

MS31 O1

Obtaining integrated intensities for powder and granular materials Jon Wright *ESRF, BP-220, Grenoble 38043, France.* E-mail: wright@esrf.fr

Keywords: New powder diffraction techniques, powder and single crystal diffraction, Bragg intensity.

Integrated intensities which are extracted from powder data tend to be corrupted by the peak overlap problem. A variety of methods can be used to reduce this overlap problem by comparing several powder patterns. Eventually one has to guess how to partition the remaining overlaps in order to obtain a set of $F(hkl)$ data. A likelihood based approach for dealing with this problem of overlapped powder data will be described [1]. The method has shown promising results in the application to severely overlapped data from powder protein samples.

Individual grains in powder specimens often give rise to diffraction spots when measured with a 2D area detector and microfocussed x-ray beam. Provided individual grains can be indexed, the problem of 2D spot overlap then replaces the problem of 1D peak overlap, and can be treated similarly.

[1] Wright, J. P., Markvardsen, A. J. and Margiolaki, I., *Z. Kristallogr.* *accepted*.

MS31 O2

Molecular envelopes from Protein Powder Diffraction Data C. Besnard^a, J. P. Wright^b, I. Margiolaki^b, S. Basso^a, F. Camus^a, A. N. Fitch^b, G. Fox^b, P. Pattison^{a,c}, M. Schiltz^a *Laboratoire de Cristallographie, École Polytechnique Fédérale de Lausanne (EPFL) Switzerland* ^b *European Synchrotron Radiation Facility (ESRF).* ^c *Swiss-Norwegian Beamlines (SNBL) at the ESRF.* E-mail: celine.besnard@epfl.ch

Keywords: Powder Diffraction, Protein Structure Determination, Isomorphous Replacement.

The preparation of single crystals suitable for x-ray analysis is frequently the most difficult step in structural studies of proteins. If a microcrystalline powder sample can be obtained, de novo solution of the crystallographic phase problem can be achieved at low resolution via, for instance, the isomorphous replacement method. With synchrotron radiation and optimized instrumentation, high-quality powder patterns have been recorded from which it was possible to generate phase information for structure factors up to 6 Å resolution. pH- and radiation-induced anisotropic lattice changes were exploited to reduce the problem of overlapping reflections, which is a major challenge in protein powder diffraction. The resulting data were of sufficient quality to compute molecular envelopes of the protein molecule and to map out the solvent channels in the crystals, which are essential structural data for the characterization of microcrystalline proteins as novel mesoporous materials.

MS31 O3

In-situ neutron diffraction and gravimetric studies of H₂ cycling in hydrides William David^{a,b}, Marco Sommariva^a, Martin Jones^b, Simon Johnson^b and Peter Edwards^b, *ISIS Facility, Rutherford Appleton Laboratory,*

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Keywords: hydrogen storage, neutron powder diffraction, gravimetric analysis

The safe and efficient storage of hydrogen is recognised as one of the key technological challenges in the transition towards a hydrogen-based energy economy. While hydrogen is stored at present principally using cryogenics or high-pressure, it is thought that the eventual solution may be a third way based upon novel condensed phase hydride stores. However, the multiple target criteria necessary for the successful implementation of such stores have not yet been met by any single material.

Simultaneously combining high storage capacity (>6wt% H₂) with a relatively low release temperature (<150°C), complete reversibility of the thermal absorption/desorption cycle and also low toxicity / low cost is a difficult conundrum. All these scientific factors are intimately linked to the crystal structure of the hydrogen store and thus understanding hydrogenation requires a full structural description coupled with a detailed study of the physical and chemical properties of the absorption/desorption process of the system. To achieve this, we have recently developed a technique that allows us to perform simultaneous structural and gravimetric measurements on the GEM and HRPD diffractometers at the spallation neutron source, ISIS. The equipment, IGAⁿ, is based upon the Intelligent Gravimetric Analyser developed by Hiden Isochema Ltd. (UK).

This combined approach to the study of hydrogen absorption and desorption is extremely powerful; On the one hand, neutron diffraction, because of its sensitivity to hydrogen, is an ideal tool for the study of crystal structures of hydride while gravimetric analysis is an extremely precise tool for measuring mass change and thus monitoring hydrogen absorption and desorption under controlled temperature and pressure. We report here detailed absorption and desorption measurements on a number of systems that include the benchmark material Mg/MgD₂ and also the new Li₃N - Li₂ND - LiND₂ system. Our studies of Mg/MgD₂ confirm the consistency of results obtained from neutron diffraction and gravimetric analysis while our results on the Li₃N - Li₂ND - LiND₂ system reveal new mechanisms for both hydrogen absorption and desorption.

