2O leads to the formation of CO32- and CO2- species. When the sample is irradiated with UV light, new peaks appeared in the O1s and C1s spectra, which are assigned to CH3OH and gas-phase CO, respectively. On the other hand, the introduction of noble metal NPs significantly changed the selectivity of the process, yielding more reduced products, such as CH4. These observations, which were confirmed by spectroscopy studies (including NAP experiments), suggested an enhancement of the charge separation processes due to the electron scavenging ability of the plasmonic metal NPs[2-3].

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Photoemission and x-ray absorption of graphene/h-BN multilayers grown by ion-beam-assisted deposition

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There is an increasing interest in heterostructures made from alternating layers of graphene and hexagonal boron nitride (h-BN), the latter being the optimal dielectric substrate for use in graphene based devices due to their similar structure. To fabricate graphene and h-BN ultrathin layers, we performed sequential evaporation of carbon and boron assisted with low energy nitrogen ions, using an ion beam assisted deposition (IBAD) system with optimized operation for subnanometric layers. This setput was used previously to produce nanometric carbon/h-BN multilayers 1.
In order to obtain quasi-epitaxial growth in this challenging system, a number of specific problems must be solved, which have been addressed in our research using x-ray absorption near edge spectroscopy (XANES) and x-ray photoemission (XPS). The measurements were conducted at BESSY synchrotron facility using beamline PM4.
Regarding the boron nitride growth, we have studied the texture of h-BN films XANES at different angles of incidence, obtaining a map of basal plane orientation as a function of growth conditions. Also, the amount of vacancy defects and the bond order can be determined from XANES and XPS spectra. The same stands for the graphene growth, which is studied via C(1s) XANES and XPS. In addition, some results are derived on the interfacial interaction between carbon and h-BN layers in the stacking. The synchrotron results are also compared with the more conventional infrared and Raman spectroscopies.

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1 R. Torres et al. "Reversed texture in nanometric carbon/boron nitride multilayers"Carbon 74 (2014) 374-378

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Structural and electronic characterization of the principal catalytic components in C-H bond functionalization by triazamacrocyclic-Cu complexes

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Herein, the electronic and geometric structure of first row transition metal mediated C-H bond activation and C-X cross-coupling reactions, was directly probed using X-ray absorption spectroscopy. The experimental data was correlated with theoretical calculations in the hopes of better understanding the principal catalytic species, reactive intermediates, and their structure-function relationship.

The study focuses on a series of aryl-Cu complexes based on a triazamacrocyclic ligand scaffold. Chelation of Cu(II) by the arene ligand is followed by PCET C-H bond activation, yielding an aryl-Cu(III) and aryl-Cu(I) species via a disproportionation reaction. The aryl-Cu(III) species facilitates C-Y heteroatom cross-coupling reactions (Y=N, O, S, Se) and represents the first direct evidence for an organo-Cu(III) intermediate in copper-catalyzed oxidative coupling. The initial arene-Cu(II) complex is proposed to form a three center three electron interaction prior to C-H activation but has not been structurally characterized. Therefore XANES and EXAFS analysis was employed to elucidate

the electronic and geometric structure at the copper center of the principal catalytic components. Furthermore, the impact of the metal center was explored by also characterizing the analogous aryl-Ni(II) complex. In the case of nickel the initial arene-metal complex is proposed to form a classical three-center, two-electron agostic interaction, and unlike the copper system, C-H activation proceeds without metal oxidation.

Ultimately understanding these systems will lead to more economic, sustainable and environmentally benign synthetic pathways with important applications in pharmaceuticals and agrochemicals. Current approaches to C-H bond functionalization involve either harsh reaction conditions that do not allow the selective transformations desired in organic synthesis, or use heavy metals that are scarce, expensive and form toxic byproducts. Therefore the use of abundant, non-toxic and economically sustainable first row transition metals is an attractive alternative.

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Caption (s) - Add figures as attached files (2 fig. max):

Coupling of X-ray absorption experimental data with theoretical calculations to elucidate the principal species in C-H activation by triazamacrocyclic-copper complexes.

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Invited talk "EMIL - a novel research platform for energy materials at the BESSY II synchrotron light source"

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A knowledge-based approach towards developing materials for energy conversion and storage application requires a fast and direct feedback between sophisticated analytics and state-of-the-art material processing facilities. At the Energy Materials In-situ Laboratory Berlin (EMIL) we achieve

this by coupling synchrotron-based X-ray characterization techniques (such as XPS, HAXPES, XRD, XES, XAS, XRF, PEEM) with relevant in-system/in-situ sample preparation techniques on up to 6"substrates in one dedicated ultra-high vacuum (UHV) system. EMIL is a joint project between Helmholtz-Zentrum Berlin and the Max Planck Society and will be operational at the BESSY II light source in 2016. EMIL has the most complex beamline so far constructed at BESSY II and will provide light in a wide energy range from 70 –10.000 eV 1. To achieve this, a new light source consisting of two canted undulators will be installed into the BESSY II storage ring and two plane-grating and one double-crystal monochromator disperse the radiation in separate pathways, while ten mirror chambers distribute the desired photon energy to five experimental endstations. A new 2000m2 large infrastructure consisting of deposition, chemistry and spectroscopy labs as well as a cleanroom facility is attached to the BESSY II mantle and will host three of the five endstations. These three endstations are designed for accepting the full energy range with spatial overlap of the soft and hard foci allowing in-system and in-situ X-ray spectroscopy. Two endstations are connected through a huge UHV transfer system to up to 20 different deposition systems 2.
In this presentation, I will provide an overview of the analytic and material capabilities at EMIL and report on the status and timeline of the project. I will discuss the overall estimated performance and highlight how EMIL can trigger research opportunities for future user operation.

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Welcome

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X-ray circular dichroism in adsorbed films of homochiral organic molecules on ferromagnetic substrates

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We have used synchrotron based techniques (XAS, XPEEM, spin polarized UPS) to study the influence of the chirality on the magnetism, when a thin film of chiral molecules is adsorbed on a ferromagnetic layer. We have grown monolayer-thick films of 1,2-diphenyl-1,2-ethanediol (DPED), adsorbed in ultra-high vacuum on Fe and Co thin films. This molecule has two chiral centers and presents two enantiomers, which are designated according to their conformation and optical activity as (R,R)-(+)-DPED and (S,S)-(–)-DPED. We observe clearly dichroic features (natural circular dichroism) by measuring the absorption by the molecular film of circularly polarized X-rays (XAS) of opposite helicity, at the carbon K edge. This dichroic asymmetry depends on the chirality showing opposite sign for the two enantiomers.

In experiments of spin-polarized photoemission spectroscopy we observe that the photoelectons emitted through adsorbed layers of pure enantiomers display a clear spin polarization at room temperature, independent of their binding energy. The spins point along different directions in space: in-plane for (R,R)-(+)- DPED and out-of-plane for (S,S)-(–)-DPED, which makes the DPED molecule a prototype system to study enantioselective spin filtering 1.

Further photoemission microscopy (PEEM) experiments making use of the magnetic circular dichroism effect have also allowed us to image the magnetic state of the sample substrate –an epitaxial Fe film deposited on W(110)–and detect the modifications induced by the adsorption of different enantiomers of DPED. These findings lend additional support to the existence of some link between the molecular chirality and the electronic spin. They create opportunities for applications not only in organic-based molecular spintronics but also in other fields such as asymmetric chemical synthesis.

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1 M. Á. Niño *et al.*, Adv. Mater. **26**, (2014) 7474.

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Structural behaviour of CaZrO3 perovskite under pressure. Influence of pressure-transmitting medium

Author: Fernando Aguado[1]

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Perovskite materials have been intensively investigated over last decades due to the interest for understanding their stability as a function of pressure and temperature as well as the establishment of correlations between crystal structure and physical properties. They cover many scientific and technological areas in Materials Science and Geophysics (structure of Earth's interior). In this regard, especial attention has been paid to phase transitions from the perovskite to the CaIrO3-type "post-perovksite"structure at high pressures, involving changes from corner sharing to edge sharing octahedral conformations.1,2 Such transition in MgSiO3 is hypothesized to be responsible for many seismic signatures of the Earth's lowermost mantle. Many structural studies have been conducted on ABX3 compounds in order to establish general models providing understanding on the distortion mechanisms of perovskites via polyhedral tilting. However, in spite of the efforts paid so far, there is no clear knowledge on the factors determining the destabilization of the perovskite structure.
CaZrO3 is a very interesting system which has been proposed for possible applications in high temperature devices (refractory) and sensors, among others. In addition, this is a good candidate to investigate as a MgSiO3 analogue, i.e. to determine its distortion evolution under pressure and its

stability limit in comparison with silicates. The idea is to establish guidelines to predict the structural evolution of perovskite materials in wide pressure ranges, explaining the equation of state (EOS) in terms of microscopic models, as well as to rationalize the propensity to form the post-perovskite structure. Thus, the structural behaviour of CaZrO3 has been studied as a function of pressure at ambient temperature by ADXRD. In addition the effect of different pressure transmitting media (methanol-ethanol mixture, paraffin and silicone oils) on the high pressure response has also been evaluated for this compound, focusing on the tilting evolution in the hydrostatic or quasi-hydrostatic regimes (below 15 GPa). Supplementary information has been obtained by means of Raman spectroscopy. Previous results on this and similar systems have been compared with present findings. The main conclusions will be presented at the conference.

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Invited talk "X-ray imaging for spatiotemporally resolved studies of micro-structure evolution during technological and biological processes"

Author: Baumbach Tilo[1]

Co-authors: Alexey Ershov [2]; Daniel Hänschke [1]; Feng Xu [3]; Julian Moosmann [4]; Lukas Helfen [5]; Patrik Vagovič [6]; Ralf Hofmann [1]; Thomas van de Kamp [4]; Tomy dos Santos Rolo [1]; Tomáš Faragó [1]; Yang Yang [3]; Yin Chen [7]

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The talk will focus on developments at Karlsruhe Institute of Technology in the context of current challenges in materials and micro-system technologies and life sciences, where state-of-the-art X-ray imaging techniques provide spatiotemporally resolved information about micro-structure and its evolution during technological and biological processes.

X-ray laminography has been developed for defect recognition in extended objects [1-4], permitting in situ and in operando studies from defect generation up to failure. It enables scanning of complete entities with medium resolution, and zooming into region of interests with high resolution and correlation of various scanning and full field contrast mechanisms [5-8].

An important issue is the development of dose-efficient imaging methods, which enable the visualization of soft tissue, in order to facilitate in vivo and in vitro investigations, e.g. for developmental biology, functional morphology, nano-toxicology and tissue engineering. The opaqueness of many organisms impedes in vivo investigation by light microscopy. In combination with optical flow

algorithms, 4D phase-contrast μCT allows following of spatiotemporal movements, e.g. in order to observe tissues and individual cells during embryonic development [9, 10]. To investigate fast structure dynamics with feature sizes in the micron range and with high temporal resolution, we designed X-ray cine-tomography [11]. The technique enables e.g. new insights into the physiology of small animals by tracking the 4D dynamics of anatomical features as demonstrated by the analysis of screw-and-nut type weevil hip joints [12].

Further development will require an increase in dose-efficiency. Promising routes here include improvement of single-distance phase retrieval at large propagation distances, as well as the use of diffraction based magnifying optics combined with single photon counting detectors [13-16].

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Hydration studies of ye'elimite by using Ptychographic X-ray nano-tomography

Author: ANA CUESTA[1]

Co-authors: Ana Diaz [2]; Angeles G. De la Torre [3]; Julio C. da Silva [2]; Miguel A. G. Aranda [4]; Mirko Holler [2]; Pavel Trtik [2]

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CSA (Calcium SulfoAluminate) cements may have variable compositions but all of them contain ye' elimite(Ca4Al6O12SO4). The manufacture of CSA cements is more environmentally friendly than that of ordinary Portland cements as their production releases up to 40% less CO2. The hydration of ye'elimite leads to crystalline ettringite (AFt) and amorphous aluminum hydroxide (AH3•nH2O).
Ptychographic X-ray computed nanotomography (PXCT) has been used here to study the hydration of ye'elimite-containing samples. PXCT is an X-ray imaging technique having demonstrated an isotropic 3D resolution better than 20 nm1. PXCT, which nondestructively provides 3D images of the sample complex-valued X-ray refractive index, has been recently applied for hydration studies of Portland cement samples2.
Samples for this study were measured in cSAXS beamline (Swiss Light Source). The main goal of this study has been the quantification of the electron and mass densities of the phases present in these samples. These mass densities were compared with the theoretical values in order to identify

the phases and matched well the expected values.
For instance, the hydration of pure ye'elimite with gypsum sample was studied. This sample should show a large amount of AFt due to the presence of gypsum in the hydration medium. This is precisely what it was observed from the analysis of the histogram. Figure 1 shows the tomogram of one slice obtained for this sample.
The most relevant results for CSA cement hydration will be discussed. A volume of interest (VOI) histogram has been studied in order to identify all the phases. Figure 2 shows a comparison between the histogram obtained in this study and a previous one performed by Gastaldi et al. (2012) at TOMCAT Beamline (Swiss Light Source). As it can be observed, TOMCAT data cannot properly distinguish between AFt and ye'elimite phase. Conversely, PXCT technique can resolve the peaks for all the phases present in CSA cements.
All reconstructions have been successful and now we are analyzing the data (segmentation, etc.) to characterize the porosities and the shape and size of the different phase, chiefly ettringite.

References:

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2 J. C. da Silva, P. Trtik, A. Diaz, M. Holler, M. Guizar-Sicairos, J. Raabe, O. Bunk, and A. Menzel, "Mass Density and Water Content of Saturated Never-Dried Calcium Silicate Hydrates", Langmuir, 2015, 31, 3779.

Caption (s) - Add figures as attached files (2 fig. max):

Figure 1.Tomogram of one slice obtained for ye'elimite with gypsum hydrated sample with the main samples labeled. Figure 2. Bottom: VOI histogram of a calcium sulfoaluminate cement obtained in this experiment. Top: grey level histogram of a CSA cement paste obtained at TOMCAT BL (Figure adapted from Gastaldi et al., Const. Build. Mat. 29, 2012 284-290).

