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In Situ SAXS studies of Jarosite formation

Helen E. A. Brand,^{a,b} Nicola V. Y. Scarlett,^a Ian E. Grey,^a Robert Knott, Nigel Kirby,^c ^aCSIRO Process Science and Engineering, Clayton South, Vic. (Australia). ^bBragg Institute, ANSTO, Menai, NSW (Australia). ^cAustralian Synchrotron Clayton South, Vic. (Australia). E-mail: helen.brand@csiro.au

Jarosite group minerals, $\text{AFe}_3(\text{SO}_4)_2(\text{OH})_6$, (where A is typically K^+ , Na^+ or H_3O^+), and related minerals are of great importance to a range of mineral processing and research applications. They are used in the removal of iron species from smelting processes, they occur in metal bioleaching systems, bacterial conditioning in flotation circuits and they are present in acid mine drainage environments. Recently there has been a renewed interest in jarosite minerals with their detection on Mars and the realisation that they are likely an indicator of liquid water on the Martian surface and may hold clues as to the environmental history of the planet. Jarosites are also of considerable theoretical interest as model compounds for spin frustration in kagomé-Heisenberg antiferromagnetic materials.

Knowledge of the conditions of formation of these minerals is critical to the optimisation of these industrial processes and understanding of their potential environmental impacts. To this end we are engaged in a program to study the nucleation and crystallisation of these minerals.

Small Angle X-ray scattering (SAXS) gives us an insight into the size, shape and rate of growth of jarosite through nucleation. Modelling of these early-stage particles suggests they have an elliptical disc form and that the system undergoes one nucleation phase, followed by growth, with possible coalescing of the particles suggested by the late-stage development of correlations at high q .

Keywords: jarosite, SAXS, in situ synthesis

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New tools for the analysis of in-situ XRPD data: symmetry mode analysis, parametric rietveld refinement and MEM

Robert Dinnebier, *Max-Planck Institute for Solid State Research, Stuttgart (Germany)*. E-mail: r.dinnebier@fkf.mpg.de

Due to recent upgrades of synchrotron-sources and the parallel development of new position sensitive detectors it is now possible to collect a vast amount of powder diffraction patterns *in situ* in dependence on external variables with a time resolution in the second or even sub-second regime thus allowing to track many structural and microstructural changes. In order to evaluate this mass of data sophisticated algorithms and suitable software must be available.

Under the simple assumption that structural changes within a crystalline phase vary continuously upon external variables like temperature or pressure, it is possible to parameterize these changes by suitable functions. In this so-called surface or parametric refinement, all powder patterns are refined simultaneously, drastically reducing the number of parameters, thus leading to higher stability of the refinements and more accurate results. Generally, polynomials of low order proved

to be quite successful, in particular for data sets recorded at high pressure. On the contrary, in a consecutive Rietveld refinement, all refinable parameters are refined independently for all powder patterns, requiring high resolution and good counting statistics of the individual powder patterns, in order to avoid strong correlations and outliers.

Under certain premises, so called symmetry (also called distortion) modes can be parameterized¹ instead of using individual atomic coordinates. Modern user friendly computer programs based on group theory like ISODISPLACE² or AMPLIMODES³ are readily available. In case of displacive phase transitions, the application of this techniques allows for the direct determination of physical quantities like order parameters, spontaneous lattice strains, etc.⁴ Alternatively, certain types of framework structures where the application of external variables results in polyhedral tilts but not distortions, allow for further parameter reduction by parameterizing internal degrees of freedom of rigid bodies in z-matrix notation. Several comparative case studies will be presented.

Recently we developed a semi-automated computer program Powder3DParametric⁵ to ease the process of creating input files for sequential and parametric Rietveld refinement using the general least squares program Topas (Bruker AXS GmbH).

