

A Crystal Structure Determination of PbSO₃ from X-Ray and Neutron Powder Diffraction Data

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The crystal structure of lead sulfite, PbSO₃, was solved from X-ray and neutron powder diffraction data. The unit cell was obtained by auto-indexing of Guinier film data. The structure was derived by comparing the X-ray powder pattern of PbSO₃ with that of BaSO₄, which indicated the structure of PbSO₃ to be related to that of BaSO₄. The structure was refined by profile analysis of X-ray and of neutron diffraction powder data.

The unit cell is orthorhombic, space group *Pnma* (No. 62), with lattice parameters from the X-ray data, $a = 7.925(1)$, $b = 5.485(1)$, $c = 6.816(1)$ Å, $Z = 4$.

The investigation of unknown crystal structures is traditionally made by single crystal X-ray or neutron diffractometry yielding detailed models of the structures. However, in the case that single crystals are not available, an investigation of the structure may be possible by combining information from X-ray and neutron powder diffractometry.¹⁻⁴ Recently, a fair number of crystal structures of the new high- T_c superconductors have thus been solved and refined by combining information from X-ray and neutron powder patterns and from electron diffraction and electron microscopy. A number of well known compounds have, however, crystal structures that are still unknown, mostly owing to the fact that single crystals large enough for single crystal X-ray diffraction investigations are not readily available. This is often the case for inorganic compounds with low solubility, prepared from aqueous solutions.

In this paper a structure investigation of lead sulfite, PbSO₃, is reported from X-ray and neutron powder diffrac-

tion data. Lead sulfite is known as the monoclinic mineral scotlandite, PbSO₃, isomorphous with the mineral molybdomenite, PbSeO₃ (Table 1), and isostructural with KClO₃. When precipitated from aqueous solutions lead sulfite forms a microcrystalline product, and the X-ray powder pattern of this orthorhombic modification of lead sulfite resembles the powder pattern of anglesite, PbSO₄, and baryte, BaSO₄. The present investigation deals with the determination and refinement of the orthorhombic structure.

Experimental

Sample preparation. Lead sulfite was precipitated by mixing a solution of 26 g of Pb(CH₃COO)₂·3H₂O (Merck p.a.) in 250 ml water with a solution of 10 g Na₂SO₃ (Merck p.a.) in 250 ml water. The precipitate was washed with water and dried at 90°C.

Table 1. Crystallographic data for compounds with related structures.

Compound	Formula	$a/\text{Å}$	$b/\text{Å}$	$c/\text{Å}$	$\beta/^\circ$	Space group	Ref.
Molybdomenite	PbSeO ₃	6.91	5.48	4.51	112.8	<i>P2₁/m</i>	5
Molybdomenite	PbSeO ₃	4.552	5.525	6.663	106.40	<i>P2₁/m</i>	6
Scotlandite	PbSO ₃	6.72	5.34	4.51	114	<i>P2₁/m</i>	7
Scotlandite	PbSO ₃	4.505(2)	5.336(2)	6.396(3)	106.08(3)	<i>P2₁/m</i>	This work
Lead sulfite	PbSO ₃	7.903(1)	5.488(1)	6.802(1)		<i>Pnma</i>	8
Lead sulfite	PbSO ₃	7.925(1)	5.485(1)	6.816(1)		<i>Pnma</i>	This work
Anglesite	PbSO ₄	8.516(20)	5.399(10)	6.989(10)		<i>Pnma</i>	9
Baryte	BaSO ₄	8.909(20)	5.467(10)	7.188(10)		<i>Pnma</i>	9

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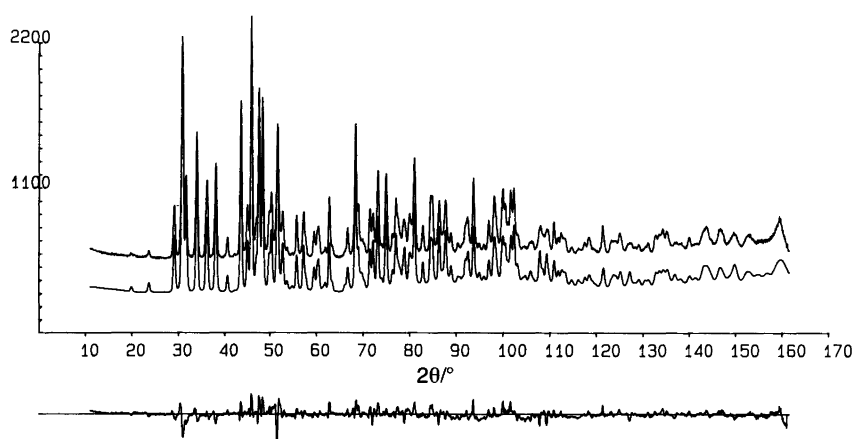


Fig. 1. Neutron diffraction powder pattern of PbSO₃. Upper curve, observed, and lower curve, calculated, profile, with difference in the lower part of the figure.