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TTS Microdifraction of microcristals embeded in thin polished films

Author: Carlos Frontera[1]

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One interesting problem in the field of petrology is the use of non-destructive techniques to investigate thin mineral polished films (25-30μm thickness) attached to a glass substrate. In this type of samples commonly show microsized crystal of different minerals formed in close contact during its genesis (see Fig. 1). In order to study such systems synchrotron radiation has two very interesting properties: a high penetration capacity when a short wavelength is used; and the possibility of using microfocused spots. Four years ago, we developed the through-the-substrate microdiffraction (tts-μXRD) technique for studying this type of films using a spot down to ($100\times100\mu m^2$). By this way we obtained powder patterns of aerinite and discovered a new mineral called ilerdite 1.
Microdiffraction station of MSPD beamline is very well suited to further develop this technique. Superconducting wiggler can reach quite high energy (30 KeV and above) and KB-mirrors render a highly focused spot ($15\times15\mu m^2$). With such capabilities, we have extended the μ-tts technique to the study of microcrystals embedded in thin polished films of compact materials 2. The procedure consists on a series of steps: i. collection of a limited number of 2D diffraction patterns (frames), for every selected microcrystal (randomly oriented, usually between 5 and 10 crystals); ii. refinement of crystal metrics from a 1D diffraction pattern obtaining by radial average of the frames; iii. determination of the orientation of the reciprocal lattice for every microcrystal, this allows assigning

hkl miller indices to the spots in every frame and combining the intensities of the different frames for each crystal (frame merging); iv. combination of the different sets of intensities for every crystal (multicrystal merging) to obtain a set of single-crystal-like integrated intensities. We show the validity of the technique by some representative examples in petrology in which glass substrates have been used and Patterson-function direct methods applied to solve the corresponding crystal structures [3]. This technique can be applied to other fields like material science and cultural heritage.

References:

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[3] J. Rius, IUCrJ, 2014, 1, 291-304.

Caption (s) - Add figures as attached files (2 fig. max):

Figure 1. Thin ofite film with polycrystalline aerinite (AE) veining and diopside (D) microcrystals.

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Synchrotron WAXS/SAXS analysis of CNT fibre based nanocomposites

Authors: Alfonso Monreal[1]; Belen Aleman[1]; Hangbo Yue[2]; Juan Jose Vilatela[1]; Juan Pedro Fernandez[1]

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The incorporation of nanocarbons (carbon nanotubes (CNTs), graphene) in polymer matrices has been broad studied in the last decades due to its mechanical reinforcement, improvement in electrical/thermal conductivity and emergence of other functional properties. The variation of these properties is largely dependent on the interesting phenomena related to the fact that a large fraction of polymer is close to solid interface, altering the polymer physics.
In this sense, based on CNT fibre, we develop polymer nanocomposites. CNT fibre is directly spun from the gas phase in a CVD reactor at 1250℃ 1 and shows excellent mechanical properties in the range of 1GPa/SG for the specific strength and 40 GPa/SG for the modulus. The fine control of the building blocks at a molecular scale 2 of this high surface area material (~ 170 m2/g), leads to tailor its structure and properties as well as the structure of hierarchical materials through its combination with polymers by hot press process.
Consequently the relation between the structure, such as the CNTs fibres as polymer nanocomposites, and the final properties is one of the main goals. On one hand, WAXS patterns of a macroscopic CNT fibre, gives rise to multi-scale structural information about packing of adjacent nanotubes and the residual catalyst. On the other hand, SAXS gives information about the orientation of the CNT in the fibre and the size and shape of the fibre pores. In the case of composites, the high intensity of synchrotron radiation allows to monitor the melting and crystallization process of the polymer matrix at standard DSC (Dynamic Scanning Calorimeter) cooling and heating rates. For instance, effect in the crystallization process as heterogeneous nucleation, polymorphism, and crystal size variation can be studied by SAXS/WAXS synchrotron studies.
In resume, this work shows the importance of synchrotron experiments in the nanocomposite characterization, which is essential to understand their properties.

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Nanofabrication of Laser Induced Periodic Surface Structures on polymer thin films as revealed by Grazing Incidence Small Angle X-ray Scattering

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Formation of laser induced periodic surface structures (LIPSS) has been observed on polymers upon irradiation with linear polarized laser beams at wavelengths efficiently absorbed. LIPSS are the result of the interference between the incoming and the surface-scattered waves which creates an inhomogeneous intensity distribution that by a feedback mechanism results in an enhancement of the structural modification1. The use of X-ray scattering techniques with synchrotron radiation can be very useful for LIPSS analysis as they can provide kinetic information in the millisecond range and structural information statistically averaged over a large area of several hundreds of microns. In this presentation we will show the formation of LIPSS on model spin-coated polymer films as followed by in situ Grazing Incidence Small Angle X-ray Scattering (GISAXS) using synchrotron radiation (Fig.1). The samples were irradiated at different repetition rates using a Nd:YAG laser (266 nm) with pulses of 8 ns. Simultaneously GISAXS patterns were acquired during laser irradiation. The variation of both the GISAXS signal with the number of pulses and the LIPSS period with laser irradiation time reveal key aspects of nanostructure development. By considering LIPSS as one-dimensional paracrystalline lattice and using a correlation found between the paracrystalline disorder parameter and the number of reflections observed in the GISAXS patterns, the variation of the structural order of LIPSS can be assessed. The role of the laser repetition rate in the nanostructure formation has been clarified. For high pulse repetition rates (i.e. 10 Hz), LIPSS evolve in time to reach the expected period matching the wavelength of the irradiating laser. For lower pulse repetition rates LIPSS formation is less effective and the period of the ripples never reaches the wavelength value. Results support and provide information on the existence of a feedback mechanism for LIPSS formation in polymer films.

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X-ray Real-time Investigation of the Crystallization of Photovoltaic Polymer-fullerene films during Solvent Drying: the Effect of Processing Additives

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The fundamental concept of solution processed solar cells resides in the nanophase separation developing in the binary blend formed by a polymer (donor) and a fullerene derivative (acceptor) when the solvent evaporates, so-called bulk-heterojunction (BHJ). The performance of a BHJ solar cells arises from a complex interplay of the spatial organization of the segregated donor and acceptor phases and the local order/quality of the respective phases. A common practice to control the nanomorphology is the introduction of processing additives, such as octanedithiol (ODT).
We report real-time grazing incidence x-ray
scattering (GIXS) study combined with optical interference that allows us to follow the evolution of the crystallinity.1 We investigate in-situ the impact a ODT on the structure film formation of Poly[2,6-(4,4-bis-(2-ethylhexyl)-4H-cyclopenta[2,1-b;3,4-b′]dithiophene)-alt-4,7(2,1,3 - benzothiadiazole)] (PCPDTBT) as donor and [6,6]-Phenyl C71 butyric acid methyl ester (PC71BM) as acceptor. Such setup allows for a simultaneous determination of the crystallization dynamics and the solvent composition of the film. If processed from pure DCB solutions, PCPDTBT does not exhibit crystalline features due to fullerene clusters that impede dense chain packing. In the presence of 3wt% ODT we observe the microstructure of PCPDTBT emerges in several stages, which is interrelated with the aggregation behavior of the fullerene component.

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A structural overview of Pontin, Reptin and their complex(es)

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Pontin, also known as RuvBL1 and Reptin, also known as RuvBL2 are highly conserved eukaryotic proteins belonging to the AAA+ family of ATPases, and closely related to the bacterial DNA helicase RuvB. They are ubiquitously expressed and have been associated with many cellular functions. In addition, a link was established between Pontin, Reptin and cancer 1.

The crystal structure of human Pontin was determined in our lab in 2006 2. It is hexameric, formed by ADP-bound monomers. Each monomer contains 3 domains: domains I and III are involved in ATP binding and hydrolysis and are structurally similar to equivalent domains in the bacterial homolog RuvB; a sequence insertion intercalated into domain I folds into domain II, unique among AAA+ proteins.

3D structures of Pontin/Reptin complexes were determined by other groups using electron microscopy [3-4]. In the human and yeast complexes, Pontin and Reptin form a dodecamer with two structurally distinct hexameric rings. It was suggested that both rings interact via domain II, but neither study

settled the issue of whether the rings are homo- or hetero-oligomeric. However, a third EM study reported a single hetero-hexameric ring structure for the yeast Pontin/Reptin complex [5].

The first crystal structure of a Pontin/Reptin complex with a truncated domain II was published in 2011 by our lab [6]. The structure of a SeMet derivative revealed a dodecamer formed by two hetero-hexameric rings composed of alternating Pontin and Reptin monomers that interact via the retained part of domain II. More recently, the crystal structure of a full-length homologue from the thermophilic fungus *Chaetomium thermophilum* was published [7] and structures of larger complexes integrating Pontin/Reptin heterohexamers were obtained by EM [8-9].

The crystal structure of truncated Reptin was published in 2012 [10]. We have been working towards the crystal structure of full-length Reptin. To date, the best diffraction data were measured to 3.4 Å at ALBA XALOC and a preliminary structure obtained by MR. However, the location of domain II could not be ascertained and the search for better-diffracting crystals continues.

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The role of mesomorphic phases in the ordering of polymers

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In recent years considerable attention has been devoted to the study of transient states (mesophases) in the ordering of polymers on the route toward a more stable (usually crystalline) structure. Mesomorphic states or mesophases are characterized by a partial and intermediate order between the amorphous disordered isotropic state and the three-dimensionally organized crystalline structure. Metastable phases are usually kinetically faster and they can display a favorable free energy when taking into account their increased surface free energy 1 in the case of very small sizes.
Besides the conditions for obtaining mesophases, another important feature is to determine their role in the ordering of the polymers, i.e., if those phases are competing with the more stable crystal structure or they are acting as precursors of crystallization.
Two kinds of polymeric systems have been analyzed: a) copolymers of isotactic polypropylene, iPP, and b) liquid crystalline polymers.

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Speciation of iron and zinc in cured ham to assess the curing process

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Traceability in cured ham process is a difficult task. In this study, we used Synchrotron XAS analysis to direct determination of Fe and Zn species in ham muscle and Zn species in visible fat (intramuscular fat) of Iberian dry-cured ham, IDCH.
Ham samples were obtained from certified IDCH from south of Spain at different curing time ranging from three to forty months. XAS spectra obtained at both Max Lab and ALBA Cells Synchrotrons allow the direct identification of Fe and Zn species in target samples containing low concentrations of Fe and Zn that have not been altered by extraction techniques. Corresponding spectra of individual reference compounds included both organic and inorganic species of Zn(II), Fe(III) and Fe(II) usually present in mammalian meat products.
Results for iron indicate that both organic and inorganic compounds are present in IDCH muscle, three main facts were observed: 1) inorganic iron is always found in less proportion than organic iron, 2) remarkable differences on iron species are found between surface and bulk muscle samples and 3) percentage of Iron (II) species increases with curing time. With respect to Zn, findings can be summarize as follows: 1) inorganic species were found relatively higher than organic species in IDCH muscle, 2) this difference increases in fat samples, 3) difference between surface and bulk samples are lower than those obtained for iron species. Correlation between results obtained and IDCH curing time will be presented.

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Characterization, assessment and optimization of polymer nanostructures using synchrotron radiation

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Controlling nanostructure formation in polymeric materials is a key aspect for the development of several applications in nanotechnology, such as organic photovoltaic cells or non volatile memories. Current synchrotron radiation sources with high flux, high energy resolution, energy tunability, and small beam size provide some of the most appropriate tools to characterize them and understand the formation process. In the first part of the talk, the use of grazing incidence small angle X-ray scattering (GISAXS) in combination with atomic force microscopy (AFM) and GISAXS modelling for the characterization, assessment and optimization of polymer nanostructures will be discussed. This approach will be applied to laser induced periodic surface structures (LIPSS) in thin polymer films 1 as well as polymer replicas of silicon moulds obtained by nanoimprint lithography (NIL) (Figure 1) 2. In the second part, microfocus beam small and wide angle X-ray scattering (μSAXS and μWAXS) experiments in nanorods of polymer and single wall carbon nanotubes (SWCNTs)/polymer composites will be presented [3]. The preparation method via infiltration in nanoporous alumina templates influences strongly the resulting crystalline structure. In fact, in the bulk material the orientation is isotropic (Figure 1b) whereas the nanorods present a clearly oriented pattern (Figure 1c). This orientation is caused by the intense interaction of the alumina with the polymer, an interaction that prevails over the templating effect of the SWCNTs in the case of the composites. All in all, the studies presented here go one step further towards controlling nanostructure formation through a deep understanding of the parameters that influence this process.

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Caption (s) - Add figures as attached files (2 fig. max):

Figure 1. AFM topography images (5 x 5 μm2, top) and GISAXS patterns (bottom) of (a) LIPSS on polymer thin film, (b) silicon mould with stripe-like motifs and (c) polymer replica fabricated by nanoimprint lithography (NIL). Figure 2. (a) Scanning electron microscopy image of the cross section of a polymer infiltrated in a nanoporous alumina membrane. μWAXS patterns of the polymer (a) outside the membrane and (b) inside.

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FTIR study of the biochemical effects in F98 glioma cells induced by x-ray irradiations combined with nanoparticles

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Radiotherapy plays a key role in the treatment of cancer. The main limitation is to reach curative doses in the tumour while sparing the surrounding healthy tissue. One strategy to improve the clinical outcome in radiotherapy is to increase the dose effects in the tumour. This can be achieved by using specific nanoparticles (NPs). Numerous studies have shown the enhanced effectiveness of tumour control when NPs were used [1-3]. However, the involved biochemical mechanisms are not yet clear. In addition to a possible dose enhancement, the size similarity of NPs to biological

molecules could provide "camouflage"to cellular
barriers, leading to changes in the cellular function and producing cell arrest at radiosensitive phases or
oxidative stress [4,5]. These effects, which could be amplified with a subsequent irradiation, might increase their
anticancer effectiveness. Within this framework, in this study we used F98 glioma rat cells as an *in vitro* model to
disentangle the biochemical changes in the cells induced by x-ray irradiations in combination with NPs. These biochemical processes can be studied by using Fourier transform infrared microspectroscopy
(FTIR). FTIR allows in situ structure determination of the most important biomolecules, and it is extremely useful
to study cell cycle, differentiation and proliferation of cell lines and cell death mode [6-8].

Within this context, F98 glioma cells were irradiated with x-rays in the presence and absence of Gadolinium NPs.
FTIR measurements were performed by using the internal globar source at SESAME synchrotron (Jordan).
Principal Component Analysis (PCA) was performed to show the variances between two different sets of
spectra. Flow cytometry and cell viability assays were also carried out.

Preliminary results are very encouraging. Figure 1 shows the PCA in the sugar and DNA region of the infrared
spectra. The differences in the presence (blue) and absence (red) of Gd NPs are clearly observed for a dose of
10 Gy. PCA reveals also clear differences in the proteins and lipids regions. Biological interpretation is in
progress nowadays. Forthcoming studies will consist in the evaluation of other radiotherapy approaches and
other types of NPs at ALBA MIRAS beamline

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Caption (s) - Add figures as attached files (2 fig. max):

Figure 1. PCA in the sugar and DNA region of the infrared spectra of F98 glioma cells for a dose of 10 Gy. Blue points correspond to the presence of Gd NPs and red points to the absence of Gd NPs.

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Bicosomes as skin delivery systems: A study based on Fourier-transform infrared microspectroscopy using synchrotron radiation

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Skin delivery is a challenge due to the strong barrier function of this tissue. Bicosomes are phospholipid systems formed by spherical vesicles and discoidal structures able to modulate skin barrier 1. In this work the penetration into skin of a model molecule incorporated in bicosomes via Fourier-transform infrared spectroscopy (FTIR) using synchrotron radiation was studied.
This technique was previously used to evaluated skin composition and location of different substances in this tissue 2. The coupling of a synchrotron radiation source and an IR microscope allows monitoring at higher spatial resolutions, rending possible the spatially resolved measurements of the superficial layer of skin, the stratum corneum (SC).

