Structure determination of the 2.5 hydrate MgSO₄ phase by simulated annealing

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ABSTRACT

The crystal structure of the 2.5 hydrate MgSO₄ phase was determined by simulated annealing from laboratory X-ray powder diffraction data measured from 2–140 °2θ using CuKα radiation. The 2.5 hydrate is monoclinic, space group C2/c, with unit-cell parameters a = 18.8636(4) Å, b = 12.3391(2) Å, c = 8.9957(2) Å, β = 94.568(2)°, V = 2087.1(6) Å³, and Z = 16. The model was refined using fundamental-parameters Rietveld refinement, converging to Rwp = 8.89%, Rp = 6.61%, Rexp = 3.33%, Rrag = 3.95%, and χ² = 2.67. The refined structure is consistent with a formula of 2.5 H₂O. Bond-valence calculations for the refined model show that the structure is chemically sensible. In the refined structure, [Mg(O,H₂O)] octahedra and [SO₄] tetrahedra build up 2-D double-sheet slabs by sharing vertex O atoms, which are held together by inter-slab H-bonds involving (SO₄)²⁻ groups and H₂O molecules coordinated with Mg²⁺ cations to form the layer structure of the 2.5 hydrate phase.

Keywords: MgSO₄·2.5H₂O, MgSO₄·2.4H₂O, crystal structure, simulated annealing, structure determination, powder diffraction, Rietveld refinement

INTRODUCTION

Various hydrated magnesium sulfates, MgSO₄·nH₂O, are stable over a wide range of temperature-humidity conditions on the surface of Earth, most of which have been identified/synthesized and structurally characterized, e.g., n = 1 (kieserite; Aleksovska et al. 1998), n = 2 (sanderite; Ma et al. 2009), n = 4 (starkeyite; Baur 1964), n = 5 (pentahydrite; Baur and Rolin 1972), n = 6 (hexahydrite; Zalkin et al. 1964), n = 7 (epsonite; Calleri et al. 1984), and n = 11 (meridianiite; Peterson et al. 2007). At least since the time of the Mars Viking landers (Clark et al. 1976), magnesium sulfate hydrates have also been predicted to exist on the surface of Mars. This prediction was strengthened by chemical and spectroscopic data from recent missions (Bish et al. 2003; Feldman et al. 2003, 2004; Vaniman et al. 2004; Bibring et al. 2005; Gendrin et al. 2005; Chipera and Vaniman 2007; Mangold et al. 2008). The hydration states of magnesium sulfates and their distribution on the surface of Mars help to understand the history of water on this planet due to the sensitivity of hydrated magnesium sulfates to temperature and humidity. Knowledge of the crystal structures and stability relations for the MgSO₄·nH₂O series are necessary to infer which species can exist on the Martian surface and, if present, how much H₂O they may contain, how the H₂O is contained, and how stable the H₂O molecules are in the structure. The stabilities of hydrated magnesium sulfate phases have been experimentally investigated recently under conditions similar to those on the surface of Mars (Chipera and Vaniman 2007), and several previously unknown phases were obtained. One of these, referred to as the “unknown phase,” persisted through several experiments and appeared to contain ~2.4 H₂O. The structure of this phase is unknown and no crystallographic information is available in the International Center for Diffraction Data (ICDD) database. In this letter, we report the structure determination of this new hydrate of MgSO₄ from X-ray powder diffraction data measured on a synthetic sample.

EXPERIMENTAL METHODS

The starting material for synthesis of the unknown phase was an ultra-pure MgSO₄·6H₂O reagent that is principally hexahydrite at the temperature (T) and relative humidity (RH) conditions in our laboratory (Alfa Aesar Puratronic 99.997%, CAS 22189-08-8). In accord with the approximate T-RH field in the MgSO₄·6H₂O stability diagram (Chipera and Vaniman 2007), the unknown phase was prepared by maintaining the starting materials in the appropriate T-RH region in an environmental cell on the X-ray diffractometer, bypassing the formation of other intermediate hydrates. The diffractometer heating stage and flat-plate sample were maintained at 75 °C, and a mixture of H₂O and N₂ gas with 95% RH (at 23 °C) was generated and introduced into the environmental cell according to Chipera et al. (1997). The effective RH at 75 °C, ~14%, was calculated from the vapor pressure of H₂O according to the Harr steam tables. These synthesis conditions were maintained during controlled-atmosphere X-ray diffraction (XRD) measurements (2–70 °2θ, 0.02° steps, 4 s/step) to monitor the progression of phases. As the T-RH conditions for the unknown phase are significantly outside the stability field for hexahydrite, the solid first transformed into an amorphous phase from which the unknown phase subsequently formed within 4–8 h. This same specimen was used to collect XRD data for structure determination (2–140 °2θ, 0.02° step size, 12 s/step), during which time the XRD heating stage and sample were maintained at 75 °C. All diffraction data were measured using a Siemens D500 diffractometer with CuKα radiation, incident- and diffracted-beam Soller slits, and a KeveX PsI solid-state detector. The specimen used for structure solution was close to pure...