Structural trends for celestite (SrSO₄), anglesite (PbSO₄), and barite (BaSO₄): Confirmation of expected variations within the SO₄ groups

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ABSTRACT

The crystal structures of the isostructural orthorhombic sulfates celestite (SrSO₄), anglesite (PbSO₄), and barite (BaSO₄) were refined by Rietveld methods using synchrotron high-resolution powder X-ray diffraction (HRPXRD) data. Their structural model was refined in space group Pbnm. The unit-cell parameters are: a = 6.87032(3), b = 8.36030(5), c = 5.34732(1) Å, and V = 307.139(3) Å³ for SrSO₄; a = 6.95802(1), b = 8.48024(3), c = 5.39754(1) Å, and V = 318.486(1) Å³ for PbSO₄; and a = 7.15505(1), b = 8.88101(3), c = 5.45447(1) Å, and V = 346.599(1) Å³ for BaSO₄. The average <M-O> [12] distances are 2.827(1), 2.865(1), and 2.953(1) Å for SrSO₄, PbSO₄, and BaSO₄, respectively, and their corresponding average <S-O> [4] distances are 1.480(1), 1.477(3), and 1.471(1) Å. The geometrical features of the SO₄ and MO₁₂ polyhedra become more symmetrical from SrSO₄ to BaSO₄. Across the series, the a, b, and c parameters vary non-linearly with increasing V. The radii of the M²⁺ cations, rM¹, <M-O> [12], and <S-O> [4] distances vary linearly with V. These structural trends arise from the effective size of the M²⁺ cation (rM¹; Sr < Pb < Ba) that is coordinated to 12 O atoms.

Keywords: Celestite, SrSO₄, anglesite, PbSO₄, barite, BaSO₄, Rietveld refinement, synchrotron high-resolution powder X-ray diffraction (HRPXRD), crystal structure

INTRODUCTION

Celestite (SrSO₄) and barite (BaSO₄) occur in hydrothermal veins and as secondary minerals in sedimentary environments. They are the main commercial sources of strontium and barium. Anglesite (PbSO₄), a minor ore of lead, typically occurs in the oxidized portion of hydrothermal lead deposits as an alteration product of galena and also as a primary mineral in some low-temperature oxidized hydrothermal deposits.

The crystal structures of isostructural celestite, anglesite, and barite were determined by James and Wood (1925). Sahl (1963) refined the structural model for anglesite and barite. The barite structure was also refined by Colville and Staudhammer (1967). The structure of celestite was refined by Garske and Peacock (1965) and Hawthorne and Ferguson (1975). The structure of a Ba-rich celestite is also available (Brigatti et al. 1997). The structure of all three minerals was refined by Miyake et al. (1978) and Jacobsen et al. (1998) to determine structural trends that are expected across the series. They concluded that the average <M-O> [12] distance increases linearly with increasing cell volume, but the SO₄ behaves as a rigid group with an average <S-O> [4] distance of 1.476 Å, which is constant across the series. Hawthorne and Ferguson (1975) and Hill (1977) reported that the SO₄ groups in all three minerals display identical geometries, and the M cation is [12]-coordinated to O atoms because of bond-strength sums.

Although previous studies indicate that the M²⁺ cations have no effect on the shape or size of the SO₄ tetrahedron (e.g., Jacobsen et al. 1998), the M²⁺ cations have different sizes and effective charge, so systematic variation in the geometry of the SO₄ group is expected. The purpose of this study is to examine the structural trends for SrSO₄, PbSO₄, and BaSO₄ using high-resolution powder X-ray diffraction (HRPXRD), this study shows that the geometry of the SO₄ group varies in a systematic and expected manner.

EXPERIMENTAL METHODS

Sample characterization

The celestite sample is from Saxony, Ngar Majunga, Madagascar (UC15824). The barite sample is from Elk Creek, South Dakota. The synthetic PbSO₄ sample was obtained as high-purity (99.995%) reagent grade powder from Aldrich and no impurity phase was observed in the HRPXRD trace.

The celestite and barite samples were analyzed using a JEOL JXA-8200 electron microprobe and its standard operating program on a Solaris platform.