The model molecule used was a rhenium tris-carbonyl tag coupled to a C12 aliphatic chain (C12Re(CO)3). This lipophilic molecule can penetrate cells and target organelles for IR imaging and exhibits a specific IR signature with absorption bands between 1920 and 2020 cm-1, which not interfere with the skin vibrations [3]. Additionally, skin delivery of the C12Re(CO)3 dissolved in dimethylsulfoxide (DMSO), a well-known penetration enhancer, was also studied. Hence, the capacity of bicosomes to promote the penetration of this molecule could be evaluated and compared with a usual enhancer.

The FTIR results showed that the C12Re(CO)3 penetrated deeper in the skin when incorporated in bicosomes than when dissolved in DMSO (Fig. 1). The application of this molecule using bicosomes resulted in 60% retained in the SC and 40% in the epidermis (Epi), deeper than the SC. When the C12Re(CO)3 was applied by means of DMSO 95% was retained in the SC and 5% reached the Epi [4].

Therefore, synchrotron FTIR microspectroscopy allows monitoring the skin permeation of bicosomes containing C12Re(CO)3 into skin. The distribution of C12Re(CO)3 may be representative of the distribution of molecules with similar physicochemical characteristics when applied in bicosomes. The C12Re(CO)3 is a good tag for skin permeation studies due to it can be differentiated from skin vibrations. Our results demonstrate that bicosomes are promising vehicles incorporating lipophilic molecules with dermatological interest into skin.

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Caption (s) - Add figures as attached files (2 fig. max):

Fig. 1 IR maps obtained from skin samples treated with C12Re(CO)3 derivative incorporated in bicosomes (A) and dissolved in DMSO (B). The C12Re(CO)3 scale goes from blue to red, indicating no amount in blue colour and high amount in red colour. The concentration of C12 Re(CO)3 is 1% w/v in both vehicles.

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Invited talk: Multimode InfraRed Imaging and Microspectroscopy at Diamond: research perspectives in Soft Condensed Matter

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Infrared (IR) MicroSpectroscopy is a quantitative analytical probe extensively applied to soft condensed matter because of its high molecular sensitivity and specificity.

Fourier Transform IR (FTIR) technique is extremely effective in revealing optically-active vibrational modes of molecules, or *IR fingerprinting* molecular groups, at the microscopic scale. The combination of microFTIR with Synchrotron Radiation (SR) broadband and brightness provides an unique diffraction limited IR microprobe. In fact, SRIR photon flux density is up to 10^3 times higher than conventional sources extending simultaneously from the near-IR (\lambda> 1 mm) up to the far-IR (\lambda < 2 mm). At MIRIAM beamline of Diamond such advantages are fully exploited to allow both the highest spatial resolution optically attainable in IR microscopy (practically \deltax ~ \alpha fwhm), and an excellent spectral quality (figure of merit signal/noise>3000 rms on 5x5 mm^2 spot in 30 sec) for vibrational spectroscopy across the whole IR range.

The initial Life Science driver for MIRIAM of biochemical analysis of fixed cell cultures and tissue sections relevant to e.g. cancer, stem cell research and pathology, is now routine in confocal IR microscopy 1. The new research frontier for biomedicine is *ex vivo* and real time IR microanalysis of living single cell, i.e. the study of subcellular metabolism as well as extracellular interactions via full field IR imaging e.g. imaging isotopic gradient around/inside living fibroblasts 2.

A new class of experiments have been pioneered at MIRIAM in the last couple of years, namely the microanalysis of gas-solid interaction controlled by temperature which are especially important for the chemistry of catalysis at single crystal level, or the dynamic of functionalized Metal-Organic-Frames [3].

Recently, SR IR for microchemical analysis on painting fragments has become a reliable technique and the research in Cultural Heritage at MIRIAM is quite successful, too [4].

Finally, the optimization of Diamond Coherent Synchrotron Radiation emission has expanded MIRIAM experimental capability for absorption spectroscopy in the "THz gap"domain. This is particular relevant in the study of large molecule collective modes e.g. the physics of MOFs [5], as well as the study of the water interaction with protein in solution [6].

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AUSE general assembly

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Key-note contribution "Technical capabilities, developments and upgrade plans of SpLine, the Spanish CRG BM25 beamline at the European Synchrotron Radiation Facility"

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The Spanish CRG BM25 SpLine Beamline is located at the bending magnet 25 of the ESRF, the European Synchrotron in Grenoble France. The beamline is split in two branches: A and B and is dedicated to structural and electronic investigations using hard X-ray techniques mostly in materials science and is specialized on X-ray absorption spectroscopy (XAS), hard X-ray photoemission spectroscopy (HAXPES) and X-ray diffraction techniques (GIXRD, XSD, XRR, HRPD and SC).

In this talk, initially, I will present a review of the technical capabilities, recent improvements and developments of the beamline. In a second part, a short review of the beamline statistics concerning users and scientific output will be exposed. And finally, I will give an outlook and forecast about the SpLine future plans in view of the ESRF phase II upgrade program.

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Visualizing phosphodiester-bond hydrolysis by an endonuclease

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The enzymatic hydrolysis of DNA phosphodiester bonds has been widely studied, but the chemical reaction has not yet been observed. Here we follow the generation of a DNA double-strand break (DSB) by the Desulfurococcus mobilis homing endonuclease I-DmoI, trapping sequential stages of a two-metal-ion cleavage mechanism. We captured intermediates of the different catalytic steps, and this allowed us to watch the reaction by 'freezing' multiple states. We observed the successive entry of two metals involved in the reaction and the arrival of a third cation in a central position of the active site. This third metal ion has a crucial role, triggering the consecutive hydrolysis of the targeted phosphodiester bonds in the DNA strands and leaving its position once the DSB is generated. The multiple structures show the orchestrated conformational changes in the protein residues, nucleotides and metals during catalysis.

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Phasing your XALOC data with ARCIMBOLDO

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Phasing your XALOC data with ARCIMBOLDO

Macromolecular Ab Initio phasing, from the native intensities alone with no experimental phase information or previous particular structural knowledge has been the object of a long quest, limited by two main barriers: structure size and data resolution. Beyond the first atomic resolution successes, current approaches have been developed, exploiting alternative constraints to atomicity, through use of the Patterson function, density modification and data extrapolation 1.
Our own approach relies on the combination of locating model fragments with the program PHASER 2 and density modification with the program SHELXE [3]. Appropriate search models are polyalanine alpha-helices[4], small polypeptide folds[5], DNA-binding motifs[6] or fragments from distant homologs[7]. Given the difficulties in discriminating correctly positioned fragments, many putative hypotheses have to be tested in parallel, thus calculations are performed on a grid or supercomputer. The method has been called after the Italian painter Arcimboldo, who used to compose portraits out of fruits and vegetables. In the case of our program, most collections of fragments remain a "still-life", but some are correct enough for density modification to reveal the protein's true portrait (http://chango.ibmb.csic.es/ARCIMBOLDO). Using these methods, a number of unknown macromolecules with a few thousand atoms and resolutions around 2 Å have been solved.
Performance of the single-workstation implementation ARCIMBOLDO_LITE available at XALOC will be presented.

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News and recent developments at NCD BL

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News and recent developments at MISTRAL BL

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News and recent developments at XALOC BL

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Stimuli responsive polymorphism in DNA-cationic liposomes complexes: effect of composition, pH and temperature

Author: Daniela Uhrikova[1]

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DNA polyanion interacts with a dispersion of cationic liposomes forming supramolecular assemblies of regular inner microstructure –lipoplexes. They are studied as delivery vectors for genetic material. Despite the fact that cationic liposomes have been used for transfection, and commercial lipid formulations are available, their efficiency needs to be improved.
We will discuss structural polymorphism of lipoplexes formed due to DNA interaction with liposomes prepared as a mixture of neutral phospholipids and pH responsive additives:
N, N-dimethyldodecylamine-N-oxide (C12NO) is a surfactant that may exist in a neutral or cationic protonated form depending on the pH of aqueous solutions. We have observed the rich structural polymorphism of pH responsive DNA –C12NO –dioleoylphosphatidylethanolamine (DOPE) complexes. Depending on pH and the composition, complexes have shown either a condensed lamellar Lc or hexagonal phase Hc. Commensurate lattice parameters aHc~dLc were detected at selected composition and pH 4.9 –6.4 suggesting that Lc and Hc phases were epitaxially related. While at the same composition and but pH ~ 7, the mixture form a cubic phase (Pn3m) when the complexes were heated to 80 oC and cooled down to 20 oC.
Fatty acids were also investigated as pH responsive additive in liposomes prepared from neutral phospholipids (PL). Cations of Ca2+ were used as a mediator of DNA –FA/PL binding. The complexes DNA-PL-FA have shown the transformation from two lamellar phases to a condensed lamellar phase with increasing concentration of Ca2+. The DNA strands were packed in a two dimensional lattice in these complexes.
In studied systems, both the composition and also pH affect the DNA binding that varied in the range 10 –95 % of the DNA total amount as derived from spectrophotometry.
SAXS experiments were performed either at BL11-NCD beamline of Alba synchrotron or A2 beamline of Doris synchrotron in Hasylab, DESY, Hamburg.

Acknowledgement: SAXS experiments were supported by BioStruct-X/Calipso programme (Alba synchrotron); and EC programme FP7/2007-2013 under grant agreement no. 2267616 (Hasylab project II-20100372 EC), by the JINR project 04-4-1121-2015/2017; and grant VEGA 1/1224/12.

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Unraveling the working architecture of real catalysts by near-ambient XPS

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The structure of heterogeneous catalysts is dynamic and both their surface structure and composition may be modified when the gaseous conditions change in order to adapt their electronic properties and geometry to the new atmosphere. Some structures and active phases only exist under reaction conditions and can differ from those identified under UHV conditions 1. Thus, the study of catalytic systems under real conditions is essential to identify the active species at work, as the restructuring driven by the environment may induce strong changes in their properties and behavior. We have carried out an operando XPS study in the CIRCE beamline (NAPP endstation) at ALBA synchrotron of bimetallic rhodium-palladium nanoparticles supported over cerium dioxide (RhPd/CeO2) for producing hydrogen through the ethanol steam reforming reaction (ESR), which represents an attractive route for renewable hydrogen generation for energy applications. We have monitored both the surface restructuring and chemical state of two systems: (i) unsupported model Rh0.5Pd0.5 nanoparticles (4±1 nm) and (ii) model Rh0.5Pd0.5 nanoparticles supported on CeO2 powder (which constitutes a real catalyst). Both systems were exposed to reducing, oxidizing and ESR conditions (0.05 mbar) to produce hydrogen. Three photon energies were chosen (670, 875, and 1150 eV) in order to perform a depth-profile study of both systems to infer the environment-induced rearrangement and the development of a core-shell structure of oxidation states. We demonstrate that the reducible ceria support plays a crucial role in the catalytic process by providing new active sites strongly affecting both the physical and chemical properties of the metal nanoparticles which, in turn, have a strong effect on the catalytic performance (Figure 1). The interaction of the metal nanoparticles with the ceria support not only provides active oxygen atoms to the superficial metal atoms of the nanoparticles, but also limits the reorganization of the metals under reaction (quenching effect) with respect to the unsupported metal nanoparticles 2. This work constitutes one of the few examples reported where the surface of a real catalyst has been characterized by XPS under controlled atmospheres closely reproducing working conditions.

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Caption (s) - Add figures as attached files (2 fig. max):

Figure 1. Scheme of the changes experienced by unsupported RhPd nanoparticles and RhPd supported on CeO2. In the absence of a support, the model nanoparticles decomposed ethanol and were more strongly reduced for all the environments tested and the reduction temperature affected the amount of metallic phase found in Rh and Pd. In contrast, the capability of CeO2 as a support to activate water and to donate oxygen atoms determined the oxidation states of the noble metals under the same reaction conditions and ESR was effective.

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Spin-lattice coupled anomalies and magneto-crystalline transition in Pr0.50Sr0.50CoO3 investigated by x-ray absoprtion spectroscopies

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The spin state of Co ions is a key degree of freedom in many *Ln*_{1-x}*A*_xCoO₃ (*Ln*: lanthanide, *A*:alkaline-earth) oxides with remarkable physical properties. In (Pr,*Ln*_{1-x})Ca_xCoO₃ cobaltites near half-doped (x≈0.5), Co³⁺ spin-state sharp changes induce a first-order Pr³⁺ to Pr⁴⁺ valence shift and an exotic MIT. The insulating state is extraordinarily unleashed by electron transfer from Pr to Co sites, producing a volume contraction and stabilizing the diamagnetic Co³⁺ in LS state. Pr_{0.50}Sr_{0.50}CoO₃ (PSCO) notably differs from Pr_{0.50}Ca_{0.50}CoO_{0.50} (PCCO). In contrast with the absence of long-range magnetic order in PCCO, metallic PSCO is FM below *T_C*≈230 K. Here, an unexpected step in magnetization at *T_{S1}*≈120 K was ascribed to changes in the magnetocrystalline anisotropy. This step may be positive or negative as a function of the applied field. The crystal symmetry reduction from orthorhombic to tetragonal at *T_{S1}*, with a significant local deformation of Co-O octahedra could be related to changes in the orbital moment *m_l*.However, the CoL_{2,3} XMCD-derived *m_l* shows a monotonous behavior with temperature and no anomaly across *T_{S1}* . This contrasts with *m_s*, which presents an upward (downward) step on cooling at 100 (10) mT. This result thus points to a leading role of the spin-lattice coupling in this anomalous transition shown by PSCO. XAS and XES spectra also suggest Co³⁺ ions to be in a mixed spin state coexisting with predominantly low spin Co⁴⁺ ions, with an average spin state slightly larger than the one recently determined for PCCO.

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Near-surface magnetic moment of Co-doped magnetite (100)

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The widely varying magnetic and electrical properties of spinel ferrites make them promising materials for spintronics applications. In particular, the magnetite is electrically conducting with <111> as easy axis, while cobalt ferrite is an insulating hard ferrimagnet with a magnetocrystalline anisotropy over an order of magnitude larger than that of the magnetite and with <100> easy axis 1. By modifying the Co:Fe ratio and the preparation method, the magnetic and electrical properties can be tuned between those of magnetite and those of cobalt ferrite 2. However, the detailed magnetic properties are difficult to predict because of the many degrees of freedom involved, such as the inversion level and the flexible cation distribution. Additional mechanisms might enter into play when cobalt ferrites are reduced to nanometer thickness.

In this work, we focus on the study of the magnetic properties of the Co-doped magnetite surface. Co was deposited at room temperature on a well-characterized magnetite (001) surface, prepared by sputtering/annealing cycles. The surface was characterized in-situ by X-ray Photoelectron Spectroscopy (XPS), X-ray absorption (XAS) and X-ray Magnetic Circular Dichroism (XMCD) in Photoemission Electron Microscopy (PEEM) (Fig. 1) in order to obtain the composition, the magnetic domains distribution, and the near-surface orbital and spin magnetic moment of the individual cations [3]. The sample was subsequently annealed to increasing temperatures in order to promote the Co adatoms incorporation and/or diffusion into the crystal lattice. The results suggest the preferential Co incorporation as Co2+, which is in good agreement with the results reported in the literature. The evolution of the Co incorporation into the crystal lattice as a function of the annealing temperature was investigated. Moreover, it was observed that the domains distribution on Co-doped magnetite surface exactly matches with those measured on pure magnetite surface (Fig. 2).

