The crystal structures of synthetic Fe₃(SO₄)₃(H₂O)₅ and the type specimen of lausenite

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ABSTRACT

An iron sulfate of nominal composition Fe₃(SO₄)₃(H₂O)₅ has been synthesized and its structure determined and refined by high resolution powder diffraction using synchrotron radiation. The structure consists of corrugated slabs in which iron octahedra are linked by sulfate tetrahedra in the monoclinic space group P2₁/m with lattice parameters a = 10.711(1), b = 11.085(1), and c = 5.5747(5) Å, β = 98.89(1)°. We compare these results with the type specimen of lausenite from Jerome, Arizona, which has monoclinic lattice parameters a = 10.679(2), b = 11.053(3), and c = 5.567(1) Å, β = 98.89(1)°. Weight loss experiments show that it is currently a pentahydrate, despite earlier reports that lausenite is a hexahydrate. We argue that our synthetic material provides a structure determination for the type specimen of lausenite.

INTRODUCTION

Iron sulfate minerals are common and locally abundant products of weathering of pyrite and occasionally other sulfide minerals. They are distinct markers of acid mine drainage (AMD) pollution (e.g., Ash et al. 1951; Nordstrom et al. 2000; Buckby et al. 2003). These minerals are able to store and release toxic metals and acidity, and therefore are of interest with respect to remediation activities at AMD sites. Many of the AMD minerals belong to the Fe₃O₄-SO₃-H₂O system which was systematically studied by Posnjak and Merwin (1922) and Merwin and Posnjak (1937). The crystal structures of most of the Fe₃O₄-SO₃-H₂O phases are known from single-crystal studies of natural specimens. One remaining mineral in this system is lausenite, a rare and poorly characterized phase. The structure and most physical properties of lausenite are unknown.

Using the phase diagram of Posnjak and Merwin (1922), we synthesized a phase corresponding to their Fe₃(SO₄)₃(H₂O)₅ compound and investigated its spectroscopic and thermodynamic properties. The results of these investigations will be reported elsewhere. Interpretation of these results and their placement into the context of the studied chemical system is predicated upon knowledge of its composition and structure. Because only fine-grained powders could be synthesized, the structure was solved from powder X-ray diffraction data. Having solved the structure of this synthetic phase, we investigated the relationship between this structure and the structure of the mineral lausenite.

EXPERIMENTAL METHODS

Fe₃(SO₄)₃(H₂O)₅ was synthesized from a mixture of deionized water, sulfuric acid (96 wt% H₂SO₄, reagent grade, Fisher) and fine-grained, homogeneous hydrated ferric sulfate [Fe₃(SO₄)₃(H₂O)₅, reagent grade, Alfa Aesar]. The amount of water, x, in the ferric sulfate reagent, was determined to be ~6.75 by a thermogravimetric analysis. The solution from which Fe₃(SO₄)₃(H₂O)₅ precipitated was prepared by mixing 1.52 mL water, 0.48 mL sulfuric acid, and 1.98 g of ferric nitrate. The solution was then kept at 90 °C for a week. A pale pink product was separated from the mother liquor by filtration, washed with copious amounts of anhydrous methanol, and dried at room temperature.

The type specimen of lausenite from Jerome, Arizona, collected by Lausen in the 1920s and deposited with the Harvard Mineralogical Museum (HMM no. 90537), was kindly made available to us. The sample has been kept in a wax-sealed vial, and showed no signs of decomposition, such as growth of new phases on the surface of the sample, evidence of deliquescence, etc.

Preliminary X-ray diffraction (XRD) experiments were carried out with a Bruker AXS D8 Advance diffractometer in Bragg-Brentano geometry. The wavelength and the zero angle of the diffractometer were determined and redefined that the XRD pattern of the synthesized phase does not match those Fe₃O₄-SO₃-H₂O phases whose structures are known. This diffractometer was also used to collect an XRD pattern from the natural lausenite sample.

Thermogravimetric (TG) and differential thermal (DT) analysis was performed with a Netzsch 449F1 instrument. The sample was loaded into a Pt crucible, covered with a Pt lid, and heated from 25 to 800 °C at a rate of 10 °C/min with a continuous oxygen flow of 40 mL/min. An experiment with empty crucibles was performed to correct for the buoyancy of the gas. Simultaneously with the thermal analysis experiment, the evolved gases were fed into a Bruker Equinox 55 Fourier-transform infrared (FTIR) spectrometer. The signal in the energy range of 1000–4000 cm⁻¹ was collected with a liquid nitrogen cooled MCT detector.

Weight loss upon firing was measured by heating a known amount of the sample in corundum crucibles at 950 °C overnight. Prior to the measurements, the corundum crucibles were repeatedly annealed at 1500 °C overnight until no weight change could be recorded. The crucibles with sample were weighed before and after heating with a balance with a manufacturer-stated precision of 0.01 mg.

The XRD pattern for structure solution was collected at the bending magnet beamline X3B1 at the National Synchrotron Light Source (Brookhaven National Laboratory). X-rays of wavelength of 1.4959(1) Å were selected by a double crystal Si(111) monochromator. The wavelength and the zero angle of the diffractometer were determined with a NIST 1976 standard reference material (corundum, α-Al₂O₃). The sample was loaded into a 10 mm glass capillary which was rotated about its axis during the data collection. The intensity of the incoming beam was monitored during the data collection with an ion chamber and the measured intensities of the diffracted beam were corrected for the decay and fluctuations of the primary beam. The diffracted beam was analyzed with a Ge(111) crystal and a Na(Tl)I scintillation detector. The XRD pattern was collected at room temperature, over an angular range of 5.9 to 65.9° 2θ, with a step size of 0.003°, and counting time of 2 s per point.