44 AIC Annual Meeting

14-18 September 2015 Vercelli

Italian Crystallographic Association

associazione italiana di cristallografia

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We are pleased to announce that in 2015, the XLIV Annual Meeting of the Italian Crystallographic Association (AIC) is held in *Vercelli* by the *Università del Piemonte Orientale A. Avogadro*. The conference is located in the renewed *Complesso Universitario San Giuseppe, Piazza S. Eusebio 5*. [Interactive Map]

The program, selected by the Scientific Committee, encourages the discussion on emerging methods in crystallography, opening new fields for the investigation of the condensed matter world. Crystal Growth, Nanoscale phenomena, Organic, Inorganic and Biomolecular Systems are studied not only as structural images but also in motion, while working as *Chemical Machines*. Two satellite workshops on emerging topics in materials science [Program Download] and structural biology [Program Download] describe new possible ways of exploring the crystallographic world. The numerous Invited lecturers from all Europe, the contribution, also from the scientific viewpoint, of several companies, the Software Fayre and a Round Table on the legacy of the IYCr in Italy further enrich the conference program. [Full Program Download]

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GOLD MEDAL MARIO MAMMI

Things Done and Things Yet To Be Done: Crystallography at Large, 2015-2030

Angelo Gavezzotti
Università degli Studi di Milano

Having been active in the field for the last 45 years, the author presents a brief but substantial list of accomplishments: for example, from one month to one hour for an X-ray crystal structure, and the extraction of crucial information on chemical structure and chemical bonding from the organic, organometallic, inorganic and protein Databases. Topics that await further progress are fortunately more numerous, ensuring a continuing business for the future crystallographer. The author speculates on a wish list, at the top of which is the prediction and control of the birth and structuring of crystalline solids by coagulation from the other states of matter, chiral resolution being a fringe benefit. Along with some promising results, a caveat is given about wrong paths presently being taken in this direction: chemistry is done by electrons, and looking at distances between nuclei is not going to help.

Crystal Engineering on “Tailor-Made” Multifunctional Zirconium Phosphonates

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Crystal engineering is defined as the design and synthesis of molecular solid-state structures with desired properties, based on the understanding and exploitation of intermolecular interactions. Zirconium phosphonates can be considered “tailor-made” materials that can be designed by exploiting the crystal engineering principles. They have been extensively used for many applications in solid state chemistry, such as heterogeneous catalysis, nanocomposites chemistry, ion- exchange and separation and intercalation. The interest on these materials mainly resides on their high insolubility and on their chemical versatility. This class of compounds, widely developed from the beginning of the 70’s, is living a second youth in the recent years due to the use of novel and more sophisticated phosphonic ligands. However, their high insolubility also represents a drawback for their correct structural characterization and for the comprehension of the structure/reactivity relationship. Indeed, the possibility to get single crystals from these materials is extremely low and therefore only ab-initio XRPD structure determination methods can give suitable information on their structure. In this contribution a survey on the structure and reactivity of zirconium phosphonates with layered and three dimensional open framework compounds is reported. A special attention will be devoted on the ab-initio XRPD structure determination methods working in the real space. The crucial role of the synthetic conditions and of non-covalent interactions as structural orientating factors will be also discussed.

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PHD'S THESIS AWARD IN CRYSTALLOGRAPHY

New Forms of Polar and Spin Ordering in $Pb_2(Mn,Co)WO_6$ Double Perovskites: Symmetry Analysis of Ferroic Properties

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In recent years, the scientific community focused on the study of new multifunctional materials, in which the simultaneous presence of different functionalities can make compounds useful to fabricate single devices able to handle several tasks. In this framework the multiferroic materials occupy a special place. In this type of systems the symmetry constrains, dictated from the magnetic point group, play an essential role regulating all the physical properties and in particular the magneto-electric coupling. In this talk I present the study of double perovskite compounds, $Pb_2(Mn,Co)WO_6$, that reveals a complex and interesting magneto-electric multiferroic character. The work is based on the accurate analysis of the magnetic symmetry, exploiting the use of the coloured groups [1] and its generalization to the superspace formalism [2,3], joined with a comprehensive physical characterization, finally allowing to define in detail the complicated picture of the system properties. The study is mainly focused on the two end members of the solid solution and on the intermediate composition containing a 60/40 ratio of the two B site cations.

The Pb_2MnWO_6 compound displays a ferrielectric state characterized by the presence of two independent lead sublattices [4]. By lowering the temperature the system exhibits two magnetic phase transitions and a magnetic ground state characterized by an incommensurate to commensurate (IC/C) magnetic phase transition at 8 K [5]. The magnetic structure was solved by the use of the superspace formalism that allows to easily characterize the IC/C transition.

The $Pb_2Mn_{0.6}Co_{0.4}WO_6$ compound shows, at room temperature, a centrosymmetric orthorhombic structure, defining an antiferroelectric system. The compound presents a first magnetic transition at 190 K characterized by a short range ordering, whereas a second long-range magnetic transition is observed at 9 K. The long-range magnetic model is an antiferromagnetic collinear structure showing an acentric magnetic space group implying the presence of a spontaneous electrical polarization, confirmed by pyroelectric measurements. The combined use of the magnetic symmetry and of the electrical characterization suggests that the symmetric exchange striction mechanism is at the basis of the observed phenomena.

The cobalt end member presents an incommensurate monoclinic phase at room temperature undergoing, at 230 K, a phase transition to an orthorhombic structure. The magnetic symmetry analysis indicate a transition to an incommensurate spin structure below 12 K, suggesting the presence of a spontaneous electrical polarization below the magnetic transition.

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PL1. New Advances in Electron Diffraction: from Ab-initio Structure Solution to Refinement

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Crystallography is a broad subject with diverse sub-fields and many different outcomes. Nevertheless, in the heart of crystallography there is still the search for the answer to the question *Where are the atoms…* Crystallographic investigations using electron diffraction have been used to assist in finding this answer since many decades ago. However, until recently, electron crystallography has been generally considered a useful complement to other methods, but not self-standing, independent method for structure analysis.

This status of electron crystallography has changed very much over the last decade. The change was made possible by two key developments – electron diffraction tomography (EDT) and precession electron diffraction (PED). EDT is a way of collecting three-dimensional diffraction data from a single nanocrystal by rotating the crystal around the goniometer axis in small steps, and acquiring the diffraction image at each step [1,2]. This approach is equivalent to the rotating crystal method used commonly also in single-crystal x-ray diffraction. In contrast to the traditional collection of oriented diffraction patterns, EDT data set is easier and quicker to collect, and, more importantly, it is much more complete. Moreover, because special zone-axis patterns are avoided, dynamical diffraction effects are suppressed in such a data set. Further suppression of the dynamical character of the diffracted intensities can be achieved by employing PED. Although developed already in 1994 [3], it has become popular much later, and the real boom of its use has come after it was associated with EDT [4].

EDT data sets, possibly combined with PED, yield 3D diffraction data suitable for *ab initio* structure solution by methods entirely equivalent to the procedures used in x-ray single crystal diffraction. Since its development, a large number of structures have been solved with this method. The main advantage of this approach is the possibility to perform a full single-crystal experiment on a single micro- or even nano-crystal. The main disadvantage is that the dynamical diffraction effects cannot be entirely suppressed, and using the kinematical theory of diffraction is just a very coarse approximation. Therefore, the quality of the *ab initio* structure solution is in general lower than from x-ray diffraction data. For the same reason the standard structure refinement yields high figures of merit and relatively inaccurate structure models.

A remedy to the problem of kinematical approximation is the use of full dynamical diffraction theory in the refinement process. The refinements using dynamical diffraction theory are more time consuming, but they lead to more reliable and more accurate structure refinements [5]. The accuracy of such refinements can compete with the refinements against x-ray diffraction data, especially if only powder data are available.

The developments of the last few years, starting from the adoption of EDT methods and precession electron diffraction, through ab initio structure solution to the accurate refinement using dynamical diffraction theory mean that electron crystallography now offers to the crystallographic community a new wonderful tool – a full and accurate structure analysis from a single nanocrystal as small as few tens of nanometres.

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PL2. Ab-initio Modeling in Crystallography

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Since the advent of the Kohn-Sham formalism 50 years ago, Density Functional Theory has shown a paramount success in the ab initio modelling of solids from physics to chemistry, from materials science to crystallography.
Here, we will show how ab initio modelling, by means of DFT methods, can be used to predict variuos properties of crystalline systems and how results can be fruitfully used by crystallographers and non-crystallographers to better understand their physical properties. Examples will be reported for the prediction of structure, vibrational features, ADPs, thermodynamic properties, linear and nonlinear optical properties, charge density studies of different crystalline solids ranging from molecular crystals to metal-organic frameworks.
All reported results have been computed by means of the periodic ab-initio program CRYSTAL14 [1,2].

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PL3. Watching Matter in Motion: Time Resolved Studies from Synchrotrons to FELs

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Atoms move in the tens of fs time scale (1fs = 10^{-15} s). While synchrotrons have long been used to understand kinetics, only recently XFELs are opening the doors towards the dynamical aspect of matter. In this contribution, I will briefly introduce fast (synchrotrons) and ultrafast (XFEL) X-ray sources with some key parameters for time resolved studies. I will then show how techniques ranging from solution scattering to crystallography and X-ray absorption have been applied to study chemical reactions, biophysical processes, and materials.

PL4. Electron Diffraction and Imaging of Protein and Pharmaceutical 3D Nanocrystals

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High-energy electrons provide 1000 times more information per Gray (absorbed energy, i.e. radiation damage), compared to X-rays. Hence electrons outperform X-rays for structure determination when radiation damage is the limiting factor.

Unlike X-rays, electrons can not only be diffracted, but also imaged. However, when imaging transparent samples, the *total number* of quanta per unit area determines the signal-to-noise ratio. When diffracting transparent samples, the *number of interacting* quanta per unit area determines the signal-to-noise ratio.

Measuring electron diffraction accurately has only recently become possible with the advent of quantum area detectors. One of the challenges is that an electron microscope is flooded with photon radiation resulting from Bremsstrahlung generated by the high-energy electrons.

Only an area detector that can discriminate between photon noise and electron signal is insensitive to this noise. This difference in signal-to-noise ratio was demonstrated in practice for electrons using a Timepix quantum area detector.

When imaging a 100 nm thick lysozyme protein crystal with electrons, typically one to two images of the same location could be measured with significant details up to 3.5Å resolution. Subsequent images had suffered too much from radiation damage to show such detail.

When diffracting similar crystals, hundreds of electron diffraction patterns with Bragg spots beyond 3 Å resolution could be measured from the same location. However, there is no such thing as a free lunch. Diffraction comes at a price: the structure factor phases are lost. They can only be retrieved using additional (prior) information, for instance obtained from (a few) electron images.

We demonstrated this strategy by phasing the 3D structure factors of a nano-crystalline amyloidic peptide.

MS1. ADVANCED THEORETICAL AND EXPERIMENTAL METHODS IN CRYSTALLOGRAPHY

The MS focuses on the most recent and innovative methodological approaches developed in crystallography, in theoretical, computing and experimental field. It covers traditional x-ray crystallographic methods as well as complementary techniques (scattering, spectroscopic, calorimetric, molecular modeling, microscopy, etc.). MS1 spans from single crystal to micro- and nano- powder, from small molecule to macromolecule.

Chair: Angela Altomare (IC CNR Bari)

1KN1. Advances in methods for macromolecular structure solution: *ab initio* and *MR* approaches

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New methods have been recently developed to improve the structure solution of macromolecules by *ab initio* (Patterson or Direct Methods) and non *ab initio* (Molecular Replacement) approaches.

Phasing proteins at non-atomic resolution is still a challenge for any *ab initio* method. The combined use of different algorithms [Patterson deconvolution and superposition techniques, cross-correlation function (*C-Map*), the *VLD* (*Vive la Difference*) approach included in the *Direct Space Refinement* (*DSR)* procedure, a new probabilistic formula estimating triplet invariants and capable of exploiting a model electron density maps, the *FREE LUCH* extrapolation method, a new *FOM* to identify the correct solution] allow to overcome the lack of experimental information. The new methods [1,2] have been applied to a large number of protein diffraction data with resolution up to 2.1Å, under the condition that Ca or heavier atoms are in the structure. Results show that solving proteins at limited resolution is a feasible task, achievable even by new Direct Methods algorithms, against the traditional common believe that atomic resolution is a necessary condition for the success of a direct *ab initio* phasing process.

A new procedure (*REVAN*) [3,4], aiming at solving protein structures *via* Molecular Replacement and density guided optimization algorithms, has been assembled. It combines a variety of programs (*REMO09*, *REFMAC*, *COOT*) and algorithms (Cowtan-*EDM*, *DSR*, *VLD*, *FREE LUNCH*), and can successfully lead to the structure solution also when the sequence identity between target and model structures is smaller than 0.30 and data resolution up to ~ 3Å. The application to a wide set of test structures (including difficult cases proposed by DiMaio *et al*. [5], solved by using *MR* procedures together with energy guided programs) suggests that *REVAN* is quite effective even far from atomic resolution and, in combination with *EDM* techniques and sequence mutation algorithms, it is able to efficiently extend and refine the set of phases, reducing its average error.

The final step of the automatic solving process (*ab initio* or *MR* approaches) is the application of an *Automated Model Building* program (i.e. *Buccaneer*, *Nautilus*, *ARP-wARP* or *Phenix-Autobuild*) in order to recover the correct structure. Results suggest that the quality of the phases at the end of the phasing process is good enough to lead the *AMB* program to success.

These new efficient procedures are implemented in the current version of the software package *SIR2014* [6].

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1KN2. Advances in microstructure analysis of materials with defects

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In a wide number of technologically relevant cases, the features present in the diffraction pattern can hardly be described using modern tools such as the Rietveld method. Broad, asymmetric or anisotropic peak shapes or displacement of the peaks from their expected positions are some of the most common manifestations of the microstructure of the material.

When the defects are diluted, the effects of structure and microstructure clearly contribute, respectively, to the integrated intensity and the profile shape. This is a consequence of the peculiar 3D nature of the problem and of the Fourier transform relationship between real and reciprocal space. When the quantity of defects increases, we can enter the regime where the global lattice approximation is no longer sustainable: configuration entropy and complexity start playing their role. A local description is still possible, but the local view is insufficient to describe a given specimen in full. Stochastic processes such as Markov chains can be employed as compact descriptors to link the local to the global structure: the diffraction pattern provides information on a given specimen and is no longer expected to be unique for a given material.

We will investigate some recent advances in microstructure analysis [1], leading to a unified formalism for the Rietveld [2], WPPM [3] and matrix methods [4].

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1O1. Quantum Mechanical Simulation Of Protein Crystals: The Case Of The Small Protein Crambin

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Molecular simulations of proteins have been usually accomplished through empirical or semi-empirical potentials, due to the large size and inherent complexity of these biological systems. On the other hand, a theoretical description of proteins based on quantum-mechanical methods would provide an unbiased description of their electronic properties, possibly offering a precious link between these and the final biological activity. Yet, such approaches have been historically hindered by the large amount of requested computational power and limited, in practice, to mixed QM/MM simulations.

Here we demonstrate the application of the periodic Density Functional Theory CRYSTAL14 code [1], in its efficient massively parallel version [2], to the description of the small plant's seed protein crambin (46 aminoacids) crystal, a common test case. We have employed the accurate hybrid B3LYP functional, coupled to an empirical description of London interactions (D*) to optimize the crambin crystal geometry, starting from an high resolution neutron diffraction structure [3], with an increasing amount of water molecules in the cell (up to 172 H_2O/cell, close to the actual crambin crystal). A good agreement with the experiment has been achieved for both protein geometry and protein-water interactions (see Figure 1). Inclusion of water proved to be essential for a correct description of the system. The energetics has been computed, obtaining accurate crystal formation energies, protein-water, protein-protein and water-water interaction energies. The unique information obtained from a fully ab-initio treatment of the system allowed to study the electronic properties of the protein, such as its electrostatic potential and the charge transfer involved in its interaction with water. Finally, the full infra-red spectrum of crambin has been modeled. These results proved that quantum-mechanical simulations of small proteins are now possible in a reasonable amount of time, thanks to modern High Performance Computing architectures.

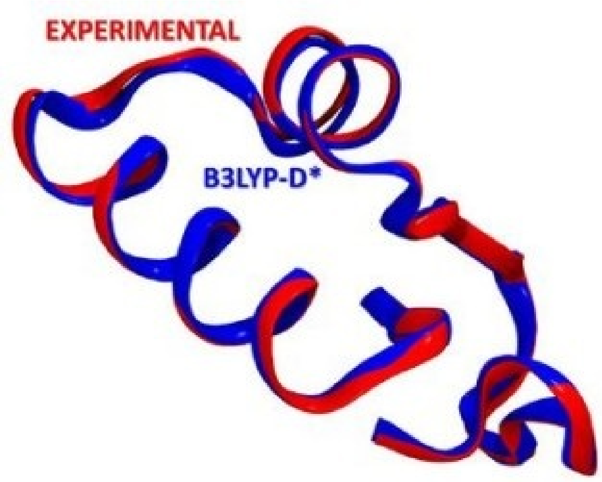

Figure 1. Superposition of experimental (red) and B3LYP-D* optimized (blue) crambin structures.

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1O2. Experimental and theoretical charge density study of iodoperfluoroalkylimidazoles self-assembled through halogen bond

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Halogen bonding, namely any noncovalent interaction involving halogens as electrophilic sites, is a relatively new item in the supramolecular toolbox and shares numerous properties with the better known hydrogen bonding. The topological analysis of the X-ray multipole refined charge density proved to be an effective tool to elucidate the nature of halogen bonding [1] and in general of intermolecular interactions responsible for molecular crystals formation.

We present here the results obtained on two iodotetrafluoroethylimidazole derivatives, whose crystal structure is dominated by formation of I···N halogen bonds between equivalent molecules, and stabilized by the presence of F···F, C–H···F, π···π and other weak interactions. The experimental charge densities have been derived from single-crystal X-ray data collected at 100 K, using the aspherical atom formalism of Stewart [2] as implemented in VALTOPO [3], as well as by accurate DFT and MP2 molecular modeling calculations. Information such as the topological features and nature of the involved interactions, as derived from topological analysis of electron density and its Laplacian, and the interaction energies associated to halogen bonding and the weaker interactions, will be presented.

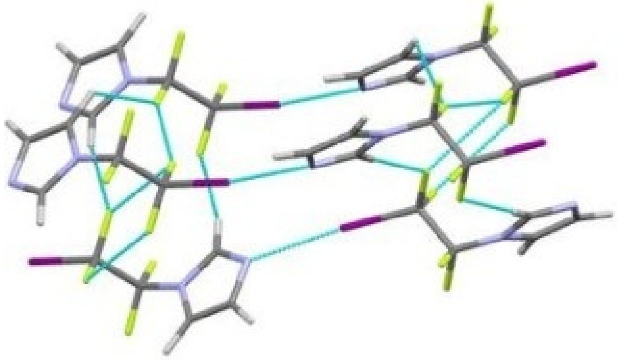

Figure 1. Interactions Network in Iodotetrafluoroethylimidazole

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1O4. Structural characterization of LDH samples by ADT and TGA-GC-MS: thermal response and contamination in nitrate and organic-exchanged hydrotalcites

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Layered double hydroxides (LDH) are versatile materials used for intercalating bioactive molecules, both in pharmaceutical, nutraceutical and cosmetic fields, with the purpose of protecting them from degradation, enhancing their water solubility to increase bioavailability, to improve pharmacokinetics properties and formulation stability. The crystal chemistry of hydrotalcite-like compounds is investigated by X-ray powder diffraction (XRPD)[1], automated electron diffraction tomography (ADT)[2],[3] and hyphenated TGA-GC-MS [4] to shed light on the mechanisms involved in ion exchange and absorption of contaminants, mainly carbonate anions. For the first time ADT allowed to obtain a structural model of LDH_NO_3 from experiment, shedding light on the conformation of nitrate inside LDH and on the loss of crystallinity due to the layer morphology. The ADT analysis of a hybrid LDH sample (LDH_EUS) clearly revealed the increase of defectivity in this material. XRPD demonstrated that the presence of carbonate is able to influence the intercalation of organic molecules into LDH, since CO_3 contaminated samples tend to assume d-spacings roughly multiples of LDH_CO_3 d-spacing. TGA-GC-MS allowed distinguishing and quantifying intercalated and surface adsorbed organic molecules, confirming the presence and amount of carbonate, especially at low (below 2% in weight) concentrations and separating the different types and strength of adsorption, in relation with the temperature of elimination.

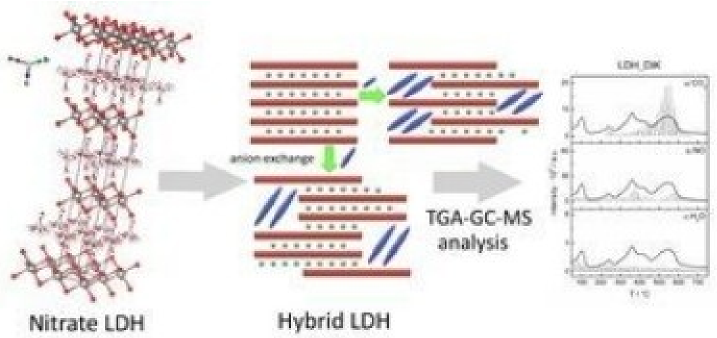

Figure 1. LDH_NO_3 structure by ADT, anion exchange reaction model and TGA-GC-MS data.

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1O5. Polymer Brushes and Their Composites with Silver Nanoparticles: An X-Ray Reflectivity and Positron Annihilation Spectroscopy Study

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Stimuli-responsive polymer brushes loaded with plasmonic nanoparticles are perfect optical sensors for temperature and pH. Probing the distribution of nanoparticles in brushes is of paramount importance to properly investigate and correlate the properties of the resultant nanocomposites. However, conventional characterization techniques do not allow to reach such insight, at least without damaging the sample (*e.g.* section electron microscopy). That makes obtaining a detailed characterization of polymer brushes and of their composites with embedded nanoparticles a challenging task.

Here we show how X-Ray Reflectivity (XRR) and Positron Annihilation Spectroscopy (PAS) can be used to obtain deep insight on the characteristics of such complex systems with unprecedented detail.

Both are non-destructive techniques. XRR is able to measure thicknesses on the order of 1 nm in the range 0 ÷ 200 nm. Other informations such as massive density and interface roughness can also be obtained. PAS is a more unconventional technique, based on the implantation of positrons in a matrix and on the study of the annihilation features. The usefulness of PAS for the study of polymer composites arises from its sensitivity to holes and defects with nanometer and sub-nanometer size and also on the possibility to extract details on the chemical composition of the probed environment.

In this work, PAS has been applied for the first time to a nanocomposite obtained by loading silver nanoparticles (NPs) into “grafting-from”–prepared poly(dimethylaminoethyl methacrylate) brushes. PDMAEMA is a weak polyelectrolyte and since positrons implantation depends also on the ionic character of the material, a rapid and accurate discrimination between protonated and deprotonated states was obtained. XRR outputs provided basilar input to allow PAS data fitting, making possible to identify changes in the mass density of the brushes films embedded with silver NPs and the introduction of new defects associated to the brushes/NPs interface.

1P1. Modelling The Carbonate Substitution In Hydroxyapatite Towards Bone Composition

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Hydroxyapatite [HA, $Ca_{10}(PO_4)_6(OH)_2$] is the main constituent of the inorganic phase of bones and teeth and is studied and applied as a biomaterial for tissues repairing and reconstructing. The biological HA is characterized by the presence of vacancies and defects, the most relevant being the carbonate ion substitution in the lattice (about 6% in weight). The CO_3^{2-} ion can be accommodated either in place of the hydroxyl groups (type A defect) or of the phosphate group (type B) of the unit cell. The detailed knowledge of these possible HA defective structures has recently become fundamental to design improved prosthetic materials, since the carbonate incorporation can influence the adsorption processes at the mineral surface in the biological environment. Theoretical methods can be successfully applied to provide structural information and surface properties and to offer a comparison with experimental measurements.

In the present contribution, some recent results of our computational study on the role of carbonate ion in both fully and partially carbonated hydroxyapatite will be presented. Static calculations at the DFT level have been run to simulate structural, electronic and vibrational bulk properties of the A-, B- and AB-type defects [1,2,4]. Moreover, ab initio molecular dynamics simulations have been employed to provide insights on the CO_3^{2-} mobility [3]. Work is in progress to model and characterize different surfaces of carbonated apatite, both plain and in interaction with biologically interesting molecules.

