

**MS46.27.3***Acta Cryst.* (2005). A61, C62**In-situ Observation of Elementary Growth Steps on a Protein Crystal, Surface Diffusion of Protein Molecules and Dislocations inside a Protein Crystal**

Gen Sazaki<sup>a, b</sup>, Masashi Okada<sup>a, b</sup>, Takuro Matsui<sup>c</sup>, Hideo Higuchi<sup>d</sup>, Tomonobu Watanabe<sup>d</sup>, Katsuo Tsukamoto<sup>e</sup>, Kazuo Nakajima<sup>a</sup>, <sup>a</sup>*IMR, Tohoku Univ., Japan.* <sup>b</sup>*CIR, Tohoku Univ., Japan.* <sup>c</sup>*ATRL, Matsushita Electric Ind. Co., Ltd., Japan.* <sup>d</sup>*TUBERO, Tohoku Univ., Japan.* <sup>e</sup>*Grad. School Sci, Tohoku Univ., Japan.* E-mail: sazaki@imr.tohoku.ac.jp

To elucidate the mechanisms of defect formation in protein crystals, one has to observe in-situ 1) behaviors of individual protein molecules in the vicinity of crystal surface, 2) consequent movements of elementary growth steps, and 3) defects formed in a crystal.

For the process 1), we have applied a single molecule imaging technique, which is popular in the field of biological physics. Using fluorescence labeled lysozyme molecules, we have succeeded in observing individual lysozyme molecules diffusing in the vicinity of tetragonal lysozyme crystals in situ, for the first time. We found that the diffusivity of lysozyme molecules close to the crystal surface is 4 orders of magnitude smaller than that in a bulk solution.

For the process 2), we have combined laser confocal microscopy (LCM) with differential interference contrast microscopy (DIM), and succeeded in observing elementary growth steps (5.6 nm in height) non-destructively [1]. Using this LCM-DIM system, now we are observing bunching processes of elementary growth steps.

For the process 3), we have applied LCM-DIM and phase contrast microscopy, and succeeded in observing dislocations normal to an incident light and inclusions in-situ during growth.

[1] Sazaki G., et al., *J. Crystal Growth*, 2004, **262**, 536.

**Keywords:** protein crystallization, confocal laser scanning microscopy, near-field optical microscopy

**MS46.27.4***Acta Cryst.* (2005). A61, C62**Interface Crystallography of a Growing Interface: KDP{101} and {100}**

Elias Vlieg, Daniel Kaminski, *IMM Dept. of Solid State Chemistry, Radboud University Nijmegen, The Netherlands.* E-mail: e.vlieg@science.ru.nl.

In crystal growth from solution, the solvent is often found to determine the morphology of the crystal or the particular polymorph that is formed. Using in situ X-ray diffraction it is possible to determine the atomic-scale structure at a solid-liquid interface [1], and thus one can try to determine the microscopic origin of the solvent effect.

Here we present our results on the solid-liquid interface structure of the {101} and {100} faces of KDP (KH<sub>2</sub>PO<sub>4</sub>) in aqueous growth solutions as a function of the solution pH. The morphology of KDP crystals changes as a function of the pH, the largest effect coming from a decrease in growth velocity of the {101} face for non-stoichiometric conditions. Using the high-intensity X-ray beams from the ESRF synchrotron, we find remarkably large changes in the liquid ordering as a function of pH for the {101} face, while the {100} face is largely unchanged. For high pH, we observe crystalline pre-ordering of K-ions in the solution at the {101} face.

The KDP{101} face terminates in a positive K-layer, but our results indicate that an electrochemical interpretation of the interface is less correct than a crystallographic point of view.

[1] Vlieg E., *Surf. Sci.*, 2002, **500**, 458

**Keywords:** crystal growth, solid-liquid interface, surface X-ray diffraction

**MS46.27.5***Acta Cryst.* (2005). A61, C62**X-ray Diffractometer for In-situ and Real-time Monitoring of MOCVD**

Alexander Kharchenko<sup>a</sup>, Johannes Bethke<sup>a</sup>, Joachim Woitok<sup>a</sup>, Klaus