As a complementary approach to Rietveld analysis, in particular if static or dynamic disorder is present, the method of maximum entropy has been successfully applied to series of *in-situ* powder diffraction patterns. It will be demonstrated that the combination of structure factor amplitudes from pattern decomposition methods and phases from charge flipping enables an estimate of the "true" nature of the disorder in dependence on temperature without any strong bias from Rietveld refinement.

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Keywords: MEM, symmetry modes, parametric rietveld refinement

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A high energy view of structure in negative thermal expansion materials

Angus P. Wilkinson,^a Cody R. Morelock,^a Benjamin K. Greve,^a Leighanne C. Gallington,^a Andrew C. Jupe,^a Karena W. Chapman,^b Peter J. Chupas,^b ^aSchool of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, GA, (USA). ^bAdvanced Photon Source, Argonne National Laboratory, Argonne, IL, (USA). E-mail: aw42@mail.gatech.edu

High energy x-rays, when paired with appropriate sample environments, can be used to study a variety of interesting phenomena under non-ambient conditions. They simultaneously give good penetration, providing flexibility in sample cell design, and access to the high Q scattering data that is typically needed for local structure (Pair Distribution Function) studies. Some of the possibilities for non-ambient studies using high energy x-rays will be illustrated using our work on the evolution of average and local structure when various "ReO₃ type" $\text{M}(\text{O}/\text{F})_3$ phases, displaying thermal expansion ranging from strongly positive to strongly negative, are subjected to changes in temperature and pressure. Our low pressure measurements (< 300

MPa) of thermal expansion and phase behavior for some of these materials have made use of a new “Background reducing Internal Mask” to obtain Rietveld quality X-ray data from samples contained in substantial heated titanium pressure vessels. Our studies of local structure evolution in the negative thermal expansion material cubic ZrMo_2O_8 as it is heated at ambient pressure and amorphized on compression in a diamond anvil cell will also be discussed.

Keywords: high-pressure diffraction, thermal expansion, local structure

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Behavior of SiO₂ in helium pressure medium

Takehiko Yagi,^a Tomoko Sato,^a Nobumasa Funamori,^b ^a*Institute for Solid State Physics, University of Tokyo, Kashiwa (Japan).* ^b*Department of Earth and Planetary Science, University of Tokyo (Japan).* E-mail: yagi@issp.u-tokyo.ac.jp

Although helium has been widely used as a good hydrostatic pressure transmitting medium, it sometimes affects considerably to the compression behavior of minerals. Here we report an example that SiO₂ glass becomes quite “rigid” when compressed in helium. We have compressed SiO₂ glass in helium up to 10 GPa with a diamond-anvil cell [1]. Volume measurements of the bulk size show that SiO₂ glass is much less compressible than normal when compressed in a helium medium, and the volume in helium at 10 GPa is close to the normal volume at 2 GPa. X-ray diffraction and Raman scattering measurements suggest that interstitial voids in SiO₂ glass are prevented from contracting when compressed in helium. This is probably because a large amount of helium penetrates into these voids. The estimated helium solubility in SiO₂ glass is very high and is between 1.0 and 2.3 mol per mole of SiO₂ glass at 10 GPa, which shows marked contrast with previous models.

These results may affect discussions on the Earth’s evolution as well as interpretations of various high-pressure experiments, and also lead to the creation of new materials.

[1] T. Sato, N. Funamori, T. Yagi. 2011, to be submitted.

Keywords: SiO₂ glass, helium, voids

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High-pressure polymorphism of ammonia hydrates