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Caption (s) - Add figures as attached files (2 fig. max):

Fig. 1. Co L-edge XAS spectra measured with positive and negative helicity and XMCD calculated spectrum of the Co-doped magnetite surface (nominal Co coverage of 0.5 ML). Fig. 2. XMCD-PEEM images of the same zone of the Co-doped magnetite (100) sample measured at (left) the Fe L-edge and (right) the Co L-edge (50 μm of field of view).

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ALBA phases II and III

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High Pressure X-ray diffraction study of alpha-As2Te3

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The structural properties of arsenic telluride with monoclinic C2/m structure (alpha-As2Te3) have been studied both experimentally and theoretically under compression at room temperature by means of X-ray powder diffraction measurements up to 23 GPa and total-energy *ab initio* calculations. It has been found experimentally that alpha-As2Te3 remains in its initial monoclinic structure up to 14 GPa. At this pressure, a phase transition is observed in contrast to previous results that reported a phase transition between 6 and 8 GPa to the R-3m phase (beta-As2Te3) 1. The pressure dependence of the structural parameters and equation of state for the low-pressure phase of As2Te3 have been determined by Rietveld refinement. The reported results are compared with those available in the literature for related *A2X3* compounds.

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News and recent developments at MSPD BL

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Operando X-ray absorption spectroscopic studies on high-pressure and electrochemical heterogonous catalytic reactions towards CO2 utilization

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To level off the atmospheric concentration of CO2, the molecule largely responsible for global warming, several CO2 utilization pathways have been actively developed in the past years. Among others, heterogeneous catalytic conversion of CO2 has a strong potential to convert large amount of CO2 in short time span. For the rational improvement of heterogeneous catalytic reactions, it is of prime importance to elucidate active state of catalyst materials under realistic operating conditions. X-ray absorption fine structure (XAFS) allows investigation of gas, liquid, and solid samples in wide pressure and temperature ranges to understand the local structure around an absorber together with its electronic structures such as oxidation states.
In this work, we studied CO2 conversion and related reactions (H2 production for CO2 reduction) by XAFS to gain insights about the oxidation state of active catalysts under challenging and realistic operating conditions. The first experiment was on high pressure CO2 hydrogenation to methanol to examine the state of copper using a conventional Cu/ZnO/Al2O3 catalyst. A high pressure (up to 200 bar) and high temperature (up to 280 ℃) micro-reactor XAFS cell with a unique coiled heating system was fabricated using the polyimide coated fused silica capillary. It was found that the active copper component of the catalyst remain in the metallic state under working reaction conditions of 200 bar and 260 ℃. 1 The second studied reaction is water electrolysis using polymer electrolyte membrane (PEM) using a novel material, cobalt oxide, for hydrogen evolution reaction (HER). A conventional PEM electrolyser was modified with X-ray transparent windows and XAFS studies was performed under operando electrochemical conditions. The study clarified a dynamic oxidation state change of active Co material under electrochemically working conditions.
These experiments were performed at BL22-CLÆSS beamline at ALBA Synchrotron Light Facility with the collaboration of beamline staff members.

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ITQ-52, a new microporous zeolite with interconnected small and medium pores obtained using an aminophosphonium dication as structure directing agent

Author: Jose L. Jordá[1]

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Zeolites are usually obtained using tetraalkylammonium cations as organic structure directing agents (OSDAs). Recently, we have reported the synthesis of new zeolites using tetraalkylphosphonium (ITQ-26, ITQ-27, ITQ-34, ITQ-49, ITQ-53) or phosphazenes (ITQ-47) as OSDAs, which contain P-C and P-N bonds, respectively. 1

Here, we report the use of a novel family of OSDA, the aminophosphonium cations, with both P-C and P-N bonds in their structures. Particularly, the cation 1,4-butanediylbis[tris(dimethylamino)]-phosphonium was used as OSDA and a new zeolite, named ITQ-52, has been achieved. 2

Due to the severe peak overlapping, the structure of ITQ-52 could not be determined using laboratory X-ray diffraction data. In fact, even the true unit cell resulted to be elusive, being monoclinic with one angle extremely close to 90º, and then easily confused with an orthorhombic cell. So, all the preliminary attempts for solving the structure as orthorhombic failed.

New X-ray diffraction data were collected at beamline MSPD of the Spanish Synchrotron ALBA. The high resolution achievable using the MAD26 detector allowed determining the small deviation of one of the angles, and then that its true unit cell was monoclinic (α = 17.511 Å, b = 17.907 Å, c = 12.367 Å and β = 90.22º, space group I12/m1). Subsequently, the complete structure could be solved using the program FOCUS, showing that the unit cell of zeolite ITQ-52 contains 10 independent Si positions and 19 O positions, and presents a bidirectional pore system formed by channels of 8R and 10R that intersect one to each other generating large cavities, accessible through two 10R and four 8R apertures.

The structure found for ITQ-52 is in good agreement with the data obtained from solid state MAS-NMR and N2 and Ar adsorption, among other techniques.

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Caption (s) - Add figures as attached files (2 fig. max):

Figure 1. Rietveld refinement of the X-ray powder diffraction pattern of calcined ITQ-52

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News and recent developments at CLAESS BL

Special Session - Coffee and poster discussion: ALBA users and AUSE members / **132**

Towards structural studies of trypanosoma target proteins

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The trypanosoma species include human pathogens, most notably Trypanosoma brucei, which causes sleeping sickness (African trypanosomiasis) and Trypanosoma cruzi, which causes Chagas disease (American trypanosomiasis). These diseases occur in developing regions in the world and have a devastating effect on the economic viability in these regions. The diseases also occur in developped countries, and in particular in Spain, due to the high mobility of the population. The currently available chemotherapies are not satisfactory due to serious side effects, low efficacy and recently

emerging resistance. We aim to provide structures of three proteins that are viable targets for therapeutic intervention in trypanosome. Two of these are from T. cruzi and are involved important metabolic pathways of this organism. The third protein is involved in the unloading of replication factors from the DNA in T. brucei during the final stages of DNA replication. We describe the purification of two of the selected targets and small angle scattering measurements (SAXS) on one of them. Furthermore, we will discuss the progress in crystallizing these proteins.

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Characterization of buried interfaces of polymer films using high kinetic energy photoemission

Author: Jordi Fraxedas[1]

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We have characterized the buried interfaces of oxidized PS-OH layers grafted on silicon substrates with high kinetic energy photoemission at the BESSY II HIKE endstation (Helmholtz-Zentrum Berlin für Materialien und Energie). PS-OH layers (4.7 nm thick) have been prepared by spin-coating and oxidized using gold-coated PDMS stamps, replicating DVD patterns. The oxidation was achieved by applying a 35-40 V bias voltage at relative humidities above 70%. The figure shows the Si1s photoemission lines taken with photons in the 2020-3000 eV range. At 2020 eV (black continuous line) only the feature associated to sub-stoichiometric silicon oxide (SiOx) is detected, which builds the interface with the grafted polymer. At increasingly higher photon energies, first the stoichiometric oxide (SiO2) and then the silicon substrate are observed. We thus observe that the PS-OH/SiOx, SiOx/SiO2 and SiO2/Si interfaces can be selectively approached by tuning the electron kinetic energies and thus the electron mean free paths. Surprisingly, the PS-OH layer is not oxidized in this process as clearly observed from the C1s signal.

Caption (s) - Add figures as attached files (2 fig. max):

Si1s photoemission lines taken at 2020, 2100, 2300, 2500 and 3000 eV photon energies. The binding energy regions corresponding to the bare silicon, stoichiometric silicon oxide (SiO2) and non-stoichiometric silicon oxide (SiOx) are indicated.

Special Session - Coffee and poster discussion: ALBA users and AUSE members / 125

EXAFS study of Ni-M supported systems for catalytic reforming of methane

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The study of Supported nickel nanoparticles systems has gained interest in the last years because of its high performance in dry reforming of methane (DRM) to produce syngas, used for several liquid hydrocarbon production (Fischer-Tropsch processes), or to obtain hydrogen, by purification of syngas, promising to become one of the major sources of energy in the near future. Coke formation by methane decomposition or by Boudouard reacction has a negative influence on catalyst stability. A good active phase dispersion in the support surface could reduce the particle size and it limit carbon formation 1. Some studies for avoiding the coke deposition in Ni based catalysts are related with doping with noble metals or by oxidative effect of basic promoters. CeO2 is reported in this way for several authors [2,3]. The mechanism by which the basic promoters like CeO2 limit deactivation on Ni catalysts is that the Ni forms a closely bonded structure or alloy with the promoting metal, which preferentially forms C-O bonds instead of C-C bonds, which helps in oxidation of surface carbon [4]. Furthermore, the presence of CeO2 in strong interaction with nickel metal nanoparticles could lead to effects in the metallic particle shape during the reaction with possible consequences in the performance of the reaction 2.
We propose the study of nickel nanoparticle systems, and modified systems with CeO2, supported on high specific surface mesoporous silica using different methods of preparation to clarify differences in structure and particle size of the catalytic active phase and its consequences in DRM activity.

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Special Session - Coffee and poster discussion: ALBA users and AUSE members / 126

Combining atomic spatial resolution with X-ray absorption spectroscopy at ALBA: connection of a scanning tunneling microscope to the BOREAS beamline.

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The study of supported adatoms, films or more complex nanostructures by X-ray absorption and circular magnetic dichroism (XMCD) requires their in-situ growth in ultra-high vacuum (UHV), and hence must be followed by some means of structural characterization that can be correlated to the spectroscopic data. Scanning tunneling microscopy (STM) provides structural information of surfaces with ultimate atomic resolution. Here we present a combined STM-XMCD study at ALBA, which has been realized by coupling a variable temperature STM of ICN2 to the BOREAS beamline via an ultra-high vacuum (UHV) transfer system.

We used this multitechnique set-up for the first time to study the magnetic and orbital moment anisotropy of 3d metal adatoms and few-atom clusters deposited on heavy-metal surface alloys. By depositing 1/3 of a monolayer of heavy metal (Bi, Sb) on a Ag(111) single crystal, ordered surface alloys with a record ($BiAg_2$) and negligible ($SbAg_2$) spin-orbit interaction were grown. The $\sqrt{3}$ x $\sqrt{3}$

R30° structure of the surface alloy was atomically resolved by STM, which allowed us to minimize the density of defects and obtain high quality, large domain surface alloys. After the surface characterization, Fe was deposited at room temperature, and the coverage-dependent size distribution of Fe nanoclusters was studied by STM (Fig. 1a). The samples were then successfully transferred in UHV to the HECTOR end-station for the XMCD measurements (Fig. 1b).

Acknowledgments: we thank Jose Ferrer and his team for his support in the installation of the STM at the BOREAS beamline.

Caption (s) - Add figures as attached files (2 fig. max):

Fig. 1: a) Atomically-resolved STM image of Fe adatoms, dimers and trimers deposited on the BiAg2 surface alloy. b) XAS spectra at the Fe L edge obtained with circularly polarized light (red/blue) and corresponding XMCD spectra (black), measured at the same sample.

Special Session - Coffee and poster discussion: ALBA users and AUSE members / 127

Crystallographic and functional characterization of the effects of the radiation damage on proteins and prospection of new scavengers

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Biological material, such as proteins, is highly sensitive to radiation damage (RD) coming from the intense ionizing radiation, which causes severe structural and functional damage to organic matter either directly by the generated free electrons or indirectly by formation of reactive oxygen species (free radicals). Synchrotron radiation is a suitable tool to both generate the radiation and study its effects on biological material.

The first step to characterize the effects of the radiation on biological material is to establish the appropriate metrics of the damage. The functional effects are commonly measured by means of activity assays upon the absorbed dose. The structural effects can be measured in different ways, depending on the technique used. Structural changes studied by Small angle X-ray scattering (SAXS) are often measured by means of the radius of gyration Rg of the protein in solution. Much more controversy is generated on the correct metrics to measure the structural changes induced by radiation studied by macromolecular crystallography (MX). Suggested metrics are R-factors and I/Sigma, among others.

The correlation between the RD effects measured in functional assays and these measured in structural studies, both SAXS and MX, have not been explored extensively. Here we report an initial study aiming to correlate the metrics of these studies. The effects of RD have been explored in diverse soluble proteins, namely, Lysozyme (Lys), Aldose Reductase (AK1RB1) and Catalase (BLC).

Added small molecules to mitigate RD are extensively used in SAXS studies, like DTT or glycerol, which act primarily as free-radical scavengers of secondary radiation damage. The use of scavengers is also common in MX studies. Several putative scavengers have been tested in functional assays and in structural studies using Lys and AK1RB1 proteins. All experiments are performed at room temperature to highlight the effect of radiation damage. The different metrics to quantify the RD in the different studies are checked to correlate the results using scavengers.

This project is being carried out as collaboration between NCD-BL11 and XALOC-BL13, the beamlines at Alba dedicated to SAXS and MX, respectively.

Special Session - Coffee and poster discussion: ALBA users and AUSE members / 115

Orientation and conformation changes within a craze in poly(ethylene terephthalate) as revealed by synchrotron infrared and Raman microspectroscopies

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Crazes constitute one of the most common failure mechanisms in polymers. Since crazes act as fracture precursors, they provoke severe impairment of the mechanical properties of the material. Thus, a deeper understanding of chain rearrangement occurring inside crazes is of fundamental and practical importance.
In this work, we have applied synchrotron infrared microspectroscopy (SIRMS) and Raman microspectroscopy to investigate the changes in orientation and chain conformation taking place inside micron-sized crazes in poly(ethylene terephthalate), PET. These crazes developed naturally during cold drawing of the material, i.e., without making a notch in the specimen prior to uniaxial deformation.

In the case of SIRMS we have exploited the natural polarization properties of the bending magnet radiation (BMR) for the orientation analysis, thus taking advantage of the complete synchrotron flux available, which is crucial when employing small microscope apertures.[1,2]

Regarding the conformational rearrangement within crazes, we have observed a promotion of the fully-extended chain conformational structure at the expense of mainly the trans amorphous conformers of the mesomorphic phase. In addition, the conformational changes were accompanied by an increase in crystallinity of around 4 %. Overall, these results are consistent with a local strain-hardening phenomenon, although some dissimilarities have been found regarding the conformational rearrangement along the deformation neck in drawn PET samples below Tg. Our results suggest that different conformational transformation pathways could occur during crazing.[3]

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Caption (s) - Add figures as attached files (2 fig. max):

Figure 1. SIRMS results. Left: orientation parameter spatial distribution as a 2D false color map. Right: spatial distribution of the 1340 cm⁻¹ to 1371 cm⁻¹ band ratio (25x25 μm² map) and of the degree of crystallinity (20x8 μm² map) as 2D false color maps. The maps are superimposed on optical microscopy images.