Lischka<sup>b</sup>, Klaus Schmidegg<sup>c</sup>, Alberta Bonanni<sup>c</sup>, Clemens Simbrunner<sup>c</sup>, Helmut Sitter<sup>c</sup>, <sup>a</sup>*PANalytical B.V., Almelo, The Netherlands.* <sup>b</sup>*University of Paderborn, Paderborn, Germany.* <sup>c</sup>*Institute of Semiconductor and Solid State Physics, Johannes Kepler University Linz, Austria.* E-mail: Alexander.Kharchenko@PANalytical.com

X-ray diffraction is a well-established, non-destructive, standardless tool for the analysis of epitaxial structures. We will present a new X-ray diffractometer that enables *in-situ* and *real-time* monitoring of metal-organic chemical vapour deposition (MOCVD). X-ray diffraction is a promising technique for *in-situ* monitoring of MOCVD growth because reflection high-energy electron diffraction, most frequently used for molecular beam epitaxy, cannot be applied in the MOCVD chambers due to high ambient pressure.

Our diffractometer uses a conventional X-ray source, it has no parts mounted inside the growth reactor and precise adjustment of the samples is not necessary. Therefore, it can be easily attached to a standard MOCVD reactor without the reactor chamber having to be significantly redesigned.

We will report on *in-situ* X-ray measurements on the nitride epitaxial structures during their growth in a standard AIXTRON single wafer MOCVD system. Using our diffractometer we were able to measure the growth rate and the composition in less than 20 seconds. In addition we could monitor the thermal expansion during heating and the strain relaxation in the epilayer as soon as the critical thickness was reached.

**Keywords:** X-ray diffraction, MOCVD, *in-situ* X-ray diffractometer

**MS47 NOVEL MATERIALS UNDER HIGH PRESSURE**

**Chairpersons:** Colin Pulham, Nancy Ross

**MS47.27.1***Acta Cryst.* (2005). A61, C62**Synthesis of Nano-polycrystalline Diamond and Related Hard Materials using Multianvil Apparatus**

Tetsuo Irifune<sup>a</sup>, Hitoshi Sumiya<sup>b</sup>, Hitoshi Yusa<sup>c</sup>, Toru Inoue<sup>a</sup>, <sup>a</sup>*Geodynamics Research Center, Ehime University, Matsuyama, Japan.* <sup>b</sup>*Sumitomo Electric Industries Ltd., Itami, Japan.* <sup>c</sup>*National Institute for Materials Science, Tsukuba, Japan.* E-mail: irifune@dpc.ehime-u.ac.jp

We synthesized pure polycrystalline diamond by direct conversion of graphite in multianvil apparatus, which turned out to be made of sintered nano-grains of cubic diamond and to possess very high Knoop hardness of 130-140 GPa [1]. Two distinct fine textures were recognized in TEM observations of the present diamond; granular particles with 10-20 nm and tabular crystals with dimensions of 100-200 nm in the elongated direction. The former crystals are interpreted to be formed via a nucleation and growth mechanism, while the latter parts may be formed by the two-step martensitic transitions [2].

Some mechanical tests have been conducted on thus synthesized polycrystalline diamonds, which exhibited significantly high abrasion resistance. Attempts to make sintered bodies of polycrystalline diamond with various forms of carbon, including carbon nanotubes, flurene, glassy carbon, etc. have been made using the present technique.

[1] Irifune T., Kurio A., Sakamoto S., Inoue T., Sumiya H., *Nature*, 2003, **421**, 599. [2] Sumiya H., Irifune T., *J. Mat. Sci.*, 2004, **39**, 445.

**Keywords:** diamond, multianvil apparatus, hard material

**MS47.27.2***Acta Cryst.* (2005). A61, C62-C63**Combined Diffraction and Raman Studies on Incommensurately Modulated Host-guest Structures of Elements**

Olga Degtyareva, *Geophysical Laboratory, Carnegie Institution of Washington, USA.* E-mail: o.degtyareva@gl.ciw.edu

Since their discovery in Ba in 1999 [1], the incommensurate host-guest structures have been found in a series of elemental metals at high pressures [2], consisting of two interpenetrating components

incommensurate with each other along one direction. The group-V elements Bi, Sb and As are shown to have similar host-guest structures in their high-pressure phases [3], where both components exhibit displacive modulations [4].

Using synchrotron x-ray diffraction and diamond anvil cells, we study the host-guest structures of Sb and As under pressure [5-6], and find an incommensurate-to-incommensurate phase transition with change in symmetry from monoclinic to tetragonal in both host and guest components. In our Raman spectroscopy studies on lattice dynamics of these metallic phases we observed five modes with the frequencies in the range of 90-200  $\text{cm}^{-1}$  for Sb, shifting to higher values with pressure increase. We analyze the Raman modes with the help of first-principles calculations for commensurate approximants [6].

