

Crystal structures and sulphate force constants of barite, celestite, and anglesite

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Abstract

The crystal structures of three isostructural sulphates, barite (BaSO_4), celestite (SrSO_4), and anglesite (PbSO_4), were refined by least-squares methods using three-dimensional X-ray data. All three sulphates belong to the orthorhombic space group $Pbnm$ with $Z = 4$. The final R values are 0.043, 0.053, and 0.067 for BaSO_4 , SrSO_4 , and PbSO_4 , respectively. The average cation to oxygen bond lengths are 2.952Å in barite, 2.831Å in celestite and 2.87Å in anglesite. The average sulphur to oxygen bond lengths are 1.478Å in barite, 1.474Å in celestite and 1.49Å in anglesite.

The force constants of the Urey-Bradley force field in the SO_4 tetrahedron were calculated from the bond lengths and the infrared absorption frequencies. The stretching force constants for barite, celestite, and anglesite are $K = 6.27, 6.34, \text{ and } 5.98$ md/Å, respectively; the bending force constants $H = 0.46, 0.47, \text{ and } 0.42$ md/Å; the repulsive force constants $F = 0.73, 0.75, \text{ and } 0.70$ md/Å. The increase of the field strength of a metal ion gives rise to the increase of the force constants in the SO_4 tetrahedron.

Introduction

The crystal structure of barite (BaSO_4), isostructural with celestite (SrSO_4) and anglesite (PbSO_4), was first determined by James and Wood (1925). Sahl (1963) redetermined the structural parameters of barite and anglesite by photographic data. Garske and Peacor (1965) refined the structure of celestite, and Colville and Staudhammer (1967) that of barite with isotropic thermal parameters. Bostrom *et al.* (1967) investigated the BaSO_4 - SrSO_4 - PbSO_4 ternary system and concluded that a complete series of solid solutions exists between the components.

In this study, crystal structures of the end members of these systems were refined to clarify the structural variations due to the differences between the alkaline-earth group (Mg, Ca, Sr, Ba) and IVA group (Sn, Pb). Force constants of the Urey-Bradley force field were calculated from the infrared absorption frequencies and the interatomic distances derived from the structure refinements.

Specimens

The specimens used were colorless, transparent crystals of barite from Tamagawa, Akita, Japan, celestite from Clay Center, Ohio, and anglesite

from Osarizawa, Akita, Japan. The chemical compositions of these specimens by an EPMA technique were $(\text{Ba}_{0.99}\text{Pb}_{0.01})\text{SO}_4$, $(\text{Sr}_{0.986}\text{Ba}_{0.013}\text{Pb}_{0.001})\text{SO}_4$ and $(\text{Pb}_{0.977}\text{Ba}_{0.013}\text{Sr}_{0.010})\text{SO}_4$ for barite, celestite, and anglesite, respectively.

Structure refinements

The cell dimensions determined by powder diffraction are $a = 7.157(2)$, $b = 8.884(2)$ and $c = 5.457(3)$ Å for barite, $a = 6.870(3)$, $b = 8.371(3)$ and $c = 5.355(2)$ Å for celestite, and $a = 6.959(2)$, $b = 8.482(2)$ and $c = 5.398(2)$ Å for anglesite. The space groups of these crystals all belong to $Pbnm$, with four formula units in each cell. Crystals used were a spherical crystal of barite 0.15 mm in diameter, a rectangular crystal of celestite $0.14 \times 0.10 \times 0.09$ mm, and a lamellar crystal of anglesite $0.17 \times 0.17 \times 0.03$ mm. Intensities were measured on a four-circle diffractometer with $\text{MoK}\alpha$ radiation up to $2\theta = 100^\circ$ by the ω - 2θ scan technique. In all, 1398, 798 and 749 independent intensity data were collected for barite, celestite, and anglesite, respectively. Intensities of anglesite were corrected for absorption using the actual crystal shape (program ACACA, Wuensch and Prewitt, 1965). Intensities of barite and celestite were