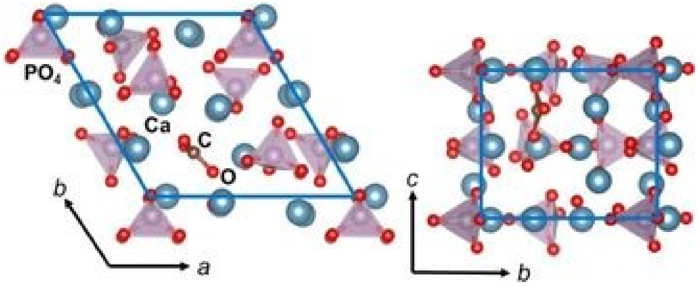

Figure. 1. Fully carbonated HA unit cell [$Ca_{10}(PO_4)_6CO_3$] viewed along the *c* (left) and *a* (right) axes.

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1P2. Chemical selectivity in structure determination by time dependent analysis of in situ XRPD data: a clear view of Xe thermal behavior inside a MFI zeolite

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X-ray diffraction methods in general provide a representation of the average structure, thus allowing only limited chemical selectivity. As recently shown [1], some structural information on a subset of atoms can be obtained by modulation enhanced diffraction (MED), thus proposing a new tool that is able to enhance selectivity in diffraction. MED uses a periodic stimulus supplied in situ on a crystal, while diffraction data are collected continuously during one or more stimulation periods. Such large data sets can then be treated by different methods. Here we present and compare Phase Sensitive Detection (PSD) and Principal Component Analysis (PCA) for in situ X-ray powder diffraction (XRPD) data treatment. The application of PCA to MED data is described for the first time in the present paper. Simulated and experimental MED powder data were produced by using an MFI zeolite as static spectator, in which Xe, acting as active species, is adsorbed and desorbed in a periodic manner. MED allowed obtaining, by demodulating first simulated and then experimental data, the powder diffraction pattern of the responding scattering density, and selectively extracting crystallographic information on Xe by solving the crystal structure of the active species independently of the static zeolite framework. The "real world" experiments indicated that the PSD-MED approach has some limitations related to the degree of fulfilment of some theoretical assumptions. When applied to in situ XRPD data, PCA, despite based on blind statistical analysis, gave results similar to those obtained by PSD (based on Fourier analysis) for simulated data. Moreover, PCA is complementary to PSD, thanks to its capability of gathering information on the Xe substructure even in the presence of a non-periodic stimulus, i.e. using for instance the most simple stimulus shape as a single temperature ramp. In particular PC1 resulted able to perfectly reproduce the corresponding 1Ω signal from a traditional PSD analysis. Moreover PCA can be applied directly to raw non periodic XRPD data, opening the possibility of using it during an "in situ" experiment. PCA can thus be envisaged as a very useful fast and efficient tool to improve data collection strategy and to maximize data quality and their information content. To date however PSD remains superior for substructure solution from analysis of 2Ω demodulated data [2].

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1P3. New advances of *QUALX2.0*, a qualitative phase analysis software querying a freely available database

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Phase identification of crystalline materials by powder diffraction technique is a useful application in different scientific fields (*e.g.*, organic and inorganic Chemistry, Mineralogy, Pharmaceutics, materials science, cultural heritage,..) as well as in industrial sectors (*e.g.*, control of quality of drugs).

QUALX [1] is a qualitative phase analysis free software querying the PDF-2 commercial database, maintained and updated by ICDD [2]. It is a computer program searching for the database single-phase pattern(s) best matching the experimental powder diffraction data.

QUALX2.0 [3] is the updated version of *QUALX*. *QUALX2.0* can perform all the procedures carried out by *QUALX* and its main feature is querying also a freely available database (POW_COD). Consequently, *QUALX2.0* is the only qualitative phase analysis program freely distributed and based on a free database. POW_COD is generated by the structure information contained in the Crystallography Open Database (COD) [4], an open-access collection of crystal structures of inorganic, metal-organic, organic compounds and minerals, continuously growing (currently COD contains more than 315000 entries). POW_COD is exported in *SQLite3* format.

Other novelties of *QUALX2.0*: i) the possibility of reading a larger variety of formats of the experimental diffraction pattern ASCII file, ii) new search-match options.

Since November 2014, *QUALX2.0* and POW_COD are available at http://www.ba.ic.cnr.it/content/qualx-downloads, free for academic and non- profit research institutions after registration (number of downloads 400).

Very recently, new features have been introduced in *QUALX2.0* concerning the possibility of actively using in the search-match process restraints on cell parameters, crystal density and/or symmetry. The structure of POW_COD has been suitably optimized in order to make the search with restraints fast and efficient.

The main procedures of *QUALX2.0*, its new features and some applications to experimental diffraction data will be outlined.

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MS2. INVESTIGATING STRUCTURE-PROPERTY RELATIONSHIPS IN COMPLEX MOLECULAR SYSTEMS BY A MULTI-TECHNIQUE APPROACH

The MS concerns the application of complementary techniques to study structure-property relationships in different classes of complex molecular systems such as, for example, MOF or co-crystals.

Chair: Patrizia Rossi (U. Firenze)

2KN1. New insight into the properties of indomethacin pharmaceutical co-crystals

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In the last years, the synthesis of co-crystals containing active pharmaceutical ingredients (APIs) has become the new frontier of the crystal engineering due to the great opportunity to modify the physico-chemical properties of solid forms of drugs. Actually, the pharmaceutical co-crystals display intermolecular motifs and hence crystal structure different from the pure API component, and consequently can exhibit diverse specific physical properties, such as solubility and dissolution rate. Since the therapeutic efficacy of a pharmaceutical formulation depends on its bioavailability, *i.e.* the absorption extent and rate of the active pharmaceutical ingredient into the bloodstream following its administration, the solubility and dissolution properties of co-crystals can allow to increase the bioavailability of poorly water soluble APIs.

Even though it is currently believed that the co-crystallization strategy should not induce changes on the pharmacological profile of the APIs, it is not yet clear whether a co-crystal would be defined as a physical mixture or as a new chemical entity. In order to clarify these aspects, we chose indomethacin (Figure 1a) as guest poorly aqueous soluble molecule and compared its properties with those of its cocrystals obtained with 2-hydroxy-4-methyl-pyridine (cocrystal ***1***), 2-methoxy-5-nitroaniline (cocrystal ***2***) and saccharine (cocrystal ***3***). In particular, we evaluated *via* HPLC analysis the API dissolution profile (Figure 1b), its ability to permeate across intestinal cell monolayers (NCM460) and its oral bioavailability in rat using the pure drug, its co-crystals and their parent physical mixtures [1].

This interdisciplinary study has shown for the first time that different effects can be induced by co-crystals and their parent physical mixtures on a biologic system, and at the same time has raised serious concerns about the use of co-crystal strategy to improve API bioavailability without performing appropriate investigations.

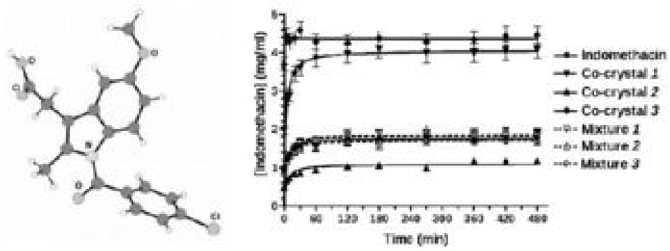

Figure 1. a) Indomethacin; b) dissolution profiles of indomethacin co-crystals and physical mixtures

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2KN2. Biomolecules as ligands to construct high-dimensional coordination networks (*bio*MOFs): towards a rational design of more feasible biocompatibility and homochiral materials

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Among the different areas of chemical sciences, the synthesis of high-dimensional metal-ligand networks, so-called Metal-Organic Frameworks (MOFs), has experienced probably the more rapid development during the last decades.[1] The reasons are two-fold: first, from a crystal engineering point of view, because of the large variety of intriguing topologies and fascinating structures they can show, and secondly, due to the wide plethora of physical and chemical properties they can exhibit, related to their intrinsic porous character.

A quite recent step forward towards the obtention of original examples of MOFs consisted to construct bioMOFs.[2] These novel materials, which can be obtained using ligands derived from the biological world, may offer remarkable advantages over traditional MOFs, more feasible biocompatibility affording potential medical applications as well as the possibility to achieve homochiral materials in a rational and predictable manner due to the enantiopure nature of the employed biomolecules, capable of transmitting their “chiral information” to the stereochemistry of the metal atoms, and suitable for application in chiral discrimination or separation. As an extension of our recent work with the related monosubstituted oxamato derivatives[3a] and cytidine,[3b] we have now focused on a family of enantiopure disubstituted oxamidato ligands derived from natural amino acids (scheme 1) and cytidine 5’-monophosphate,[3c] which offer multiple coordination sites and good perspectives as chiral inducers. We report herein a novel example of proton conducting, homochiral *bio*MOF family.

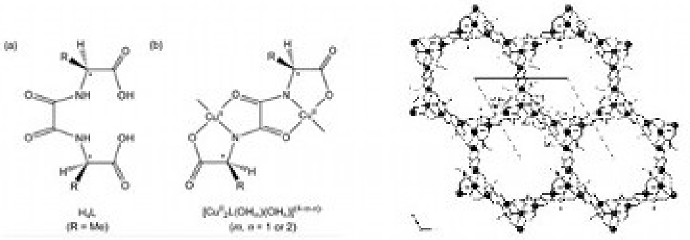

Figure 1. (left) Chemical structures of the chiral bis(amino acid)oxalamide ligands; (right) Perspective view of the 3D open-framework of $\{Ca^{II}Cu^{II}_6[(S,S)\text{-}L]_3(OH)_2(H_2O)_4\} \cdot 32H_2O$.

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2O1. Molecular Rotors in Porous Covalent Frameworks and Supramolecular Architectures

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Highly porous materials are attracting large attention in the recent literature for their applications in the field of gas storage, selective recognition and molecular confinement. The discovery of ultra-fast molecular rotors in porous covalent frameworks allowed us to look at them from a new perspective [1,2]. The unusual combination of remarkable porosity with fast dynamics enabled the reversible speed-regulation of matrix rotors by the interaction with I_2 vapors entering the galleries of the porous compounds. Molecular rotors, especially when bearing dipoles, are a challenging research field entailing a number of useful phenomena, such as switchable ferroelectricity, and the fabrication of dynamic elements of molecular motors in solids. Recently, fast rotating organic elements bearing carbon-fluorine dipoles have been fabricated in porous organic-inorganic hybrid periodic architectures [3]. The reactivity of the pivot bonds allowed halogen addition and motion regulation.

A first example of molecular rotors in porous molecular crystals is presented. Disulfonated rotor-containing molecular rods were self-assembled with alkylammonium salts to fabricate porous supramolecular architectures held together by charge-assisted hydrogen bonds [4]. The rotors are exposed to the crystalline channels, which absorb CO_2 and I_2 vapors at low pressure. The rotor dynamics could be switched off and on by I_2 absorption/desorption, suggesting the use of porous crystals in sensing and pollutant management.

Moreover, crystals with permanent porosity were exploited in an unusual way to decorate crystal surfaces with regular arrays of dipolar rotors. The inserted molecules carry alkyl chains which are included as guests into the channel-ends [5]. The rotors stay at the surface due to a bulky molecular stopper which prevents the rotors from entering the channels. The host-guest relationships were established by 2D solid-state NMR and low rotational barriers were found by dielectric spectroscopy.

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2O2. Characterization of the solid state dynamic behaviour of cyclic peptoids

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Cyclic alpha-peptoids hold the attention of both synthetic and supramolecular chemists for their biostability and potential diversity but also for their elegant and intriguing architectures [1].

Peptoids differ from peptides in the side chains, which are shifted by one position along the peptide backbone to the nitrogen atom to give N-substituted oligoglycine.

The lack of the amide proton prevents the formation of NH···OC hydrogen bonds and weaker interactions, as CH···OC hydrogen bonds and CH-pi interactions, play a key role. Inter-annular CH···OC hydrogen bonds can provide face to face or side by side arrangement of macrocycles mimicking beta-sheet secondary structure in proteins [2].

In particular, the role of side chains in the solid state assembly of peptoid macrocycles will be discussed to show how they can promote the formation of a peptoid nanotube by acting as pillars, extending vertically with respect to the macrocycle planes [3,4].

Conformational flexibility is a key feature of peptoids and may be exploited to lead to functional materials. Examples will be given as the suitable choice of the side chains has a key role in determining the solid state dynamic behaviour upon solvent uptake and release.

Thermal analysis, hot-stage microscopy, in-situ gas absoprtion X-ray powder diffraction and single crystal X-ray diffraction concurred to the assessment of the solid state dynamic behaviour of the examined compounds.

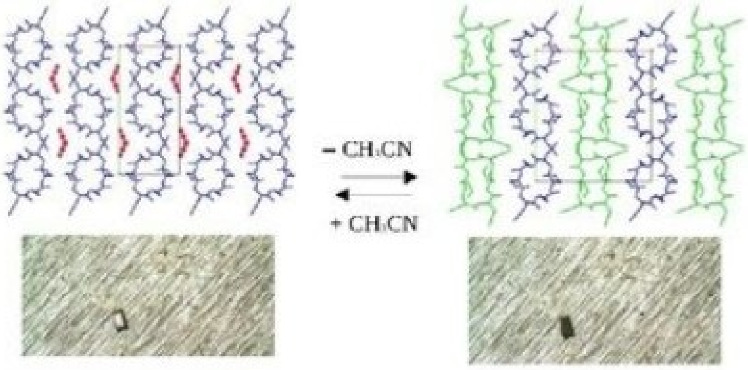

Figure 1. Reversible single crystal to single crystal transformation upon acetonitrile release and uptake for the cyclic peptoid *cyclo-(Nme-Npa*$_2$*)*$_2$, *Nme* = *N*-(methoxyethyl)glycine, Npa = *N*-(propargyl)glycine.

EU FP7-People- IRSES grant number 319011 "Synthesis and characterization of porous molecular solids" is gratefully acknowledged.

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2O3. Promising Low-Dielectric-Constant Materials: Metal-organic Frameworks and Coordination Polymers Compared

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Identifying novel low-dielectric-constant (low-*k*) materials for integrated circuit (IC) use is a main challenge for the microelectronics industry. *Fluorous* metal-organic frameworks (FMOFs) and non-porous coordination polymers (FN-PCPs) built up with poly(azolate) ligands are promising alternatives to currently applied low-*k* dielectrics, as their properties can be modulated through a sensible choice of nodes and spacers, with the added value of the high thermal stability imparted by the *N*-donor struts. Surprisingly, in spite of this, few reports, regarding solely MOFs, have appeared to date on dielectric properties.

To improve the knowledge on this scarcely explored field, we report here, as a case study, on the structural features, the thermal behaviour and the dielectric constant of a number of FBTB- and FTZ-based materials (FBTB = 1,4-bis-(tetrazol-5-ate)tetrafluorobenzene; FTZ = 3,5-bis(trifluoromethyl)-1,2,4-triazolate).

As retrieved by state of the art PXRD, both **Cu(FBTB)** and **Ag$_2$(FBTB)** show 3-D networks: the former, possessing **pts** topology, features 1-D rhombic channels accounting for 30% of the unit cell volume and for the so-called 'breathing' observed as a function of temperature (both up to 523 K and down to 90 K); due to the *exo*-octa-dentate coordination mode adopted by the spacer, **Ag$_2$(FBTB)** is non porous and remarkably rigid, as also proved by N_2 adsorption at 77 K. Finally, **Ag$_2$(Ag$_4$FTZ$_6$)** [1] possesses a nanotubolar 3-D architecture.

As foreseen, ligands fluorination is definitely beneficial, as it

1. enhances thermal stability: as demonstrated by coupling TGA and VT-PXRD, **Cu(FBTB)** and **Ag$_2$(FBTB)** decompose in air at 260 and 400 °C, respectively (*vs.* $T_{\text{phase change}}$ = 100 °C and T_{dec} = 380 °C for the isostructural counterparts Cu(BTB) [2] and Ag$_2$(BTB) [3]).
2. favours stability toward water (*k* ~ 80): not only **Ag$_2$(FBTB)** is recovered intact after one month exposure to water vapours, yet it shows measured contact angles up to ~75° (*vs.* ~50° for Ag$_2$(BTB)). Even more performing, in this respect, is **Ag$_2$(Ag$_4$FTZ$_6$)**: in spite of porosity, measured contact angles reach ~160º, allowing to classify it as a *super-hydrophobic* material.
3. reduces values: impedance room temperature measurements up to 2 MHz disclosed a dielectric constant as low as 2.59(3) and 2.44(5), for **Ag$_2$(FBTB)** and **Cu(FBTB)**, respectively (*vs.* 3.79(4) for Ag$_2$(BTB)). Moreover, after 72 h exposure to water vapours, **Ag$_2$(FBTB)** increases to only 2.63(5). Finally, preliminary tests on **Ag$_2$(Ag$_4$FTZ$_6$)** revealed values lower than 2.5. Noteworthy, to the best of our knowledge, the observed dielectric constants constitute *a new world record* (*k* < 2.8) *for MOFs and PCPs.*

Work is in progress to complete this study and exploit metal-ligand combinations which, though preserving the observed promising properties, increase the stability up to the ~450 ºC needed for the dielectrics to survive processing and post-processing steps for IC applications.

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2O4. Fifty Years of Sharing Crystal Structures

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Crystallographers have been responsible for some remarkable achievements, demonstrated by the multitude of Nobel prizes awarded in the field. The crystallographic community can also claim a remarkable achievement: the output of every structure determination ever published is available for all. Not only can we learn from these individual structures, but we can learn from the collection.

The Cambridge Structural Database (CSD) [1] is one of the collections of crystallographic data and it contains all the small molecule organic and metal-organic crystal structures ever published. Thanks to the hard working crystallographic community this valuable resource now contains nearly 800,000 crystal structures, and the rate of growth of the CSD continues to rise.

This presentation, timed to coincide with the 50th anniversary of the Cambridge Structural Database, will discuss trends in structural chemistry, from authorship to use of structures, from crystallographic statistics to polymorph propensities. We will also look at examples of the extraordinary, curious and bizarre within the database.

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2P1. Homochiral Self-Assembly of Biocoordination Polymers: Anion-Triggered Helicity and Absolute Configuration Inversion

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We report herein on two *quasi*-identical homochiral 1D *bio*-coordination polymers built from the direct self-assembly of cytidine 5'-monophosphate (CMP) and Cu(II) ions, in the presence of two different counter-anions (perchlorate or triflate) coming from the copper(II) source. We found the anion to play a central role in the homochiral resolution process, leading to a helix with *P* (right-handed) or *M* (left-handed) chirality in the case of the perchlorate or the triflate, respectively (see Figure 1). The handness of the two obtained helices can be quickly inverted, in a reversible way, by switching the anion, as revealed by circular dichroism experiments, both in solution and in the solid state. Single crystal and powder X-ray diffraction, together with electrospray experiments, well support our hypothesis.[1]

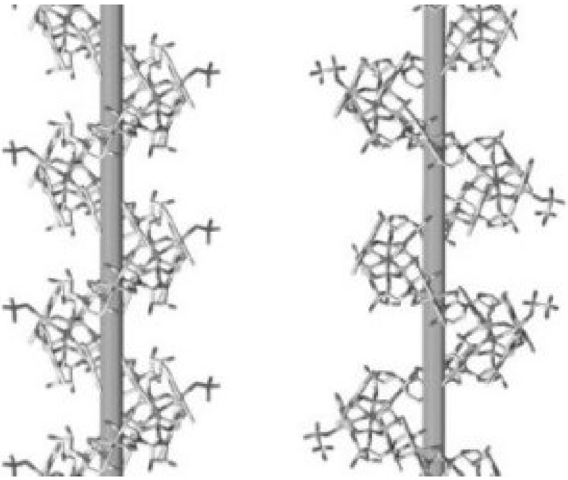

Figure 1. Side view of the P (right-handed), left, and M (left-handed), right, helices presented in this work.

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2P2. Naphthalene diimide cocrystals based on halogen bond

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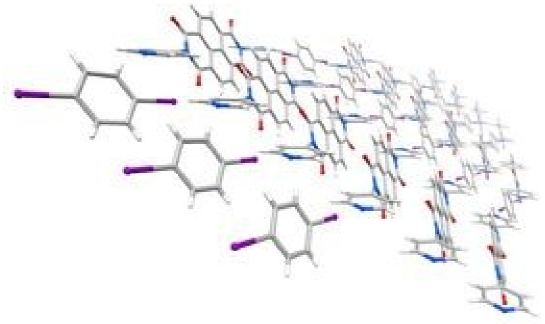
Naphthalene imides (NI), naphthalene diimides (NDI), perylene diimides and their derivatives are commonly employed for their absorption and luminescence properties [1]: they are indeed one of the most promising class of electron accepting materials. Their rigid aromatic core favours π-π stacking interactions which, along with different types of weak interactions, could lead to a broad range of compelling compounds.

In this work we present the first sets of cocrystals made up with DPNDI (N,N-di-(4-pyridyl)-naphtalene-1,4,5,8-tetracarboxydiimide) and halogenated aromatic derivatives interacting through halogen bonds. Recent interest in this specific kind of interactions [2] is certainly ascribable to the capacity to tune and design specific and valid self-assembly structures.

Formation of new crystalline compounds, obtained through the combination of two different molecules (co-crystals), is possible by using suitable molecular partners. Despite NDI molecules remain unchanged in cocrystal form, its specific properties are subjected to an evident variation. For this reason we have investigated and correlated different cocrystals and their absorption properties to the crystalline packing and how NDIs molecules and partners interact in the solid state in order to establish a univocal relation between each other.

The degree of inclination in a π stacking system can be described by two angles called "pitch" (P) and "roll" (R) as reported in previous works [3] so as to properly correlate halogen bonds to the ultimate crystalline structure.



igure 1. Diiodobenzene-DPNDI cocrystal.

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2P3. From crystallography to applications: non linear optical properties of β-D-fructopyranose alkaline halides MOFs

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Many physical properties of crystals are strictly correlated to their symmetry elements and packing of their constituents. It is the case of the second harmonic generation (SHG) property, that is strongly dependent on the absence of the inversion centre in the crystal structure [1]. Furthermore, in a non-centrosymmetric crystal, the presence of asymmetric molecules can introduce an additional electronic asymmetry and high hyperpolarizability, that seems to be strictly related to the SHG intensity [2].

Metal Organic Frameworks (MOFs) represent an ideal category of compounds to design functional materials with physical properties dependent on crystal symmetry. In particular,

carbohydrates represent good asymmetric poly-dentate ligands for the formation of MOFs. The SHG efficiency of many mono-, di- and tri-saccharides have been examined, and a correlation between their crystal systems and SHG efficiencies has been evidenced, *i.e.* the lower is the space group symmetry of the crystal the larger is the SHG efficiency [3].

In our previous work [4], two MOFs obtained from fructose and $CaCl_2$, $[Ca(C_6H_{12}O_6)(H_2O)_2]Cl_2$ (**1**) and $[Ca(C_6H_{12}O_6)_2(H_2O)_2]Cl_2 \cdot H_2O$ (**2**), were studied and it was demonstrated that the coordination of fructose on the calcium ion causes an improvement of the SH intensity with respect to the fructose itself. The theoretical calculations suggests that, at the excitation angular frequency, the SH intensity is influenced by both the position of the resonant frequency and the second-order susceptibility.

In this work we aim to better understand the correlation between the structural features and the SHG efficiency of new MOFs obtained from fructose and MX_2 (M=Ca,Sr; X=Cl, Br), of formula $[Ca(C_6H_{12}O_6)(H_2O)_2]Br_2$ (**3**) and $[M(C_6H_{12}O_6)_2(H_2O)_2]X_2 \cdot H_2O$ (**4**,**5**).

The metal-carbohydrate based MOFs analyzed in this work show a favorable combination of thermal and chemical stability, transparency, and second-order optical nonlinearity, and are thus potential candidate for applications in electro-optics devices.

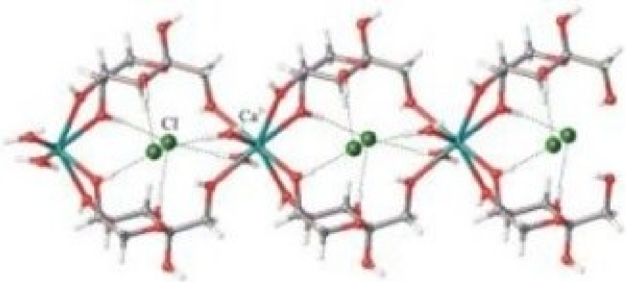

Figure 1. Infinite network of calcium, chloride and sugar in the [010] direction for compound **2**.