[1] Nelmes R.J., Allan D.R., McMahon M.I., Belmonte S.A., *Phys. Rev. Lett.*, 1999, **83**, 4081. [2] McMahon M.I., Nelmes R.J., *Z. Kristallogr.*, 2004, **219**, 742, and references therein. [3] McMahon M.I., Degtyareva O., Nelmes R.J., *Phys. Rev. Lett.*, 2000, **85**, 4896. [4] Degtyareva O., McMahon M.I., Nelmes R.J., *High Pres. Res.*, 2004, **24**, 319. [5] Degtyareva O., McMahon M.I., Nelmes R.J., *Phys. Rev.*, 2004, **B 70**, 184119. [6] Degtyareva O., Struzhkin V.V., Caracas R. et al., 2005, to be published.

**Keywords:** high pressure phases, Raman spectroscopy, incommensurate structures

#### MS47.27.3

*Acta Cryst.* (2005). A61, C63

#### High-pressure Behavior of Feldspathoids: the Case of Analcite

G. Diego Gatta<sup>a</sup>, F. Nestola<sup>b</sup>, T. Boffa Ballaran, <sup>a</sup>Department of Earth Sciences, University of Milan, Italy. <sup>b</sup>Bayerisches Geoinstitut, Bayreuth, Germany. E-mail: diego.gatta@unimi.it

Feldspathoids are low silica minerals and, similar to zeolites, have large openings in the crystal structure. Elastic and structural behaviour of a natural cubic feldspatoid analcite ( $\text{NaAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$ ) was investigated up to 8.5 GPa by *in situ* single-crystal X-ray diffraction. A first-order phase transition was observed at  $P = 0.98 \pm 0.07$  GPa. Lattice parameters and reflection conditions show that the HP-polymorph has a  $P \bar{1}$ , Sp. Gr. Volume data of the low- $P$  (cubic) and high- $P$  (triclinic) polymorphs were fitted with a second- and third-order Birch-Murnaghan Equation of State [1], respectively. The refined elastic parameters are:  $V_0 = 2571.2(4) \text{ \AA}^3$ ,  $K_{T0} = 56(3)$  GPa and  $K' = 4$  (fixed), for the cubic polymorph,  $V_0 = 2613(10) \text{ \AA}^3$ ,  $K_{T0} = 18(1)$  GPa and  $K' = 7.2(7)$ , for the triclinic polymorph. The elastic behaviour of the HP-polymorph, calculated on the basis of the linearised bulk moduli, appears to be strongly anisotropic ( $K(a):K(b):K(c) = 2.07:1.36:1.00$ ). Tetrahedral tilting produces the main deformation mechanism in response of the cubic  $\rightarrow$  triclinic phase transition. The distortion of the secondary building units gives rise to a change of the 8- and 6-ring channels ellipticity. As a consequence, the extra-framework topological configuration changes: it appears in fact that the coordination number of part of the Na atoms becomes 7 ( $2\text{H}_2\text{O} + 5$  framework oxygens) instead of 6 ( $2\text{H}_2\text{O} + 4$  framework oxygens).

[1] Birch F., *Phys. Rev.*, 1947, **71**, 809.

**Keywords:** analcite, high-pressure, compressibility

#### MS47.27.4

*Acta Cryst.* (2005). A61, C63

#### New High-pressure Forms of Simple Salts-sulfates, Formates, and Acetates

David R. Allan, School of Chemistry, The University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ, UK. E-mail: D.R.Allan@ed.ac.uk

Over the last few years, we have been studying the effects of high pressure on the structures of a variety of molecular compounds that include: simple organic compounds [1], pharmaceuticals [2], amino acids [3], and simple inorganic compounds such as the oxoacids and their hydrates [4]. All of these systems have been studied principally with single-crystal x-ray diffraction techniques in combination with diamond-anvil cells (DAC). Methods for studying single crystals in

DACs include growth of single crystals *ex situ* followed by loading into the DAC or growth of single-crystals *in situ* from the melt. Both of these methods suffer from disadvantages and so we have recently developed methods for the high-pressure *in situ* growth of single crystals from solution [Ref]. Using these methods, we have studied the high-pressure recrystallisation of the sodium salts of the simple carboxylic acids, formic acid and acetic acid, and of the sodium salt of sulfuric acid. All of these compounds form previously unobserved hydrate phases at high pressure. For the new sodium sulfate hydrate phase, the growth of the single-crystal occurred *via* a high-pressure/high-temperature chemical reaction and its structure is certainly the most complex of all five known phases of  $\text{Na}_2\text{SO}_4$ , or its two previously observed hydrates,  $\text{Na}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$  and  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ . These sulfates are all geologically relevant and so the identification of this new high-pressure phase is likely to be highly significant.

