

The crystal structure of tin sulphate, SnSO₄, and comparison with isostructural SrSO₄, PbSO₄, and BaSO₄

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The crystal structure of tin (II) sulphate, SnSO₄, was obtained by Rietveld refinement using synchrotron high-resolution powder X-ray diffraction (HRPXR) data. The structure was refined in space group *Pbnm*. The unit-cell parameters for SnSO₄ are $a = 7.12322(1)$, $b = 8.81041(1)$, $c = 5.32809(1)$ Å, and $V = 334.383(1)$ Å³. The average ⟨Sn–O⟩ [12] distance is 2.9391(4) Å. However, the Sn²⁺ cation has a pyramidal [3]-coordination to O atoms and the average ⟨Sn–O⟩ [3] = 2.271(1) Å. If Sn is considered as [12]-coordinated, SnSO₄ has a structure similar to barite, BaSO₄, and its structural parameters are intermediate between those of BaSO₄ and PbSO₄. The tetrahedral SO₄ group has an average ⟨S–O⟩ [4] = 1.472(1) Å in SnSO₄. Comparing SnSO₄ with the isostructural SrSO₄, PbSO₄, and BaSO₄, several well-defined trends are observed. The radii, r_M, of the M²⁺ (=Sr, Pb, Sn, and Ba) cations and average ⟨S–O⟩ distances vary linearly with V because of the effective size of the M²⁺ cation. Based on the trend for the isostructural sulphates, the average ⟨Sn–O⟩ [12] distance is slightly longer than expected because of the lone pair of electrons on the Sn²⁺ cation. © 2012 International Centre for Diffraction Data [doi:10.1017/S0885715612000450]

Key words: SnSO₄, SrSO₄, PbSO₄, BaSO₄, Rietveld refinement, HRPXR, crystal structure

I. INTRODUCTION

The crystal structure of tin (II) sulphate was determined by Rentzeperis (1962) based on the suggestion of James and Wood (1925) that SnSO₄ has a barite structure. However, Donaldson and Moser (1960) indicated that such a relation is unlikely because of the large difference in the ionic radii of Ba²⁺ and Sn²⁺ [$r_{\text{Ba}} = 1.61$ Å (Shannon, 1976); $r_{\text{Sn}} = 0.85$ Å (Donaldson and Puxley, 1972)]. Using single-crystal data, the structure of SnSO₄ was refined by Donaldson and Puxley (1972). The main structural features of SnSO₄ are illustrated (Figure 1). A lone pair of electrons of the sp³ hybridized Sn²⁺ orbitals may explain the high degree of distortion in SnSO₄ and its relation to the barite structure. In SnSO₄, the Sn²⁺ atom is in a pyramidal coordination that forms three bonds with the O atoms and the fourth orbital in the sp³ hybridization is occupied by a lone pair of electrons [Figure 1(a)]. The lone pair of electrons is viewed as pseudo-ligands, which prevents close approach of other anions in this direction and significantly changes the space requirements (Gillespie, 1967; Gillespie and Robinson, 1996). Crystal structures that have cations with a lone pair of electrons are quite open and they undergo pressure-induced phase transitions (Crichton *et al.*, 2005; Hinrichsen *et al.*, 2008).

The crystal structure of celestite, anglesite, and barite was recently refined by Antao (2012), and interesting structural trends were observed across the series. Miyake *et al.* (1978) indicated a possible systemic variation in the SO₄ tetrahedron with field strength of the M²⁺ cation across the series. Jacobsen *et al.* (1998) concluded that the average ⟨M–O⟩ distance increases linearly with unit-cell volume, but SO₄ behaves as a rigid group with an average ⟨S–O⟩ distance of about 1.476 Å, which is constant across the series.

Hawthorne and Ferguson (1975) and Hill (1977) reported that the SO₄ groups in all three structures display identical geometries. These studies indicate that the M²⁺ cations have no effect on the shape or size of the SO₄ tetrahedron. The M²⁺ cations have different sizes and effective charge, so systematic variation in the geometry of the SO₄ group across the series is expected, and this was recently confirmed by Antao (2012). Although the structure of the isostructural MSO₄ materials is well known, previous studies have not shown the change in the geometry of the SO₄ group observed by Antao (2012) using high-resolution powder X-ray diffraction (HRPXR), which is the same technique used in this study to examine the structure of SnSO₄.

The purpose of this study is to refine the crystal structure of SnSO₄ and to examine its relation to the structural trends that were recently observed by Antao (2012) for the isostructural sulphates SrSO₄, PbSO₄, and BaSO₄. Of particular interest is the variation in the geometry of the SO₄ group for these sulphates and the radius of the [12]-coordinated Sn²⁺ cation.

II. EXPERIMENTAL

A. Synchrotron HRPXR

The SnSO₄ sample was studied by HRPXR that was performed at beamline 11-BM, Advanced Photon Source (APS), Argonne National Laboratory (ANL). The synthetic tin (II) sulphate, SnSO₄, was obtained as 99% reagent grade powder from ACROS organics, and the HRPXR trace showed no impurity phase. The sample was crushed to a fine powder using an agate mortar and pestle. The powder sample was loaded into a Kapton capillary (0.8 mm internal diameter) and rotated during the experiment at a rate of 90 rotations per second. The data were collected to a maximum 2θ of about 43° with a step size of 0.001° and a step time of 0.1 s per step. The HRPXR trace was collected with 12 silicon (111) crystal analysers that increase detector efficiency,

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