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2P4. Studies of the conformational changes on the ribosomal GTPase EFL1 using SAXS

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Ribosome biogenesis is closely linked to the cell growth and proliferation. Dysregulation of this process causes several diseases collectively known as ribosomopathies. One of them is the Shwachman-Diamond Syndrome, and the SBDS protein mutated in this disease participates with EFL1 in the cytoplasmic maturation of the 60S subunit. SBDS couples the energy liberated from the hydrolysis of GTP by EFL1 to release eIF6 from the surface of the 60S ribosomal subunit [1,2]. The eIF6 protein prevents the premature association of the ribosomal subunits by binding to the B6 inter-subunit bridge and additionally contacting the sarcin-ricin loop, Rpl23 and Rpl24 (3,4). EFL1 belongs to the P-loop family of GTPases and is homologous to the elongation factor EF-G/EF-2 (5). EFL1 probably removes eIF6 from the 60S surface through a conformational change similar to that triggered by EF-2 during elongation in the protein synthesis. Recently, we have shown that the interaction of EFL1 with SBDS resulted in a decrease of the Michaelis-Menten constant (K_M) for GTP and thus SBDS acts as a GEF for EFL1 [3]. Subsequent studies demonstrated that SBDS greatly debilitates the interaction of EFL1 with GDP without altering that for GTP. The interaction of EFL1 alone or in complex with SBDS to guanine nucleotides is followed by a conformational rearrangement. Understanding the molecular strategy used by SBDS to disrupt the binding of EFL1 for GDP and the associated conformational changes will be key to understand their mode of action and alterations occurring in the disease. The structure of the GTPase EFL1 is not known and its crystallization has been unsuccessful at least in our hands.

In this study, we aim to show the conformational changes resulting from the interactions between EFL1 and its binding partners, the SBDS protein and the guanine nucleotides using SAXS technique [4,5]. SAXS will provide structural information of the proteins and their conformational changes [6]. For the SAXS data analysis we have built models of EFL1 using by EF-2 as homology template and of SBDS using the crystal structures of the archaea orthologues.

The authors acknowledge financial support PGR2015 "Con il contributo del Ministero degli Affari Esteri e dalla Cooperazione Internazionale, Direzione Generale per la Promozione del Sistema Paese".

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2P5. Stacking motives in metallate salts of methylene blue

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The study focuses on the π-π stacking geometry exhibited in the solid state by 3,7-bis(dimethylamino)phenothiazin-5-ium, also known as methylene blue cation (MBC) associated with different counter-anions, in particular metallate ions.

The preparations of all the compounds were carried out in the solid state, by grinding MBC chloride together with several transition metal salts. The resulting powders have been characterized through X-ray powder diffraction, in order to check the reactions products and to confirm the crystalline nature of the compounds obtained. All the products were subsequently dissolved in adequate solvents and several crystallization trials were set up. Some of them aforded crystals suitable for single crystal X-ray diffraction and their structures have been successfully solved.

In the observed crystalline phases MBC gives rise to several different π-π stackings, which can be divided in two main classes. In the first class, the most abundant one, MBC exhibits an infinite π-π stacking. In these cases the geometrical operator connecting one molecule to the next in the stacking array is not a simple translation, as the molecule is also rotated on its own plane. The second class consists of rare cases where MBC forms dimers bound together through π-π interaction, with no significant stackings.

In order to find a rationale for the different dispositions of MBC, several parameters must be taken into account, e.g. the geometry of the involved counter-anion, its charge, the presence of solvent molecules and their geometry and polarity. Hence, a statistical approach is required to simplify the data processing and to evaluate the electrostatic and steric influence on the crystal packing in all the crystal phases observed.

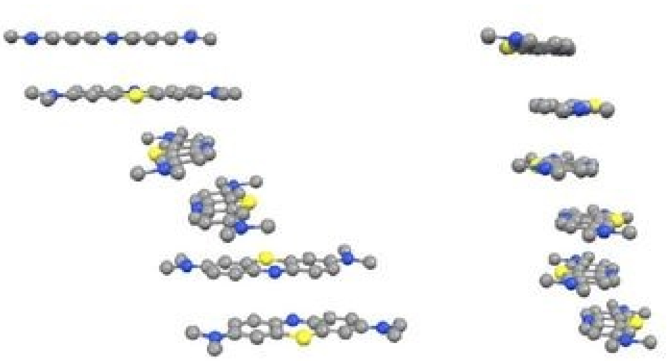

Figure 1. Two different examples of stacking geometry of MBC as observed in two crystalline phases in which, respectively, a $[HgCl_4]^{2-}$ anion (left) and a $[AuCl_4]^-$ (right) is present. The anionic species are omitted for clarity.

MS3. FROM NATURE TO ADVANCED MATERIALS: STRUCTURE CHARACTERIZATION AT THE NANOSCALE

The development of complex advanced materials and the need for a deeper understanding of nature require crystallographic knowledge at a nanoscopic level. Macroscopic materials properties are strictly linked with atomic structure, defectivity and hierarchical arrangement of crystalline nanodomains. Lab X-ray diffraction methods need to be integrated by other structure information, available by synchrotron sources, spectroscopies, neutron and electron diffraction, electron and atomic force microscopy. Speakers are invited to present innovative approaches and case-studies for the characterization of complex materials, with special regard to the identification of nanoscopic structural features.

Chair: Mauro Gemmi (IIT Pisa); Enrico Mugnaioli (U. Siena)

3KN1. Rotation electron diffraction as a complementary technique to powder X-ray diffraction for phase identification and structure solution

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Phase identification and structure determination of submicrometre-sized crystals are important in materials science and crystallography. The most widely used technique for these purposes is powder X-ray diffraction (PXRD). However, the use of PXRD is limited in multiphase samples, especially those containing unknown phases. Due to the strong interaction between electrons and matter, submicrometre-sized crystals can be studied as single crystals using electron diffraction. Electron crystallography has proven a promising alternative for studying individual phases in multiphase crystalline samples containing submicrometre-sized particles.

The recently developed electron diffraction tomography methods, for example automated electron diffraction tomography (ADT) [1] and rotation electron diffraction (RED) [2,3] and can be used to collect complete three-dimensional electron diffraction (ED) data from single crystals of sub-micrometre sizes in a TEM. RED combines discrete goniometer tilt steps (typically 2–3°) with very fine steps of beam tilt (typically 0.05–0.20°) and data collection is controlled entirely by software on a conventional transmission electron microscope. Since there is no need to align the crystal, data collection is made very simple and fast. In RED data processing, 3D reciprocal space of the crystal is reconstructed and the unit cell as well as the space group can be easily determined. The reflections are then indexed and a list of *hkl* with intensities is output for *ab initio* structure solution using standard phasing methods, for example direct methods [4].

Today it has become routine work to collect essentially complete three-dimensional electron diffraction data from crystals as small as tens of nanometers and solve the structures. However, at present electron diffraction data needs to be combined with PXRD for a complete structure determination which includes both structure solution and reliable refinement, due to the fact that the electron diffraction intensities are of lower quality. The best approach is to combine three-dimensional ED and PXRD [5,6]. We expect that three-dimensional ED methods will become more and more important for phase identification and structure solution of complex materials in the near future.

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3KN2. How difficult is to solve complex structures: the case of Eni Carbon Silicates

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Eni Carbon Silicate (ECS) materials form a new family of crystalline hybrid organic-inorganic metallo-silicates recently discovered in the eni's laboratories [1]. They are prepared by hydrothermal treatment at 100°C of a reaction mixture composed by a source of trivalent metal ion (e.g. $NaAlO_2$), a base (NaOH and/or KOH), demineralized water and a bridged silsesquioxane of general formula $(R'O)_3Si–R–Si(OR')_3$ (R = alkyl, aromatic or alkyl-aromatic group; R' = Me or Et) as source of silica. Today, the ECS family is composed by 20+ phases obtained by varying the nature of the bridging organic group, the trivalent metal ion (i.e., Al [1], B [2], Ga [3]) and the composition of the reaction mixture. A detailed characterization of these phases is necessary for answering to some important questions related to the integrity of the bridged silsesquioxane moieties, to their assembly in the crystalline lattice, to the role of the trivalent metal ions, to the presence of open porosity, etc. All this information can be obtained once the structure of the material is determined and refined. In the case of ECSs, the structural characterization proved to be a challenging problem because of their complexity, while the nanocrystalline nature of the samples hampered the application of the conventional single crystal X-ray diffraction techniques. Therefore, a suitable protocol, which includes elemental, thermal (TG-DTA-MS) and textural (N_2 adsorption/desorption isotherms) analyses, MAS NMR (^{29}Si, ^{27}Al, ^{11}B, ^{71}Ga, ^{13}C, ^{1}H), electron microscopy (FESEM-EDS, HRTEM) and laboratory X-ray diffraction (XRD), was applied for a preliminary characterization of the ECS samples and for deriving the necessary data for the successive structure determination. High-resolution synchrotron X-ray powder diffraction data were collected for all the ECS phases and in some cases (ECS-17 and ECS-14, Fig. 1) they were employed for solving the crystal structure by direct methods [4,5]. For other materials, however, it was necessary to approach the problem in a different way, exploiting advanced crystallographic techniques recently developed, such as the Automated Diffraction Tomography (ADT), which allowed the collection of single-crystal electron diffraction data on very small specimen (< 0.5 µm). In this way, it was possible to determine the structure of ECS-3 (with 63 independent non-H atoms in the asymmetric unit, actually the most complex structure determined by ADT [6]) (Fig. 1) and of ECS-5, which crystallize in form of very thin platelets (< 0.1 µm) [2].

The successful results obtained so far demonstrate once more how the integration of conventional and non-conventional techniques is fundamental for solving challenging problems in the structural characterization of new materials and this can be achieved only through a teamwork involving the necessary skills.

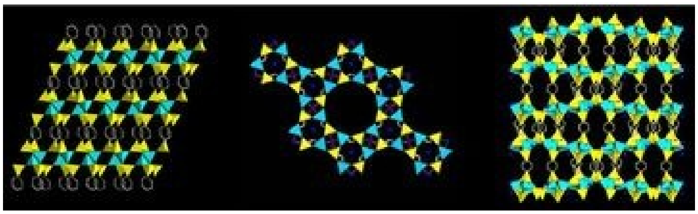

Figure 1. Structure of ECS-17 (left), ECS-14 (middle) and ECS-3 (right). $[SiO_3C]$ tetrahedra in yellow, $[AlO_4]$ tetrahedra in cyano, Na ions in blue, phenylene ring in grey.

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3O1. 3D Investigation of the Reciprocal Space of Nano-Crystals by Electron Diffraction Tomography

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Electron Diffraction Tomography (EDT) [1] is a recent crystallography technique that until now has mainly been used to solve unknown structures. It consists of taking a set of diffraction patterns while tilting the sample around the goniometer axis of the microscope, with a specific angular step (typically 0.5-1°) and within an angular range depending on the goniometer that is used (in our case from -60° to 60°). It can be coupled with precession, in order to obtain quasi-kinematical intensities. However, even if solving structures is the main goal of EDT, it is only one of the possibilities of this powerful and versatile technique.

In fact, apart from going through the whole structure solution process, a 3D-reconstruction of the reciprocal space (RS) can be performed and used as a powerful visualization tool. Furthermore, this feature also allows to build sections of the RS that do not pass through its origin, making a finer investigation of the reciprocal space possible. This 3D-reconstruction then makes it easier to understand what happens in the structure, and specific weak features like structure modulation and diffuse scattering can be detected and directly visualized in connection with the underlying Bragg scattering.

The case of a modulated structure ($Bi_8Pb_5O_{17}$) will first be discussed. The visualization allows us to understand the geometry and the symmetry of the modulation, that in this case is two-dimensional, and how this one affects the average structure. A preliminary structural model has been derived in a five-dimensional superspace using the Superflip software and JANA2006. A second example will concern the reciprocal space analysis of InSb nanowires, in which the reciprocal space reconstruction shows astonishing star shape spots probably connected to a core shell structure induced by different relaxed structures in the radial direction of the wire. A third example will show the diffuse scattering of the mineral cesarolite as a road map towards a modulated crystal structure.

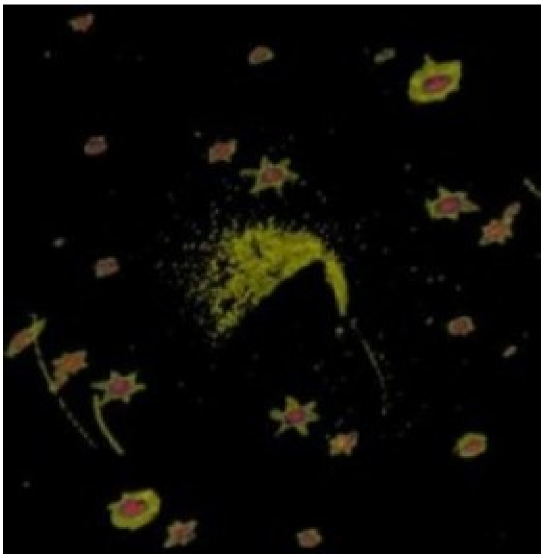

Figure 1. 3-dimensional reconstruction of the reciprocal space of an InSb nanowire.

The main drawback of EDT, like all the techniques in which electrons are involved, is the difficulty to use it on beam sensitive materials. This is overcome with a fast EDT[2] procedure: the diffraction patterns are taken while the sample is tilted continuously, reducing dramatically the dose suffered by the sample. Then new possibilities are emerging, like the study of pharmaceutical compounds and proteins for example.

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3O2. Structure determination using ab-initio methods and simulated annealing from PED tomography

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Despite the success of X-Ray crystallography in solving structures there is a limitation to work with nm size crystals. Since the invention of precession electron diffraction (PED) [1] in Transmission Electron Microscope (TEM), many structures have been solved either collecting several zone axis (ZA) data or collecting the data by diffraction tomography technique. During the ab-initio structure determination from electron diffraction data in combination with PED, it is possible that the light atoms are not found using *ab-initio* structure solution or their positions are found distorted due to poor quality of the collected ED data. In this work we present how combination of ab-initio structure solution and simulated annealing can help to recover correctly all atom positions from low quality electron diffraction (ED) data.

Using automated diffraction tomography (ADT) in combination with PED, a tilt sequence of several non-orientated electron diffraction patterns around an arbitrary tilt axis with fixed tilt step can be collected [2]. The collected PED patterns can be analyzed by ADT3D software to extract the unit cell and intensity. Such data may have low completeness due to the restriction of the TEM goniometer and/or the quality of the ED data may be poor due to beam sensitivity or to the low dynamic range of CCD camera used; all those factors may have a negative impact on the *ab-initio* structure solution.

As a test case, ED data from $LiFe_{0.20}Al_{0.80}Si_2O_6$ sample with space group *C* 2/c was collected with a tilt range of $+-30^0$, ES500W Erslangshen 12 bit CCD camera. From the extracted intensity ab-initio structure solution was performed with direct methods (SIR 2012) and charge flipping algorithms but it was not possible to determine Li atom position. After using same extracted intensity data set and using simulated annealing/potential energy minimization algorithm (Endeavour software package) [3] it was possible to detect Li atom [Figure 1] at position which match with the position obtained from X-ray diffraction data.

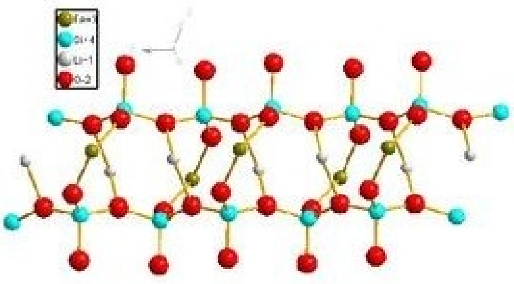

Figure 1. Crystal structure model of $LiAl_{0.2}Fe_{0.8}Si_2O_6$, as obtained by Endeavour Software

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303. Organized architecture of dyes in zeolite channels: an effective transport of electronic excitation energy

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The Assembly of chromophore molecules, using the one-dimensional channel framework of zeolite L (ZL) allow to induce organized architectures [1], or functional supramolecular systems (e.g. Dye−ZL composites) [2], with efficient FRET and impressive antenna properties for light harvesting, transport, and trapping [3]. It has been shown [4], that the properties of dye-ZL systems depend on the molecular packing inside the channels, controlling the intermolecular and the dyes/framework interactions

In this work we presents a study on the optical properties of a two –dyes antenna system in which fluorenone molecules (FL, donor molecule) and thionine (Th, acceptor molecule) are organized in Zeolite L porosities.

To interpret the optical properties of the hybrids a detailed structural study at atomistic level was mandatory. Due to the impossibility of studying from the structural point of view a two –dyes systems, two "one-dye" hybrids (ZL/FL and ZL/Th) were firstly synthesized and characterized to investigate the intermolecular and the dyes/framework interactions [5].

The results of thermogravimetric, IR, and X-ray structural refinements carried out for the one-dye ZL/FL and ZL/Th systems established that 1.5 and 0.3 molecules per unit cell are the maximum loadings possible for FL and Th, repectively. The FL carbonyl group strongly interacts with a K+ ion in the ZL channel. On the other hand, short distances between the carbon, sulfur and nitrogen atoms of Th with two water molecule sites, in turn at bond distance from the oxygen atoms of the main channel, suggested a water-mediated Th-ZL interactions. The energy transfer from excited FL molecules, forming the non-covalent nano-ladder in the ZL channel, and Th, deposited on the external surface of ZL particles, is currently under investigation.

In conclusion, concerning the optical properties of our composites, no evidence of Davydov splitting emerged from our study, indicating that one of the main competitors of the FRET mechanism is not operative notwithstanding the close packed arrangement of FL. We believe that this feature is of overwhelming relevance in view of application of such a system in artificial antenna devices.

The authors acknowledge the Italian Ministry of Education, MIUR-Project: "Futuro in Ricerca 2012 - ImPACT-RBFR12CLQD".

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3O4. Structural evolution of tungsten oxide nanocrystals investigated by Pair Distribution Function and Modulation Enhanced Diffraction

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A static and dynamic structural characterization of selected crystal-phase-controlled samples of colloidal tungsten oxide nanorods, synthetized by a non-hydrolytic route under rigorous water- and air-free conditions [1], then subject to prolonged air exposure, has been carried by combining the Modulation Enhanced Diffraction (MED) technique [2] and Pair Distribution Function (PDF) analysis [3]. The samples have been characterized with an unprecedented accuracy, which has allowed determining the thermal motion and position of single atoms, and revealing subtle stoichiometry deviations from the reference crystal phases available in the database. The crystal phases present in the samples were identified by means of a Rietveld analysis against several reference phases and an atomic pair PDF refinement of the best candidates. The samples were then put in contact with air at ambient temperature and their structure was monitored by time-dependent X-ray measurements, using a synchrotron facility for monitoring within the first 24 hours, and a home diffractometer for monitoring over a period of several months. The PDF analysis of these datasets revealed a peak broadening and an increased atomic thermal motion. This static analysis was complemented with a dynamic investigation, performed by means of the MED technique applied to the whole set of measurements. The MED technique has been recently proposed as a tool to capture structural features of crystal systems that are varying in phase upon application of some external stimuli, like for example temperature or pressure [4]. MED is based on the joint analysis of a series of XPD profiles, collected as long as the external stimulus is being varied [5,6]. This technique has been here applied to PDF analysis for the first time, and complemented by a novel multivariate approach. The time-dependent behavior of the samples produced under air exposure, obtained from XPD and PDF analysis on the basis of a multivariate analysis, has been interpreted as resulting from an appreciable increase of the thermal motion of oxygen atoms within the most oxygen-rich crystal planes. The methods and the algorithms proposed in this study can be potentially applied to any nanomaterial, to monitor its structural properties in response of an *in situ* applied external perturbation.

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3P1. Electron diffraction study of polyphasicnanocrystalline M_2O-Al_2O_3-WO_3 (M = Na, K) system

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In the last century, X-ray crystallography allowed the determination of the atomic structure of hundreds of thousands of materials. Still, single-crystal X-ray diffraction can be performed only on crystalline domains of some cubic microns, while many new synthetic phases do not grow in crystals of such dimensions. X-ray powder diffraction may be problematic for polyphasic samples and structures characterized by large cell parameters or pseudo-symmetry. On the other hand, electron diffraction is able to deliver 3D structural data from single crystallites of few nanometers. This ability derives from the high cross section between electrons and matter and the possibility to focus the electron beam into a nanometric probe. In the last years, automated diffraction tomography (ADT) emerged as an efficient method for acquiring complete and quasi-kinematic electron diffraction data for ab-initio structure determination of sub-micrometric phases [1-2].

M_2O-Al_2O_3-WO_3 (M = alkaline metals) system attracted the attention of the scientific community because some of its members showed potential applications as single crystalline media for tunable solid state lasers. A systematic investigation of these phases is nonetheless hampered because it is impossible to produce large crystals and only in few cases a pure synthetic product can be achieved. In this work we present the structure characterization of two hitherto undetermined compounds, $K_5Al(W_3O_{11})_2$ and $NaAl(WO_4)_2$, by a combination of ADT and precession electron diffraction [3]. Ab-initio structure determination was obtained by data taken from single crystallites less than 100 nm in size, eventually sampled in polyphasic mixtures. Structure determination was complicated by the presence of pseudo-symmetry, that was revealed by 3D single-crystal diffraction data [4].

$K_5Al(W_3O_{11})_2$ was found to crystallize in monoclinic space group $C2$. Weak reflections $hk0$ with h = 1, 3, 5 may mislead space group assignment for poor crystallographic data, and probably are the reason for the failure of previous attempts of structure solution.

$NaAl(WO_4)_2$ can be synthesized only in a polyphasic mixture together with $Na_2W_2O_7$, whose structure is known from literature [5]. Both $NaAl(WO_4)_2$ and $Na_2W_2O_7$ have a pseudo-hexagonal cell that must be reduced respectively to C-centered orthorhombic and C-centered monoclinic cells in order to achieve structure determination. Actually, the structure of $NaAl(WO_4)_2$, solved in space group $C2/c$, was found to be isotypic with $NaFe(MoO_4)_2$ structure, in agreement with previous proposals on the basis of compositional, metric and symmetry resemblances observed in oriented electron diffraction zone patterns.

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3P2. Average and Local structural comparison of $BaTi_{1-x}Ce_xO_3$ by Pair Distribution Function

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$BaTiO_3$ is considered as a typical ferroelectric material. It presents, with a temperature decrease, the classical phase transition from a paraelectric cubic structure to ferroelectric phases (progressively: tetragonal, orthorhombic and rhombohedral). The solid solutions with other $BaM^{IV}O_3$ perovskites (M=Sn, Zr, Hf, Ce) can strongly modify these transitions and the related polar behaviors. Some materials show, dependently from the dopant type and amounts, a variation from conventional ferroelectric, via diffuse ferroelectric transition to a clear relaxor state and further to dipolar glass behaviour [1]. Considering that $BaTiO_3$-based solid solutions are environment-friendly dielectrics with similar performances as many toxic Pb-based electroceramics [2], the study of these compounds becomes a topic of great interest and a current matter. Different researches have investigated these systems, but the relation with the average crystallographic structure, the local order and electric properties is still mostly unknown. Just few previous studies, as for the $BaTi_{1-x}Zr_xO_3$ [3], have addressed the issue demonstrating the existence of a structural local disorder linked to the evolution of the polar behaviour. In this work $BaTi_{1-x}Ce_xO_3$ ceramic solid solutions with different cerium amounts (x = 0.05, 0.10, 0.20) are presented. This system represents a limit and interesting case due to a large difference in the Ti and Ce atomic radius ($r_{Ce4+} = 0.87$ Å and $r_{Ti4+} = 0.605$ Å), and because this kind of substitution does not involve the creation of charge compensating lattice defects. As indicated by dielectric permittivity measurements, the three samples under study correspond to a different polar behaviour: conventional ferroelectric (x = 0.05) but close to the so-called pinched transition, diffuse phase transition (x = 0.10) and non-ergodic relaxor (x = 0.20). Total scattering data has been collected ID22 high resolution beamline, ESRF (European Synchrotron Radiation Facility; Grenoble, France) in a range between 100 and 400 K every 100 K to explore the phase transitions associated to each sample. Pair Distribution Function (PDF) refinements have been performed with the aim of understanding the induced differences between average and local structure as a function of composition and temperature. The Rietveld and average PDF results show a good agreement with the structural hypothesis suggested by the dielectric permittivity measurements. On the other hand, PDFs analysis also highlights a clear local disorder for all the samples. Often local and average structure have required different space groups to be fitted appropriately. PDFs comparison and structural refinements demonstrate in fact a clear local evolution of Ti-O and Ce-O bond distances with temperature and by the increase of the cerium amount.