X-Ray diffraction. A Guinier photograph was taken with a Guinier–Lenné camera with Si ($a = 5.430\,50\text{ \AA}$) as internal standard using Cu $K\alpha_1$ radiation ($\lambda = 1.540\,598\text{ \AA}$). The pattern was indexed with the auto-indexing program FZON¹⁰ with an orthorhombic cell, and a De Wolff figure of merit $M_{20} = 24.6$. The reflections were in agreement with the space group $Pnma$ (No. 62); the unit cell found was qualitatively in agreement with Ref. 8. The unit cell parameters were then refined by a least-squares procedure using the program CELLKANT,¹¹ and this yielded the unit cell parameters listed in Table 1. The powder pattern of PbSO₃ was also measured on a Stoe diffractometer with a position-sensitive detector, using Cu $K\alpha_1$ radiation. The detector is curved and covers a 2θ range of 40° . By measuring at two positions of the detector, a 2θ range of 80° is covered. The diffractometer was calibrated with a standard of Ag₆Ge₁₀P₁₂ ($a = 10.312\text{ \AA}$).

The published powder pattern of scotlandite⁷ was indexed with a monoclinic unit cell chosen by analogy with the unit cell of molybdomenite in Ref. 6, and the unit cell parameters were then refined with the program CELLKANT.¹¹ The results obtained are listed in Table 1.

Neutron diffraction. The neutron diffraction powder pattern of PbSO₃ was measured at room temperature in the 2θ range $10\text{--}160^\circ$ in steps of 0.05° using $\lambda = 1.594\text{ \AA}$ neutrons on a multi-detector powder diffractometer, D2B, at the Institut Laue–Langevin, Grenoble.¹² The sample was kept in a 8 mm diameter vanadium container, and the neutron powder pattern thus obtained of PbSO₃ is displayed in Fig. 1.

Structure determination

The average scattering contribution per atom in the X-ray case is Pb, 93.8%; S, 3.6%; O, 0.9%; the X-ray powder pattern is thus strongly dominated by the scattering from the lead atoms. The density of PbSO₃ measured by the method of Archimedes is 6.28 g cm^{-3} . In the space group $Pnma$ and $Z = 4$, corresponding to a calculated density of 6.42 g cm^{-3} , the position of the lead atoms will most likely

be in site $4c$, $(x, 1/4, z)$. From the intensities of some of the low-angle reflections where (200), (002) and (101) are rather weak and (111) and (011) are rather strong, the lead atom coordinates are expected to have values in the ranges: $x = 0.20\text{--}0.25$ and $z = 0.16\text{--}0.25$.

The structure of the compounds PbSO₄ and BaSO₄ are also described in the space group $Pnma$, and their unit cells have dimensions comparable with those of PbSO₃ (Table 1). The powder patterns of these three compounds are strongly dominated by the scattering contributions from the metal atoms. The intensity distributions of the pattern of PbSO₃ and that of BaSO₄ are qualitatively in agreement with each other, indicating lead atom coordinates in the structure of PbSO₃ similar to the barium atom coordinates in BaSO₄. The barium and sulfur atom coordinates⁹ Ba (0.1882, 0.25, 0.1670) and S (0.437, 0.75, 0.186) were used in a calculation of the X-ray powder pattern of PbSO₃ using the program LAZY PULVERIX,¹³ and this calculated powder pattern was qualitatively in agreement with the observed pattern of PbSO₃. The lead and sulfur atom coordinates in the model of the structure of PbSO₃ were then refined by the profile refinement method¹⁴ using the program EDINP,¹⁵ and neutral atom values of the atomic scattering factor,¹⁶ and the X-ray diffractometer data. The parameters refined were a scale factor, four positional parameters, two isotropic temperature factor parameters, a zero point and three unit cell parameters, and four profile parameters. A pseudo-Voigt peak shape function was as-

Table 2. Positional parameters for the lead and sulfur atoms in PbSO₃ from X-ray powder diffractometer data.