corrected assuming the crystals to be spheres. The structure refinements were carried out with the full-matrix least-squares program LINUS (Coppens and Hamilton, 1970), starting with the atomic parameters given by Colville and Staudhammer (1967) for barite and Garske and Peacor (1965) for celestite and anglesite. Unit weights were allotted to all reflections. The atomic scattering factors for neutral atoms were taken from the *International Tables for X-ray Crystallography* (1962). On applying anisotropic temperature factors¹, final *R* values of 0.043, 0.053, and 0.067 for barite, celestite, and anglesite were obtained. The observed and calculated structure factors are listed in Table 1². The final parameters are given in Table 2.

Results of X-ray analysis

The interatomic distances and bond angles calculated by the program UNICS (Sakurai, 1967) are given in Table 3. Figure 1 shows an ORTEP (Johnson, 1965) plot of the crystal structure of barite. Isolated SO₄ tetrahedra are present in which the *z* coordinates of S, O(1) and O(2) in Table 2 are fixed by the mirror plane, whereas O(3) is in a general position, resulting in C_s(*m*) symmetry of the SO₄ tetrahedron in these structures. The average values of sulphur–oxygen distances are 1.478, 1.474 and 1.49A for barite, celestite, and anglesite, respectively, which are close to the mean sulphur–oxygen distance of 1.473A in sulphate structures as reported by Baur (1970). The longest S–O distance is S–O(3) and the widest O–S–O angle is O(1)–S–O(2) in all three crystals in the present refinements. The metal ions (Ba²⁺, Sr²⁺, or Pb²⁺) in these crystals are surrounded by 12 oxygen atoms. The Ca ions of smaller ionic radii are surrounded by 8 oxygen atoms in the structure of anhydrite (CaSO₄) (Morikawa *et al.*, 1975). The average metal–oxygen distances decrease from Ba to Pb to Sr.

Infrared experiments and calculation of force constants

The infrared spectra of barite, celestite, and anglesite were run from 4000 to 400 cm⁻¹ on a Japan Spectrometer Company IR-G. These spectra showed very strong absorption bands from 1300 to 1000 cm⁻¹, relatively strong bands in the vicinity of 600 cm⁻¹ and a shouldered band in 980 cm⁻¹. The assign-

¹ The form of the anisotropic thermal ellipsoid is $\exp [-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl)]$.

² To obtain a copy of this table, order Document AM-78-073 from the MSA Business Office, 1909 K Street, NW, Washington, DC 20006. Please remit \$1.00 in advance for the microfiche.