Special Session - Coffee and poster discussion: ALBA users and AUSE members / 114

Annealing effect on the crystal structure in Heusler Ni45.5Mn43.0In11.5

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Heusler based magnetic shape memory alloys exhibit functional properties as magnetocaloric effect, high magnetoresistance or shape memory behavior; probably due to the existence of martensitic phase transition with a strong magneto-structural coupling. These alloys are candidates for applications as sensors, actuators or magnetic coolers. In this work, the crystal structures of the Ni45.5Mn43.0In11.5 annealed ribbon was followed at 150 K, 300 K and 350 K, whereas as quenched ribbon was analyzed at 100 K and 300 K. Experiments were performed at Diamond Light Source, UK, in the range between 10º and 100º by employing radiation of λ=1.127 Å. It was found that austenite is the stable phase at room temperature before annealing. After annealing, martensite is the stable phase (monoclinic with a 10M modulation). Thus, martensitic transformation is shifted to higher temperatures. There are also important changes on the texture in reflection peaks located in the 42º to 44º region. Complementary thermomagnetic measurements were performed and it was found that the sample is in a paramagnetic state above and below the martensitic start temperature.

References:

Annealing effect on the crystal structure and exchange bias in Heusler Ni45.5Mn43.0In11.5 alloy ribbons. L. González-Legarreta et al.
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Special Session - Coffee and poster discussion: ALBA users and AUSE members / 88

GIXRD studies of solvent annealing effect in donor-acceptor structures

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Bulk heterojunctions (BHJs), in which electron–donor and electron–acceptor material are blended together from a common solution, represent the most promising device structure for high-efficiency organic solar cells. It is has been shown that BHJs solar cells can reach higher efficiencies and fill factors by controlling the morphology applying solvent vapor annealing treatments (SVA) 1. In this technique, the solvent vapor penetrates into the blend re-organizing the donor-acceptor arrangement. A powerful tool to study these changes in the morphology is grazing incidence wide angle X-ray scattering (GIWAXS) with a synchrotron source. In this work, 2D- GIWAXS is employed to investigate the effect of the solvent annealing on the structure of BHJs formed by two oligothiphenes (donor) with [6,6]-phenyl C71-butyric acid methyl ester(PC71BM) (acceptor) 1. In addition, the incident angle was varied in order to obtain depth-resolved information of the structure. The structural results are correlated with the photovoltaic performance of the solar cells.

References:

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Special Session - Coffee and poster discussion: ALBA users and AUSE members / 116

A new scavenger that reduces radiation damage in solution and crystalline protein samples

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Radiation damage is a serious problem in synchrotron light sources, limiting the quality of the collected data. This issue is critical for structural biology techniques, like Biological Small Angle X-ray Scattering (BioSAXS), and Macromolecular Crystallography (MX). Common strategies to reduce radiation damage in SAXS are flowing the sample through the beam, or adding small molecules such as dithiothreitol (DTT) or polyols such as glycerol to the sample. However, DTT is not advisable in proteins with disulphide bonds, and glycerol may reduce signal-to-noise ratio at high concentrations. In MX, the primary strategy is cooling the samples to cryogenic temperatures. However, radiation damage is a complex phenomenon not completely understood, and still a milestone for structural biology studies at current synchrotron radiation facilities.
The scavenging properties of several small molecules that have not been investigated as scavengers for SAXS and MX were analysed. Lysozyme was used in both experiments, as this is a model protein for SAXS and MX. All the assays were performed at near room temperature. The results show that the so-called SMX1 compound has similar efficacy as DTT or glycerol in decreasing radiation damage in solution scattering experiments. SMX1 also shows scavenging properties in MX experiments on lysozyme crystals at room temperature. Protective effects of SMX1 on enzyme function of lysozyme irradiated in solution were also studied. Altogether, the results show that SMX1 can be considered a new alternative scavenger for structural biology techniques. This study is part of an ALBA Synchrotron Light Source project in radiation damage on biological macromolecules, in collaboration with the Spanish Nuclear Safety Council (CSN). This project is being carried out as collaboration between NCD-BL11 and XALOC-BL13, which are the ALBA beamlines dedicated to SAXS and MX, respectively.

Special Session - Coffee and poster discussion: ALBA users and AUSE members / 113

Remote Plasma Enhanced –Chemical Vapor Deposition (rPE-CVD) of Graphene on Various Substrates

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Mechanical exfoliation of highly oriented pyrolytic graphite (HOPG) has been the most common method of producing single layers of graphene. However, the lateral dimensions of monolayer samples are typically limited to the micro-scale. Since large area graphene films on insulating substrates are required for practical applications, several techniques have been explored such as chemical vapor deposition (CVD) on transition metals, graphitization of SiC wafers under high vacuum, and reduction of oxidized graphite films.

Plasma Enhanced Chemical Vapor Deposition (PE-CVD) [1-3] makes the deposition method more tunable as it allows for an independent control of the reaction parameters and the growth parameters, which should lead to a better control of the size and shape of the nanostructures. Moreover, converting the precursor gas into a plasma state involves, by definition, a higher amount of active carbon radicals in the reaction process and thus enhances the deposition rate. By means of using a highly reactive deposition technique such as a hydrocarbon plasma, one can decrease the exposure time and/or decrease the substrate temperature. This latter feature opens the deposition process towards a wider variety of substrates with lower melting points. Last but not least, a remote plasma is –by definition - generated at a distance from the substrate, thus minimizing preferential perpendicular growth directions that the electrical fields may induce in a traditional plasma setup.

CELLS-ALBA together with ibss Group, Inc. has adapted the GV10x downstream inductively coupled RF plasma source typically used for cleaning hydrocarbon contaminated from SEM chambers to also remove carbon deposits on optical precision surfaces [4]. For these applications the feedstock gas of the plasma consists of a chemically active agent such as oxygen or hydrogen converting carbon into CO2, CO, or hydrocarbons gas via a corresponding oxidation or reduction process, respectively.

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Caption (s) - Add figures as attached files (2 fig. max):

Figure 1: SEM image of one of our graphene samples. Figure 2: Raman spectra corresponding to some of our graphene samples.

Special Session - Coffee and poster discussion: ALBA users and AUSE members / 112

Time-resolved kinetics ordering of FeAl

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In this study, time resolved X-ray scattering using a synchrotron X-ray source has been used to gain insight of time-temperature atomic ordering of an intermetallic Fe40Al ball-milled powder with the aim to estrapolate these results as an explanation of rapid ordering processes occurring during thermal spray coating deposition. Interestingly, present results show that in the range between 400 to 650ºC, the evolution of the atomic order with time can be observed through the processing and fitting of the first acquired diffractograms, while above such temperatures, the ordering process is too fast to be able to be resolved with the available time resolution. Specifically, after performing Rietveld analysis of the data to fit the occupation factors of the Fe and Al atoms within the B2 lattice, it has been observed that at low temperatures such factor for the Fe changes slowly with the time and faster at higher temperatures as expected; the evolution seems to be non-exponential at moderate temperatures. The changes on the crystal lattice parameter upon heating and cooling, and its time dependence in the up-quench to moderate temperatures have been also investigated.

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Special Session - Coffee and poster discussion: ALBA users and AUSE members / 82

Structural study of the bulk and local compressibilities of the mixed organic/inorganic [(CH3)4N][FeCl4] compound

Author: Jose Antonio Barreda-Argüeso[1]

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Mixed organic/inorganic crystals as [(CH3)4N]FeCl4 (Ref. 1) are receiving considerable attention due to their simple structure consisting of organic (CH3)4N+ and inorganic FeCl4- tetrahedra, being precursors of magnetic ionic liquids with FeCl4- as the most common anion (Ref.2). The incorporation of magnetic anions (as FeCl4-) makes them attractive for modifying their thermodynamic properties by applying external magnetic fields or illumination (Ref.3).
In spite of its relevance, the vibrational and electronic structures of FeCl4- anions remain yet unexplored, in part due to the scarce number of mixed organic/inorganic crystals incorporating FeCl4- anions in the structure, apart from the strong absorption of these materials in the visible-ultraviolet range. This is due to low-lying, spin and parity allowed electric-dipole charge-transfer transitions, forming the material band gap. Furthermore, these materials can be easily compressed due to the small bulk modulus (K ≤ 10 GPa) in comparison to the local bulk moduli of both organic and inorganic tetrahedra, being more than an order of magnitude higher, as it was recently shown in [(CH3)4N]2MnX4 (X: Cl,Br) compound (Ref.4).
This work reports investigations on the structure of isostructural compounds [(CH3)4N]FeCl4 and [(CH3)4N]GaCl4 as a function of pressure with the aim of determining the compression mechanisms governing the crystal bulk and molecular tetrahedra. We have obtained the equation-of-state for the crystal and both tetrahedral ions, the organic (CH3)4N+ and inorganic (Fe,Ga)Cl4- by means of x-ray diffraction and Raman spectroscopy in the 0 –15 GPa range. The comparison between the local and bulk compressibilities allows us to conclude that molecular tetrahedra are harder to compress

than the crystal bulk, due the strong intramolecular covalent bonds in comparison to the weak intermolecular hydrogen bonds.
A full report on the structure of these compounds and their associated properties will be presented at the conference.

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Caption (s) - Add figures as attached files (2 fig. max):

Bulk and local equation of states of [(CH3)4N]FeCl4 and GaCl4-, respectively.

Special Session - Coffee and poster discussion: ALBA users and AUSE members / 80

Synchrotron Radiation based techniques for the study of altered metal foil coatings in Baroque altarpieces

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Baroque artists applied metal foils on altarpieces to produce colourful sparkling and shining light effects. Additionally, pigments or dyes were mixed with oils and resins and applied over the silver or gold foils to create also colour shades. However, the effect intended by the artist appears distorted by the alterations occurred over the years resulting from the chemical reactions among the materials themselves and with the environment. Besides, these processes are favoured by the environmental conditions in which the materials are kept. The silver foil itself reacts with the environment through the micro fissures open in the organic protection coatings producing silver sulphides and chlorides, which, while crystallizing, produce themselves stresses that enlarge the cracks resulting in a gradual loss of the metal layer. The study of the reactivity and stability of the metal foils, coating layers and adhesives which fix the foils onto the ground layers (often a bole) is essential to define restoration strategies. The samples extracted are very complex, to the original materials (bole, adhesives, metal foils, resins, drying oils, pigments/dyes, fillers and binders), reaction, weathering and aging compounds (i.e. carboxylates and oxalates) we have to add those materials incorporated by historical restorations and dirtiness. Furthermore, those substances are present in variable concentrations, and often in extremely low concentrations. Finally, the location and distribution of the reaction and aging substances in the different layers is also important and consequently, homogenizing and dissolving the samples is not adequate since this valuable information is lost. Synchrotron radiation based micro-sensitive techniques such as μFTIR and μXRD are outstanding to overcome the difficulties involved in the analysis. The cathedral of Tortosa, a few kilometres inland from the mouth of the

Ebro river, contains a set of Baroque altarpieces made over a prolonged period of about one hundred years, the oldest dating 1671 and the newest, 1775. During this extended period the materials used and the techniques employed changed and those changes are manifested in the aging and alteration processes undergone by the artworks. The nature, reactivity and alterations of the green, red and amber protective coatings are studied.

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Special Session - Coffee and poster discussion: ALBA users and AUSE members / 89

Materials, techniques and conservation of historic stained glass "grisailles"

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A grisaille is a brown-blackish paint applied onto the inner surface of stained glass to draw the contours and details of the figures and producethe effect of shades and volumes. Grisailles were traditionally made of finely ground oxides of iron but also of copper, zinc, lead or manganese mixed with a flux such as lead ground glass and a binder and fixed onto the flat glass by firing. The grisailles have typical layer thickness varying between 10 and 100 μm and are formed by a complex mixture of pigment particles, crystalline and amorphous reaction compounds, aging and weathering compounds. The high brilliance, collimation, energy selection and monochromacity of the SR beam are ideal to obtain micro-XRD patterns from thin cross sections of the grisailles. The analyses are complemented with SEM-EDX and LA-ICPMS. A selection of grisailles from several cathedrals and buildings in Spain, Avila, Burgos, Alcalá de Henares and in particular from Segovia, dating from early 16th to the 20th century and belonging to several master glaziers are studied. Changes in the methods of production and materials in the different historical periods are obtained and also related to the conservation state of the materials.

Special Session - Coffee and poster discussion: ALBA users and AUSE members / 81

High-pressure diffraction study on cobalt ferrite spinels

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High pressure angle-dispersive x-ray diffraction measurements on CoxFe2-xO4 (x=1, 1.5, 1.75) spinels have been performed at the beam line MSPD in the ALBA synchrotron 1. The patterns were collected at room temperature between ~0 and 34 GPa with an incident monochromatic wavelength of 0.4246 Å. Samples were loaded in 130 microns diameter holes of 40 microns thick stainless steel gaskets in DAC with diamond culet sizes of 300 microns. Two ruby grains were loaded with the sample for pressure determination 2 and a mixture of methanol and ethanol (4:1) was used as the pressure-transmitting medium. The three samples show a similar structural phase transformation from the cubic spinel structure to an analogous post-spinel phase at around 20 GPa as can be seen in Fig. 1 for the CoFe2O4 sample, for instance. Spinel and post-spinel phases coexist in a wide pressure range (~20 –25 GPa). The transformation is irreversible as measurements performed after releasing pressure revealed that the post-spinel phases are stable down to ~4 GPa and then, they decompose into a new phase with very broad diffraction peaks indicating a poor crystallinity. Neither the spinel nor the post-spinel phases can be recovered after a subsequent compression cycle. This phase transformation induced by pressure explains the irreversible loss of the ferrimagnetic behaviour reported for these spinels [3,4].

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Caption (s) - Add figures as attached files (2 fig. max):

Figure 1. Powder x-ray diffraction patterns of CoFe2O4 at selected pressures. The asterisk marks the appearance of contribution from post-spinel phase while cross indicate the vanishing spinel phase. The pressure was increased and released as indicated by arrows on the right of the picture.

Special Session - Coffee and poster discussion: ALBA users and AUSE members / 118

XALOC: The MX beamline at the synchrotron ALBA

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BL13-XALOC is the only operating macromolecular crystallography beamline at the 3 GeV ALBA Synchrotron near Barcelona (Spain) and started user operation on July 2012. It receives light from an in-vacuum undulator and it is fully tunable from 5 to 22 keV which allows anomalous diffraction-dependent experiments. The optical design consists of a Si(111) channel-cut crystal monochromator and a pair of focusing KB mirrors. The beam at the sample position is typically focused with a

size of 52 μm x 5.5 μm FWHM (H x V) and it can be defocused to match the dimensions of the crystal up to a maximum of sizes 300 μm x 200 μm FWHM (H x V) which is very uniform due to the small slope errors of the mirrors (55 nrad and 83 nrad RMS for the vertical and horizontal focusing mirrors, respectively). Both mirrors can also be removed from the beam path to use an unfocused beam. Thorough commissioning with X-ray beam and user operation the beamline has demonstrated an excellent energy and spatial stability of the beamline. The end-station includes a high-accuracy single-axis diffractometer, a removable mini-kappa stage, an automated sample-mounting robot (CATS) that performs reliably with SPINE/MD vials/caps and a photon-counting detector (Pilatus 6M) that allows shutterless operation. This equipment, together with the operation flexibility of the beamline, allows a large variety of types of crystals to be tackled, from medium-sized crystals with large unit-cell parameters to microcrystals. Recent software updates include a new user GUI, raster scan to determine the best area to expose the sample, automatic data collection strategy (EDNA), inverse beam data collection method and an automated pipeline to perform data reduction and integration (AutoProc) that runs after each data collection. The control system is based on Sardana-Tango architecture and MXCuBE is being integrated. As per May 2015, 51 structures have been deposited to the PDB with data collected at XALOC and more than 17.000 crystals have been tested.