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3P3. Photocatalytic Shaping of Silver Nanoprisms Self-Assembled on Anatase Thin Films

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Films made of highly photoactive titanium dioxide (anatase) were deposited on silicon substrates by an electrochemically-assisted technique. Citrate-stabilized silver nanoprisms (mean side length 40 nm, mean thickness 5 nm) were then self-assembled on titania. The process was aided by functionalizing the film surface with 3-aminopropyltriethoxysilane (APTES) to exploit the electrostatic interaction between positively charged amine groups and negatively charged silver nanoprisms. Silver nanoprisms distributed evenly on the surface and their shape was not affected by the deposition process as confirmed by electron microscopy.

However, by irradiation with 365 nm-UV light for less than 1 h, dramatic changes in both the shape and surface distribution of attached silver nanoprisms were observed (Figure 1). While the bigger prisms changed into discoidal particles, the smaller dissolved. Such new particles displayed different plasmonic properties compared to pristine nanoprisms. Titanium dioxide is known to produce highly reactive oxygen species, such as hydrogen peroxide and hydroxyl radical, under UV irradiation. Silver nanoprisms are sensitive to reactive oxygen species and display relevant optical properties (surface plasmon resonance). Both photocatalytic and plasmonic aspects must then be considered to delineate the photoshaping mechanism.

By performing the irradiation through a photomask, defined patterns with micrometer resolution could be easily obtained even on transparent substrates, opening new scenarios, for example, development of surface enhanced Raman scattering (SERS) sensors.

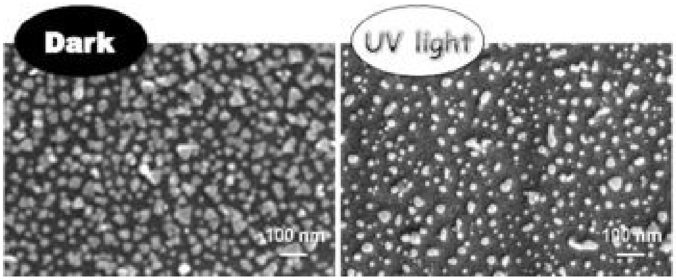

Figure 1. Self-assembled silver nanoprisms on APTES-functionalized titanium dioxide in the dark (left) and after UV irradiation (right).

MS4. NEW TOPICS IN CRYSTAL GROWTH RESEARCH

What’s new on experimental and theoretical aspects of crystal growth and its applications. Topics may also include but are not limited to: crystallization in nano-composites or nanospace; crystals for energy conversion and storage; growth, characterization and technological developments of new crystalline materials; innovative growth methods; new perspectives in crystallization and resolution of chiral systems;new theoretical and experimental approaches for the control of crystal polymorphism and crystal habit modifications.

Chair: Silvia Rizzato (U. Milano)

4KN1. Uncovering the role of solvent in organic crystals nucleation and growth

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Nucleation and growth of crystals from solution are important and yet only partially understood physical-chemical transformations, playing key roles in a wide variety of systems both in nature and in the process industry. Understanding crystallization at the molecular level is key to control and predict properties of crystals. Reaching towards this goal is a multidisciplinary challenge that greatly benefits from the interplay between theory, simulations and experimental techniques.

In this seminar the use of advanced molecular simulation methods [1] to investigate both crystal nucleation and growth will be discussed.

The paradigmatic case of urea will be analyzed. In fact, despite being a rather simple organic molecule, it displays a rich crystallization behavior. Urea nucleation from solution has been found to follow either a single-step or a two-step mechanism depending on the solvent. Moreover in the early stages of urea nucleation, a competition between polymorphic structures has been observed to take place [2-4]. Also concerning the development of solvent-specific crystal morphologies urea represents an interesting case study. Experimental evidences highlight that the solution composition affects urea crystal habits allowing accessing a wide variety of morphologies: from elongated needle-like prisms to compact tetrahedra. In this context enhanced sampling simulations allow to assess the role of both solvents and additives, to uncover face-specific growth mechanisms [5] and to predict steady state morphologies obtained for different solutions [6].

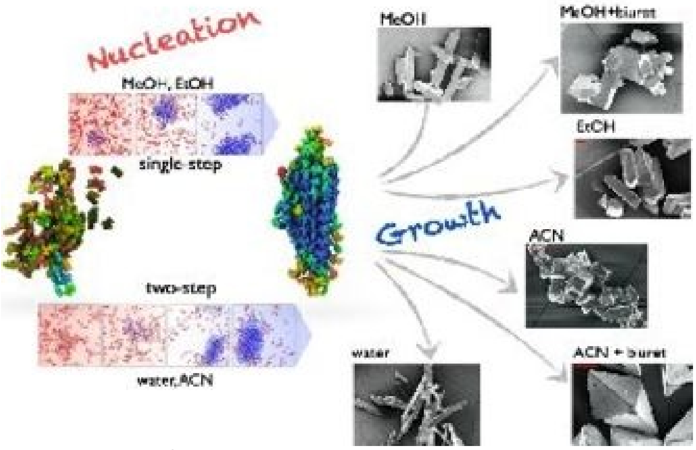

Figure 1. Urea nucleation and growth follow solvent-dependent routes and generate a variety of morphologies.

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4KN2. The role of the adhesion energy in surface and interface growth processes: apatites and alkali-halides.

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The adhesion energy (β_{adh}) is the underlying theme of several surface and interfacial phenomena as twinning and epitaxially ruled growth of crystalline phases. Related to the adhesion energy, the concept of the surface wetting can give an immediate image of what could happen in two- or more phases systems: the wetting could range from inexistent to better than perfect, generating or not structured interfaces, according to the thermodynamic conditions.

A geometrical approach (the theoretical analysis of the surface and interface structure) followed by the calculation of the surface energy and of the interface energy [1,2,3,4] are quantitative and unambiguous ways to decode a sometimes weird-looking growth behavior of crystals. This method can be applied to homogeneous and heterogeneous systems, and then can be related to apparently unrelated phenomena as twinning or adsorption followed by epitaxy.

In this contribution, the unifying role of the adhesion energy will be discussed from the experimental point of view, focusing on the growth morphology and association of some interesting phases as apatites and alkali-halides.

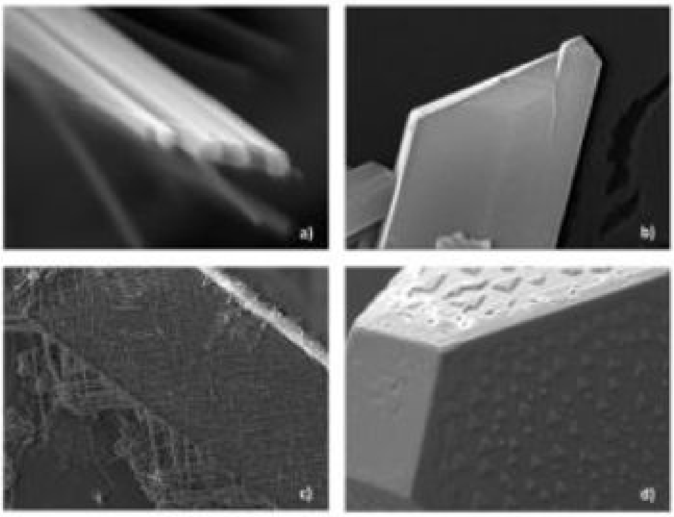

Figure 1. a) and b) twinned synthetic apatites, c) alizarin red, epitaxially grown on NaCl, d) KCl grown in the presence of lead

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4O1. Turning liquid drugs into crystals

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The objective of this work is to find a systematic way to embed liquid or volatile molecules inside crystalline materials, with the multiple aims of stabilizing them, of tuning their possible ways of delivery in medicine or agrochemistry, and to explore new regulatory and intellectual properties issues. Liquid or volatile formulations of active pharmaceutical ingredients (APIs) are intrinsically less stable and durable than solid forms; in fact most drugs are formulated as solid dosage because they tend to be stable, reproducible, and amenable to purification. Most drugs and agrochemicals are manufactured and distributed as crystalline materials, and their action involves the delivery of the active molecule by a solubilization process either in the body or on the environment. The poor solubility of pharmaceutical active ingredients (API) or the reverse too high solubility of agrochemicals are problems often encountered in their formulation since these phenomena limit respectively the bioavailability of the API or the duration of the action of the agrochemical. However some important compounds for the human health or for the environment occur as liquids at room temperature. We have defined a benchmark of molecules relevant to human health and environment that have been combined with suitable partners according to the well known methods of crystal engineering in order to embed them in crystalline hosts. Our approach is twofoled, by using cocrystals and MOFs.

The formation of co-crystals has been demonstrated as a means of tuning solubility properties of solid phases, and therefore it is widely investigated by companies and by solid state scientists especially in the fields of pharmaceuticals, agrochemicals, pigments, dyestuffs, foods, and explosives. In spite of this extremely high interest towards co-crystallization as a tool to alter solubility, practically no emphasis has been paid to using it as a means to stabilize volatile or labile or liquid products. In this work we trap and stabilize volatile and liquid APIs and agrochemicals in crystalline matrices by engineering suitable co-crystals. These new materials alter the physic state of the active ingredients allowing to expand the phase space accessible to manufacturing and delivery. We also explore the possibility to include liquid APIs inside the pores of suitable designed MOFs, again with the aim of stabilizing their solid state formulation (Figure).

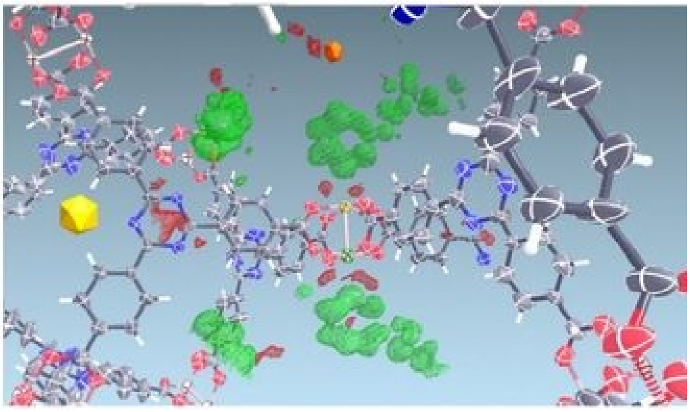

Figure 1. Electron density map of nicotine embedded in the MOF PCN6.

4O2. Exploiting dimensional variability in coordination polymers: solvent promotes reversible conversion between 3D and chiral 1D architectures

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Coordination polymers generated from metal centres and polytopic ligands have attracted increasing interest along the last two decades. Indeed, they are an excellent bench test for self-assembly concepts and a wide source of new functional materials. Despite the massive attention devoted by researchers to these compounds, the predictability of the final network and dimensionality is still an open challenge. In fact, the self-assembly process involves competing reversible and simultaneous interactions among the metal, the ligand, the counteranion and the solvent. In particular, the solvent has the most ambiguous and unpredictable role. The coordinating ability of some solvents can play a crucial role in promoting the network dimensionality, as evidenced by few but significant works. In this context, we studied the self-assembly between Cu(II) ions and 4,4´-bipyridine (bpy) in the presence of the highly coordinating DMSO solvent and we showed that it promotes a reversible conversion between a 3D network and a chiral 1D Cu-bpy based polymer. DMSO promotes the formation of both the architectures as well as the dimensional variability by blocking a different number of coordinative sites of Cu(II) ions. This allows to selectively and reversibly obtain a 3D nanoporous network and a 1D chiral polymer. The crystal growth of the 1D or 3D architecture can be tuned through chemico-physical parameters such as the presence of a co-solvent or the evaporation rate. Notably, the 1D chiral architecture is obtained from achiral building blocks and it displays spontaneous resolution during the crystallization leading to a racemic mixture of enantiomeric pure single crystals.

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4O3. Catalyst-free vapour-phase growth of Ga_2O_3 nanowires and nanobelts

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Gallium oxide is a transparent conducting oxide (TCO) with a wide transparency range (band gap energy is about 4.9eV), high chemical stability, n-type conductivity, and strong blue photoluminescence (PL). It crystallizes in five known crystalline modifications (α, β, γ, δ and ε phases), among which β-Ga_2O_3 is the most stable polymorph. The β-phase Ga_2O_3 is characterized by a monoclinic crystal structure with two distinct gallium sites (six-and four-coordinated) and three oxygen sites (three- and four-coordinated). Native point defects are known to form readily in this complex oxide lattice and are responsible for a range of important physical properties. Specifically, oxygen vacancies have been proposed to lead to the formation of shallow donor states which are considered to be the source of n-type electrical conductivity.

In recent years, low-dimensional β-Ga_2O_3 structures including NWs, nanobelts, nanorods and nanosheets have attracted growing attention of researchers due to their superior properties as compared to their bulk counterpart. One very important advantage of β-Ga_2O_3 NWs is their large surface to volume ratio providing more surface states to interact with the surroundings. The strong blue light emission property of the Ga_2O_3 nanobelts also suggests them as new candidates for fabricating functional optoelectronic nanodevices and nanosize sensors.

In this work we report the successful synthesis of β-Ga_2O_3 nanowires/nanobelts using simple a physical evaporation technique, derived from previous experiments on the vapour phase growth of metal oxide nanostructures from a simple metal source. Nanostructures have been grown on different kind of substrates (silicon, alumina, sapphire) starting from metallic Ga source that, in the proper alternation of argon and argon-oxygen mixture atmospheres, evaporates, deposits and finally feeds the growing nanocrystals by reaction with oxygen in the proper temperature range. No catalyst have been used to force the nucleation of nanowires and no metal-organic precursor have been used, so that only high purity β-Ga_2O_3 nanostructures can be obtained. As a case of study, nanowires have been grown also on Au and Pt films for comparison.

The morphological, structural and optical properties of the obtained nanostructures have been characterized, revealing thin (mainly ranging from 5 to 20 nm) and long (up to tens of micrometers) nanowire- or nanobelt-shaped crystals. Their properties have been studied by means of SEM and TEM microscopy as well as cathodoluminescence, mainly comparing results obtained for different growth conditions and substrates.

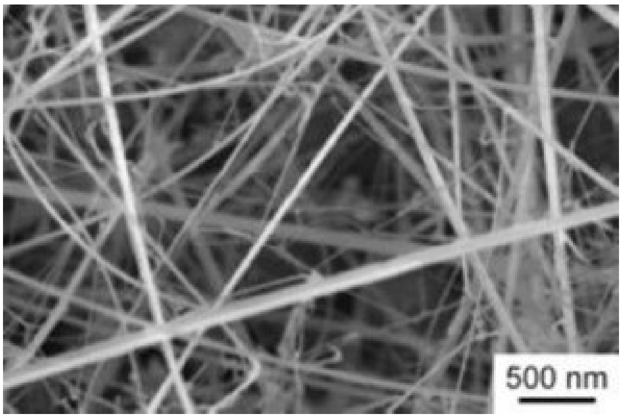

Figure 1. SEM image of β-Ga_2O_3 nanowires and nanobelts obtained on alumina substrate.

4O4. New Fluorinated Metal-Organic Frameworks Self-Assembled via Halogen Bonding

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Metal–organic frameworks (MOFs) are composed of organic linkers and coordinating metals that self-assemble to form a crystalline material with tunable porosity. Their synthetic modularity and inherent long-range order create opportunities for use as new functional materials with applications in areas as gas storage, separation and catalysis [1].

Recently, the useful properties of fluorinated molecules prompted the preparation of MOFs containing fluorinated linkers (F-MOFs). Enhanced thermal and chemical stability, high hydrophobicity of the pores and low surface energy are expected. Up to now only a few F-MOFs have been reported and they are mainly related to gas absorption, especially H_2 [2]. Tuning the properties of the network via structural control is one of the key challenges in the MOFs field. Coordination bonds (CBs) are clearly the main driving force in MOFs self-assembly, but other supramolecular interactions could play a significant role. The strong electron-withdrawing effect of fluorine makes iodinated perfluoro-motifs ideal for the formation of strong halogen bonds (XBs). Here we report the exploitation of a cooperative approach between XB and CB for the self-assembly of F-MOFs. A new Cu(II)-F-MOF containing unsaturated metal centres shows selective and reversible solvent absorption accompanied by solvatochromic effect. [3]

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4P1. $Cu_{2-x}S$ ultra thin films obtained by electrodeposition: a structural characterization

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Recent developments in the field of thin film manufacturing resulted in the production of a wide range of new materials for photovoltaic application [1]. A particular interest focuses on thin films realized by mild approaches, as electrochemical deposition, giving the opportunity of working under standard laboratory conditions without requiring expensive vacuum equipments. In this contribution we report about our studies devoted to the growth of semiconductors, of interest in the solar energy conversion field, prepared using the E-ALD (Electrochemical Atomic Layer Deposition) method to synthesize a p-n junction in a single step. The electrodeposited films are usually ultra thin and require specific investigation methods to be fully characterized. In our case, the structure of the growth films was studied by means of SXRD (Surface X-Ray Diffraction).

In-situ and ex-situ SXRD measurements were performed at the ID03 Surface Diffraction beamline of the ESRF (Grenoble). The in-situ measurements aimed to the investigation of the growth mechanism of Cu-S ultra thin films on the (111) crystal plane of a silver single crystal, commonly used as a working electrode. The growth of the film was monitored by following the evolution of the diffraction pattern after each E-ALD step. Bragg peaks, characteristic of the growth film, became observable after R 15 E-ALD cycles and their evolution has been followed up to 60 E-ALD cycles.

Breadth and profile analysis of the Bragg peaks lead to a qualitative interpretation of the growth mechanism, in the normal and in-plane directions, with respect to the Ag surface. Namely, the contribution of crystal strain and crystallite size were identified by the width analysis of the Bragg reflections.

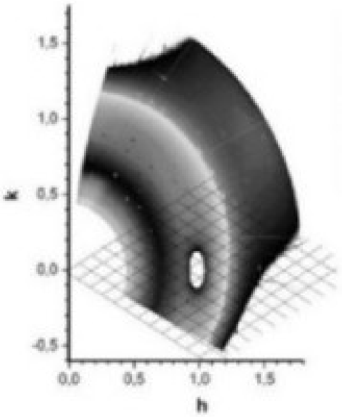

Figure 1. Mapping of the reciprocal space of the thin films on the (h,k,1.05) plane of the silver lattice, by means of an hexagonal cell

The preliminary interpretation of the experimental reciprocal lattice, coupled to the SEM investigation, suggests that the samples show a pseudo single crystal diffraction pattern. This can be described by a new hexagonal unit cell. The crystal structure of this electro-deposited $Cu_{2-x}S$ could be related to that of chalcocite, in particular considering the layering of triangular Cu sites and octahedral Cu sites.

The influence of the applied electric potential on the stability of the electro-deposited crystal structure has been monitored by means of SXRD measurements performed during the switch off of the potential. A structural change was, in fact, registered, and correlated to the occurrence of the stable phases under conventional laboratory conditions.

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4P2. Recrystallization behavior of amorphous venlafaxine free base prepared by melt technique

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Venlafaxine, a bicyclic phenylethylamine-based compound, is an antidepressant administered orally as hydrochloride (VHC). VHC is relatively aggressive towards handling equipment and it is irritating to the skin [1]. Venlafaxine free base (VB) is easier to handle, but significantly less soluble in water compared to VHC. As reported in literature, VB may exist in three crystalline phases (Form I, Form II and Form III) [2]. Crystalline-to-amorphous phase transformation represents one of the approaches able to improve the solubility of poorly water-soluble drugs. Compared to the crystalline counterpart, the amorphous materials are endowed with higher molecular mobility and enhanced thermodynamic properties. These features lead to high apparent solubility and dissolution rate, and so potentially enhancing the bioavailability [3]. However, due to their metastable nature, amorphous solids are often characterized by a notable spontaneous crystallization. The purpose of this study was to evaluate solid-solid phase transformation that may occur in the amorphous form of VB prepared by melt process. VB was melted at 80 °C and analyzed by DSC and XRPD immediately (VBmelt) and after 24 hours storage at room temperature (VBmelt-1d).

Figure 1a shows that crystalline VB was in Form I (Tmelt ~75 °C); during the temperature scanning, VB transformed into a different crystalline phase, consisting in a mixture of Form II and III (Tmelt ~77 °C and 78 °C, respectively). The drug analyzed immediately after the melt process (VBmelt) was fully amorphous. A spontaneous solid-solid interconversion occurred within 1 day: DSC profile of VBmelt-1d showed that it was composed of Form III with small percentages of Form II. The comparison of XRPD diffractograms of the three forms of VB [4] with those reported in Figure 1b evidenced that VBmelt-1d was a mixture of Form II and Form III.

Amorphous VB completely reverted back to the crystalline state within 1 day. To avoid patenting issues and to follow the regulatory requirements, nucleation and crystal growth of amorphous drugs during the shelf life of pharmaceutical products must be prevented.

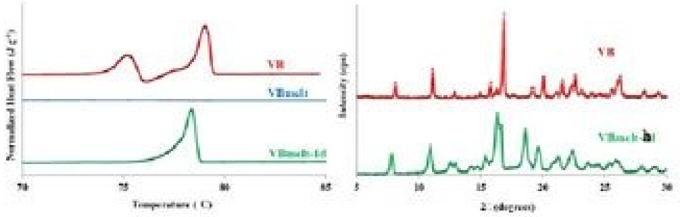

Figure 1. a: DSC profiles of VB, VBmelt, VBmelt-1d (endo up) and b: XRPD of VB and VBmelt-1d.

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4P3. A computational approach to the study of epitaxy

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Crystalline interfaces are the most common microstructures. They determine chemical and physical properties of devices for applications in mechanics, electronics, medicine, in material chemistry for designing and engineering of composite materials.

This work is a contribution to the characterization of epitaxial interfaces. When, at the interface where epitaxy occurs, the misfit between 2D lattice is low, interfaces relax with negligible in plane stress and adhesion energy can be calculated without the need of considering interface dislocations. We are interested to natural systems and to the contribution that crystal growth theory can give to unravel questions such as: can olivine, $(Mg, Fe)_2SiO_4$, nucleate on some diamond faces in condition of negative affinity? A valid contribution to these items can only come by the coupling of the laboratory and field observations with the calculations of adhesion and interface energy.

In this contribution the theoretical and computational aspects related to the determinations of the (i) interface structure, (ii) adhesion energy and (iii) interfacial energy of a system composed by two crystalline phases in epitaxial relationship, are discussed. Specifically, we describe the possible 2D lattice coincidences between two phases in epitaxial relationship, as well as all of the possible initial interface configurations which generate when different surface terminations of the phases put in contact are taken into account. Then, in order to elucidate these theoretical aspects, we have studied the following epitaxies in a natural system: {110}-diamond (C)/{101}-forsterite (Mg_2SiO_4), {001}-diamond/{001}-forsterite and {111}-diamond/{001}-forsterite [1]. The optimized interface structures and their adhesion energies were determined at *ab initio* level.

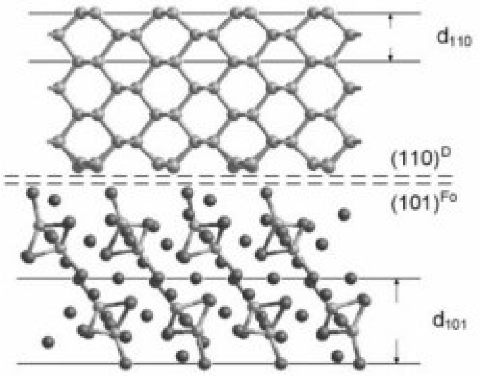

Figure 1. {110}-diamond/{101}-forsterite interface viewed along the [010] direction of forsterite.