Table 2. Positional and thermal parameters

Barite			Celestite			Anglesite		
Atom		Parameters	Atom		Parameters	Atom		Parameters
Ba	x	0.1585 (1)	Sr	x	0.1583 (1)	Pb	x	0.1667 (1)
	y	0.1845 (1)		y	0.1839 (1)		y	0.1879 (1)
	z	0.25		z	0.25		z	0.25
	B ₁₁	0.0042 (1)		B ₁₁	0.0034 (1)		B ₁₁	0.0072 (1)
	B ₂₂	0.0027 (1)		B ₂₂	0.0023 (1)		B ₂₂	0.0039 (1)
	B ₃₃	0.0087 (1)		B ₃₃	0.0105 (2)		B ₃₃	0.0166 (3)
B ₁₂	-0.0002 (1)	B ₁₂	-0.0001 (1)	B ₁₂	0.0004 (1)			
S	x	0.1911 (2)	S	x	0.1853 (2)	S	x	0.1842 (7)
	y	0.4375 (2)		y	0.4382 (2)		y	0.4367 (6)
	z	0.75		z	0.75		z	0.75
	B ₁₁	0.0037 (2)		B ₁₁	0.0020 (2)		B ₁₁	0.0035 (7)
	B ₂₂	0.0028 (1)		B ₂₂	0.0023 (2)		B ₂₂	0.0025 (4)
	B ₃₃	0.0062 (3)		B ₃₃	0.0060 (4)		B ₃₃	0.007 (1)
B ₁₂	-0.0001 (1)	B ₁₂	-0.0001 (1)	B ₁₂	-0.0003 (5)			
O(1)	x	0.106 (1)	O(1)	x	0.093 (1)	O(1)	x	0.096 (3)
	y	0.5878 (7)		y	0.5942 (8)		y	0.592 (2)
	z	0.75		z	0.75		z	0.75
	B ₁₁	0.009 (1)		B ₁₁	0.010 (1)		B ₁₁	0.008 (3)
	B ₂₂	0.0043 (5)		B ₂₂	0.0027 (6)		B ₂₂	0.004 (2)
	B ₃₃	0.017 (2)		B ₃₃	0.023 (3)		B ₃₃	0.025 (8)
B ₁₂	0.0026 (6)	B ₁₂	0.0035 (7)	B ₁₂	0.003 (2)			
O(2)	x	0.0494 (7)	O(2)	x	0.0419 (9)	O(2)	x	0.043 (2)
	y	0.3177 (9)		y	0.3075 (9)		y	0.306 (2)
	z	0.75		z	0.75		z	0.75
	B ₁₁	0.0039 (6)		B ₁₁	0.0048 (9)		B ₁₁	0.005 (2)
	B ₂₂	0.0088 (8)		B ₂₂	0.0049 (7)		B ₂₂	0.004 (2)
	B ₃₃	0.014 (2)		B ₃₃	0.017 (2)		B ₃₃	0.027 (7)
B ₁₂	-0.0030 (7)	B ₁₂	-0.0031 (7)	B ₁₂	-0.002 (2)			
O(3)	x	0.3114 (5)	O(3)	x	0.3108 (6)	O(3)	x	0.309 (2)
	y	0.4199 (4)		y	0.4217 (5)		y	0.418 (1)
	z	0.9702 (7)		z	0.9746 (8)		z	0.974 (2)
	B ₁₁	0.0054 (4)		B ₁₁	0.0051 (6)		B ₁₁	0.007 (2)
	B ₂₂	0.0048 (3)		B ₂₂	0.0044 (4)		B ₂₂	0.006 (1)
	B ₃₃	0.0071 (7)		B ₃₃	0.008 (1)		B ₃₃	0.008 (3)
B ₁₂	-0.0003 (3)	B ₁₂	-0.0008 (4)	B ₁₂	-0.001 (1)			
B ₁₃	-0.0012 (5)	B ₁₃	-0.0028 (6)	B ₁₃	-0.001 (2)			
B ₂₃	0.0001 (4)	B ₂₃	0.0001 (6)	B ₂₃	-0.001 (2)			

ment of the vibrations of the sulphate ion followed after Hezel and Ross (1966). Figure 2 shows the symmetry correlation in the SO₄ tetrahedron between T_d($\bar{4}3m$) of free ion symmetry and C_s(*m*) of site symmetry. Bands of ν_3 and ν_4 modes are split and inactive ν_1 and ν_2 modes appear in infrared absorption spectra by the lowering from T_d($\bar{4}3m$) to C_s(*m*) symmetry. In