Special Session - Coffee and poster discussion: ALBA users and AUSE members / 85

Photoemission and x-ray absorption of hexagonal Boron Nitride prepared by interaction of Boron vapor with Nitrogen ions

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We present a study of the texture and crystalline perfection of hexagonal boron nitride (h-BN) films based on x-ray absorption near edge structure (XANES) and x-ray photoemission (XPS) spectroscopies. The measurements were conducted at BESSY synchrotron facility using beamline PM4. The synchrotron results are also compared with the more conventional infrared and Raman spectroscopies.

Hexagonal BN films were grown by ion-beam-assisted deposition (IBAD) through B evaporation and concurrent N2+ ion bombardment. XANES and XPS reveal that the quality of h-BN layers can be controlled through ion bombardment and heat treatments, and provide unique information to optimize the growth conditions. Furthermore, the nitrogen ions contribution leads to a compressive stress in the films that tends to orient the basal planes perpendicular to the substrate. The texture of h-BN films is studied by XANES at different angles of incidence, a technique very well suited to study the orientation of π bonded systems. In this way, we have obtained a map of basal plane orientation as a function of growth conditions.

The quality of the h-BN films is discussed in terms of the XANES and XPS data, by comparing the amount of vacancy defects and the width of the spectral features.

Special Session - Coffee and poster discussion: ALBA users and AUSE members / 109

Selenium speciation in Se-enriched wheat by XAS and HPLC-ICP-MS

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Selenium is an essential micronutrient for humans and it has been shown to be antioxidant, anti-tumoral, anti-viral and to contribute in the treatment of cardiovascular diseases. Therefore, appropriate selenium intake can benefit human health, but millions of people worldwide consume it at levels below the body's need for the correct expression of selenoproteins.
Se-poor soils around the world produce Se-deficient crops, resulting in deficient food for humans lacking selenoaminoacids. Soil Se enrichment in edible plants has been proposed as a solution for this problem. Selenium-enriched wheat may contribute to human welfare in the form of functional foods.
The properties of Se in wheat (bioavailability, toxicity, etc.) are strongly dependent on their chemical speciation. Consequently, characterization of the different species present is required in order to assess the potential health benefits as well as its safety. In this context, it is important to gain an understanding of the plant's mechanism of bioassimilation of Se, and its metabolism, where inorganic species are transformed to selenoaminoacids. It is also critical to determine the distribution of the species in the different plant tissues (roots, stems, leaves, and grain). Furthermore, the novel element in the research is the use of a chemical tuning of the Se species in the soil to obtain the desired ratio in wheat, to define the properties of the final functional food.
Oppositely, mercury is not an essential micronutrient, but its concentration in crops has risen, and mercury has been shown to change Se uptake and speciation. Its presence can hamper the health benefits of Se-enriched wheat crops. The interaction between the two elements is due in part to the formation of Se-Hg complexes.
Accordingly, we have measured Se content and speciation in wheat tissues by conventional speciation techniques as HPLC-ICP-MS and by direct X-Ray Absorption Spectroscopy with Synchrotron Radiation in CLAESS beamline at ALBA. The comparison of the results have provided reliable data that have allowed to study the distribution and speciation of Se in enriched wheat and the significance of the presence of Hg for the crops.

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Special Session - Coffee and poster discussion: ALBA users and AUSE members / 102

Evaluation of skin collagen under infrared exposure: a study based on Small Angle X-Ray Scattering using synchrotron radiation

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Infrared radiation (IR) penetrates the epidermal and dermal layers of skin increasing temperature significantly 1, and consequently it can damage both skin compartments. Collagen is located in the dermis and accounts approximately 75% of total dry weight of skin providing integrity of this tissue [2, 3]. This protein could be damaged at high temperatures coming from IR exposure, which can cause skin disorders.
The regular staggered structure of collagen induces periodic variations of electron density visible by X-ray scattering as sharp Bragg peaks. Position, intensity and number of reflections of the typical axial periodicity of skin collagen change by effect of tissue physiology or physical conditions [2, 3]. The use of synchrotron radiation with Small angle X-ray scattering (SAXS) is required to detect skin collagen reflections, due to these changes are not detected with a conventional radiation source.
In this work the evaluation of collagen structure in native skin and in skin exposed to IR was performed by SAXS using synchrotron radiation. Different skin treatments were carried out with phospholipid nanostructures (bicosomes [4]) incorporating beta-carotene to evaluate their protection effect on skin collagen against IR exposure.

The characteristic collagen peaks in the X-ray profiles showed a decrease in intensity in the skin samples exposed to IR in comparison with native skin. This fact could indicate the disorganization in the structure of the collagen, which was consequence of the degradation of the protein (Fig. 1).

The skin samples previously treated with bicosomes incorporating beta-carotene and subjected to IR kept the X-ray profile with the characteristic features of collagen. This fact would evidence the preservation of collagen fibres of the skin treated with this system under IR exposure, indicating the potent efficacy on collagen preservation of bicosomes with beta-carotene.
In conclusion, the heat produced by IR exposure damages skin causing degradation of skin collagen, and bicosomes protect collagen fibers of the skin under IR exposure. Further, the use of synchrotron radiation in SAXS is a good technique to evaluate microstructural changes of skin collagen.

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Caption (s) - Add figures as attached files (2 fig. max):

Fig. 1: SAXS profiles of different skin samples with the correspondents reflections of collagen. Native skin (black), skin exposed to IR (red), skin exposed to IR previously treated with bicosomes incorporating beta-carotene (blue).

Special Session - Coffee and poster discussion: ALBA users and AUSE members / 103

Cationic distribution and magnetic properties of cobalt-ferrite thin films probed by x-ray magnetic circular dichroism

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Investigation of the epitaxial thin films of insulating ferromagnets (cobalt-ferrites) has received a renewed attention due to its central role in spintronic devices involving spin Hall effect 1. The spin magnetoresistance (SMR) is generally known to depend upon the film orientation and consequently the chemical nature of the exposed film surface. Among other recent works on cobalt-ferrite films 2, we report the cationic distribution, especially at the surfaces, due to the fact that the SMR is mainly controlled by the interface orbital magnetic moments.

In this work, we have fabricated the epitaxial CoFe₂O₄ (CFO) thin films on SrTiO₃ for 14 nm and 23 nm thicknesses by pulsed laser deposition. We employ x-ray absorption spectroscopy to investigate the electronic charge distribution and element-specific x-ray magnetic circular dichroism (XMCD) to unravel the spin and orbital magnetic moments of Fe/Co ions and their site occupancy. The 14 nm thick CFO films exhibit non-saturation in the magnetization and reduced moments while the 23 nm CFO film show a bulk-like magnetic moment. The presence of Co²⁺(T_d) and Fe²⁺(O_h) cations owing to the smaller net moment in the CFO films by increasing the antiparallel alignment [which could cause antiphase boundaries] and possible (oxygen) non-stoichiometry of cationic distribution. In addition, the CFO films exhibit anomalous magnetic properties, including a two-step magnetization reversal with different 'magnetic phases'and a reduced coercivity with the thickness. Disentangling the effects of non-stoichiometry and/or antiphase boundaries is explained to discuss these anomalous properties. Our investigations shall offer further insight into the interface, cation ordering, and magnetic properties of cobalt-ferrite films as interesting systems for novel spintronic device applications.

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Special Session - Coffee and poster discussion: ALBA users and AUSE members / 100

PEEM analysis of the pin-on-disc weartrack of carbon/boron nitride nanometric multilayers

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A series of multilayer thin films composed of nanometric hexagonal carbon and boron nitride sublayers was grown on silicon substrates by ion beam assisted deposition (IBAD), following the method described elsewhere 1. The period of the multilayers was varied between 3 and 40 nm in the whole series of samples. Carbon was deposited always with c-axis perpendicular to the substrate surface while BN was deposited in both, parallel and perpendicular orientations depending on the sample.

On these multilayered films, erosion pin-on-disc experiments were performed to create a measureable weartrack where only a few of the topmost sublayers are exposed to the environment. In this way, layers with nanometric thickness appear as micrometric and nanometric bands along the sliding direction in the wear track. The spectroscopic analysis of these compositional features in the weartrack constitutes a perfect playground to evaluate the microscopy and spectroscopy capabilities of PEEM in a real Materials Science problem.
After PEEM analysis, several interesting conclusions were obtained, which are briefly discussed as follows. The multilayered stacking is confirmed by observation of terraces of pure BN and carbon phases. The spectral features of B(1s) edge within one sample varies from an almost perfect hexagonal structure (already observed by TEM 2 for some multilayers), to a distorted hexagonal structure with a big amount of vacancy defects and, finally to the formation of metallic borides and/or borates [3]. This structural/compositional evolution is attributed to the tribochemical interaction with the Cr-steel ball during the mechanical test. It was found too, that Fe reacts selectively with boron while Cr does with carbon during formation of the tribolayer. Evolution on the formation of the tribolayer from metal Fe transfer, to formation of Fe borides is also discussed.
A detailed study based on comparison of compositional PEEM images and local XANES spectra extracted from the stacking of PEEM data is presented.

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Caption (s) - Add figures as attached files (2 fig. max):

Figure 1: pi* B(1s) map of the weartrack of a C/BN multilayer with 40 nm period and the set of spectra obtained from several positions along a cross-line of the sample.

Special Session - Coffee and poster discussion: ALBA users and AUSE members / 101

Structural characterization of alkyltrimethylphosphonium surfactants by powder real-time and monocrystal XRD analysis

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Surfactants based on tetraalkylphosphonium salts have recently become the focus of a good number of investigations because they offer superior properties when compared with tetraalkylammonium surfactants 1, such as much higher thermal stability. Since the structure of phosphonium surfactants still remains hardly explored 2, we have undertaken the structural study of a series of alkyltrimethylphosphonium bromides (nATMP·Br, n is the number of carbon atoms in the alkyl chain taking values from 12 to 22). This study is based on the information provided by DSC, XRD and optical polarizing microscopy. WAXS and SAXS patterns were simultaneous recorded from powder samples using synchrotron radiation (ALBA, NCD BL11 line). Monocrystals for selected cases (n = 12, 18) were also analyzed by XRD using conventional cameras.

The DSC traces registered over the 20-280 ºC range revealed the presence of two (for $n \leq 14$) or three (for $n \geq 16$) endothermal peaks arising from reversible thermal transitions involving crystalline, liquid-crystal or liquid phases. These phases were characterized by real-time XRD recorded at variable temperature (Fig.1). SAXS patterns displayed the presence of a long spacing peak in the ~1.8-4.0

nm range corresponding to the nanoperiodicity of the structure. In the WAXS region, the crystal structure that is adopted by the salts in the different phases was reflected as multiple discrete scattering. Conspicuous changes in both WAXS and SAXS patterns were observed upon heating and cooling at temperatures consistent with those estimated by DSC.
Results of the monocrystal analysis showed that the unit cell of nATMP·Br salts is monoclinic for n = 12 or triclinic for n = 18, and contains four or two molecules respectively. In both cases molecules are in a fully extended conformation and packed with the long alkyl chains and the phosphonium and bromide ions arranged in alternating non-polar and polar layers (Fig. 2). The alkyl chains are tilted respect to the layer planes and are deeply interpenetrated.

It could be preliminary concluded that nATMP·Br surfactants adopt a layered biphasic structure with features similar to that described for alkyltrimethylammonium surfactants previously studied by us.

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Special Session - Coffee and poster discussion: ALBA users and AUSE members / 106

In situ High Pressure Powder Diffraction study of proton conductors based on metal phosphanates

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Soft Porous Metal Organic frameworks (MOFs) are referred to as a class of coordination polymers that exhibit structural flexibility in response to guest interactions or physical stimuli 1. By combining softness and regularity, the responsive crystalline frameworks show, for instance, unique mechanisms of separation and storage of gases.

Here we report the effects of high pressures of CO2 on the frameworks of two types of coordination polymers based on multifunctional metal phosphonates, which exhibit proton conductivity at high relative humidity in addition to porous properties. The first one, Ni2(H2O)2(O3PCH2N(C4H8)NCH2PO3)·8H2O (Ni-STA-12) is a well-known MOF material structural featured by 1D channels build from MO5N octahedra linked by the piperazinyl moieties 2. The second solid, Mg[(HO3PCH2)2NHCH2C6H4CH2NH-(CH2PO3H)2]·2H2O, (MgHDTMP·2H2O), is a pillared layer metal phosphonate containing flexible alkyldiaminetetraphosphonate as linker of the inorganic layers. For both solids, *in situ* synchrotron powder diffraction data were collected on BL04-MSPD under different pressures of CO2 (up to ~10 bar) and temperatures at ALBA (Barcelona, Spain). The resulting structural changes observed on their frameworks as well as their proton conductivities will be discussed.

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Caption (s) - Add figures as attached files (2 fig. max):

Figure 1. X-ray diffraction patterns of MgHDTMP at different CO2 pressures. The inset shows the evolution of the peaks upon CO2 adsorption/desorption. (*desorption).

Special Session - Coffee and poster discussion: ALBA users and AUSE members / 104

On the determination of the microscopic residual stress in aluminum alloys

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A procedure to separate the (average) microscopic residual stress, m-RS, from the total residual stress (sum of the macroscopic residual stress, M-RS, and the m-RS) in monolithic (one-phase) alloys from measurements conducted by synchrotron radiation diffraction is proposed. The method focuses on stress equilibrium at different scales and the assumption that grains with different orientations are treated as different phases. Due to crystal anisotropy, the elasto-plastic behavior of individual grains in a polycrystalline aggregate depends on its orientation with respect the applied stress state. Texture of materials is required in the analysis to take into account the different phases involved and the intensity of each one. Two different cases are here presented for which specific measurements were conducted:
1.- Cylindrical samples machined from a bar of extruded 2014 aluminum alloy in which both M-RS and m-RS develop upon quenching from high temperature. The un-stressed lattice spacing value required in the calculation of the RS is obtained from the equilibrium of the M-RS across the sample. The measurements for this experiment were conducted on EDDI instrument at BESSY synchrotron, Berlin, which operates in energy dispersive mode, in the range 10-150 keV. Here, the signal from several hkl planes is obtained simultaneously at a given diffraction angle 2□. The m-RS among grains 311, 111, 220, and 200 can be up to some 20 MPa
2.- A "comb"type of sample machined from a sheet of rolled 2024 aluminum alloy. In this case, the M-RS is assumed to be relieved. Only the presence of the m-RS resulting from the rolling process must be considered. These measurements where conducted on MSPD instrument of ALBA synchrotron, Barcelona, which operates with a monochromatic radiation of □ = 0.31 Å, corresponding to the energy of 40 keV. Here, the signal from several hkl is obtained by adjusting 2□ accordingly (Bragg´s Law). In this case, the maximum m-RS obtained among grains belonging to different texture component is of about 100 MPa.