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4P4. Facile intercalation of organic molecules into hydrotalcites by liquid assisted grinding: yield optimization by a chemometric approach

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In a recent work, a fast and convenient method, namely liquid assisted grinding (LAG), for the preparation of functional materials based on organic molecules intercalated into hydrotalcite (LDH) was developed and demonstrated[1]. LAG can profitably produce hybrid materials with facile preparation routes, mild conditions, low solvent consumption, short reaction times and high yields. It can also allow an easy scale up of the synthesis to industrial production. The current work employs a chemometric approach to optimize the LAG parameters for sulfonic intercalation in nitrate exchanged hydrotalcite (HTLC-NO_3). Six suitable molecules, three aliphatic sulfonic surfactants and three naphthalensulfonic acids, were employed as negatively charged intercalants to evaluate the conditions and the efficiency of LAG method. The completeness of the intercalation and the yield (% intercalation, calculated as (LDH_2-NSA/(LDH_2-NSA+LDH_NO_3))*100) were estimated and quantified using XRPD analysis with Rietveld refinement, using Topas TA[4] and single peak refinements. Using the same standard recipe (hydroalcoholic liquid phase, stoichiometric intercalant/nitrate ratio, grinding time) different intercalation yields for the molecules were found, demonstrating the clear role of the molecules structural and chemical features in the process. As a case study, the intercalation yield variability of 2-naphtalenesulfonic acid (2-NSA) was investigated using a design of experiment (DoE) approach, in order to achieve the best conditions for maximum intercalation yields case.

Experiments were performed in accordance to factorial design[2] and Simplex[3] algorithms, varying two experimental factors, the amount of NaOH and percent of Ethanol in the liquid component of the recipe, while the procedure and the other parameters kept constant.

From a starting intercalation yield of 2-NSA of about 40-50% using the reference recipe, a preliminary DoE approach using the Factorial Design resulted able to improve it of up to 66%. However, this method was considered not fully suitable for yield optimization, for the limited variable domain exploration and their a priori definition on the basis of previous OVAT (One Variable At Time) experiments. Conversely, the Simplex algorithm resulted the optimal DoE tool to reach the best conditions in few experiments, also in absence of preliminary experiments. Experiment track with Simplex led to a 2-NSA intercalation yield improvement up to 76%, which can be considered a physico-chemical limit of the system for one-step intercalations (higher yields were achieved by repeated LAG exchanges of LDH-NSA sample with fresh NaOH/Ethanol solution). Simplex evidences highlighted also an antagonist effect between NaOH and EtOH, undetectable with OVAT methods. The LAG-obtained compounds, despite the completely different reaction conditions (i.e. solvent-free), resulted similar to solvent-intercalated products, as demonstrated by XRPD, TGA and DR-UV-Vis data.

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4P5. New Co-crystals of Salicylic acid: from screening to synthesis and structural characterization

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Few areas of crystal engineering have, in recent times, received the same amount of attention that has been lavished upon almost any topic dealing with co-crystals. Many co-crystals have been prepared through strong hydrogen bonds, notably between a carboxylic acid and an N-group hydrogen-bond acceptor.[1] To assess the utility of these synthons, we present here our studies on the supramolecular reactions between salicylic acid (**SA**) with six co-formers (tyramine (**Tyr**), 1,2-Phenylendiamine (**Phen**), paracetamol (**Par**), ibuprophen (**Ibu**), diglycine (**Dig**) and triglycine (**Trig**)). The co-crystals are first screening using Differential Scanning Calorimetry (DSC) and synthesized by Liquid Assisted Grinding (LAG). A single crystal of **SA•••Phen** and **SA•••Trig** were obtained by slow evaporation method using methanol as solvent in the first case and a mixture of methanol:water (9:1) in the second case. The mixtures were characterized by thermal analysis (DSC and Thermogravimetric Analysis (TGA)), Powder X-Ray Diffraction (PXRD), infrared spectroscopy (IR) and Single Crystal X-Ray Diffraction (SCXRD) when possible. From the initial screening and data obtained so far, it can be concluded: (*i*) The co-formers studied, **SA•••Phen** and **SA•••Trig** formed a single crystal and the structures were characterized using SCXRD. (*ii*) **SA•••Ibu** and **SA•••Dig**, showed potential to form co-crystals by screening conducted using DSC. Furthermore, the PXRD spectrum showed some significant changes in the samples prepared through the LAG method. (*iii*) **SA•••Par** need further investigation, including new crystallizations and study of new ratios between the components. Data obtained for the **SA•••Par** (1:1), prepared through the slow evaporation of the solvent and LAG method, are not conclusive to observe interactions between these components.

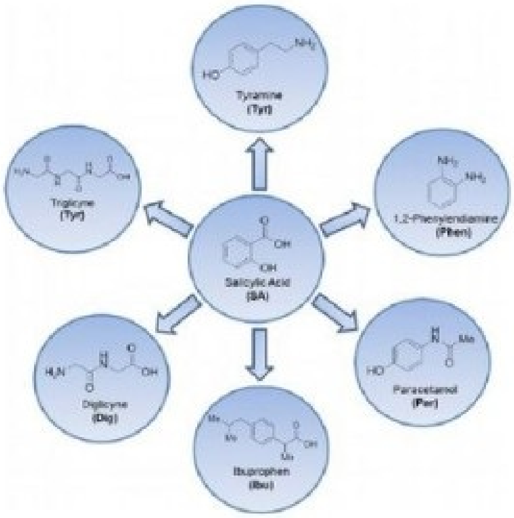

Figure 1. New co-crystals from salicylic acid.

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4P6. Morphological and Structural Effects of Gels on Coordination Polymers Crystallization.

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The use of gels or viscous materials as growth media for a wide range of compounds, including proteins and inorganic and organic compounds has been reported in the literature. In the presence of gel, sedimentation and convection currents are greatly suppressed and the mass transport of the molecules mainly occurs by diffusion, resulting, usually, in a lower nucleation density and a better crystal quality.[1a]

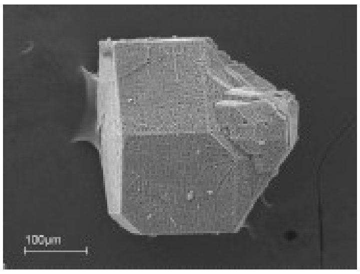
Here we report some new interesting phenomena observed in crystallization experiments of coordination compounds, such as, "coordination polymers", by using gels as diffusion media.[1b]

By using a semi-liquid silica-gel system as a dispersion matrix, we were able to increase the quality of the crystals but also slow down the solvent loss, stabilizing the partially dehydrated structure of a very flexible porous framework. This has enabled an accurate determination of the dynamic behavior of the system during the desolvation process by using single crystal X-ray diffraction. Unit cells and structure solution has been obtained at any point during the process.

The improved stability of the crystals and the large flexibility of the network have also made possible to carry out in-situ high-pressure diffraction measurements.

Other important results concern the effects of gels on the macroscopic crystal shape and on the micromorphology of the crystal surfaces (Figure), and the capacity of gel media to promote the concomitant crystallization of topological isomers with a monotropic relationship.[2]

Funding from the Cariplo Foundation under the grant ‘‘2012-0921” is gratefully acknowledged.



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MS5. NANOSTRUCTURES AND NANOSCALE PHENOMENA

Advanced structural studies are essential to establish structure-properties relationships and taylor new nanomaterials for a wide range of applications. The micro symposium “Nanostructures and Nanoscale phenomena” is focussed on experimental techniques (such as XAS, NPD, XRPD, also under operative conditions) and procedures of structural analysis (simulation of EXAFS spectra, Pair Distribution Function, Debye Function Analysis) particularly suited for Materials Science.

Chair: Antonino Martorana (U. Palermo)

5KN1. Characterization of nano-structured materials by synchrotron radiation techniques

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Synchrotron radiation X-ray micro- and nano-beams are emerging characterization tools with broad implications for science, covering solid state physics catalysis, geology, cultural heritage, biology and medicine. In the field of materials characterization, they are becoming a key tool for the space-resolved determination of structural (XRD) and electronic (XANES/EXAFS) properties and for chemical speciation (XRF) of nano-structured or composite materials [1].

In this contribution, recent advances in focusing devices available at III generation synchrotron radiation sources will be briefly reviewed and selected examples will be afterward presented. In particular, (i) the complete characterization of a Multi-Quantum Wells Electroabsorption-Modulated Laser [2], employed in high frequency optical communications over long propagation spans, (ii) the structural investigation of superconducting whiskers [3] (Figure 1a) and (iii) the $Fe^{3+}/\Sigma Fe$ in a zoned garnet microcrystal geologically relevant to understand subduction processes (Figure 1b) [4] will be more deeply discussed.

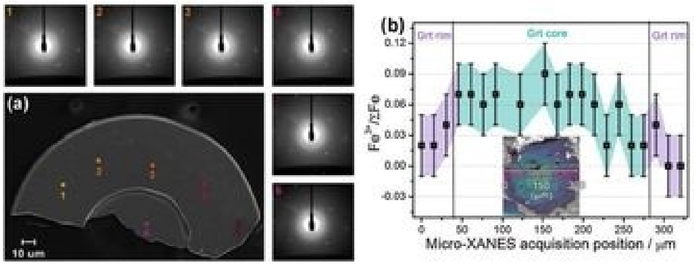

Figure 1. (a): Nano-XRD investigation of a curved YBCO whisker. (b): Quantitative spatial variation of the $Fe^{3+}/\Sigma Fe$ ratio obtained for a geologically-relevant garnet sample from the micro-XANES analysis.

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5KN2. Application of Total Scattering Methods to the Investigation of Clean Energy Materials

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The knowledge of the structural properties of crystalline materials is one of the most essential piece of information we need to obtain in order to make reliable correlations with physical properties, especially in functional materials. Traditional crystallographic methods based on single crystal and powder X-ray and neutron diffraction are the preferred methods to look at the *average* structure of a crystalline material. The progress in the synthesis of complex materials with enhanced properties showed that a full understanding of their structural features may not be obtained with the use of diffraction alone. Materials which are not fully periodic, like nanocrystalline or highly disordered compounds, require new experimental approaches that can tackle the structural issues to a high degree of accuracy [1]. In this context, materials for clean energy applications, such as highly defective oxides and nanocrystalline compounds (which are becoming extremely popular in this area) for a range of applications (solid oxide fuel cells, lithium batteries, hydrogen storage materials) need to be treated with a new approach that could open the possibility to study their *local* structure and unveil structural features which cannot be assessed with traditional crystallographic methods. This approach centres around the *atomic pair distribution* (PDF) technique. In the past, PDF analysis has been used for many years for studying materials with no long-range order such as liquids and glasses. The advent of high power X-ray and neutron sources allowed to apply the PDF analysis to the investigation of crystalline materials. The essential difference with respect to the traditional crystallographic methods, which make use of the structural information contained in the Bragg peaks, is the use of the *total scattering* coming from the sample which include the Bragg and diffuse scattering [1]. This part of the sample scattering become more and more important as the long-range order breaks on the atomic-scale and the PDF technique allow to reveal the short and intermediate order of the material regardless of the degree of disorder.

In this talk we are going to give first a concise description of the PDF technique and then an overview about the successful application of total scattering methods to the investigation of crystalline materials for clean energy applications. We should stress that, with respect to other classes of materials, the application of the PDF technique to materials for energetics is more recent. However, such new approach already showed its power in order to provide information at the atomic scale level that are essential to give new insights, for example, about the mechanisms involved in the carrier motion, study the defects structure and find correlations between different crystal structure of a material [2-6].

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5O1. Disclosing the Rhombohedral Structure of Colloidal Lead Chalcogenides Quantum Dots, their stoichiometry and their shape evolution through the Debye Function Analysis

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Colloidal lead chalcogenides Quantum Dots (QDs) are an increasingly important class of nanocrystalline materials. Due to strong quantum-size effects, they are very promising materials in solar cells applications [1], photodetectors[2] and thermoelectric devices [3].

Size-tuneable QDs are usually synthesized using long organic ligands (controlling their growth and preventing them from aggregation) providing metal-rich nanocrystals (NCs). Controlling their structure at the atomic level is the key to fully understanding their peculiar properties and tuning their functionalities.

A lot of work has been done on this side, that mainly indicate the formation of non-stoichiometric core-shell NPs, with an excess of Pb atoms at the surface, coordinated by the capping ligands [4]. Also the presence of local Pb disorder has been deeply analysed with several techniques (PDF [5], EXAFS [6]) in microcrystalline powders, but it is still strongly debated. Using unconventional Wide-Angle X-ray Total Scattering techniques and a core-shell model relying on the Debye Scattering Equation, we characterized highly monodispersed oleate-capped PbS and PbSe QDs (with nominal sizes in the 3-8 nm range) in colloidal suspensions in terms of crystal structure, size, size distribution and stoichiometry. Data were collected at the MS-X04SA beamline of the Swiss Light Source. Structural modelling was performed using the Debussy Program Suite [7].

By this innovative approach we were able to obtain very unexpected findings about QDs crystal structure, stoichiometry and morphology that could bring new lights on the understanding of their complex functional properties.

These results will be presented in details within this communication.

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5O2. Spatially resolved photoemission spectromicroscopy: a powerful tool for the characterization of nanostructured novel materials.

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Due to the short escape depth of electrons, usually less than a few nm, photoelectron spectroscopy is the best surface sensitive analytical technique for probing chemical composition and electronic properties of surfaces and top layers of samples. Nevertheless the standard approach to this technique suffers from two major limitations: 1) spatial resolution (material gap) and 2) the requirement for high-vacuum environment (pressure gap).

The Scanning PhotoEmission Microscope (SPEM) uses a direct approach to add the spatial resolution and characterize chemically surfaces and interfaces at the submicron scale i.e. the use of a small focused X-ray photon probe to illuminate samples. Focusing of X-ray beams is performed by Fresnel lenses (zone plates) while elemental selective maps are obtained by scanning samples with respect to the focused beam. In the SPEM hosted at the ESCAmicroscopy beamline at the Elettra synchrotron light source, the X-ray beam can be downsized to a diameter of 120 nm which allows imaging resolution of less than 50 nm [1].

The unique properties of photoemission spectroscopy to shed light on the chemical and electronic properties of surfaces offer a powerful tool of analysis for a wide class of scientific and technological topics. The main results obtained by using the SPEM in the characterization of materials used for the fabrications of solid oxide fuel cells [2], nanomaterials in model redox reactions [3] and electrochemical devices will be presented aiming to disseminate properties and performance of this novel type of microscopy.

Only recently the development of electron energy analyzers with differentially pumped lens systems allowed to perform in situ XPS measurements up to few mbar (near ambient pressure (NAP)). Due to severe technical constrains it was not possible to implement these solution on photoemission microscope so far. The first results of in operando spatially resolved NAP photoemission measurements obtained at Elettra with innovative setups will be presented and discussed.

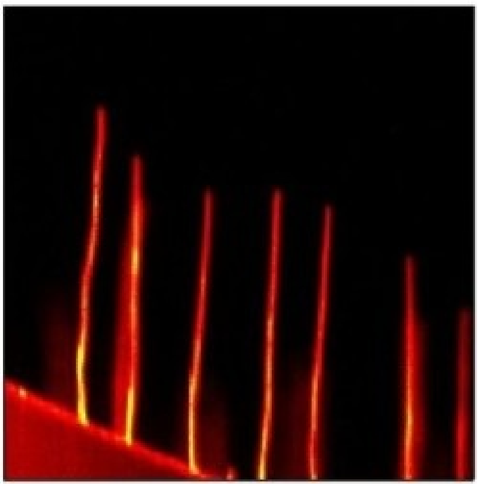

Figure 1. SPEM image of vertically aligned multiwall carbon nanotubes having a diameter of 60 nm.

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5O3. microEXAFS and microXANES for the study of Solid Oxide Fuel Cells

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Chemical and structural compatibility between materials is a critical point in all-ceramic devices working at very high temperatures: in this respect, the degradation of the cell performance is often the critical factor limiting the working life of SOFC. A well-studied example is the formation of a resistive layer of $La_2Zr_2O_7$ at the interface between lantanum-containing perovskite cathodes and zirconia electrolytes.

$LaNbO_4$ doped with 2% Ca^{2+} (LNC) represents the last real breakthrough in the field of proton-conducting oxides for use as electrolytes in SOFC, showing improved stability and high conductivity with respect to perovskites [1]. To develop efficient and robust devices based on LNC, the electrical performance and chemical compatibility of various electrode materials with LNC was extensively tested in recent literature. [2]

We recently applied X-ray microspectroscopy to evaluate the chemical and local structural fate of cations interdiffusing across an LNC/cathode bilayer (where the cathode is either $La_{0.6}Sr_{0.4}MnO_3$, $La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_3$, etc.) after prolonged annealing at high temperatures (1150 °C), to simulate the operating conditions of a fuel cell. The interfaces of the devices were studied with space-resolved X-ray absorption spectroscopy (XAS) using the focused submicrometer-sized beam available at the SXM-II endstation on the ID21 beamline of ESRF. We collected microXANES and microEXAFS spectra at the Nb L_3, La L_3, Ca K, Fe K and Mn K edges. The microXRF composition maps spectra were also collected, giving information on the distribution of cations. In some cases, microXANES spectra show marked variations, so that chemical-contrast maps can be acquired by changing slightly the beam energy.

A wealth of interesting results are obtained by combining chemically-resolved maps and microspectroscopy. In general, an unexpected and impressive exsolution of the Ca^{2+} dopant from the LNC electrolyte towards the cathode is observed in all samples. [3] The Ca and Nb change of coordination number and geometry between the perovskite cathode and the LNC electrolyte is well supported by microXANES simulations, pinpointing the greater structural flexibility of the perovskite structure as the driving force behind the incorporation of cations from the electrolyte. Fe and Mn edge microXANES spectra also show interesting variations as a function of the distance from the interface, hinting at some kind of oxygen vacancy accumulation at the interface. At the La, Fe and Mn edges, high quality microEXAFS spectra were collected and modeled up to about 8 $Å^{-1}$.

These results represent the first application of X-ray absorption microspectroscopy to the study of materials compatibility in SOFC. Such an approach can be extended to other kinds of SOFC materials, including ceramic anodes, cermets, and oxide-ion conductors, reproducing different working conditions of real devices: this is expected to give unprecedented insight on the mechanisms governing electrolyte-electrode compatibility and electrochemical performance in solid oxide fuel cells.

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5P1. A super cell approach for the refinement of carbonate hydrotalcites affected by stacking faults

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Carbonate hydrotalcite is known to crystallize into two different politipes: a three-layer rhombohedral polytype (3R1), and a two-layer hexagonal polytype (2H1). The 3R1 polytype has a metal hydroxide layer stacking sequence of AbC CaB BcA AbC, and the 2H1polytype has astacking sequence of AbC CbA AbC, where AbC stands for a metal hydroxide layer. The uppercase letters stand for the hydroxyl ion positions, and the lower case letters stand for the cation positions.
Depending on the synthesis method is possible to obtain ordered 3R1 samples or faulted sample.
A recent paper(1) shows that faulted samples are simulated with DIFFaX corresponding to the 3R1 polytype with 30% 2H1 stacking faults. However, it is important to note that the DIFFaX formalism, unlike the Rietveld technique, does not include a least-squares fit of the whole profile, but is a simple simulation of the XRD pattern of any given model structure that permits the inclusion of structural disorder and predicts the resultant line shape.
In this work we present the new super cell approach for the treatment of stacking faults implemented in Topas V5, were we refined both simulated and real data to ordered and faulted hydrotalcite samples.

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5P2. Stress measurements at the nanoscale by ZnO Nanorods-modified Carbon Fibers

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Carbon fiber based composites (CFC), owing to the exceptional ratio between mechanical properties and weight, represent a fundamental technology for several applications, ranging from aerospace to automotive, from civil infrastructure to biomedical engineering. Due to the intense mechanical stress often involved, strain and deformation on CFC made structures have to be constantly monitored. Furthermore univocal mechanical models doesn't exist, since carbon fiber (CF) patches can be textured with CF oriented in different directions depending on necessity.

Nowadays strain sensing on CFC is carried out with optical fiber and piezoelectric ceramics. However this technologies present three main drawbacks, that are large size (compared to CF size), weight addition to the structure and use of precious metals wires. Recently the use of different materials functionalized with piezoelectric zinc oxide (ZnO) nanostructures started to get a foothold for sensing and energy harvesting.

Piezoelectric effect, owing to its dual peculiarity relating deformation with electric properties, lends itself to both sensing and actuating applications. Therefore functionalization of CF with ZnO piezoelectric nanostructures allow to realize a fully integrated piezoelectric sensor/actuator within CFC structure, thanks also to the fact that conductive CF themselves act as electrical wires.

The ZnO *in-situ* growth is made by a low-temperature and low-cost two-step process: functionalization of CF with ZnO seed-layer by Successive Ionic Layer Adsorption and Reaction (SILAR) technique and growth of ZnO nanorods by chemical bath deposition.

Measuring the piezoelectric effect in ZnO nanostructures is still a debatable topic, since the typical I-V characterization is not generally accepted. In this work piezoelectric investigation is carried out for the first time on such structure using ferroelectric virtual ground, PUND and DHM techniques. The emergence of a voltage-invariant capacitance variation upon stress application is ascribed as the fingerprint of piezoelectricity.

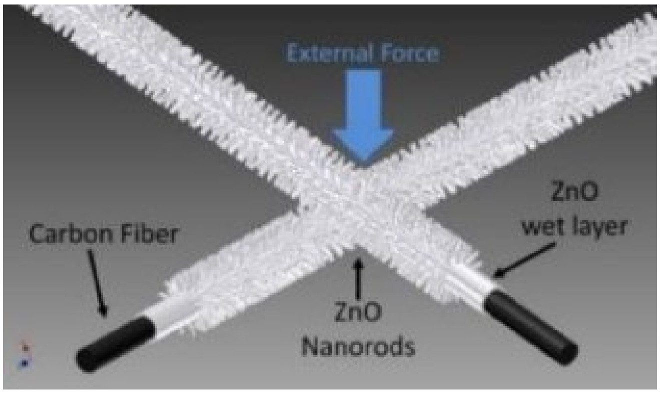

Figure 1. Depiction of the device structure: crossed CF functionalized with ZnO seed-layer and nanorods

5P3. The DebUsSy Suite 2.0: a powerful tool for characterizing nanosized materials through the Debye Scattering Equation

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The Debye Scattering Equation (DSE) provides the total (X-ray, Neutron or Electron) scattering pattern of an ensemble of nanoparticles through the distribution of their interatomic distances, without any assumption of periodicity and order [1]. DSE is therefore a powerful approach for quantitatively determining structural and microstructural properties of nanoscaled materials and nanocomposites, at both the atomic and nanometer length scales.

DebUsSy is a suite of programs implementing the DSE for the analysis of powder diffraction data from nanocrystalline, defective and non-periodic objects [2]. It encodes an algorithm making the DSE calculation, in principle very intensive from the computational time point of view, extremely fast and accurate. The Suite has been successfully applied in modeling different kind of nanomaterials (metals, alloys, oxides, bioceramics, molecular drugs, QDs and metal-organic compounds) [3,4,5].

In this contribution, the new 2.0 release of the DebUsSy Suite [6] will be presented. It includes different kinds of optimization algorithms enabling to extract quantitative micro-structural values of mono- or bi-variate log-normal function to deal with the sample-size distribution, size-dependent lattice expansion, atomic site occupation factors and thermal parameters. Disorder of paracrystalline nature can be modeled according to the Welberry's theory [7]. A python-based Graphical User Interface makes easy to run any of the programs within the Suite and to display predefined or customized plots of the results. Additionally, a satellite suite of utilities has been developed for correcting the experimental data from absorption and instrumental effects, and subtracting extra-sample scattering contributions.

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5P4. Core-shell cobalt/cobalt oxide nanoparticles: a Debye function XRD pattern simulation

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Cobalt nanoparticles have long attracted the interest of structural investigations, from the point of view of structural modelling [1] and for structure-properties correlations [2-4]. We have recently coped with the structural analysis of cobalt nanoparticles prepared by thermal decomposition of $Co_2(CO)_8$, and proposed a new model allowing for stacking faults in the sequence of the Co basal planes [5]. According to the model, the position of each layer of the stack is probabilistically influenced by the block of the four neighbouring ones, giving rise to XRD patterns showing the simultaneous presence of both the hcp and ccp signatures. The model, validated by simulation runs based on the Debye Function Analysis (DFA), allowed to treat the structure of cobalt nanostructured samples on the basis of a unique statistical ensemble, overcoming the questionable approach of summing up two different contributions bearing separately the hcp and ccp characters [6].

The nanostructured Co experimental patterns showed also a contribution that was attributed to a disordered oxide phase. This likely constitutes a shell of variable thickness growing over the metal core, as it is also confirmed by TEM data. The occurrence of the oxide phase can be effectively taken into account in the pattern fitting procedure by a background line, such as a Tchebicheff polynomial of suitable degree. On the other hand, a simulation involving a thorough physical model [7] could give important information in view of applications of nanostructured cobalt as magnetic or catalytic material.