Table 3. Interatomic distances and tetrahedral bond angles

Atoms	SO ₄ ²⁻ group		
	Barite	Celestite	Anglesite
S - O(1)	1.468 (7) A	1.452 (7) A	1.46 (2) A
S - O(2)	1.471 (7)	1.472 (7)	1.48 (2)
S - O(3) (2x)	1.487 (4)	1.486 (4)	1.50 (2)
Average S - O	1.478	1.474	1.49
O(1) - O(2)	2.43 (1)	2.43 (1)	2.46 (3)
O(1) - O(3) (2x)	2.415 (7)	2.402 (7)	2.43 (2)
O(2) - O(3) (2x)	2.405 (6)	2.403 (7)	2.41 (2)
O(3)' - O(3)''	2.404 (5)	2.405 (6)	2.42 (2)
O(1) - S - O(2)	111.8 (4) °	112.1 (4) °	113.4 (11) °
O(1) - S - O(3)	109.7 (2)	109.7 (2)	110.1 (7)
O(2) - S - O(3)	108.9 (2)	108.6 (2)	107.7 (6)
O(3)' - S - O(3)''	107.9 (2)	108.0 (2)	107.6 (7)
Atoms	Metal ion - oxygen polyhedra M=Ba, Sr, or Pb		
	Barite	Celestite	Anglesite
M - O(1)	2.770 (7) A	2.536 (7) A	2.61 (2) A
M - O(2)	2.798 (5)	2.636 (6)	2.62 (2)
M - O(3) (2x)	2.811 (4)	2.653 (4)	2.65 (1)
M - O(3) (2x)	2.811 (4)	2.696 (4)	2.74 (1)
M - O(3) (2x)	2.911 (4)	2.816 (4)	2.91 (1)
M - O(2) (2x)	3.075 (3)	2.980 (3)	3.005 (8)
M - O(1) (2x)	3.320 (4)	3.263 (4)	3.27 (1)
Average M - O	2.952	2.831	2.87

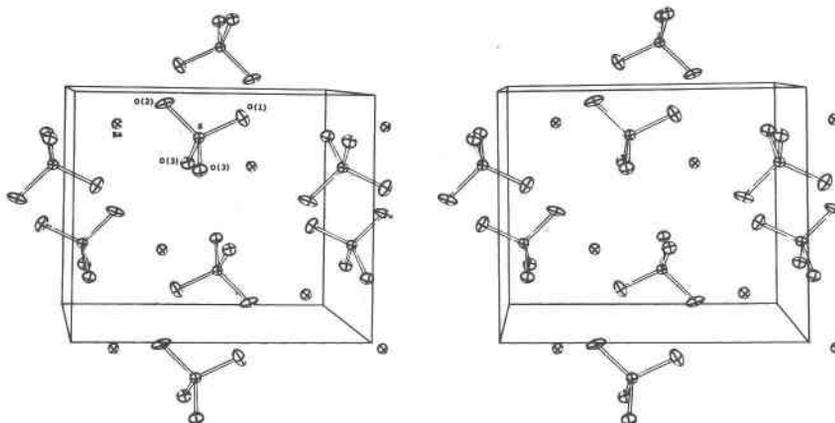


Fig. 1. Stereoscopic illustration of the crystal structure of barite viewed along c [Program ORTEP (Johnson, 1965)].

this experiment, ν_2 mode was not observed due to its weak intensity. The absorption bands for ν_1 , ν_3 , and ν_4 modes of celestite shift toward the higher wave number side and those of anglesite shift toward the lower wave number side compared with those of barite.

The SO_4 tetrahedron with $T_d(\bar{4}3m)$ symmetry was assumed for simplification, and the overall force constants were calculated, since the SO_4 tetrahedron with $C_s(m)$ symmetry is too complex to calculate its force constants. The force constants were determined by Wilson's method with use of the potential energy matrix F and the kinetic energy matrix G (Wilson *et al.*, 1955). The Urey-Bradley force field function for the potential energy calculation is as follows:

$$V = 1/2\sum K_i(\Delta r_i)^2 + 1/2\sum H_{ij}(\Delta\alpha_{ij})^2 + 1/2\sum F_{ij}(\Delta q_{ij})^2 + 1/2\kappa$$

where K is the stretching force constant, H is the bending force constant, F is the repulsive force constant, κ is the internal molecular tension, r is the S-O bond length, α is the O-S-O angle, and q is the