[1] Allan D.R. et al., *Chem. Commun.*, 1999, 751. [2] Fabbiani P.A. et al., *Chem. Commun.*, 2003, 3004. [3] Moggach S.A., et al., *Acta Cryst.*, 2005, **B61**, 58. [4] Allan D.R. et al., *Dalton Communications*, 2002, **8**, 1867.

**Keywords:** high-pressure, crystal structure, small molecule

#### MS47.27.5

*Acta Cryst.* (2005). A61, C63

#### Hydrogen Storage in Molecular Compounds

Wendy Mao<sup>a</sup>, Ho-kwang Mao<sup>a,b</sup>, <sup>a</sup>Department of the Geophysical Sciences, University of Chicago. <sup>b</sup>Geophysical Laboratory, Carnegie Institution of Washington. E-mail: wmao@uchicago.edu

At low temperature ( $T$ ) and high pressure ( $P$ ), gas molecules can be held in ice cages to form crystalline molecular compounds that may have application for energy storage. We synthesized a hydrogen clathrate hydrate,  $\text{H}_2(\text{H}_2\text{O})_2$ , that holds 50 g/liter hydrogen by volume or 5.3 wt %. The clathrate, synthesized at 200–300 MPa and 240–249 K, can be preserved to ambient  $P$  at 77 K. The stored hydrogen is released when the clathrate is warmed to 140 K at ambient  $P$ . Low  $T$  also stabilizes other molecular compounds containing large amounts of molecular hydrogen, although not to ambient  $P$ , e.g., the stability field for  $\text{H}_2(\text{H}_2\text{O})$  filled ice (11.2 wt % molecular hydrogen) is extended from 2,300 MPa at 300 K to 600 MPa at 190 K, and that for  $(\text{H}_2)_4\text{CH}_4$  (33.4 wt% molecular hydrogen) is extended from 5,000 MPa at 300 K to 200 MPa at 77 K. These unique characteristics show the potential of developing low- $T$  molecular crystalline compounds as a new means for hydrogen storage.

**Keywords:** hydrogen storage, molecular compounds, high pressure synthesis

#### MS48 MICROBEAM X-RAY SCATTERING

**Chairpersons:** Christian Riekkel, Atsuo Iida

#### MS48.27.1

*Acta Cryst.* (2005). A61, C63-C64

#### Microbeam Diffraction of Hierarchical Nanocomposites

Oskar Paris<sup>a</sup>, Peter Fratzl<sup>a</sup>, Aurelien Gourrier<sup>a</sup>, Himadri Gupta<sup>a</sup>, Wolfgang Wagermaier<sup>a</sup>, Dieter Loidl<sup>b</sup>, Herwig Peterlik<sup>b</sup>, Manfred Burghammer<sup>c</sup>, Christian Riekkel<sup>c</sup>, <sup>a</sup>Max Planck Institute of Colloids and Interfaces, Potsdam, Germany. <sup>b</sup>University of Vienna, Austria. <sup>c</sup>ESRF, Grenoble, France. E-mail: Oskar.Paris@mpikg.mpg.de

Advanced composite materials with optimized mechanical properties are often hierarchically structured from the atomic/molecular level up to macroscopic length scales. Typical examples are biological tissues such as bone or wood, but also many complex technical composites, which often benefit from the imitation of natural materials by biomimetic principles or by biotemplating. Structural investigations of such materials require new experimental techniques with a position resolution covering several length scales. Beside electron microscopy, small- and wide-angle X-ray scattering (SAXS/WAXS) are well suited to study structural features in the nanometer regime. The high brilliance of third generation synchrotron radiation sources together with novel X-ray optics can be used to extend the position resolution to the micrometer regime by using microbeam scanning techniques in combination with SAXS/WAXS.

The present contribution reviews some recent experimental studies