MS31 O4

Investigating Ionic Conductors by Powder Diffraction Hans Boysen, *Department of Earth and Environmental Sciences, Section Crystallography University of Munich, Germany.* E-mail: boysen@lmu.de

Keywords: ionic conductivity, neutron powder diffraction, diffusion

High ionic conductivity in solids plays an important role in technological applications such as in batteries, fuel cells, gas sensors, catalysts, etc. Valuable information to understand the underlying diffusion mechanisms can be gained from powder diffraction experiments, preferably with neutrons and under *in situ* (operating) conditions (high temperature, electric field). Analysis of the refined

average structure reveals the distribution of the ions as described by the probability density function, which can be obtained either by Fourier transformation of the Debye Waller factor (including anharmonic terms [1]) or by Fourier methods. The former is more appropriate for interstitial diffusion processes, i.e. when the migration of the ions proceeds directly to adjacent vacant sites. In this case a continuous density is found directly representing the diffusion pathway. Moreover, by applying Boltzmann statistics effective single particle potentials can be derived containing the potential barriers to migration which can be compared with otherwise measured activation energies. On the other hand, if interstitialcy (exchange) processes prevail, it is more meaningful to analyse difference Fourier maps and/or to introduce additional (metastable) positions. All this will be illustrated by various examples. For fluorite like ZrO_2 doped with cations and anions (e.g. Sc and N [2]) one generally finds anion diffusion pathways directly through an edge of the surrounding cation tetrahedron along $\langle 100 \rangle$ to a neighbouring site. Derived activation energies agree with those obtained from conductivity measurements showing that no additional energy is needed for the creation of defects. By comparing samples with and without N it is possible to derive separate activation energies for O and N. In perovskite like $LaGaO_3$ doped with Mg and Sr the pathways are curved. These and the corresponding potentials are significantly altered when measured under electric fields [3] or microwave irradiation [4]. An example of interstitialcy diffusion is provided by mayenite ($Ca_{12}Al_{14}O_{33}$) [5]. Its structure may be described as a calciumaluminate framework containing 32 of the 33 O atoms, while the remaining "free" oxygen statistically occupies 1/6 of larger cages in the structure. In spite of the presence of vacancies and rather large openings between adjacent cages no continuous density was found, therewith ruling out interstitial diffusion (probably because of too long jump distances). On the other hand, difference Fourier maps revealed various other weakly occupied positions which can be related to an exchange process with particular framework O. Moreover, each jump process is connected with a relaxation of Ca, i.e. there is considerable interaction with the framework. Interestingly, the mechanism is different when the "free" O is replaced by N, i.e. nitrogen shows the interstitial type of diffusion within the same framework.

[1] Boysen H. *Z. Kristallogr.* 2003, 218, 123.

[2] Lerch M., Boysen H., Rödel T.C., Kaiser-Bischoff I., Hoelzel M., Senyshyn A. *Z. Kristallogr.* 2007, in press.

[3] Guenter M.M., Boysen H., Corte C., Lerch M., Suard E. *Z. Kristallogr.* 2005, 220, 218.

[4] Guenter M.M., Korte C., Brunauer G., Boysen H., Lerch M., Suard, E. *Z. anorg. allg. Chemie* 2005, 631, 1277. [5] Boysen H., Lerch M., Stys A., Senyshyn A. *Acta Cryst. B*, submitted.

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MS31 O5

Remarkable microstructure evolution in biogenic crystals upon mild annealing Emil Zolotoyabko^a, Boaz Pokroy^a, Andy Fitch^b, ^a*Department of Materials Engineering, Technion-Israel Institute of Technology, Haifa, Israel.* ^b*ESRF, Grenoble, France.*
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Keywords: Biomineralization, Microstructure, Powder Diffraction

By using high-resolution X-ray powder diffraction at a dedicated synchrotron beam line ID-31 at ESRF (Grenoble, France) we studied structural and microstructural modifications in biogenic calcium carbonate crystals, calcite and aragonite, obtained from different mollusk shells and subjected to heat treatments at elevated temperatures. The usage of the advanced analyzing optics on the diffraction beam resulted in diffraction spectra of superior quality and above all in narrow diffraction peaks with an instrumental contribution to the peak widths not exceeding 0.004° . The measured X-ray powder diffraction profiles were treated with the aid of the Rietveld refinement within the GSAS program and the EXPGUI interface. As a result, the structural parameters were extracted with the highest possible precision (about 10 ppm for lattice parameters). All investigated shells revealed anisotropic lattice distortions of the unit cell [1] as compared to geological aragonite [2]. In both biogenic calcite and aragonite the maximal distortions reached about 0.2% along the *c*-axis. Analysis of the complete set of experimental findings allowed us to unequivocally attribute the discovered lattice distortions to intracrystalline biomacromolecules confined within individual crystallites. Strong support for this conclusion is given by the results of structural measurements in samples subjected to mild short-period annealing at temperatures of 150-200 °C. At these temperatures, pronounced lattice relaxation due to the heat-induced degradation of organic macromolecules occurs [3]. Analysis of diffraction peak shapes fitted to Voigt functions allowed us to separate the contributions to peak widths caused by the finite crystallite size and microstrain fluctuations. This analysis revealed that at room temperature the crystallite sizes are highly anisotropic. Upon annealing, a drastic reduction of the crystallite sizes occurs that causes substantial broadening of the X-ray diffraction peaks clearly resolved by a naked eye. The peak broadening is well correlated with the lattice relaxation mentioned. The reduction of crystallite size is also correlated with the growth of averaged microstrain fluctuations due to increasing number of intercrystalline boundaries. These findings allowed us to suggest a model of the biogenic crystal development as a result of the amorphous/crystalline phase transformation within the network of oriented biomacromolecules.

[1] Pokroy B., Quintana J.P., Caspi E.N., Berner A., Zolotoyabko E., *Nature Mater.* 2004, 3, 900.

[2] Caspi E.N., Pokroy B., Lee P., Quintana J.P., Zolotoyabko E. *Acta Cryst. B* 2005, 61, 129.

[3] Pokroy B., Fitch A.N., Zolotoyabko E. *Adv. Mater.*, 2006, 18, 2363.