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Keywords: SAXS, SANS, industrial

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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] *[a]CSIRO Process Science and Engineering, Clayton South, Vic. (Australia). [b]Bragg Institute, ANSTO, Menai, NSW (Australia). [c]Australian Synchrotron Clayton South, Vic. (Australia).* E-mail: helen.brand@csiro.au

Jarosite group minerals, $AFe_3(SO_4)_2(OH)_6$, (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 parameterized[1] instead of using individual atomic coordinates. Modern user friendly computer programs based on group theory like ISODISPLACE[2] or AMPLIMODES[3] 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 Powder3DParametric[5] 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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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] *[a]School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, GA, (USA). [b]Advanced 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 "ReO_3 type" $M(O/F)_3$ phases, displaying thermal expansion ranging from strongly positive to strongly negative, are subjected to changes in temperature and pressure. Our low pressure measurements (< 300