Atom	x	y	z	$B/\text{\AA}^2$
Pb	0.185(3)	1/4	0.139(3)	5(1)
S	0.437(15)	3/4	0.150(20)	3(1)

Refined parameters: zero = -0.0529° ; $U = 0.611$, $V = -0.568$, $W = 0.185$, $T = 0.160$; $a = 7.925(1)\text{ \AA}$, $b = 5.485(1)\text{ \AA}$, $c = 6.816(1)\text{ \AA}$. The FWHM is calculated from the profile parameters as:

$$\text{FWHM} = (U \tan^2 \theta + V \tan \theta + W)^{1/2} + T/\cos \theta.$$

Fig. 2. Projection of the structure of PbSO_3 along 010.

sumed for the X-ray reflections. The parameters arrived at are listed in Table 2, and confirm the position of the lead atom arrived at by the hypothesis that the structure of PbSO_3 resembles that of BaSO_4 (see above). With the low scattering contribution from the oxygen atoms in this case it would not be possible to determine the position of these atoms from the X-ray pattern, and the position of the sulfur atom is determined with rather high uncertainty.

With the neutron diffraction powder pattern 158 reflections with $F > \sigma(F)$ were extracted, using the program ALLHKL.¹⁷ This list of structure factors were given phases in a structure factor calculation using the position of the lead atom arrived at from the X-ray powder pattern (Table 2) and the single crystal least-squares refinement program LINUS.¹⁸ A calculation of a Fourier map gave then the positions of two oxygen atoms at (0.31, 3/4, 0.02) and (0.43, 0.53, 0.26) and of a sulfur atom at (0.45, 3/4, 0.15). This model of the structure was then used in a least-squares profile refinement of the structure of PbSO_3 using the program EDINP,¹² and the scattering lengths Pb, 0.94003; S, 0.2847; O, 0.5805 (all in 10^{-12} cm units).¹⁹ The parameters refined were a scale factor, nine positional parameters, four isotropic temperature factor parameters, a zero point and three unit cell parameters and four profile

parameters, assuming a pseudo-Voigt function peak shape for the reflections. The parameters arrived at are listed in Table 3, and observed and calculated profiles and a difference plot are displayed in Fig. 1. In Table 4 are included some characteristic interatomic distances, and Fig. 2 shows a drawing of the structure. A small discrepancy of 0.2% is observed between the unit cell parameters determined from the X-ray data (Table 2) and the unit cell parameters determined from the neutron data (Table 3). This is most likely due to uncertainty in the determination of the neutron wavelength.

Discussion

The analysis shows that the structure of PbSO_3 is rather similar to the structures of BaSO_4 and PbSO_4 , when the SO_4^{2-} ions are substituted with SO_3^{2-} ions. The approximate position of the lead atom in the structure was deduced from the intensities of some selected reflections of the X-ray powder pattern, and the model of the structure was derived from the structures of BaSO_4 and PbSO_4 by comparison of the powder patterns of the three compounds. The positions of the sulfur and the oxygen atoms were in addition found in Fourier map calculations using the neutron diffraction data.

The interatomic distances in the SO_3^{2-} ions of the PbSO_3 structure are comparable with the distances of the sulfite ions in the structures of Na_2SO_3 ,²⁰ Ag_2SO_3 ,²¹ and $\text{CdSO}_3 \cdot 1.5\text{H}_2\text{O}$.²² The S–O distances in the SO_3^{2-} ions of PbSO_3 do not deviate significantly from each other, so that the symmetry of the ion is C_{3v} . The lead–oxygen distances in the structure are comparable with the Pb–O distances in PbSO_4 ,⁹ and in PbC_2O_4 .⁴

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Table 3. Refined parameters for the structure of PbSO_3 (neutron powder diffraction data).

Atom	x	y	z	$B/\text{\AA}^2$
Pb	0.1840(3)	1/4	0.1357(3)	1.98(3)
S	0.4647(6)	3/4	0.1482(9)	1.34(9)
O1	0.3076(6)	3/4	0.0177(5)	2.46(6)
O2	0.4369(3)	0.5299(3)	0.2866(3)	2.15(4)

Refined parameters: zero = $-1.041(1)^\circ$; $U = 0.098(10)$, $V = -0.155(17)$, $W = 0.205(7)$, $T = 0.102(5)$; $a = 7.9233(3)$ \AA, $b = 5.4845(2)$ \AA, $c = 6.8134(3)$ \AA; $R_p = 5.1\%$, $R_{wp} = 6.5\%$, $R_F = 8.2\%$, $R_I = 9.7\%$, $R_E = 5.1\%$. For definitions of the R -values see Refs. 3 and 4.

Table 4. Interatomic distances in different compounds (in \AA).

PbSO_3	PbSO_4 (Ref. 9)	PbC_2O_4 (Ref. 4)	Na_2SO_3 (Ref. 20)	Ag_2SO_3 (Ref. 21)	$\text{CdSO}_3 \cdot 1.5\text{H}_2\text{O}$ (Ref. 22)
Pb–O2	2.726(3)	2.63	2.432(7)		
Pb–O1	3.020(3)	3.25	2.903(8)		
S–O1	1.541(7)			1.504	1.52
S–O2	1.546(4)				1.52–1.57

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