Special Session - Coffee and poster discussion: ALBA users and AUSE members / 105

In-situ early age hydration of cement-based materials by synchrotron X-ray powder diffraction

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Cement based binders are building materials of worldwide importance. Since these samples are very complex, the knowledge/control of their mineralogical composition are essential to design and predict materials with specific/improved performance 1. Rietveld quantitative phase analysis (RQPA) allows the quantification of crystalline phases and, when combined with specific methodologies, as the addition of an internal standard or the external standard approach (G-factor), amorphous and non-crystalline phases can also be quantified. However, to carry out a proper RQPA in hydrated cementitious materials, a good powder diffraction pattern is necessary. In this work, synchrotron X-ray powder diffraction (SXRPD) has been used, allowing in-situ measurements during the early-age hydration process.

This work studies the early hydration of cement-based materials. The analised samples were: a laboratory-prepared belite calcium sulphoaluminate (BCSAF) clinker (non-active) 2 mixed with 10wt% gypsum, labelled G10B0; two active laboratory-prepared BCSAF clinkers (activated with 2wt% borax) 2, one mixed with 10wt% gypsum and the other one with 10wt% monoclinic-bassanite, hereafter named G10B2 and B10B2, respectively; and an environmentally-friendly cement sample from Henkel, composed of bassanite mixed with 15wt% Portland cement and 10wt% Metakaolin, labelled H1.

Anhydrous G10B0 contains beta-belite and orthorhombic-ye'elimite as main phases, while alpha'H-belite and pseudo-cubic-ye'elimite are stabilized in G10B2 and B10B2. Anhydrous H1 contains monoclinic and hexagonal bassanite and alite as main phases.

Ye'elimite, in G10BO pastes, dissolves at a higher pace than in G10B2 (degree of reaction is α~25% and α~10% at 1h, respectively), with the corresponding differences in ettringite crystallisation (degree of precipitation is α~30% and α~5%, respectively).

Moreover, the type of sulphate source has important consequences on the hydration of the active BCSAF cement. Bassanite is quickly dissolved and it precipitates as gypsum within the first hour of hydration (in B10B2) and ettringite starts to crystallize (Figure1). Moreover, after 12hours ettringite is almost fully crystallized, similar to G10B2.

In H1, bassanite transforms into gypsum within the first hour, being the principal hydration product; ettringite starts to be formed just after few hydration minutes (Figure2).

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Caption (s) - Add figures as attached files (2 fig. max):

Figure 1. Direct Rietveld quantitative phase analysis results (wt%) for B10B2 sample as a function of hydration time. Figure 2. Rietveld plots for anhydrous (top), hydrated after 1.5 hours (middle) and 32.7 hours (bottom) H1 cement. Bassanite, gypsum and ettringite marked with triangle, circle and square, respectively.

Special Session - Coffee and poster discussion: ALBA users and AUSE members / 66

Magnetic coupling of cobalt nanodots and rare-earth-Au2, monolayer-thick surface compounds

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High-temperature deposition of rare-earths (RE) on noble metal surfaces, such as Au(111), gives rise to stable, REAu2 mono and bilayers of high crystalline quality. These surface alloys exhibit characteristic, long-range moiré patterns that can be utilized as growth templates 1. In fact, cobalt deposition on such pre-patterned REAu2/Au(111) surfaces leads to self-organization of Co nano-dots. Depending on the RE material of the surface one can achieve different interactions that determine the magnetic properties of the dots arrays. In order to investigate the magnetic properties of the REAu2/Au(111) support and the Co/REAu2/Au(111) arrays, a detailed study combining X-ray Circular Magnetic Dichroism and Scanning Tunneling Microscopy was carried out. Several substrates were analyzed (SmAu2, GdAu2, and YbAu2), which share the same RE-Au2 surface structure and lattice constant, but reveal ferromagnetic, anti-ferromagnetic 2, and non-magnetic interactions with the Co nano-dot array, respectively. These interactions not only determine the magnetic properties below the Curie temperature TC of the substrate but also far above TC and lead to enhancements of the magnetic anisotropy and blocking temperature of the Co nano-dot array.

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Special Session - Coffee and poster discussion: ALBA users and AUSE members / **99**

Exotic magnetic behavior due to competing anisotropies in a multiferroic crystal revealed by soft x-ray resonant magnetic scattering

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The induction of magnetic frustration and complex magnetic orders by tuning synthesis thus breaking the spatial inversion symmetry is an effective way of producing multiferroic (MF) and magnetoelectric (ME) materials. The (Mn,Co)WO4 family are reference models for the study of the mutual interaction between spins and polar orders. Co favors a strong competition between its magnetocrystalline anisotropy (McA) and Mn-Mn exchange interactions, stabilises the characteristic ferroelectric (FE) behavior of MnWO4 at low temperatures (T), and uplifts the T-x phase diagram richness with the appearance of new FE phases and magnetic structures.
By means of soft x-ray resonant magnetic scattering (SXRMS) we have investigated in detail the magnetic order in a MF crystal with the Mn0.85Co0.15WO4 critical composition above its FE transition,

focusing on the well-known collinear AF4 phase. Thanks to SXRMS chemical selectivity we have demonstrated that Co moments arrange antiferromagnetically following their own strong uniaxial McA, although the collinear order of Mn spins point to a different direction. This implies intrinsic remarkable deviations of the spin arrangement at the local scale from the average description provided by neutron diffraction. These element-resolved magnetic results call for reexamining the phase diagram of this model family of MFs. The occurrence of a similar non-collinearity of ordered spins from different magnetic ions must be investigated in other mixed compounds with competing anisotropic interactions.

Special Session - Coffee and poster discussion: ALBA users and AUSE members / 98

Substrate binding implications in the X-ray structure of a nicotinamidase from a metagenomic bacteria with biotechnological interest

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NAD+ is a central cofactor that plays important roles in cellular metabolism and energy production in all living cells. Nicotinamidases are essential enzymes for the recycling of nicotinamide into NAD+ in most prokaryotes and most of lower eukaryotes, but not in mammals. These enzymes convert nicotinamide to nicotinic acid and its significance for nicotinamide salvage and for NAD+ homeostasis has stimulated interest in nicotinamidases as possible antibiotic targets. In fact, some of them have pyrazynamidase activity being able to metabolize pyrazinamide, an analog of nicotinamide, into pyrazinoic acid, which is a first-line drug against tuberculosis. Nicotinamidases are also regulators of intracellular nicotinamide concentrations, and hence participating in the signaling regulation of NAD+-consuming enzymes, such as sirtuins with NAD+-dependent deacetylase activity. Here, we report two high-resolution crystal structures of a nicotinamidase from a marine metagenomic microorganism in unligated form or covalently bound to the product nicotinic acid at 2.35 and 2.52 Å resolution, respectively. These structures provide detail about substrate binding, revealing several important features, including a metal ion that coordinates the substrate and the catalytically relevant water molecule. Comparison with known pyrazinamidase structures provides clues about the different selectivity of these closely related enzymes. The high activity reported by the biochemical analysis carried out reveals potential biotechnological implications of this metagenomic nicotinamidase.

This study was partially supported by MINECO-FEDER (BIO2013-45336-R), ALBA synchrotron (proposal 2013110777-2) and Programa Ayuda a Grupos de Excelencia de la Región de Murcia, Fundación Séneca (04541/GERM/06, Plan Regional Ciencia y Tecnología 2007–2010). R.Z.P. and A.G.G.S are predoctoral fellows from Plan Propio of University of Murcia.

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Special Session - Coffee and poster discussion: ALBA users and AUSE members / 91

Semiconducting polymer nanostructures studied by a combination of synchrotron techniques and AFM

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Conjugated polymers have been proposed for application in a wide variety of next generation technologies including displays, solid-state lighting, transistors and organic photovoltaic devices. In organic photovoltaics (OPVs), the dissociated free charges (electrons and holes) are generated at the interface between the donor (e-donor) and acceptor (e-acceptor) phases, and then transported to their respective electrodes, forming the external circuit. Therefore, increasing the interfacial area between the e-donor and e-acceptor phases and limiting the morphology of the heterojunction to the nanoscale are critical for improving the device performance 1.
In this work we will report on the laser induced periodic surface structures (LIPSS) in conjugated polymers such as poly-3-hexylthiophene (P3HT), poly[N-9'-heptadecanyl-2,7-carbazole-alt-5,5-(4',7'-di-2-thienyl-2',1',3' benzothiadiazole)] (PCDTBT) and the blend P3HT/PCDTBT. The investigation of the thin films as well as the nanostructured films was performed by using different synchrotron techniques. The evolution of the polymer nanostructures was followed by in situ Grazing Incidence X-Ray Scattering (GISAXS and GIWAXS) 2. The polymer blend was studied by Scanning Transmission X-Ray Microscopy (STXM) based on the Near Edge X-Ray Absorption Fine Structure (NEXAFS) spectra of the two polymers P3HT and PCDTBT. By this technique it is possible to obtain the compositional maps of the blend P3HT/PCDTBT before and after irradiation. In both cases the results reveal a phase separation of the two polymers. In addition a synergy in the LIPSS formation was found for the polymer blend. The structure-properties relationship was investigated by conductive AFM [3].

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[3] Á. Rodríguez-Rodríguez, E. Rebollar, M. Soccio, T.A. Ezquerra1, D. R. Rueda, J. V Garcia-Ramos, M. Castillejo. M-C. Garcia-Gutiérrez, submitted to Macromolecules

Caption (s) - Add figures as attached files (2 fig. max):

Figure 1. (up) in situ GISAXS patterns of PCDTBT thin films irradiated at 532 nm using a fluence of 26 mJ/cm2 for different number of pulses, (down) STXM images of the P3HT/PCDTBT blend before and after irradiation.

Special Session - Coffee and poster discussion: ALBA users and AUSE members / 92

Minor groove interactions of AT-rich DNA with dicationic drugs and proteins.

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AT-rich DNA is mainly found in non-coding regions in eukaryotes, it represents a large portion of genomes. It is known that some of these non-coding regions play an important role in regulation, transcription and signaling. Some proteins interact with AT-rich DNA as architectural proteins that affect cellular functions by modulating chromatin structure. Moreover DNA of several pathogens is very rich in AT base pairs. Typical examples include the malaria parasite *Plasmodium falciparum* which has 80% AT-DNA and is the causative agent of malaria.

This fact has prompted studies of drugs which interact with the minor groove of DNA. We present the crystal structure of the complex of the DNA duplex d(AAAATTTT)₂ with the dicationic drug 4,4'-bis(imidazolinylamino) diphenylamine (CD27), an antiprotozoal drug. It completely fills the minor groove of DNA preventing the access of proteins and displaces bound water. The drug protrudes from the DNA and interacts with neighboring molecules, so that it may act as a cross-linking agent. These findings allow a better understanding of this family of compounds and will help in the development of new, more effective drugs.

This type of agents may prevent the access of proteins such as high mobility group (HMG) proteins to DNA. We have studied the interaction of HMGA and HMGB proteins with AT-rich DNA. We have found a novel mode of DNA recognition of box-A from HMGB protein, it reveals a mechanism by which structure-specific HMG boxes kink and underwind linear DNA.

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Web page of MACROM group

Acta Cryst (2014), D70 pp.1614-1621 F.J. Acosta-Reyes et al. (PDB: 4OCD)

Acta Cryst (2015), D, (in press). R. Sánchez-Giraldo et al.

Caption (s) - Add figures as attached files (2 fig. max):

Fig. 1.- Complex of drug CD27 with AT-rich DNA. Fig. 2.- Protein HMGB boxA with AT-rich DNA

Special Session - Coffee and poster discussion: ALBA users and AUSE members / 94

Crystal structure solution of a new polymorph of the Agomelatine/hydroquinone cocrystal from Synchrotron X-ray data

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Although it has been traditionally suggested that cocrystals show a lower tendency to polymorphism than monocomponent crystals, the increasing number of polymorphic cocrystals described is recently questioning that old statement. The impact that this phenomenon has on the pharmaceutical industry is particularly relevant since affects to both intellectual property and formulation of new drugs. Thus, more experimental data about polymorphism of cocrystals are required to understand deeply whether the polymorphism affects in the same way to pure compounds than to multicomponent crystals. In this contribution we intend to enrich the debate by presenting the crystal structure of the second polymorph of the cocrystal between Agomelatine (an effective drug for the treatment of major depressive disorders) and hydroquinone. The structure have been determined using synchrotron X-ray powder diffraction data obtained in the high resolution powder diffraction end station of the MSPD beam line in Alba. The right data have been obtained with the sample in a 0.7 glass capillary, at 100 K, with wavelength 0.619 Å using the Mythen detector. Attempts to index high resolution powder diffraction data with Cu Kα laboratory X-ray powder diffraction data at room temperature has not been successful. The 100 K synchrotron powder diffraction data was perfectly indexed to an orthorhombic cell of about 1830 Å3 by means of Dicvol04,2 and the space group perfectly determined to be P212121 from the systematic absences. Being the asymmetric unit one molecule (1:1 agomelatine / hydroquinone stoichiometry), Z=4, the crystal structure was determined by direct space methodologies starting from a molecular model optimized with the commercial software SPARTAN by means of FOX.3 The refinement of the structure has been performed by the Rietveld method using FullProf.4 The details and difficulties of the resolution and refinement will be discussed. The final structure will be described and compared with the one of the other polymorph of Agomelatine / hydroquinone cocrystal.

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Special Session - Coffee and poster discussion: ALBA users and AUSE members / 117

Two-dimensional quantum well states on vicinal Beryllium surfaces.

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A vicinal surface with monoatomic steps is an interesting example of quasi one-dimensional nanostructured system. Vicinal surfaces of noble metals have been an active field of research in the past years because they offer a natural playground to investigate the behavior of electronic surface states in low dimensional nanostructured systems. Group II metals like Be exhibit several prominent surface states with a large density of states, which in some cases is even larger than the bulk electronic

density. For several surfaces, like Be(0001), the surface state has an almost ideal two-dimensional character, since the bulk band gap is very large and the surface is almost decoupled from the bulk. On the other hand, vicinal Be(10-10) offers a novel scenario to investigate how several kinds of surface states are affected by the introduction of a new periodic step potential.