distance between two oxygen atoms in the SO_4 tetrahedron. In this study, the value of the internal molecular tension was assumed to be $0.57 \text{ md}\cdot\text{A}$, that is, the value of the free SO_4 ion (Iishi, 1975). The force constants were evaluated using the frequency of the ν_1 mode, the average of three frequencies of the ν_3 mode, and that of the ν_4 mode. The initial values of the force constants $K = 6.03 \text{ md/A}$, $H = 0.42 \text{ md/A}$, and $F = 0.77 \text{ md/A}$ for the free SO_4 ion (Iishi, 1975; Omori, 1970) were substituted, respectively.

For comparison, the force constants of magnesium sulphate, anhydrite, and tin sulphate were calculated by the same method, using the structural parameters of magnesium sulphate (Rentzeperis and Soldatos, 1958), anhydrite (Morikawa *et al.*, 1975), and tin sulphate (Donaldson and Puxley, 1972). In the present calculation, the infrared absorption data and the Raman scattering data of magnesium sulphate, anhydrite, and tin sulphate (Farmer, 1974, p. 423-444; Krishnan, 1946) were employed. The observed and calculated frequencies and the determined force constants are given in Table 4.

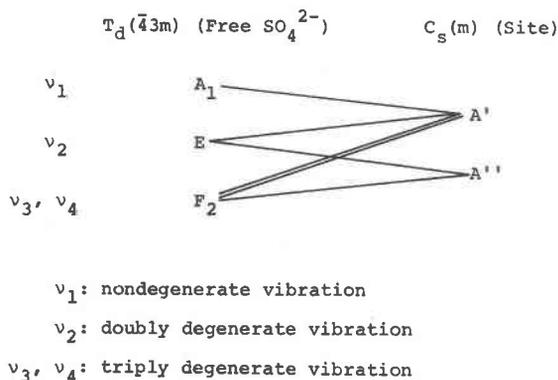


Fig. 2. Symmetry correlation diagram.

Discussion

As is seen in the structure of barite, Figure 1, the angle of O(3)-S-O(3) adjacent to the barium atom is narrower than $109^\circ 28'$, while that of O(1)-S-O(2) is wider, and the bond lengths of two S-O(3) corresponding to the former are longer than those of S-O(1) and S-O(2). The observed narrow angle and long bond length are the result of the displacement of two O(3) atoms toward the barium atom reducing a repulsive force between the barium atom and the sulphur atom. The similar displacement was found in all of the alkaline-earth and IVA group compounds. The displacement of the oxygen atoms distorts the

structure of the SO_4 tetrahedron. The distortion of the SO_4 tetrahedron suggests that each oxygen atom of SO_4 is not bounded by equal bonding strengths from surrounding metal ions in these structures. The mean sulphur-oxygen bond length in the sulphates becomes shorter in this order: PbSO_4 , SnSO_4 , BaSO_4 , SrSO_4 , and CaSO_4 .

In order to examine the effect of the metal ions on the SO_4 tetrahedron, the relationships between the force constants within SO_4 and the field strength of a metal ion are discussed. Figure 3 shows a plot of the stretching force constant versus the values $Z_{e1} \times Z_{e2} / r_{M-O}^2$ for the alkaline-earth and IVA group compounds. Z_{e1} and Z_{e2} are the formal charge of the metal ion and the oxygen ion, respectively, and r_{M-O} is the average metal-oxygen distance derived from the structure refinements. The field strength or the polarizing power, $Z_{e1} \times Z_{e2} / r_{M-O}^2$, is the derivative of the attractive coulombic potential energy. Although the structure of anhydrite is very different from that of celestite and barite, the alkaline-earth group compounds exhibit a linear relationship between force constant and field strength, Figure 3. The IVA group compounds do not show a similar relationship. The electronegativities of the alkaline-earth group are close to 1.0 (Mg = 1.2, Ca = 1.0, Sr = 1.0, and Ba = 0.9), while those of the IVA group are 1.8 (Sn = 1.8 and Pb = 1.8). The observed discrepancy can be ascribed to the difference in electronegativities of metals of the alkaline-earth and IVA groups.

