ISIS Experimental Report

Rutherford Appleton Laboratory

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Title of Experiment: The high pressure phase IV of epsomite ($MgSO_4.7D_2O$).

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Instrument: POLARIS

Experimental Team: A. D. Fortes

Date of Experiment: 20-22/09/2006

Introduction: In a previous study of epsomite at high-pressure [1], a series of phase transitions were observed. These transitions are relatively sluggish, and below 1.5 GPa the phase behaviour is not clear from the coarse sampling. However, a single phase is stable from roughly 1.5 - 3.0 GPa. Although excellent data were collected from this phase on PEARL, a satisfactory indexing has thus far not been made. The purpose of the present work was to form the high-pressure phase in the P-E cell offline, quench it to liquid nitrogen temperatures, and attempt recovery at atmospheric pressure. The specimen would then be investigated on POLARIS unencumbered by the P-E cell; i.e., high-resolution backscattering data could be collected, and long d-spacing data collected in low-angle detectors. The new measurements, it was hoped, would allow indexing of the high-pressure phase.

Experimental: Fully deuterated epsomite crystals, grown from aqueous solution, were powdered in air at room temperature. In the first instance, five separate loadings of a V4 Paris-Edinburgh cell were carried out with epsomite powder (plus MeOD/EtOD) mounted in toroidal gaskets. After a load of 25 tons was applied, aluminium tape was stuck across the gap between the anvils to form a dam. Liquid nitrogen was poured into this cavity until the core of the breech became frosted (~ 30 minutes). The load was then released and the breech unscrewed, allowing the gasketed sample pellet to drop out into a tray of liquid nitrogen. The solid pellets were pushed out of the gasket ring and then dropped into an 8 mm vanadium can. The can was screwed to a cryostat centre stick and loaded into an Orange cryostat on the POLARIS beamline. Inspection of the diffraction pattern from the five pellets revealed that they were the familiar atmospheric phase of epsomite (Figure 1); that is, no phase transformation had occurred.

Another attempt was made using a toroidal gasket. In this second instance, a period of two hours was left between applying the load of 25 tons, and commencing the quenching process. Unfortunately, the pellet broke into several pieces during recovery, and only a fraction of the pellet (probably about one third) could be found in the nitrogen bath. Two small fragments were dropped into a vanadium can. The diffraction pattern from this specimen (Figure 2a) was clearly different to that of the low-pressure phase, and there are sufficient similarities to the pattern of phase IV seen on PEARL (Fig. 2c) to conclude that the high-pressure form had indeed been formed and quenched. However, the scattering was rather weak, and even after 20 hours of data collection, the pattern was too noisy to allow indexing.

A final attempt was made using encapsulated gaskets, the recovered gasketed sample being held in a 5 mm slab can. A further 20 hour integration failed to yield an improvement in observed signal to noise ratio (Figure 2b). Why it should be the case that an essentially identical specimen counted for the same amount of time should yield such a poor diffraction pattern on POLARIS compared with PEARL is not obvious.

Summary: The high-pressure phase of epsomite can be quenched back to atmospheric pressure, but the transition takes some time to occur, even at room temperature. The data collected on POLARIS are not adequate to allow indexing.

References

[1] Fortes et al., (2006) ISIS Experimental Report RB520039.
[2] Fortes et al., (2006) Eur. J. Min. 18, 449.

Figure 1: Rietveld refinement of the data collected from the first five recovered pellets using the structural model from an earlier study. The refined unit cell obtained here is *a* = 11.8972(4) Å, *b* = 11.9264(3) Å, *c* = 6.7976(2) Å, and V = 964.52(3) $Å^3$. Compare this with the values obtained at 85 K on HRPD [2]: *a* = 11.88891(9) Å, *b* = 11.91578(8) Å, *c* = 6.79126(10) Å, and V = 962.09(2) $Å^3$.

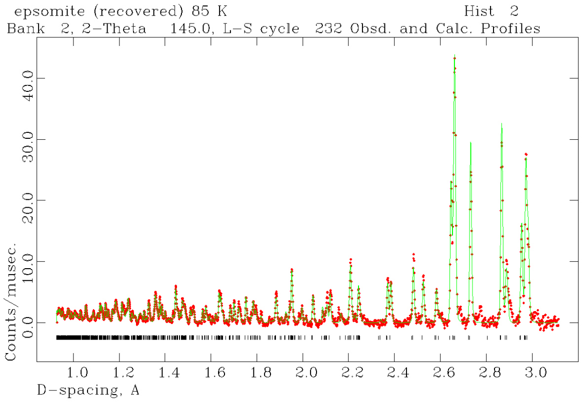

Figure 2. Diffraction patterns of high-pressure epsomite, in each case data are from detector banks at 2θ = 90°. (a) Small fragments recovered from between toroidal gaskets. (b) Sample contained in encapsulated gaskets in a slab-can. (c) Sample contained in encapsulated gaskets in the P-E cell on PEARL (RB520039). Red asterisks in (a) and (b) mark scattering from the vanadium windows of the cryostat, and in (c) are due to scattering from tungsten carbide and nickel in the anvils. If the phase observed in (a) and (c) *are* the same, then the shift (Δd/d ≈ ΔV/V) of the peak near 3.1 Å is consistent with a bulk modulus of ~ 27 GPa, in good agreement with the measured incompressibility of deuterated epsomite [2].