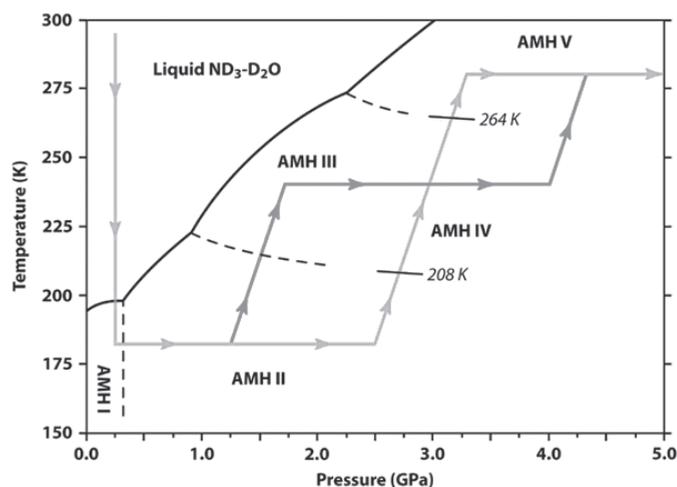
A. Dominic Fortes,^a Gareth Griffiths,^b Richard J. Needs,^b Christopher J. Pickard,^c Thomas Hansen,^d ^a*Department of Earth Sciences, University College London, (U.K.)* ^b*Theory of Condensed Matter Group, Cavendish Laboratory, Cambridge University, (U.K.)* ^c*Department of Physics and Astronomy, University College London, (U.K.)* ^d*Institut Laue Langevin, Grenoble, (France).* E-mail: andrew.fortes@ucl.ac.uk

Ammonia hydrates, $\text{NH}_3 \cdot n\text{H}_2\text{O}$ (where $n = \frac{1}{2}, 1, 2$), are likely to be major constituents of icy bodies in the outer solar system; their phase behaviour and physical properties up to pressures of several GPa are therefore relevant to modelling the structure and thermal evolution of such planetary objects [1]. We report the status of our program to investigate these properties using a combination of high-pressure powder diffraction (carried out at the ISIS neutron spallation source and the Institut Laue Langevin) and quantum mechanical calculations.

Calculations have provided us with predicted crystal structures, constrained only by the experimentally obtained unit-cell dimensions and contents, of both ammonia monohydrate phase II [2] and ammonia dihydrate phase II, as well as predicted structures of other high-pressure phases which can be tested against new powder diffraction data. Moreover, the elastic properties calculated by these methods are a direct complement to equations of state determined from high-pressure experiments [3], [4].

Most recently, we carried out an initial survey of the ammonia monohydrate phase diagram using a Paris-Edinburgh press on the high-intensity D20 beamline at the ILL. Neutron powder data collected over the five day study allowed us to fit an isothermal equation of state for ammonia monohydrate II over a range twenty times larger than previously measured, reproduced earlier observations [5] of phases IV and V, and constrained their phase transition pressures and temperatures (see figure below); ammonia monohydrate phase V was observed up to a pressure of 9 GPa. We will discuss the practical aspects of loading a volatile liquid sample into the CCR-mounted P-E press in use at the ILL, the nature and high quality of the data produced, and implications for our future studies of such systems at high pressure.

Figure 1 below shows the phase diagram of ammonia monohydrate, and the P-T path (pale line) followed during our December 2010 study at the ILL. The darker line shows the P-T path we propose to follow in future work.



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Keywords: polymorphism, diffraction, pressure

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Structural Evolution of $\text{Ca}_{0.4}\text{Sr}_{0.4}\text{Nd}_{0.2}\text{Mn}_{1-x}\text{Cr}_x\text{O}_3$; $0 \leq x \leq 0.2$ perovskites

Teck-Yee Tan,^a Qingdi Zhou,^a Brendan J. Kennedy,^a Qingfen Gu,^b Justin A. Kimpton,^b James R. Hester,^c ^a*School of Chemistry, The University of Sydney, New South Wales 2006, (Australia).* ^b*Australian Synchrotron, 800 Blackburn Road, Clayton, Victoria 3168, (Australia).* ^c*Bragg Institute, Australian Nuclear Science and Technology Organisation, Lucas Heights, NSW 2234, (Australia).* E-mail: ttan6692@uni.sydney.edu.au

A series of complex oxides of the type $\text{Ca}_{0.4}\text{Sr}_{0.4}\text{Nd}_{0.2}\text{Mn}_{1-x}\text{Cr}_x\text{O}_3$; x