In this paper we report about the whole pattern simulation of core-shell cobalt nanostructured samples. The shell contribution is calculated by DFA, weighing the distance t between couples of scatterers with the volume common to the shape function and its t-shifted image. The issues taken into consideration are: i. the interaction between the metal core and the oxide shell; ii. the cobalt oxidation state; iii. the thickness of the oxide shell; iv. the oxide lattice constants; v. the degree of long range order of the shell. The integration of shell simulation into the algorithm of whole pattern fitting allowed a structural analysis based entirely on a physical model.

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MS6. CRYSTAL CHEMISTRY OF INORGANIC COMPOUNDS FOR THE UNDERSTANDING OF THEIR PROPERTIES AND STABILITY

This session welcomes innovative contributions dealing with the crystallography and crystal chemistry of both natural and synthetic inorganic compounds sensu lato such as nanophases and microporous materials, aimed to the understanding of their physical-chemical and technological properties and stability fields (temperature/pressure).

Chair: Alessandro Gualtieri (U. Modena e Reggio Emilia)

6KN1. Time for Changes: Nanosized Magnetite Clusters on the Run

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Very small superparamagnetic iron oxide nanoparticles were characterized by innovative synchrotron X-ray total scattering methods and Debye function analysis. Using the information from both Bragg and diffuse scattering, size-dependent core–shell magnetite–maghemite compositions and full size (number- and mass- based) distributions were derived within a coherent approach. [1] Very broad superstructure peaks produced by the polycrystalline nature of the surface layers were experimentally detected even in room temperature oxidized samples. Effective magnetic anisotropy constants, derived by taking the knowledge of the full size-distributions into account, show an inverse dependence on the NPs size, witnessing a major surface contribution. These iron oxide nanoparticles concomitantly show size-driven expansion and oxidation-driven contraction, both effects influencing the accuracy of lattice parameter and of stoichiometry determination. [2] Finally, i*n situ* oxidation experiments performed at different temperatures allowed kinetic and thermodynamic parameters of magnetite oxidation to be suitably determined.

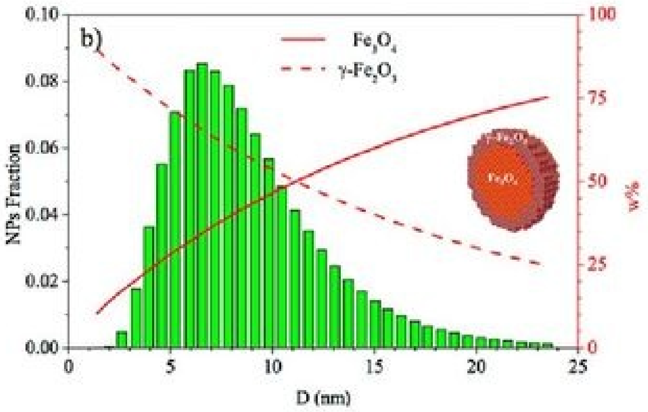

Figure 1. An example of the relative variation of the weight fractions, wt %, of the Fe_3O_4 core and the γ-Fe_2O_3 oxidized shell (see inset) as a function of the particle size within the mass-based population.

[1] R. Frison, G. Cernuto, A. Cervellino, O. Zaharko, G. M. Colonna, A. Guagliardi, N. Masciocchi *Chem. Mater.* **2013**, *25*, 4820.
[2] A. Cervellino, R. Frison, G. Cernuto, A. Guagliardi, N. Masciocchi *J. Appl. Cryst.* **2014**, *47*, 1755.

6KN2. Tracking structural and electronic properties of coordination compounds: the role of synchrotron radiation

Elisa Borfecchia[a]

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This contribution aims to provide an overview of the potential of synchrotron-based X-ray techniques to elucidate the structural and electronic properties of crystalline coordination compounds, and to track their evolution during chemically-relevant processes [1]. Besides the well-established anamalous diffraction and X-ray absorption spectroscopy (XAS), in both near (XANES) and post (EXAFS) edge regions, more specialized techniques currently emerging in the panorama of synchortron characterization will be introduced, with an emphasis on X-ray emission spectroscopy (XES) and small/wide X-ray scattering (SAXS/WAXS) methods. Furthermore, advanced experimental approaches designed to monitor the evolution and to track the reactivity of the investigated system in controlled conditions will be presented, including multi-technique *in situ*/*operando* setups and quick/dispersive EXAFS methods. Synchortron approaches will be critically compared to more conventional diffractometric and spectroscopic laboratory techniques (such as XRD, UV-vis, NMR, EPR and FTIR), evidencing both the added value of synchrtron probes and the importance of a multi-technique approach to maximize the information level in the analysis of complex nanomaterials. In addition, the key role of computational modelling for a reliable interpretation of structural and electronic data will be discussed.

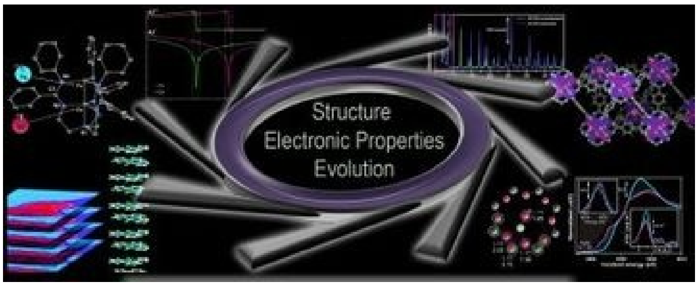

Figure 1. Pictorial representation of the potentialities of synchrotron-based X-ray techniques in elucidating structural and electronic properties of coordination compounds, and tracking their evolution along chemically relevant processes.

The potentialities of the above-mentioned methods and setups, further empowered by their synergic integration, will be exemplified by a selection of relevant applications, focusing on long/short range structure and reactivity in MOFs and functionalized derivatives [2], electronic/structural properties and catalytic activity of exchanged metal sites in zeolite-based catalysts [3], intra-molecular interactions and electronic structure in transition metal molecular complexes [4], and multi-technique *in situ* investigation of crystallization processes [5].

Finally, a perspective summary of the key advances expected to impact the synchrotron characterization field in the forthcoming future will be presented.

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6O1. Adsorption/Desorption Of Fuel Based Pollutants Confined within ZSM-5: a Combined *In Situ* High-Temperature Synchrotron Powder X-Ray Diffraction and Chromatographic Study

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Removal of fuel-based compounds from natural water is of considerable interest due to their harmful effects on the environment, even at very low concentration. Toluene (TOL), 1,2-dichloroethane (DCE) and methyl-tert-butyl-ether (MTBE) are of special relevance since they are toxic and commonly found in surface and ground water. Recently, high-silica zeolites, have been shown to be environmental friendly materials able to efficiently adsorb from water fuel based pollutants[1]. Moreover, zeolites can be easily thermally regenerated at low cost without changing their initial adsorption [2]. In this work, the *in situ* high-temperature (HT) synchrotron X-ray powder diffraction (XRPD), is used as a key to continuous monitoring the DCE, MTBE and DCE-MTBE mixture decomposition process as well as the structural modifications undergoing on ZSM-5 upon a temperature-programmed thermal treatment. Kinetics and adsorption isotherm batch data were obtained via Headspace Solid Phase Microextraction-GC. Thermal analyses were performed in air up to 900°C at 10°C/min. HT-XRPD data (temperature range 30°-600°C) were collected on the ID31 beamline (ESRF, Grenoble). Rietveld refinements demonstrated that regeneration of ZSM-5 is effective when thermally treating the adsorbent in mild conditions (~300°C). Once regenerated and reloaded, thermogravimetric, chromatographic (Figure 1) and diffractometric analyses (Figure 2) indicates that both organics location and content remain substantially unchanged thus highlighting ZSM-5 is able to re-adsorb the selected pollutants in amounts comparable to that adsorbed in the first cycle. XRD analysis demonstrates that the regenerated and reloaded zeolite does not show any significant crystallinity loss, as well as perfectly regains the crystallographic features of fresh material (Figure 2). The regeneration/adsorption process also occurs without any significant deformations in the channel apertures. In conclusion, the use of this adsorbent with unchanged adsorption performances after thermal regeneration under mild conditions appears very promising also over several cycles of the adsorption/desorption process.

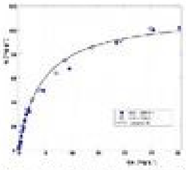

Figure 1. Adsorption isotherms (T=298 K) of DCE on fresh (ZSM-5) and thermally regenerated (ZSM-5-r) zeolites.

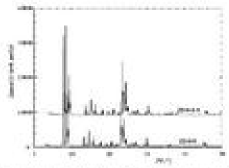

Figure 2. Powder diffraction patterns of unloaded (ZSM-5) and thermally regenerated (ZSM-5-R) zeolites.

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6O2. After a century of Bragg diffraction, how well do we know the structures of inorganic compounds?

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The atomic structure provided by refinement to the Bragg intensities obtained in a diffraction experiment provides a picture of the average structure of a material at the atomic scale. This average structure is not only the foundation for understanding the thermodynamics and physical properties of bulk materials, but is also the basis for defining a variety of structural modifications such as defects, compositional order/disorder, dynamical disorder, incommensurate modulations and the structures of nanoparticles. With the recent advances in technology, we asked the question: "How well are structures determined in routine experiments, one century after the discovery of X-ray diffraction?"

To answer this question we have undertaken a systematic study of how well we can determine with modern laboratory equipment the structures of two major Earth minerals; anorthite as an example of the feldspar family which comprises 60% of the Earth's crust, and olivine the major component of the Earth's upper mantle. We used sub-100um size crystals, measured with a commercial instrument, the Oxford Diffraction SuperNova diffractometer equipped with a Mo-target microsource, and a Pilatus 200K area detector.

We found that a partial data collection of just 90 seconds on anorthite is sufficient to determine the bond lengths to an accuracy of 0.02Å and thus the essential architecture of the structure! A full dataset to $2\theta_{max} = 60^o$ collected in 48 minutes yields esd(T-O) = 0.004Å, equivalent to the results from 6 days data collection in 1990, or several years in the 1950s! A data collection with $2\theta_{max} = 100^o$ (81 hours) has >28,000 reflections and gives esd(T-O) = 0.0005Å. Refined structures of anorthite show no significant differences in bond lengths with either changing resolution ($2\theta_{max}$ from 60^o to 100^o for MoKα) or with increasing exposure time at constant resolution in full datasets. The esds scale approximately with the inverse square root of the number of reflections used in the refinement. This means that modern diffraction data themselves are precise and accurate.

Conventional refinements of olivine with independent atom models show that the site occupancies are strongly dependent on data resolution and give systematically wrong chemical compositions. The reason is that the diffraction intensities are sufficiently precise to include the diffraction effects of the non-spherical electron distribution due to bonding in the crystal. The use of refinement models such as the electron-in-bond model provides correct compositions (and by inference correct site occupancies) independent of data resolution.

These tests show that modern structure refinements, properly performed, are not limited by the accuracy or precision of modern laboratory X-ray diffraction data which provide an unbiased map of the electron density of the crystal. The limitations of modern structure refinements are in the refinement models used to interpret the data. Thus, while bond lengths and angles are determined consistently by different models, site occupancy refinements are biased to the wrong results by the conventional independent atom model, but can be accurately determined with physically-meaningful but simple refinement models.

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6O3. Crystal-fluid interactions in open-framework materials at high pressure

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The number of experiments on the high-pressure behavior of open-framework materials increased significantly in the last decade [1,2]. The framework topology, the chemical composition and the so-called "host-guest" interactions (between the framework and the extraframework components) were found to significantly influence the response of zeolites to the applied pressure. However, the H*P*-behavior of zeolites may also be influenced by crystal-fluid interactions when *P*-transmitting fluids (PTF) are used to generate hydrostatic compression, and in particular when the PTF is "pore-penetrating". In such a case, the *P*-induced penetration of PTF molecules into the zeolite structural voids leads to a change of the physical-chemical properties of the studied material, for example inducing a stiffening of the elastic behavior or leading to the hyperconfinement of supramolecular aggregates (in the zeolite channels) with functional properties [3].
In this study, we describe the H*P*-behavior and the crystal-fluid interactions of two synthetic zeolites with empty channels and cages, *i.e.* all-silica ferrierite (Si-FER) and $ALPO_4$-5 ($AlPO_4$), compressed with non-penetrating (silicone oil, s.o.) and potentially pore-penetrating PTF. The compression of Si-FER in s.o. evidences the remarkable flexibility of this framework: a first displacive phase transition was observed from the *Pmnn* to the $P12_1/n1$ space group at ~ 0.7 GPa. A second displacive phase transition, involving a significant unit-cell volume contraction, was observed at ~ 1.24 GPa from the $P12_1/n1$ to the $P2_1/n11$ space group (through an intermediate *P*-1 structure, "type-II" transition according to Christy [4]). The high-*P* $P2_1/n11$ polymorph was found to be stable at least up to 3.00(7) GPa, whereas - upon pressure release - the starting *Pmnn* structure was fully recovered. The three polymorphs were found to share a virtually identical bulk elastic behavior, being their average volume compressibility β_V: 0.051(4), 0.056(9) and 0.055(3) GPa^{-1}, respectively. The compression of Si-FER and ALPO-5 in potentially pore-penetrating PTF showed a lower bulk compressibility, different phase-transition paths (for Si-FER) and diverse atomic-scale deformation mechanisms with respect to the compression in silicone oil, suggesting the onset of significant crystal-fluid interactions, likely due to the *P*-induced penetration of PTF molecules. In addition, the H*P*-behavior of Si-FER is strongly influenced by the process kinetics, which was found to control the *P*-induced molecules intrusion phenomena and, as consequence, the *P*-induced phase transitions in this material.

The authors acknowledge the Italian Ministry of Education, MIUR-Project: "Futuro in Ricerca 2012 - ImPACTRBFR12CLQD".

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6O4. In situ high-temperature X-ray diffraction and spectroscopic study of fibroferrite, $FeOH(SO_4)\times5H_2O$

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Fe-sulfates are found in a variety of geological settings, and are also considered to be relatively widespread in Mars where they are considered important carriers for water [1]; they are currently recognized as sensitive environmental indicators and play an important role in the acid drainage mobilization of metals and the monitoring of water quality [2].

Decomposition products of iron-bearing sulfates are extremely important in technological processes; applications include uses in selective catalysis, pigments, coatings, sensor technologies, ion exchangers, and data storage materials and in developing new electrode materials for lithium-ion batteries [3].

The present study is focused on a particular iron hydrated sulfate, fibroferrite, $FeOH(SO_4)\times5H_2O$.

The crystal structure of fibroferrite is based on $[Fe^{3+}(OH)_2(H_2O)_2O_2]$ octahedra linked via cis octahedral vertices to form helical chains running parallel to the *c* axis. SO_4 groups share two oxygen corners with Fe^{3+}-octahedra providing further intra-chain linkages. Adjacent chains link both by direct hydrogen bonding, and by an additional and complex hydrogen-bonding network involving free water groups.

The thermal decomposition of fibroferrite was studied by a multimethodological approach, combining Rietveld refinement of *in-situ* high-temperature (HT) synchrotron X-ray powder diffraction data, HT-FTIR spectroscopy, thermogravimetric analysis and mass spectrometry. The results from these techniques allowed to closely address the structural changes of the initial compound, determining the stability fields and reaction paths and the higher temperature products. Six main dehydration/transformation steps have been identified in the heating temperature range 25-800 °C. Above 760 °C, hematite is the final phase. Temperature behavior of the different phases was analyzed and the structural changes induced by heating are discussed.

Infrared spectra are characterized by a complex system of SO_4^{2-} and H_2O internal modes. *In situ* HT-FTIR data, collected up to 600 °C both on powders and single-crystals, show a succession of structural transitions accompanying the loss of water molecules and OH groups, in agreement with HT X-ray powder diffraction results and mass loss steps from thermogravimetry.

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*RSC Advances.***2013**, 37, 16840-16849.

6O5. Structural characterization of magnetoresistive Pb_2FeMoO_6

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Pb_2FeMoO_6 belongs to the class of double perovskites (general formula $A_2BB'O_6$), which represent an interesting playground in the material research field, being characterized by the high stability and tolerance to chemical substitutions typical of perovskites, with the addition of B-site splitting, allowing in principle the fine-tuning of cation ordering, magnetic exchange interactions and electrical properties. As a result, a large number of peculiar structural and physical properties can be observed, including multiferroism, spin polarized carriers, magnetoresistance or catalytic properties. Pb_2FeMoO_6 is a poorly studied member of the family, needing high pressure and high temperature conditions to be synthesized. It is reported [1] to display ferromagnetic-like properties below about 250 K and magnetoresistance effects. We present here a series of thorough structural characterizations allowing the effective interpretation of the physical properties of the system making use of electron diffraction, synchrotron powder X-Ray diffraction and neutron time of flight measurements. The room temperature crystal structure of Pb_2FeMoO_6 was determined for the first time, being characterized by a superstructure with *Fm-3m* symmetry and lattice parameter $a'=2a_p$ (a_p indicates the simple perovskite). B-site cation ordering is detected, with the relevant presence of antisite defects. The lead atoms are statistically shifted off the high symmetry position giving rise to local polar properties. The magnetic structure was solved in the *I4/mm'm'* colored space group (see Fig.1), involving the atomic moments of iron and molybdenum to be coupled in antiparallel way, giving rise to a ferrimagnetic resultant over which a central role is played by the antisite defects. The results of the structural analysis are compared with the physical characterizations revealing excellent agreement.

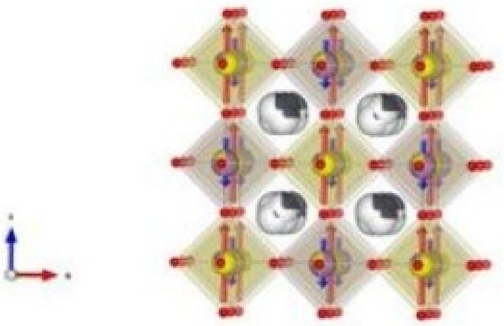

Figure 1. Magnetic structure of Pb_2FeMoO_6.

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6P1. Twinning: structural peculiarities and opportunities in coordination polymers

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The phenomenon of twinning in the chemical crystallographic community is commonly perceived as a problem in an accurate structural resolution. However, twins can be an opportunity in the material science, i.e. the peculiar meccanical properties of metallic materials obtained from deformation twinning. [1] In a wider sense, all the properties with a tensorial nature can be modeled through a rational development of the different kind of twinning: the point group symmetry of the entire crystal edifice differs from the point group symmetry of the twin’s individuals, and this make possible to change the relations between the tensor components from the single crystal to the twinned edifice. [2] Rational control of tensorial properties is of great interest for their applications in NLO materials and advanced optics . Within this background, a less developed study of the nature, problems and opportunities of twinning is the investigation of this phenomenon in the structure of coordination polymers, organometallic compounds with an infinite repetition of metal centers and ligand in one or more dimensions. The study of this family of polymers has been developed in the last decades for the investigation of the peculiar structural features and the consequent properties . However, a screening on the structural literature on this field shows a very common occurrence of twinning in this kind of structures. The occurrence of these phenomena has been deeply studied and understood in mineralogy, but scarcely developed from an inorganic-organometallic point of view. The main aim of this contribution is a tentative to correlate the structural pattern of the coordination polymers and their weak interactions responsible of the crystalline architecture, with the presence of twinning, in order to obtain a better knowledge of his occurrence in the crystal growth. The peculiar symmetries of the twin’s individuals will be examined in the framework of the polychromatic group theory, a development of the study of Shubnikov groups. [3] This approach is interesting to do a more formal and rigorous description of the twinning and could be important for an exact description of the crystal structure, in the framework of the modern geminography.

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6P2. Improper Ferroelectric state in a double perovskite system with a collinear magnetic structure

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The physical characterization and the careful crystallographic study of the double perovskite system $Pb_2Mn_{0.6}Co_{0.4}WO_6$ indicate an improper ferroelectric state induced by the magnetic ordering. The compound shows a centrosymmetric orthorhombic double perovskite structure, s.g. *Pmcm.1'*, strongly distorted from the lead stereoactivity, joined with two magnetic transitions at 190 K and 10 K. The time of flight neutron diffraction data, performed at the ISIS facility on the WISH instrument [1], indicates the presence of diffuse scattering below the first transition temperature and the rise of extra reflections below 10 K. These new reflections, ascribable to a long range magnetic ordering, can be indexed with two propagations vectors κ_1=(000) and κ_2=(½00). The symmetry analysis of the magnetic transition, performed with the help of the ISODISTORT and Jana2006 software [2,3], indicate the breaking of both time and spatial inversion symmetry at the magnetic transition from the *mmm.1'* to the $m'm2_1'$ point group. The symmetry reduction allows the generation of a spontaneous electrical polarization confirmed by the electrical characterizations. The magnetic structure is described by a collinear pseudo-E type structure propagating in the {111} plane of the primitive perovskite cell. The observed electrical polarization is produced by symmetric exchange striction mechanism between the interacting spins, as supported by the magnetic symmetry analysis that exclude the presence of spiral magnetic structure and, as consequence, of inverse Dzyaloshinskii-Moriya mechanism. The experimental electrical polarization is modelled on the basis of the observed magnetic structure and of the symmetric exchange mechanism, taking into account also the small range ordering, evidenced in the time of flight data from the diffuse scattering in the high d-spacing region. This case of study is a meaningful example of the role that the magnetic symmetry analysis and in particular the use of the coloured symmetry can play in explaining the structure-properties relationship in complex multifunctional materials like multiferroics.

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6P3. CO_2 adsorption in Faujasite systems: a synchrotron X-Ray Powder Diffraction investigation

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The separation of CO_2 from other light gases has been largely practiced in the past. In particular, much of the work concerned the separation of CO_2 for the purification of natural gas [1]. Several different approaches have been proposed to remove CO_2 from flue gases on a large scale [2-5]. Among these, zeolites are strongly preferred for their high adsorption capacity, selectivity, irreversibility of the adsorption processes and relatively low production cost [6].

In this work - through in situ X-Ray Powder Diffraction (XRPD) experiments - we describe the CO_2 molecules penetration and their interactions with zeolite cavities/extraframework cations. Three different zeolite samples [NaX, NaY and CaLSX] - sharing the same FAU framework type but with different Si/Al ratios and different cation contents - were investigated.

XRPD experiments were carried out at the MCX beamline at Elettra Sincrotrone Trieste source. The powdered samples were degassed at T=400°C in order to remove the water and then saturated with CO_2 at 1 bar for 30 minutes. XRPD patterns were collected. In order to study the CO_2 desorption, a series of patterns were collected upon heating from room T to 600°C.

After the degassing at 400°C and the consequent water release, the extraframework species underwent a re-organization. Once the systems were saturated at 1 bar, it was possible to locate the host molecules adsorbed in the cavities.

The diffraction data collected on Na-Y allows localizing 48 CO_2 molecules in the FAU supercage, distributed over two independent crystallographic sites. The molecules form clusters at the center of the cage. Forty Ca-coordinated CO_2 molecules were located in the supercage of Ca-LSX, as well. On the contrary, the data collection performed on the saturated NaX allows to locate five Na-coordinated CO_2 molecules in the sodalitic cage, and a carbonate-like species near the supercage. Due to the low number of CO_2 molecules found by this structure refinement, it is not possible to exclude the further molecules occupying the cages with a disordered distribution.

Upon heating up to 600°C, the Na-samples underwent a complete release of all previously adsorbed CO_2 molecules. On the contrary, Ca-LSX retained 25 CO_2 molecules in the channels, suggesting a stronger bonding interaction with the cations.

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6P4. Crystallographic and chemical transformation of asbestiform erionite and chrysotile asbestos in cell environment

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Chrysotile is historically a well known material with exceptional technological properties, as well as famous for the related health issues caused when breathed in high doses. Erionite never had an industrial use, but as any zeolite it bears rare physical and chemical properties and unfortunately also its fibers can cause diseases, specifically mesothelioma (a kind of cancer). Chrysotile is the main serpentine sheet silicate that occurs with asbestiform habit and owing to its tubular sheet arrangement it is a microporous mineral having high tensile strenght, flexiblility, excellent thermal and acoustic absorption properties, chemical and biological strentgh . Erionite can occur in fibers or prismatic crystals, having a framework characterized by several channels developped along its structure for which it can be classified as a microporous mineral. The internal surface area is particularly extended, giving to it the possibility to absorb the 20 % of its weight in water, also ion exchange properties comes from this aspect. These two different microporous minerals can cause the same diseases in human. The present study aims to evidence common characteristics and differences in the interaction among these minerals and the human cell environment (*in vitro* experiment).

