ISIS Experimental Report

Rutherford Appleton Laboratory

RB Number: 1010009

Date of Report: 12/08/2010

Title of Experiment: Recovery and characterisation of high-pressure phases in the systems H_2O – NH_3, H_2O – H_2SO_4, and H_2O – $MgSO_4$.

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Instrument: GEM

Experimental Team: A.D. Fortes, I. G. Wood, M. G. Tucker

Date of Experiment: 04/05/2010

Introduction: The objective of this experiment is to synthesise four particular high-pressure polymorphs of various hydrates discovered by us in recent years during work carried out using the Paris-Edinburgh cell on PEARL/HiPr (see Fortes *et al.*, 2009 and experiment reports for RB 820064, 920226, 920237, 920238. At present, the crystal structures of these materials are unknown. We proposed to synthesise: (*i*) ADH IV; (*ii*) SAT-III; (*iii*) the high-pressure phase formed by compression of epsomite to 12 kbar at 295 K; and (*iv*) the phase mixture formed by compression of meridianiite to 9 kbar at 240 K. After synthesis in the P-E press, each phase was to be quenched to 100 K, decompressed, and then recovered for analysis using the GEM diffractometer.

A detailed description of the sample synthesis method is provided in experimental report RB 1010008. The end product of this effort was three gasketted specimens, comprising sulfuric acid tetrahydrate phase III (SAT-III), ammonia dihydrate phase IV (ADH IV), and a phase or phase mixture formed by compression of epsomite, similar to that seen previously on PEARL/HiPr under loads of 22-31 tons (see RB 920237). This last specimen was not the one we had proposed to make; time constraints forced us to hurry the compression of our epsomite specimen, with the outcome that we missed the narrow phase field for which we were aiming. The proposed meridianiite specimen, although loaded and kept in cold storage, was not used due to lack of time.

Experimental method: The gasketted samples were stored in a pool of liquid nitrogen in a spare P-E cell cryotank until use. For analysis on GEM, these were transferred – under liquid nitrogen - into a bespoke aluminium foil pouch screwed onto the end of a centre stick. The stick was inserted into a CCR mounted on the GEM beamline, and data from all three specimens were collected initially at 100 K. Since we were aware that some of these specimens were strongly textured (particularly the SAT-III), by examining the variations in reflection intensity around the arc of 90° detectors on PEARL/HiPr, we collected data from the gasketted specimens in several orientations. This was achieved by the simple expedient of lifting the centre stick, turning it through 45°, and dropping it back down. Full datasets were then collected upon cooling to 20 K for SAT-III and epsomite. The ADH IV specimen produced no obvious signal, either crystalline or amorphous; we concluded that the specimen was either lost somehow during storage, or else was not properly positioned in the neutron beam.

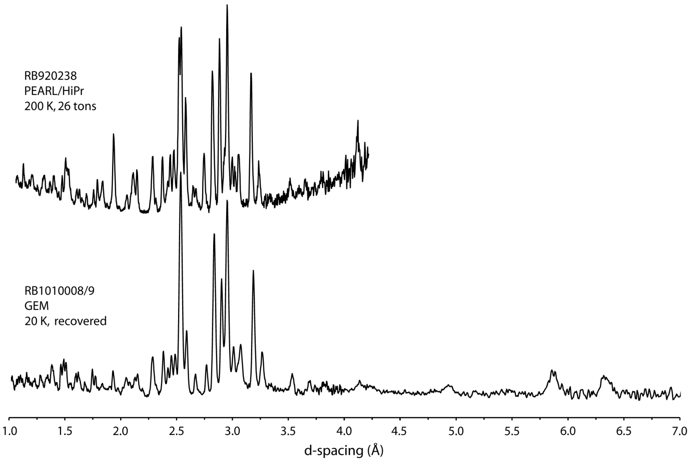
All three specimens were removed from the beamline under liquid nitrogen and preserved in a low-loss dewar for possible future analysis.

A total of 825 μAhr (5 hours) were integrated on SAT-III and 892 μAhr on the high-pressure epsomite phase.

Results:

Removing the gasketted samples from the P-E press for analysis on GEM firstly eliminates the undesireable absorption caused by the through-anvil geometry used on PEARL/HiPr. As seen in Figure 1, the improvement in the increasingly noisy data at d-spacings longer than 3.5Å is significant. We can now observe reflections to conderably longer d-spacings; in the case of SAT-III, this greatly increases our confidence in the unit-cell indexing that we had obtained previously.

Figure 1: Comparison of the zero-pressure 20 K SAT-III diffraction pattern collected on GEM (bottom) with the same material under load on PEARL/HiPr (top). The upper diffraction pattern has been shifted in order to line up the Bragg peaks for easy visual comparison.



Attempts to solve the structure of SAT-III, and work to understand the phase behaviour of epsomite, using the new powder data are ongoing. We believe it will be useful to try and remove the specimens from their gaskets for grinding in future.

References: Fortes *et al.* (2009b): *J. Appl. Cryst.* **42**(5), 846-866.