The structure and electronic properties of several Be crystals vicinal to the (10-10) directions have been investigated by Low Energy Electron Diffraction (LEED) and Angle Resolved Photoemission Spectroscopy (ARPES) with Synchrotron Radiation 1. The long-range ordered terraces and step superperiodicity was investigated by LEED for surfaces with different miscut angles, going from 2.95 to 9 degrees. The electronic structure revealed several prominent features corresponding to a surface resonance (SR) centered at Γ and two surfaces states located at A, in agreement with previous measurements of flat [10-10] surface 2. Moreover, several additional states between the SR and the Fermi level were found. These bands behave as free-electron like electrons along the direction parallel to the terraces, while they are confined (dispersionless) along the direction perpendicular to the steps. These additional states are in agreement with two-dimensional quantum well states in an infinite potential well model.

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Special Session - Coffee and poster discussion: ALBA users and AUSE members / 119

Crystal structure refinement of an axinite specimen from synchrotron tts-μDiffraction data

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Synchrotron through-the-substrate microdiffraction (tts-μXRD) allows the study of polycrystalline samples included in polished thin sections 1. In a tts-μXRD experiment the primary beam passes first through the glass substrate before reaching the thin section where the target material is embedded. This technique has now been extended to the study of crystal microvolumes 2. A polished thin section (30μm) cut out of an epidote-pyroxene-axinite pneunomatolitic outcrop from Pont de Suert (Catalonia, Spain) has been studied and intensity data of microvolumes of triclinic axinite crystals were directly collected. The basic steps of this new tts-uXRD application include:

- Collection of 2D patterns (frames) for each randomly-oriented crystal microvolume.
- Determination of the reciprocal lattice orientation for each randomly-oriented crystal microvolume which allows assigning the *hkl* indices of the crystal dataset. Previously the metric has been refined from angular peak positions or from circularly averaging the sum of collected patterns.
- Merging of the individual crystal datasets to produce an extended dataset suitable for structure solution and refinement.

Axinite is a triclinic complex silicate with unit cell formula Ca₄X₂Al₄\Si₈B₂O₃₀\₂ (space group P-1)

with X being Fe²⁺, Mn²⁺ and even Mg²⁺. The resulting dataset from 7 axinite microvolumes (614 unique reflections, 65% data completeness for 1.08Å resolution) allowed the crystal structure solution using Patterson-function direct methods [3] and an accurate single-crystal least-squares refinement. From the combination of an electron microprobe analysis and μXRD information, the cationic distribution in the unit cell of this axinite specimen was determined.

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Special Session - Coffee and poster discussion: ALBA users and AUSE members / 75

Structural Analysis of Condensed Metaphase Chromosomes by Synchrotron Small-Angle X-Ray Scattering

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Each chromosome contains a single DNA molecule that is associated with histone proteins and forms a long filament containing many nucleosomes (the dimensions of the nucleosome core particle are shown in Fig. 1a). During mitosis, this chromatin filament is densely packed into metaphase chromosomes. TEM images of partially denatured chromosomes obtained using different procedures showed that bulk chromatin in chromosomes is organized forming multilayered plate-like structures (see example in Fig. 2b). This planar structure was studied using cryo-EM, electron tomography, AFM imaging in aqueous media, and AFM-based nanotribology and force spectroscopy (1). The results obtained suggested that nucleosomes in the plates are irregularly oriented, and that the successive layers are interdigitated (layer thickness 5-6 nm), presumably allowing face-to-face interactions between nucleosomes of adjacent layers (Fig. 1c). Multilayer plates (identical to those found in metaphase chromosomes) can be self-assembled from chromatin fragments obtained by micrococcal nuclease digestion of metaphase chromosomes (2), and it has been suggested (3-5) that metaphase chromosomes could be self-organizing liquid crystal structures formed by many stacked layers of chromatin oriented perpendicular to the chromosome axis (Fig. 1b). We have used the NCD beamline of ALBA Synchrotron to study the internal structure of native chromosomes. Sediments containing chromosomes from human (HeLa) cells under different conditions were placed in plastic capillaries and were exposed to X-rays for 20-80 s. The typical peaks at ~2.8 and ~3.7 nm corresponding to the internal nucleosome structure were observed in all samples. The peaks at ~11 and ~30 nm corresponding, respectively, to the distances between parallel nucleosome columns and laterally packed 30-nm fibers were absent or showed very low intensities. Under all conditions containing structuring cations, and in particular under metaphase ionic conditions (17 mM Mg, 120 mM K, 20 mM Na), a peak centered at 6 nm is prominent (Fig. 2c). This broad peak can be correlated with the short-range repetition of the ~6 nm distance between nucleosomes (face-to-face interactions) and between stacked layers.

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Caption (s) - Add figures as attached files (2 fig. max):

Figure 1. Nucleosome core particle (a). In the thin-plate model (references 3-5) it is considered that the metaphase chromosome is formed by stacked chromatin layers (b) in which nucleosomes are interdigitated (c). Figure 2. Native metaphase chromosomes (a) and plates emanated from soft-denatured chromosomes (b). Scattering curve of chromosomes in metaphase ionic conditions (c).

Special Session - Coffee and poster discussion: ALBA users and AUSE members / 74

EUSpec - Modern tools for spectroscopy on advanced materials: a European modelling platform

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The study of materials is of central significance for progress in science and technology. At present the focus is on materials with reduced dimensions such as nano-structures or molecule based systems. These materials offer new tunable properties. In order use them in devices a deep understanding of the properties of the materials on the atomic scale is a prerequisite. Non-destructive spectroscopies are a fundamental tool of analysis at the nanoscopic level, allowing to probe matter and its constituents with an atomic resolution, and to monitor their time evolution down to the femtosecond range, transforming them into unique methods to trace chemical reactions. However, in order to make use of the continuously increasing resolution in space, energy, momentum, spin and time, complementary theoretical support is indispensable. This is where new EU-funded COST action EUSpec gets in. This COST action brings together the expertise of experts working in the science of advanced materials in order to build a coherent theory and computing platform with a new common data format to model sophisticated spectroscopy experiments performed at advanced radiation sources as well as at academic and industrial research laboratories. The goal is to strengthen the communication between between theoreticians and experimentalists because on the one hand new types of experiments are important benchmarks for the status of theory and often require or trigger new formal theoretical and corresponding code developments. On the other hand, experimental groups are not always aware of the available tools and program packages provided to them by the colleagues from theory to analyze and interpret the experimental findings. EUSpec will lead to a large-scale network in order to give a strong impetus to the spectroscopy research and to give Europe a decisive lead. It will establish a platform that goes far beyond the applicability of the actual individual computational codes in order to address the relevant questions and problems for many

more materials and spectroscopies. In line with these ambitious goals, EUSpec will be presented to initiate strong interactions between theory and experiment in the future.

References:

http://www.euspec.eu/

Special Session - Coffee and poster discussion: ALBA users and AUSE members / 73

How much do we need to focus? Advantages of high resolution crystal structures

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Last decade, advances in synchrotron facilities have allowed an exponential increase on the number of protein structures solved at atomic resolution. Last year, the Protein Data Bank reached the 100k structures but less than 10 % of these can be considered "atomic-resolution structures". These structures show more detailed and accurate information of the proteins. The presence of alternate conformations in some residues or modified residues is only noticeable in those high-resolution structures. Besides, these structures allow a better modeling of water molecules. Our group is interested in the solution of the structures of modular domains that interacts with proline rich motifs (PRMs) to study the anomalous thermodynamic signature of these complexes. The binding site of these domains is characterized by the presence aromatic residues where the proline residues are buried upon binding. Unexpectedly, most of the times, the binding is driven by a negative value of the enthalpy that might be addressed to the burial of water molecules. We have solved the structures of PRMs-binding modular domains (WW, TSG101-UEV and SH3) and we were able to determined special features related with their binding behavior that are only visible in high resolution structures [1-3]. For example the binding orientation of these PRMs to some SH3 domains is conducted by the formation of a salt bridge between an arginine/lysine residue flanking the canonical binding motif PxxP and an aspartate/glutamate residue located at the specificity pocket. High resolution structures have allowed us to identify alternate conformation of a leucine residue next to the acidic residue that forms the salt bridge, which might be correlated to the orientation of the PRMs binding. This residue is well conserved among the SH3 domains. Here we show how high resolution structures can help to solve the ambiguity in the modeling of some residues that might participate in the binding of PRMs through conformational changes that promotes long distant interactions. We compared these high resolution structures with lower resolution ones to show how these alternate residues cannot be modeled at lower resolution, although some clues are already present.

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Special Session - Coffee and poster discussion: ALBA users and AUSE members / 72

In-situ hydration studies of C4AF at early ages in the presence of other phases

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The ferrite phase, C4AF in cement nomenclature, is the major iron-containing phase in Ordinary Portland Cement (OPC) and in iron rich belite calcium sulfoaluminate cements. The term "ferrite"usually refers to a solid solution with a wide range of composition with the general formula Ca2(AlyFe2−y)O5, where y can vary from 0 to about 1.331. In cement chemistry the ideal composition C4AF, is used to describe the ferrite phase in OPC.

The hydration of pure C4AF with water initially forms metastable C-(A,F)-H hydrates which eventually convert to hydrogarnet phase C3(A,F)H6 (katoite) over time. The addition of sulfates to C4AF inhibits the direct hydration of C4AF to katoite. Ettringite is the most commonly hydration product observed under these conditions. In addition, ettringite could decompose to an AFm monosulfoaluminate hydrate2.

The aim of this work is to better understand the early age hydration of ferrite in the presence of other phases at early ages. Chiefly, we want to determine the hydration kinetic and mechanisms of this phase using different reaction media.

Firstly, C4AF in the presence of water hydrates to form mainly katoite phase. The hydration of ferrite with w/s ratio of 1.0 yielded C3A0.84F0.16H6 as single crystalline phase. Its crystal structure has been determined by the Rietveld method. Figure 1 shows the Rietveld synchrotron X-ray powder diffraction plot for this sample.

Secondly, the presence of sulfates strongly modifies ferrite hydration behavior. The hydration of C4AF in the presence of gypsum gives AFt first and, crystalline AFm precipitates afterwards. Figure 2 shows a selected range of the SXRPD raw patterns for a sample with C4AF, gypsum and ye'elimite recorded at different time of hydration, with the main peaks due to a given phase labelled.

Finally, the effect of w/s ratio has also been studied for this sample. Results indicate that higher amounts of water favour the formation of AFm. A summary of the results for the hydration of C4AF will be discussed.

Cement nomenclature: C=CaO, A=Al2O3, F= Fe2O3, H=H2O.

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Caption (s) - Add figures as attached files (2 fig. max):

Figure 1. Rietveld Synchrotron X-Ray Powder Diffraction plot for C3A0.84F0.16H6. The tic marks are the Bragg reflections: C3A0.84F0.16H6 (lower row); Quartz, internal standard (upper row). Figure 2. Selected range of the SXRPD raw patterns for C4AF with ye'elimite and gypsum (w/s=1.0) recorded at different time of hydration, with the main peaks due to a given phase labelled. AFt: circle; AFm: star; Qz: triangle; gypsum: rhombus; C4AF: inverted triangle and ye'elimite: square.

Workshop on High pressure powder diffraction at ALBA / 59

Visit to the BL

Workshop on High pressure powder diffraction at ALBA / 58

Invited talk - Structural studies at high pressure, were are we today?

Author: Michael Hanfland[1]

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Workshop on High pressure powder diffraction at ALBA / 55

Welcome

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Workshop on High pressure powder diffraction at ALBA / 54

Registration

Workshop on High pressure powder diffraction at ALBA / 57

Invited talk - Exploring the structure of materials under high pressure at BL04-MSPD beamline

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Workshop on High pressure powder diffraction at ALBA / 56

An introduction to BL04-HP: activity & instrumentation

Workshop on High pressure powder diffraction at ALBA / 60

High Pressure structural investigation of promising optical materials

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The significance of pressure effects in materials science comes from structure and property relationships with emphasis on the synthesis and study of phase transitions. Besides temperature, pressure can also induce changes in the structural properties of transitional metal oxides because it directly affects atomic interactions by altering interatomic distances. Structural and electronic transitions have been observed by applying high pressure: we can mention, for example, the induced superconductivity at low temperature 1. In this presentation, we will report high pressure investigations on the structural properties of several orthovanadates. These systems can be employed in a number of applications including their use as promising optical materials 2. These studies were carried out by means of X-ray diffraction (XRD) measurements using diamond anvil cells. In situ HP-XRD was performed at MSPD beamline of ALBA synchrotron. The structure of the different phases has been refined and their equation of state (EOS) determined. Theoretical calculations fully agree with the experimental results. We will discuss here the structure of the high pressure phases and the compressibility of these systems in the light of experimental results and according to theoretical calculations.

References:

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Workshop on High pressure powder diffraction at ALBA / 61

HP in XAS, prospects for HP on CLAESS

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Workshop on High pressure powder diffraction at ALBA / 62

High-pressure phase transition in Witherite: Simultaneous study by synchrotron Infrared and Raman microspectroscopy

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Workshop on High pressure powder diffraction at ALBA / 63

Open discussion/exchange on HP activity, future directions, etc.

Workshop on Photoemission Electron Microscopy (PEEM) at ALBA: Practical user guide and data analysis workshop / 4

X-PEEM for Micromagnetism and Device Physics

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Workshop on Photoemission Electron Microscopy (PEEM) at ALBA: Practical user guide and data analysis workshop / 3

Welcome

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Workshop on Photoemission Electron Microscopy (PEEM) at ALBA: Practical user guide and data analysis workshop / 7

Practical Module II in two groups (A/B) - Practical modules are A) basic PEEM operation and sample mounting B) training with PEEM data analysis software

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Workshop on Photoemission Electron Microscopy (PEEM) at ALBA: Practical user guide and data analysis workshop / 2

LEEM-PEEM in Surface Science

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Workshop on Photoemission Electron Microscopy (PEEM) at ALBA: Practical user guide and data analysis workshop / 1

Introduction to LEEM-PEEM: Working Principles

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Workshop on Photoemission Electron Microscopy (PEEM) at ALBA: Practical user guide and data analysis workshop / 5

Practical Module I in two groups (A/B) - Practical modules are A) basic PEEM operation and sample mounting B) training with PEEM data analysis software

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Exploring the structure of materials under high pressure at BL04-MSPD beamline

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Thanks to the combined use of synchrotron radiation and diamond-anvil cells, powder x-ray diffraction (XRD) has become a technique widely used to study the physical properties and crystal structure of materials under high pressure. This kind of studies is particularly relevant for earth sciences, materials science, and condensed matter physics.

In this presentation, I will review high-pressure studies carried out by our group during the past years in different compounds at the BL04-MSPD beam-line of ALBA. The examples to be presented includes simple elements (Tl), complex materials (CeScO3, MgAlBO4, BiPO4, InTaO4, etc.), and nanomaterials (TiO2, SnO2) among others. They will be used to illustrate the scientific possibilities of the beam-line showing that high-quality data has been collected by our group at BL04-MSPD beyond Mbar pressures. The occurrence of pressure-induced phase transitions and/or pressure-driven amorphization in the studied materials will be discussed. Examples of structural solution of complex structures, structural refinements of HP polymorphs, and collection of accurate compressibility data will be also described.