Fibers oh both minerals were characterized using transmission electron microscopy and diffraction before the interaction with the cell cultures and after 48 hours and 96 hours of interaction (Fig. 1). Many intense morphological and crystallinity modifications are visibile in chrysotile samples, whilst higher chemical variation happens in asbestiform erionite samples, with a large motion of extra-framework cations. After the interaction, both minerals show as more stable structural component the tetrahedral coordinated cations, in chrysotile the surface and near-surface species are hydrolized and carried into solution. In erionite fibers the cation exchange is not only a surface or near-surface phenomenon, but involves the interior of the mineral that acts as a buffer.

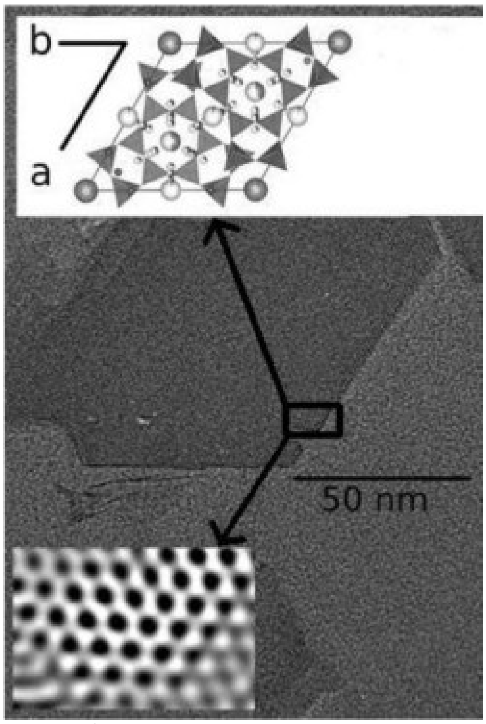

Figure 1. HRTEM evidence of an erionite fiber showing high crystallinity degree after 96 hours interaction with a bronchoalveolar cell. On the top, the unit cell oriented as in the bottom TEM image is shown

6P5. Compressibility and high-pressure behaviour of lead feldspar

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High-pressure *in situ* X-ray diffraction was performed on synthetic lead feldspar. The crystals, with composition $PbAl_2Si_2O_8$, were synthesized from melt as in a previous work and thermally treated at T = 1150°C for 12 h and further annealed at T = 1000°C for 70 h [1]. A single crystal of lead feldspar was preliminary characterized by using a Gemini R Ultra X-ray diffractometer (CrisDi, University of Torino). At room condition the unit-cell parameters are a = 8.3936(4), b = 13.0498(7), c = 14.3258(8) Å, β =115.281(6)°, V = 1418.9(1) Å^3; space group: $I$2/c; Q_{od} = 0.7.

The sample was loaded in an ETH-type diamond anvil cell (DAC) and the unit-cell parameters were measured in the P range 0.0001 - 8.4 GPa at room T, using a Siemens P4 diffractometer and SINGLE software [2]. The evolution with pressure of the unit-cell parameters and volume shows a strong discontinuity between 7.7 and 8.2 GPa indicating a first order-phase transition. In the P range 0.0001 - 7.7 GPa the trend shown by the axial compressibility ($_a$ > $_c$ > $_b$) is similar to that observed in the previous HP powder diffraction study, performed on lead feldspar using high-brilliance synchrotron radiation up to 7.1 GPa [3].

In the P range 0.0001 - 4.3 GPa at room T, the P-V data of the $I2/c$ lead feldspar were fitted with a 2nd-order Birch-Murnaghan EoS, using EosFit7c software [4]. The parameters obtained are: V_0 = 1422.2(1) Å^3 and K_{T0} = 76.4(9) GPa. At P > 4.27 GPa, the volume values deflect from the BM2 curve and show a volume softening, precursor of the reported HP phase transition. Also in strontium feldspar a volume softening was recently observed above 4.2 GPa [5].

Another crystal of lead feldspar of the same synthesis was loaded in the DAC to investigate the structural changes with increasing pressure. Single-crystal diffraction intensities were collected with Gemini diffractometer at P=0.0001, 2.4, 3.1, 5.4, 6.0, 7.2, 8.4, 9.7 GPa. The measurements up to 7.2 GPa showed only a ($h+k$ = even, l = even) and b-type ($h+k$ = odd, l = odd) reflections ($I$2/c space group). The appearance of c ($h+k$ = even, l = odd) and d-type ($h+k$ = odd, l = even) reflections at P = 8.4, the analysis of the systematic absence and the structural refinements indicate that the HP first-order transformation is an $I2/c$ - $P2_1/c$ phase transition.

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6P6. Alkali activated materials from sulfate-bearing kaolins: pros and cons

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The feasibility of using low-grade kaolins containing sulfates to synthesize alkali activated materials (AAMs) has been assessed. Alunite, $KAl_3(SO_4)_2(OH)_6$, is present in kaolin deposits deriving from trachyte, rhyolite, and similar potassium-rich volcanic rocks, and normally hinders the use of these clays in the ceramic industry due to the release at high temperature of SO_x, which damages furnaces refractories. Metakaolinite obtained by annealing alunite-containing kaolins at T = 550 °C, i.e. below desulfation temperature, has been used for alkali activation.

AAMs have been synthesized from metakaolin and sodium silicate solution, nominal composition of the slurry is given by SiO_2/Al_2O_3 and Al_2O_3/Na_2O molar ratios of 4.6 and 1.04, respectively. Specimens have been cured in air-tight molds at 52° C and for 19 h. Samples have been prepared by using the alunite-bearing kaolin from Piloni di Torniella mine (alunite 5% wt) as starting material and by mixing 10% wt. alunite to high-quality kaolinite to better identify sulfate by-products in the AAMs. The results are promising as the synthesized samples revealed to be composed mainly by an amorphous gel and characterized by high thermal stability and strength, with compressive strength higher than 80 MPa. All samples have been characterized by thermal analysis, X-ray powder diffraction and infrared spectroscopy. A petrographic approach has been used to analyze the textural features of geopolymers at different lengths of scale by using optical and scanning electron microscopies.

More studies are needed in order to improve the sulfate retention as well as to identify all the silico-sulfate phases and understand the possible interactions between precipitated nanocrystalline sulfate phases and geopolymer binder.

MS7. IMAGING BIOMOLECULAR MACHINES IN ACTION THROUGH CRYO-ELECTRON DIFFRACTION AND CRYO-ELECTRON MICROSCOPY

Structures at near-atomic resolution are no longer the prerogative of X-ray crystallography or nuclear magnetic resonance spectroscopy. The old dream of being able to use few dozen protein 3D nano-crystals to determine by electron microscopy atomic-resolution structures may finally come true. The combination of direct electron detectors and reliable image processing programs is keeping the field moving forward at a rapid rate. Precise knowledge of the structure of molecular machines in the cell is essential for understanding how they function. Structures of large macromolecules in their multitude of different conformations can now be obtained at near-atomic resolution by averaging thousands of electron microscope images recorded before radiation damage accumulates. This microsymposium will highlight the major methodological advances for high resolution imaging of biomolecular machines in action through cryo-electron diffraction and cryo-electron microscopy.

Chair: Doriano Lamba (IC CNR Trieste)

7KN1. The atomic structure of the human gamma-secretase complex

Xiao-chen Bai[a], Chuangye Yan[b], Guanghui Yang[b], Peilong Lu[b], Dan Ma[b], Linfeng Sun[b], Rui Zhou[b], and Yigong Shi[b], Sjors H.W. Scheres[a]

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For many years, structure determination of biological macromolecules by cryo-electron microscopy (cryo-EM) was limited to large complexes or low-resolution models. With recent advances in electron detection and image processing, the resolution by cryo-EM is now beginning to rival X-ray crystallography. A new generation of electron detectors record images with unprecedented quality, while new image-processing tools correct for sample movements and classify images according to different structural states. Combined, these advances yield density maps with sufficient detail to deduce the atomic structure for a range of specimens.

Now the question arises as to where the new size limits lie. The ribosome and virus might be considered easy targets for cryo-EM because they are relatively large, and the latter also has high symmetry. Currently, the smallest complex subjected to the new methodology is γ-secretase. This asymmetric membrane complex comprises four different proteins with a total molecular weight of 170 kDa. Imaging on a K2 detector in counting mode and performing reconstruction with a modified motion correction and 3D classification algorithm led to near-atomic resolution 3.4Å, which proved sufficient for de novo model building. This structure represents another breakthrough for the emerging technique of high-resolution cryo-EM, and also serves as a molecular basis for mechanistic understanding of γ-secretase function and disease-causing mutations.

7KN2. Molecular mechanisms of asymmetric cell divisions

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The Asymmetric cell divisions are attained by unequal segregation of cell-fate defining components, and by differential positioning of siblings within the tissue. In several vertebrate stem cell systems, only daughters retaining contact to specialized microenvironment called niches maintain stemness. On these premises, it becomes clear that asymmetric divisions require the coordination between cellular polarity and the division plane, and hence the mitotic spindle axis. Spindle coupling to cortical polarity is attained by pulling forces exerted on astral microtubules by NuMA:LGN:Gαi complexes bound to Dynein. What instructs the recruitment of these force-generating devices at the correct cortical sites is to date largely unclear. The adaptor Inscuteable (Insc) has been considered the molecular bridge between the apical polarity proteins Par3:Par6:aPKC and LGN. In Drosophila neuroblasts and in murine neural stem cells and skin progenitors, Insc has been shown to interact both with Par3 and LGN. However the molecular basis for its function still remain elusive.

I will present the crystallographic structure of *Drosophila* LGN in complex with Insc. The structure reveals a stable tetrameric arrangement of intertwined molecules, in which each Insc chain contacts two LGN^{TPR} domains. Biochemical analyses showed that Insc:LGN tetramers constitute stable cores for the assembly of the Par3-Insc-LGNGαi^{GDP} apical complexes. Importantly, such oligomeric arrangements are conserved throughout species, and are competitive with the binding of LGN to NuMA. Collectively these results suggest a novel cortical function of LGN, independent from microtubule motors and specific for asymmetric apico-basal divisions. Based on this evidence, we propose a model in which two independent pools of LGN contribute to asymmetry in different ways: the Insc-bound pool by coordinating the distribution of fate determinants including Par3, and the more abundant NuMA-bound pool by providing cortical information to orient the division plane.

7O1. Membrane NAPE-PLD links major players in lipid homeostasis with major players in lipid mediated signaling

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NAPE-hydrolyzing phospholipase D is a membrane enzyme that produces fatty acid ethanolamides (FAEs), essential biactive lipid mediators involved in highly conserved biological functions, such as innate immunity, energy balance, and stress control [1]. The crystal structure of human NAPE-PLD at 2.6 Å resolution shows it forms homodimers partly separated by an internal ~9-Å-wide cannel and uniquely adapted to associate with membrane phospholipids. Structural and biophysical analysis reveal bile acids bind with high affinity to specific pockets of the protein membrane interface, enhancing dimer assembly and enabling catalysis [2]. Experiments of 3D EM reconstruction of the protein associated to membrane vesicles are under way. These insights might cast an interesting light on NAPE-PLD as a point where signaling of bile acids and FAEs converge [3].

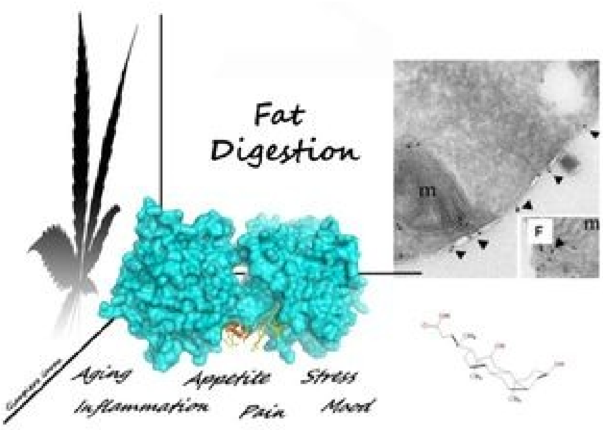

Figure 1. Regulation of bioactive lipid amide signals by bile acids

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7O2. Pore flexibility underlies the poor selectivity of CNG channels: a structural, functional and computational analysis

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Cyclic nucleotide-gated (CNG) ion channels, despite a significant homology with the highly selective K^+ channels, do not discriminate among monovalent alkali cations and are permeable also to several organic cations [1,2]. We combined X-ray crystallography with electrophysiology and molecular dynamics (MD) simulations to demonstrate that the pore of CNG channels is highly flexible. When a CNG mimic is crystallized in the presence of a variety of monovalent cations, including Na^+, Cs^+ and dimethylammonium (DMA^+), the side chain of Glu66 in the selectivity filter shows multiple conformations and the diameter of the pore changes significantly. MD simulations indicate that Glu66 and the prolines in the outer vestibule undergo large fluctuations, which are modulated by the ionic species and the voltage. The differences in position, ion occupancy and ion size in the Li+, Na+, Rb+, Cs+, MA+ and DMA+ complexes also result in small but significant structural changes in the polypeptide lining the pore lumen arise from both a small lateral displacement of the backbone chain and a reorientation of main-chain carbonyls. This flexibility underlies the coupling between gating and permeation and the poor ionic selectivity of CNG channels.

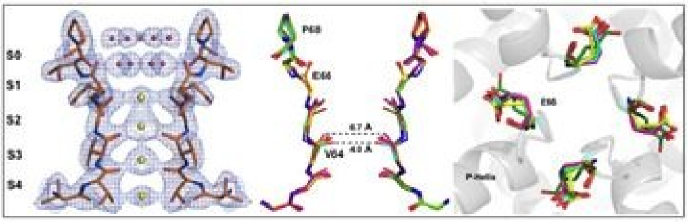

Figure 1. Structural analysis of the CNG mimic channel in complex with different ions.

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7O3. Have your phosphate and eat it: structure and function of a bacterial PhoX phosphatase

Pietro Roversi[a,b], Shee Chien Yong[a], James Lillington[b], Fernanda Rodriguez[a], Martin Krehenbrink[a], Oliver Zeldin[a], Elspeth Garman[a], Susan Lea[b], and Ben Berks[a].
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[b]*Sir William Dunn School of Pathology, Oxford University, Oxford, England, UK.*
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When phosphate is unavailable in the environment, alkaline phosphatases enable microorganisms to generate their own phosphate supply by breaking down phosphate-containing compounds. We have determined the crystal structure of the widely occurring microbial alkaline phosphatase PhoX. The purified enzyme showed an unexpected purple colour – and turned out to be structurally and mechanistically distinct from so far characterised alkaline phosphatases. Its active site comprises two antiferromagnetically coupled ferric iron ions, three calcium ions, and an oxo group bridging three of the metal ions. Notably, the main part of the cofactor resembles synthetic oxide-centred triangular metal complexes. Three additional crystal structures of PhoX in complex with a substrate analogue, a transition state analogue and phosphate, collectively implicate the cofactor oxo group in the catalytic mechanism. As well as offering some intriguing chemistry to follow up, these findings also have ecological implications: PhoX is as widely distributed as the PhoA family of alkaline phosphatases amongst ocean microbes. The discovery that PhoX requires Fe and Ca, in contrast to PhoA which requires Zn and Mg, raises the question of how these organisms may juggle with these two enzymes in order to secure their phosphate meal in areas of the ocean where Zn, Fe and phosphate are all simultaneously scarce.

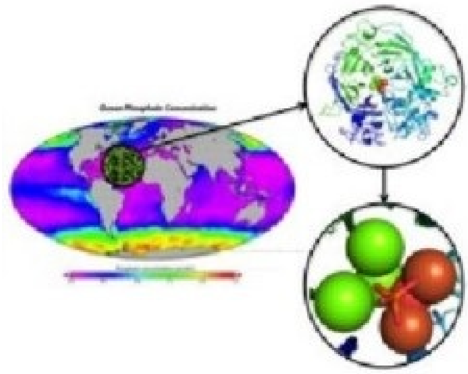

Figure 1. Low phosphate levels in the water prompt oceanic bacteria to express PhoX and secure phosphate *via* catalysis at its Ca_3Fe_2O active site.

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7O4. How to build a host-parasite interactome: a proof of concept for *Schistosoma mansoni*

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Eukaryotic vector-borne parasites represent a huge burden for human health worldwide.

Malaria, Schistosomiasis and Leishmania are the first causes of morbidity and death worldwide, affecting about 1 billion people living between the tropics. Each parasite has evolved to evade the host immune response, while finding its final destination, independently of the entry point.

It is therefore important for both diagnostics and therapeutics to know which are the molecular players in this survival game. Under this respect we have undertaken a high throughput screening of the interactions between the secreted proteins from the human parasite *Schistosoma mansoni* and the components of the human extracellular matrix.

S. mansoni is an extracellular parasitic trematode, which lives attached to the veins of the portal system around the liver. Before attaining this final site, the infectious cercaria travels from the epidermis to the derma, then reaches one capillary and heads to the lungs, where it matures into the juvenile form, which then travels to the final tropism and reaches the sexual adult stage.

Previous studies of the secretomes of these three stages have evidenced the presence of a handful proteins always expressed and secreted, and a number specific for each stage [1,2].

In order to set up a proof of concept we have selected three of these proteins, which also display a moonlighting behaviour: enolase, protein disulfide isomerase and thioredoxin glutathione reductase.

Then we have screened with surface plasmon resonance imaging for their human partners among 78 proteins, glycoproteins, and glycosaminoglycans (GAG) known to be the major components of the extracellular matrix. Those positive hits were subsequently tested for complex formation by small angle X-ray scattering, in order to reveal both the stoichiometry and the structure of the complexes.

Here we present the results on SmEnolase, whose major interacting protein partners are plasminogen, tropoelastin, tumor endothelial marker 8 (TEM8), while the major interacting GAGs are dermatan and chondroitin sulfate.

In parallel we have screened live promastigotes of 24 strains of 6 species of Leishmania, dividing them by tropism (visceral, cutaneous and mucocutaneous) against the same subset of human ECM components [3]. Very interestingly, common partners have been found between *S. mansoni* and *L. donovani*, *L. infantum*, which share a common visceral tropism, while a very small number of different partners could be used as markers for tropism.

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7P1. Platinum binding to human copper chaperone Atox1

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Interaction between platinum ion and intra and extra cellular proteins plays a key role in platinum-based anticancer drug resistance. Particularly, proteins involved in copper transport and regulation are able to mediate the cellular uptake, sequestration, and efflux from cell of platinum-based drugs, affecting their anticancer activity.

The copper chaperone protein Atox1, which is involved in copper homeostasis, has been reported to interact with cisplatin in *in vitro* and in cell experiments [1].

Here, the interaction between Atox1 protein and platinum from oxaliplatin, belonging to the third-generation platinum drugs, has been investigated by using X-ray crystallography and X-ray absorption spectroscopy. Our structure shows that Atox1 protein dimerizes in the presence of platinum, which loses the amine ligands from the starting drug. A platinum ion binds the Cys12 and Cys15 sulfur atoms of two Atox1 proteins in an unexpected tetrahedral coordination, present also in a previously reported platinum-mediated Atox1 dimer structure [2]. However, in this structure, a severe clash between the amine ligands and the sulfur atoms appears, as platinum preserves their native ammine ligands, suggesting that platinum loses all of its ligands before binding the sulfur atoms of the cage, as occurs in our structure.

Differently from the previous Atox1 dimer structure, our structure shows the presence of a lower occupied binding site on the Cys41 of one of the two chains forming the dimer, where, once again, platinum loses all its ligands from native drug.

In solution measurements (FPLC-SEC, ESI-MS, and SAXS), performed by using both cisplatin and oxaliplatin, show that monomeric Atox1 adducts containing a platinum ion coordinated to amine ligands is initially formed and that protein dimerization takes place at longer time with loss of the amines, in agreement with the crystal structure. This process is reminiscent of the copper-promoted formation of Atox1 dimers, which have been proposed to be able to cross the nuclear membrane and act as a transcription factor [3].

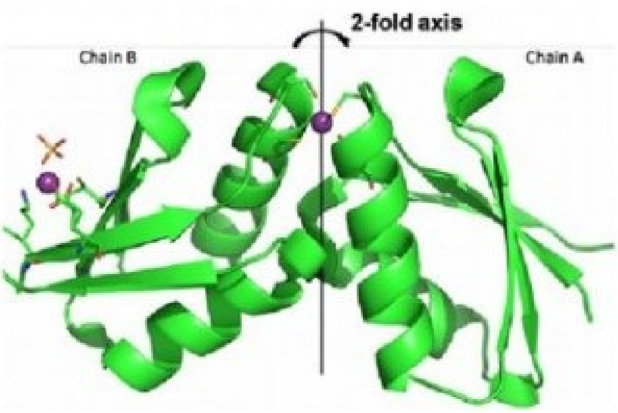

Figure 1. Crystal structure of the Atox1 protein crystallized in the presence of oxaliplatin.

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7P2. Single-particle cryo-EM study of the AMPA receptor in the desensitized state

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The neurotransmitter glutamate mediates most of the excitatory synaptic responses in the central nervous system. Glutamate released from the pre-synaptic membrane binds to ionotropic glutamate receptors in the post-synaptic membrane, causing the opening of the receptor's cation channel and a transient depolarization of the membrane [1]. Deactivation occurs when glutamate is released and the receptor returns to the *apo* resting conformation. However, while the agonist is still bound, the receptor can undergo other conformational changes that decouple agonist binding from the activation of the ion pore, leading to a desensitized state [2]. Despite the importance of ionotropic glutamate receptors, the dynamics of intact receptors and the structural changes between distinct functional states are not yet fully understood. In particular, questions remain concerning the mechanisms that underlie the desensitization of these receptors.

Among glutamate receptors, α-amino-3-hydroxy-5-methyl-4-isoxazolepropionic acid (AMPA) receptors, whose name reflects their affinity for this artificial glutamate analog, are responsible for fast signaling and have kinetics of activation, deactivation and desensitization in the scale of milliseconds [1]. First structural information for AMPA receptors came from negative-stain EM studies of heterotetrameric receptors isolated from mouse brains, which revealed that the extracellular domains are organized as dimers of dimers [3]. A later X-ray crystal structure of an engineered homotetrameric AMPA receptor in an antagonist-bound state confirmed the EM structure and provided insights into ligand binding and activation of the full-length receptor [4]. Since then, both EM and X-ray crystallographic studies aimed at understanding mechanistic aspects of AMPA receptor function [5,6]. The desensitized state, in particular, seems to be characterized by a separation of the extracellular domains, and the conformational changes that trigger this flexibility are not yet fully understood.

Here, we present a cryo-EM study of the AMPA receptor in the desensitized state, which is characterized by the separation of its extracellular domains, consisting of the amino-terminal and ligand-binding domains. As a result, the extracellular domains lose the 2-fold symmetry observed in the X-ray structure [4] and adopt a continuum of conformations. We imaged vitrified samples by cryo-EM and collected ~250,000 particles. 3D classification of these particles yielded structures of the receptor in various conformations, reflecting different separations of the extracellular domains. In particular, the structures allowed us to observe the coupling and uncoupling of the ligand-binding domains that lead to the major conformational changes involving the whole extramembranous domain.

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7P3. Three-dimensional structure and ligand-binding site of carp Fishelectin (FEL)

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María Cecilia González, Massimiliano Perduca, Michele Bovi, Monica Galliano and Hugo L. Monaco
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Carp FEL (fishelectin or fish egg lectin) is a 238 amino acid lectin that can be purified from the fish eggs exploiting its selective binding to Sepharose followed by elution with N-acetyl glucosamine. We previously reported its amino acid sequence and other biochemical properties. The glycoprotein has four disulphide bridges and the structure of the oligosaccharides linked to Asn 27 was described (1).

The poster will describe the three-dimensional structure of apo carp FEL (cFEL) and of its complex with N-acetyl glucosamine determined by X-ray crystallography to resolutions of 1.35 and 1.70 Å respectively (2). The molecule folds as a six-blade β-propeller and internal short consensus amino acid sequences have been identified in all the blades. A calcium atom binds at the bottom of the funnel shaped tunnel located in the centre of the propeller.