The observed relationship between the stretching force constant within the SO_4 tetrahedron and the field strength in the alkaline-earth group compounds

Table 4. Observed and calculated frequencies and determined force constants

	MgSO_4^*	CaSO_4^*	SrSO_4	BaSO_4	SnSO_4^*	PbSO_4
$\nu_{1\text{obs}}$	1020 cm^{-1}	1013 cm^{-1}	990 cm^{-1}	980 cm^{-1}	985 cm^{-1}	960 cm^{-1}
$\nu_{1\text{calc}}$	1020	1005	995	987	985	965
$\nu_{2\text{obs}}^*$	505	515	491	470	475	—
	430	415**	—	439	425	—
$\nu_{2\text{calc}}$	487	470	463	457	454	438
$\nu_{3\text{obs}}$	1235	1149	1190	1170	1185	1110
	1175	1126	1125	1110	1080	1040
	1155	1095	1085	1075	1050	—
	1110	—	—	—	—	—
	1085	—	—	—	—	—
$\nu_{3\text{calc}}$	1149	1141	1132	1126	1106	1099
$\nu_{4\text{obs}}$	705	671	635	625	650	615
	615	612	605	600	595	590
	—	592	—	—	590	—
$\nu_{4\text{calc}}$	648	634	624	621	619	605
K ***	6.48 $\text{md}/\text{Å}$	6.41 $\text{md}/\text{Å}$	6.34 $\text{md}/\text{Å}$	6.27 $\text{md}/\text{Å}$	6.02 $\text{md}/\text{Å}$	5.98 $\text{md}/\text{Å}$
H ***	0.51	0.48	0.47	0.46	0.43	0.42
F ***	0.83	0.78	0.75	0.73	0.78	0.70

* Farmer (1974).

** Krishnan (1946).

*** K : the stretching force constant between S-O.

H : the bending force constant between O-S-O.

F : the repulsive force constant between O...O.

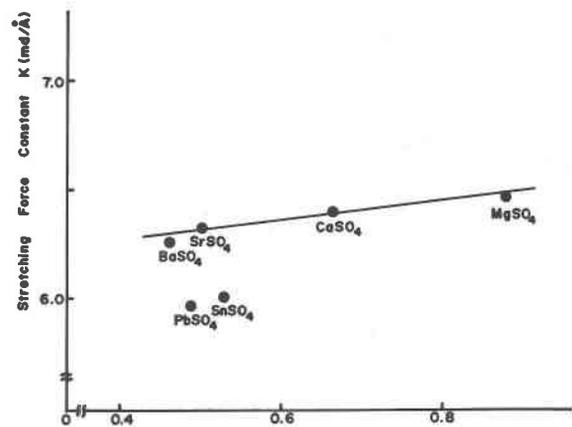


Fig. 3. Plot of the stretching force constant vs. the values $Z_{e1} \times Z_{e2} / r_{M-O}^2$ for the alkaline-earth and IVA group compounds.

is the result of an interaction of the coulombic force between a metal ion and an oxygen ion. As the coulombic force between a metal ion and an oxygen ion increases, the restoring force between sulphur and oxygen atoms increases. The increase of the restoring force results in an increase of the stretching force constant in the SO_4 tetrahedron. The mean sulphur-oxygen bond length becomes shorter with increasing the stretching force constant.

The linear increase in the bending force constant H and the repulsive force constant F of the sulphates are found with increasing field strength.

Conclusion

The electronegativity of a metal and the coulombic force between a metal ion and an oxygen ion modify the structure of the SO_4 tetrahedron. The increase of the field strength of a metal ion gives rise to the increase of the force constants in the SO_4 tetrahedron.

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