ISIS Experimental Report

Rutherford Appleton Laboratory

RB Number:	810197	**Date of Report:**	7th April 2009
Title of Experiment:	**Measurement of the thermoelastic parameters of mirabilite ($Na_2SO_4.10D_2O$)**	**Local Contact:**	K. S. Knight
Principal Proposer:	Dr. I. G. Wood	**Instrument:**	HRPD
Affiliation:	University College London		
Experimental Team:	H. E. A. Brand, I. G. Wood, A. D. Fortes, L. Vočadlo, K.S. Knight	**Date of Experiment:**	9th -13th March 2008

Introduction: Multiply hydrated salts, such as $Na_2SO4.10H_2O$ - the mineral mirabilite – are likely to be major 'rock-forming' minerals in the interiors of the solar system's large icy moons [1]. On Earth, mirabilite occurs in evaporites, often forming extremely thick deposits which are able to flow and form diapiric structures within sedimentary basins [2]. Whether we wish to model the behaviour of deeply lain evaporites on Earth, or to construct geophysical models of icy moons, it is necessary to know the phase behaviour and thermoelastic properties of mirabilite under the appropriate pressure and temperature conditions; for the large icy moons we are concerned with pressures up to ~ 5 GPa, and temperatures from 100 – 300 K. In a previous experiment [4,5] we measured the structure and thermal expansion of mirabilite between 4.2 and 300 K at atmospheric pressure. The purpose of the high-*P* study reported here was to allow measurement of the incompressibility of mirabilite and its temperature dependence.

Experimental Method: Crystals of fully deuterated mirabilite were grown from a supersaturated solution of Na_2SO_4 (Sigma Ultra) in D_2O (Aldrich). Large crystalline lumps were extracted from the mother liquor, dried, powdered and loaded into a TiZr pressure cell (during grinding and loading of the cell the apparatus was cooled in solid CO_2 to prevent dehydration). The cell was then sealed under a helium pressure of 478 bar and placed in a CCR on the HRPD beamline. The temperature was reduced to 260 K, and data were collected for 70 μAhr (Fig. 1). Data were then collected upon compression to 5.5 kbar in 500 bar steps, counting for 70 μAhr at each datum. At 5.5 kbar, the sample was cooled to 80 K in 20 K steps, counting for 60 μAhr at each point. Finally, the sample was decompressed at 80 K in ~600 bar steps from 5.5 – 0 kbar, again counting for 60 μAhr at each point. The diffraction patterns obtained were analysed using GSAS and the resulting unit-cell volumes fitted to a Birch-Murnaghan 3rd order equation-of-state (EOS) to obtain the incompressibility, K_0. As the diffraction patterns were very weak (Fig. 1), and the resulting $V(P)$ curves rather noisy, the value of K_0' (the first-derivative with respect to pressure) required in the EOS was fixed at 5.6, the value obtained in our recent *ab initio* simulations of mirabilite.

Results: There are no previous high-*P* experimental studies of mirabilite with which to compare this study. Table 1 compares the results with our *ab initio* simulations and with data for another hydrated salt, epsomite ($MgSO_4.7H_2O$).

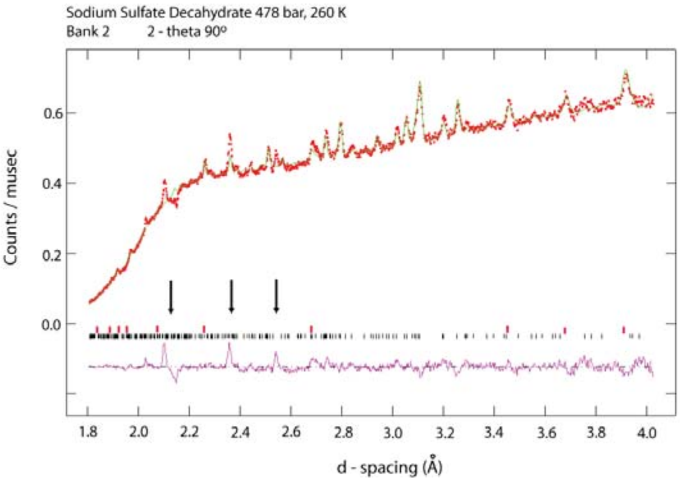

Figure 1 Neutron powder diffraction patterns of mirabilite at ~480 bar, 260 K obtained on HRPD in the 90° banks. The red circles are the observations, the green line the fit to the observations and the pink line below is the difference between the fit and the observations. The lower set of black tick marks denote the positions of the mirabilite peaks and the upper set the positions of D_2O ice Ih peaks. The black arrows denote peaks unaccounted for by either ice or mirabilite though to be due to components of the sample environment.

The values of K_0 obtained in this experiment are in excellent agreement with the *ab initio* simulations and similar to those for epsomite. The volume offset between the mirabilite simulations and experiments of approximately 2% is typical of such simulations. It is interesting that the bulk moduli of mirabilite and epsomite are so similar despite large differences in intermolecular bonding.

	Mirabilite			Epsomite 50 K Ref. [3]
	Simulation (athermal)	This Experiment		
		80 K	260 K	
V_0 (Å^3)	1468.6(9)	1440.2(4)	1456.7(6)	961.17 (7)
K_0 (GPa)	22.21(9)	22.7(6)	18.0(5)	25.0(2)
K_0'	5.6(1)	5.6	5.6	5.3

Table 1. EOS Parameters for mirabilite and epsomite.

References:[1] Kargel (1991) *Icarus* **94**, 368 - 390 [2]Colman *et al*.(2002) *Sed. Geol.* **148**, 61 -78 [3] Fortes *et al*. (2006) *Eur. J. Min*. **18**, 449 - 462 [4] RB610128 [5] Brand *et al*. (2009) *Phys. Chem. Min*. **36**, 29-46.