Two ligand binding sites,αand β are present in each of the two protomers in the dimer. The first site, α, is closer to the N terminus of the chain and is located in the crevice between the second and the third blade while the second site, β, is located between the fourth and the fifth blade. The amino acids that participate in the contacts have been identified as well as the conserved water molecules in all the sites. Both sites can bind the two anomers, αandβ of N-acetyl glucosamine, clearly recognizable in the electron density maps.

The lectin presents sequence homology to members of the tachylectin family, known to have a function in the innate immune system of arthropods and homologous genes are present in the genome of other fish and amphibians (3). This structure is the first of a protein of this group and, given the degree of homology with other members of the family, we expect it will be useful to experimentally determine other crystal structures using the coordinates of cFEL as search probe in molecular replacement.

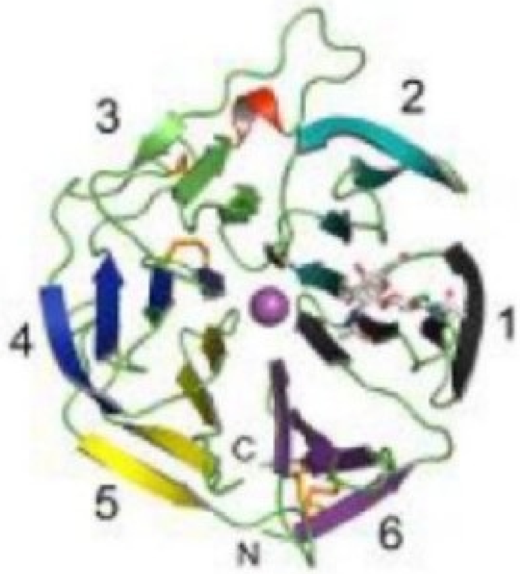

Figure 1. Ribbon diagram of the FEL molecule.

.

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7P4. Structural studies of human acidic fibroblast-growth factor (FGF1) mutants with a probable anticancer activity

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Lectins are carbohydrate-binding proteins ubiquitously present in nature. They play a role in biological recognition phenomena involving cells and proteins. The interaction lectin-carbohydrate is highly specific, and can be exploited for the development of nanoparticles containing on their surface lectins specifically directed to carbohydrate residues present only on malignant cells and absent on healthy ones [1].

Lectins have been found to possess anticancer properties and they are proposed as therapeutic agents, binding to cancer cell membranes or their receptors, causing cytotoxicity, apoptosis and inhibition of tumor growth. Some lectins are able to prevent the proliferation of malignant tumor cells because they recognize the T-antigen (Gal β 1–3GalNAc) found specifically on the surface of tumor cells [2]. The main problem is that their use as a detection agent for the T-antigen in clinical studies is not possible because the immune system can recognize them as foreign molecules and develop an immune response.

Previous studies with X-ray crystallography made in our laboratory have characterized a lectin found in mushrooms called BEL β-trefoil which has antiproliferative activity on tumor cell lines, because it contains three binding sites for the T-antigen. Unlike other lectins with this property, BEL β-trefoil shows structural homology with a human protein, acidic Fibroblast Growth Factor (FGF1) [3]. Superposition of their structures suggests that the human protein could be mutated to contain at least one of the binding sites for the T-antigen. Such mutations should create in FGF1 the potential capacity of recognizing tumor cells with less immunogenicity than the fungal protein. FGF1 is mitogenic and chemotactic, and mediates cellular functions by binding to transmembrane receptors, which are activated by ligand-induced dimerization requiring heparin as co-receptor.

To reach our purpose, the FGF1 cDNA was cloned into a bacterial plasmid and then mutated in four different positions to eliminate its mitogenic activity and to engineer in the protein the T-antigen binding capacity. Attempts to crystalize the mutants of FGF1 were made using the hanging drop technique with the final aim to carry out their structural characterization by X-ray diffraction analysis of the crystals.

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7P5. Unraveling the antitumoral properties of Arundo donax lectin

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Lectins are proteins that recognize specific carbohydrate structures and thereby participate in molecular recognition events of fundamental relevance in a variety of biological processes [1]. They are promising ligands for targeted drug delivery because they bind rapidly and specifically to membrane-linked carbohydrates or glycoproteins to initiate receptor-mediated endocytosis [2].

In recent years several lectin-functionalized nanoparticles have been described and, in particular, the well-known wheat germ agglutinin has been used for the selective delivery of nanoparticles loaded with a widely used anticancer agent [3].

In our laboratory we have begun to characterize a novel lectin that presents a significant sequence homology with wheat germ agglutinin and exhibits cytotoxic activity against epithelial cancer cells (Fig. 1). The lectin is isolated in very high yields (500 mgs per Kg of the starting material) and with a very simple purification method from the rhizomes of the common giant reed *Arundo donax*, one of the most readily available sources of biomass on the Earth because of its fast growing rate and its ability to grow in different soil types and climatic conditions. We call the protein ADL which stands for *Arundo donax* lectin [4].

The goal of our project is to structurally and functionally characterize the lectin, i.e. to define in detail its ligand binding specificity using several biophysical techniques and, in particular, X-ray crystallography. We have already prepared diffraction quality crystals and are in the process of solving its three-dimensional structure. In the future we intend to prepare ADL conjugated nano-sized particles for the selective delivery of anti-tumoral agents to neoplastic epithelial cells.

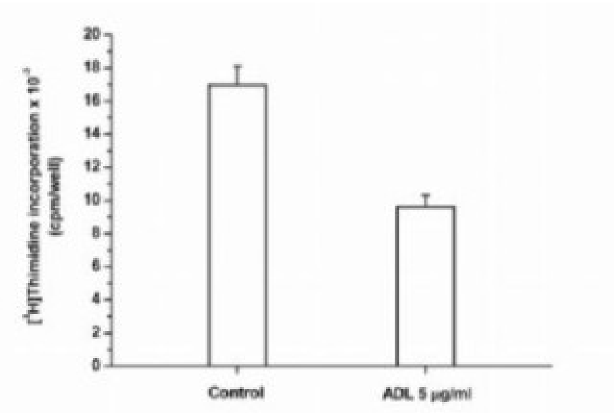

Figure 1. ADL cytotoxic activity against epithelial cancer cells.

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7P6. Structural Characterization Of Proteins Involved In *Helicobacter pylori* Motility And Adhesion

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Helicobacter pylori is strongly associated with the development of atrophic gastritis, which is a precursor lesion to gastric cancer. The Gram-negative bacterium is present in half of human population, but only 15% of infected people show gastric and duodenal ulcers [1]. The infection is often contracted before the age of ten years, by fecal-oral or oral-oral infection. All *H. pylori*-infected patients develop chronic gastric inflammation, but this condition usually is asymptomatic. Two of the principal causes of *H. pylori* stomach colonization are bacterium motility and adhesion to gastric epithelium [2]. The motion is due to flagella, which can serve as adhesive appendages in the initial phases of colonization. There is evidence that less motile strain are less able to colonize or survive in the host and the degree of motility is correlated with the degree of infection. The organization of the *H. pylori* flagellum consists of basal body, hook and flagellar filament. The basal body includes the rings, motor and switching proteins. The filament is masked by a sheath and extends 3-5 µm from the cell; the flagella are polar and are between 2 and 6 per cell. A flagellum includes flagellins FlaA (HP0601) and FlaB, necessary for the full motility. Several copies of FlgE (HP0870) compose the hook, which is a flexible structure that links the filament to the driving apparatus in the basal body. A set of about ten chaperons is included among the flagellar proteins in order to avoid protein axial polymerization [3]. FlgN belongs to this group and is thought to interact with the hook junction proteins FlgL and FlgK.

Whilst FlaA and FlgE are still ongoing in investigation, FlgN has been cloned starting from the corresponding gene *hp1457*, expressed in *E. coli* BL21(DE3) and transformed using a pETite vector. After size-exclusion chromatography purification, the protein was identified as monomeric and dimeric species. Crystals have been obtained for the monomeric form at different concentrations. Further investigation should be carried on to improve FlgN crystals quality.

Adherence of the bacterium to the host cell is a mechanism that helps to protect it from the displacement due to peristalsis. It damages the epithelium and induces inflammation, eventually delivers toxins [4]. One of the proteins involved in this pathogenic process is the *Helicobacter pylori* adhesin A (HpaA), formally designated HP0797. HpaA was expressed fused with sfGFP1-10 [5] in order to facilitate protein crystallization and to help to solve the crystal structure by molecular replacement, using GFP atomic coordinates. Crystals were obtained in several conditions, but they turned out to be only GFP. New crystallizations attempts are on the way in order to increase crystallization kinetics against degradation.

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7P7. Multi-Target-Directed Ligands in Alzheimer's Disease Treatment

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Alzheimer's disease (AD) is a complex neurodegenerative disorder arising from multiple molecular abnormalities including a progressive forebrain cholinergic deficiency, accumulation of misfolded protein deposits as amyloid β plaques and a redox system impairment which lead to increased levels of reactive oxygen species and to the consequent radicals mediated injury. To date, the only licensed AD treatments are acetylcholinesterase (AChE) inhibitors and memantine, which are valuable in restoring cholinergic deficit but offer only a modest and temporary benefits to patients[1] .

In the fight of AD recently has been proposed a move from the classic "*one protein, one target, one drug*" strategy to a strategy of developing drugs that simultaneously target multiple targets [2].

We report on the structure-activity relationships of two novel multitarget anti-Alzheimer compounds designed by combining a tacrine fragment and a juglone [3] or benzofuran moiety respectively, with a linker of a suitable length.

In vitro, both compounds displayed excellent AChE inhibitory potencies and interesting capabilities to block amyloid-β aggregation and anti-oxidants properties. The X-ray analysis of the *Torpedo californica* AChE – inhibitor complexes allowed a structure-based rationale for the outstanding activity data.

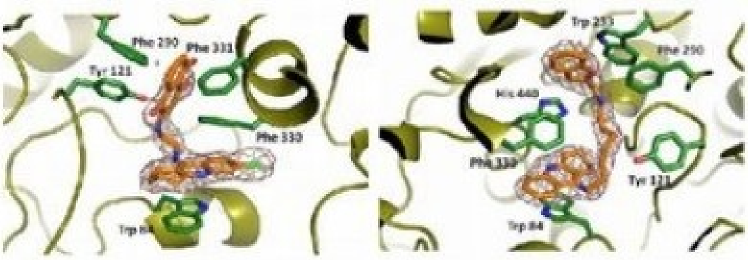

Figure 1. Interaction of the tacrine-juglone hybrid inhibitor (Panel **A**) and of the tacrine-benzofuran hybrid inhibitor (Panel **B**) within the *Tc*AChE active site.

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7P8. The Structure of the T190M Mutant of Murine α-Dystroglycan at High Resolution: Insight into the Molecular Basis of a Primary Dystroglycanopathy

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The severe dystroglycanopathy known as a form of limb-girdle muscular dystrophy (LGMD2P) is an autosomal recessive disease caused by the point mutation T192M in α-dystroglycan [1]. Functional expression analysis *in vitro* and *in vivo* indicated that the mutation was responsible for a decrease in posttranslational glycosylation of dystroglycan, eventually interfering with its extracellular-matrix receptor function and laminin binding in skeletal muscle and brain. The X-ray crystal structure of the missense variant T190M of the murine N-terminal domain of α-dystroglycan (50-313) has been determined [2], and showed an overall topology (Ig-like domain followed by a basket-shaped domain reminiscent of the small subunit ribosomal protein S6) very similar to that of the wild-type structure [3]. The crystallographic analysis revealed a change of the conformation assumed by the highly flexible loop encompassing residues 159–180. Moreover, a solvent shell reorganization around Met190 affects the interaction between the B1–B5 anti-parallel strands forming part of the floor of the basket-shaped domain, with likely repercussions on the folding stability of the protein domain(s) and on the overall molecular flexibility. Chemical denaturation and limited proteolysis experiments point to a decreased stability of the T190M variant with respect to its wild-type counterpart. This mutation may render the entire L-shaped protein architecture less flexible. The overall reduced flexibility and stability may affect the functional properties of α-dystroglycan via negatively influencing its binding behavior to factors needed for dystroglycan maturation, and may lay the molecular basis of the T190M-driven primary dystroglycanopathy.

Figure 1. Superimposition of the WT and T190M mutant S6 domains.

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7P9. A PPP Platform at Elettra: achievements and future perspectives

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Expression, purification and structure determination of recombinant proteins is a fundamental requirement for a variety of biological applications, from exploratory research to pharmaceutical drug discovery.

The PROTEO project, granted by the Cross-Border Cooperation Program Italy - Slovenia 2007-2013, has created a network of scientific collaborations among research laboratories with a common focus on cancer therapy research and development of diagnostic devices for early cancer detection (www.elettra.eu/Prj/PROTEO). Within this framework we have implemented a protein production platform in the Structural Biology Lab of Elettra providing specialized support to express and purify recombinant proteins for functional and structural studies. We perform semi-automated cloning and expression of multiple protein targets in *E.coli* and insect cell systems. Mammalian expression is also supported with a manual throughput. The core unit is equipped to clone/express/purify proteins with high efficiency, using rapid cloning methods such as Ligation-Independent, Gateway, Restriction-Free or Gibson in multi-sample parallel protocols and Ni-NTA affinity small-scale purification on a robotic platform (Freedom Evo 150 – Tecan). The unit is also equipped for scale-up protein production and purification and to evaluate protein stability by TSA and protein activity by functional assays. Other biochemical and biophysical assays are done accordingly with the protein requirements. Protein crystallization trials are set up at the crystallization facility of Elettra.

Currently, about 10 projects are run in parallel with a focus on protein targets that are relevant for cancer diagnostic and therapy. The main interest is on two classes of proteins: the human kinases and the deubiquitinases. In this work we will present the workflow of the newly established protein production platform, taking examples from the most significant results obtained from the projects in progress in the lab.

MISCELLANEOUS

MP1. Crystal Structure of Functionalized Croconaines

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Croconaine (CR) dyes have been the subject of many recent investigations owing to their excellent optical and electronic properties. Their intramolecular charge-transfer (CT) character as well as the extended conjugated π-electron network give rise to the intense bands observed in the visible to near-infrared (NIR) region. These peculiarity together with their stability promoted their exploitation in a number of applications i.e.: photoconductivity, light emitting field-effect transistors, solar cells, etc. [1-5]. Their photochemistry has been extensively studied and many derivatives of the CR moieties have been synthesized, especially as infrared (IR) probes and non-linear optical (NLO) materials [6]. The CR properties depend both on the functionalization of the molecule and on the crystal structure. In this context, here we describe the results of a SCXRD study of three CR molecules (see Figure). The I- and Br-substituted crystals resulted to be monoclinic (S. G. $P2_1/n$, 10.818 $\leq a \leq$ 11.163 Å, 10.02 $\leq b \leq$ 10.11 Å, 23.15 $\leq c \leq$ 23.15 Å, 103.1 $\leq \beta \leq$ 103.4°), while the last one is triclinic (S.G. P-1, a = 11.08 Å, b = 14.65 Å, c = 28.65 Å, = 66.2°, = 81.9°, = 72.3°) for the occurrence of embedded solvent molecules into the crystal structure. Bond valence analyses allowed to check H-positions. It turns out that CR stereochemical arrangements are affected by intramolecular N-H...O bonds, whereas the crystal packings are driven by - interaction between C=O groups and sometimes between aryl-aryl groups which allow an extended conjugated π-electron network.

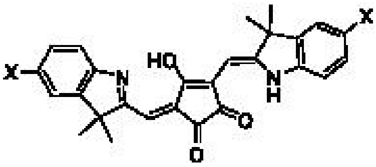

Figure 1. Sketch of the studied croconaines molecules (X = H, Br, I).

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SOFTWARE FAYRE

The EXPO program

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The main features of EXPO2014 [*] [http://wwwba.ic.cnr.it/content/software], a software for crystal structure determination from X-ray powder diffraction data, will be given by explicative examples.

The preliminary steps will be described: download and installation of software; preparing the input file for EXPO2014; indexing the diffraction pattern by means of a new tool, which combines cell solutions obtained from different indexing programs; identifying the space group. The program is able to perform the structure solution by using Direct Methods and/or the Real Space Methods approaches: examples related to both methods will be displayed and applied to organic and inorganic compounds.

Useful suggestions to be adopted when EXPO2014 default strategies fail will be given. A brief description of the Rietveld refinement performances in EXPO2014 and of tools for visualization and manipulation of crystal structures will be also proposed.

*A. Altomare, C. Cuocci, C. Giacovazzo, A. Moliterni, R. Rizzi, N. Corriero and A. Falcicchio, "EXPO2013: a kit of tools for phasing crystal structures from powder data", *J. Appl. Cryst.* (2013). **46**, 1231-1235.

The SIR program

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The SIR (Semi-Invariants Representation) package [http://wwwba.ic.cnr.it/content/software] has been developed for solving crystal structures by a variety of methods (Direct and Patterson Methods, VLD, Direct Space Methods, Molecular Replacement).

The present version of the program, Sir2014 (v. 15.07), is designed to solve ab initio structures of different size and complexity, up to proteins, provided that data resolution is no lower than 2.0. Data can be collected with X-Ray or electron sources. The program can also be applied to Molecular Replacement problems providing a powerful pipeline to solve and refine protein structures. New features and a new Graphical User Interface will be shown.

The CRYSTAL program

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Ab initio modeling has become an ever-increasing area of interest in solid state chemistry, physics and materials science.

CRYSTAL [http://www.crystal.unito.it] is a general-purpose program for the study of crystalline solids, and the first to have become available to the scientific community. It adopts Gaussian type functions as basis set and allows calculations at HF, DFT and various flavors of HF/DFT hybrid

(e.g. B3LYP, PBE0, ...) levels of theory. The program may be used to perform consistent studies of the physical and chemical properties of crystalline solids, surfaces, nanotubes, polymers and molecules. The symmetry of the system is automatically handled and fully exploited in the calculations.

Basic, advanced and new capabilities of the latest version of the code (CRYSTAL14)[*] will be presented and illustrated with hands-on tutorials organized in the practical session.

[$] R. Dovesi, R. Orlando, A. Erba, C. M. Zicovich-Wilson, B. Civalleri, S. Casassa, L. Maschio, M. Ferrabone, M. De La Pierre, P. D'Arco, Y. Noel, M. Causa, M. Rerat, B. Kirtman. "CRYSTAL14: A Program for the Ab Initio Investigation of Crystalline Solids" *Int. J. Quantum Chem.* (2014) **114**, 1287.

ROUND TABLE

The Future of Crystallography and the Legacy of IYCr in Italy

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La comunità dei cristallografi italiani ha aderito con entusiasmo all'Anno Internazionale della Cristallografia (IYCr2014), proponendo una serie di iniziative locali distribuite su tutto il territorio nazionale, e alcune azioni generali rivolte in special modo a insegnanti e studenti delle scuole superiori. Sono stati organizzati oltre 50 eventi locali per la divulgazione della cristallografia a vari livelli. Alcune iniziative sono ancora in corso e si proiettano nel 2015. Questa tavola rotonda ha l'obiettivo di presentare alcune tra le attività più positive e proporre strategie per costruire progetti di divulgazione e visibilità per i prossimi anni.

17:15-17:30 La mostra itinerante "Cristalli!" (*Alessia Bacchi)*

17:30-17:45 Cristallografia: la visione ai raggi X (*Simona Galli e Pietro Roversi)*

17:45-17:55 Concorso Nazionale di crescita cristallina *(Marco Bruno)*

17:55-18:10 Crystallography matters … more *(Michele Zema)*

18:10-18:45 Open discussion

Progress in X-ray Crystallographic Methodology:Shutterless Data Collection

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Instrumentation for single crystal structure analysis has advanced greatly over the last decade. These improvements include the introduction of area detectors, in particular CCD detectors with high dynamic ranges; as well as major software improvements.

In mid-2011 Bruker AXS introduced the PHOTON 100 detector; the first CMOS active pixel sensor for laboratory crystallography. Since then, CMOS technology has been rapidly displacing CCD detectors and a large number of D8 QUEST and D8 VENTURE systems are now used in laboratories throughout the world.CMOS technology offers numerous advantages compared to CCD detectors:

- CMOS sensors are available in larger sizes
- CMOS sensors have lower power consumption than CCDs and provide excellent signal-to-noise ratios even when only moderately cooled. This allows the design of air-cooled detectors.

CCD detectors and imaging plates operate in the conventional still-image mode involving numerous shutter-open/shutter-close, goniometer ramp-up/ramp-down and detector readout steps. Next to overhead-time this process introduces mechanical jitter. The PHOTON 100 detector can now operate in a completely shutterless read-out mode. This enables continuous data collection without the need to frequently open and close the X-ray shutter, resulting in less mechanical wear and faster, more accurate measurements.

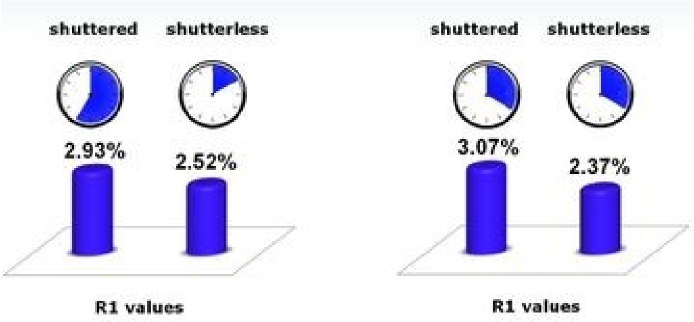

Figure 1. shutterless, continuous-scan mode allows for more efficient experiments at same or better data quality (left) or greatly improved data quality at same time as compared to shuttered mode

XRPD Solutions to Industrial Application Fields

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The paper aim is to describe how XRPD (X-Ray Powder Diffraction) analytical technique can be applied to industrial applications as a reliable tool for quality assurance and quality control practices. All the developed solutions take advantage of the main features of XRPD as structure determination and QPA (quantitative phase analysis) moreover it is a non-destructive. In this paper are taken into account manufacturing, pharmaceutical and health hazard applications.

In manufacturing processes, XRPD is successfully used to determine residual stress [1] and retained austenite [2]. Residual stresses are the compressive and tensile stresses that remain in a material once an external load has been applied. Most of the manufacturing processes (mechanical, thermal, chemical), which leads to inhomogeneous deformation, inhomogeneous volume changes, etc. induce residual stresses into components. The extent of induced residual stress depends on the process. Effects vary from “near surface” region, caused by machining, grinding, etc., to inner component regions caused by casting, welding, heat-treatment, etc.

Austenite is a very useful structural constituent of advanced high-strength steels. Its ability for strengthening in many different ways offers possibilities to obtain a unique range of mechanical and technological properties thus its amount (retained austenite) need to be determined. An especially important feature of austenite phase is its ability to transform to martensite or to form twinned microstructures during straining.

In health hazard field, XRPD is successfully used to quantify silica dust concentration. Silica is one of the most common minerals in the earth crust and can be found in three crystalline forms (polymorphs): quartz, cristobalite and tridymite. Nowadays, it is well known that crystalline silica dust inhalation can cause both silicosis and lung cancer, being a health hazard especially for mining, construction and foundry workers. In order to prevent occurrence of pathologies, several national and international norms regulate the occupational exposure to silica dust [3], by defining procedures for sampling airborne particles on filters and their concentration estimation. XRPD is particularly effective for quantification of silica dust concentration on filters: in fact, on the one hand each polymorph can be investigated and quantified; on the other hand potential occurrence of interfering crystalline mineral phases is detected.

In Pharmaceutical field, XRPD is successfully used to determine the crystal structure the presence and the relative amounts of different polymorphs and crystallinity degree.

Solid-state properties of drugs is a major contributing factor to both bioavailability and formulation characteristics. Most pharmaceutical drugs are solids and exist in many different physical forms, including amorphous, polymorphic crystalline or hydrated forms. The polymorphism, is one of the most important solid state properties of drugs because it can affect the pharmaceutically, important chemical and physical properties, such as melting point, chemical reactivity, solubility, dissolution rate and tableting behavior. XRPD is a powerful tool to identify different phases by their unique diffraction pattern.

[1] UNI - UNI EN 15305, Non-Destructive Testing - Test Method for Residual Stress Analysis by X-Ray Diffraction.
[2] ASTM E975-13, Standard Practice for X-Ray Determination of Retained Austenite in Steel with Near Random Crystallographic Orientation, ASTM International, West Conshohocken, PA, 2013.
[3]NIOSH 7500, OSHA ID 143, MDHS 14/3, UNICHIM 2398

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* COMMERCIAL PRESENTATIONS

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