

A FURTHER REFINEMENT OF THE BARITE STRUCTURE

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ABSTRACT

The crystal structure of barite, BaSO_4 , a 8.8842(12), b 5.4559(8), c 7.1569(9) Å, $Z=4$, space group $Pnma$, has been refined by full-matrix least-squares methods to $R=0.0295$ ($R_w=0.0474$) using 326 Zr-filtered $\text{MoK}\alpha$ data.

SOMMAIRE

La structure cristalline de la barite, BaSO_4 , a 8.8842(12), b 5.4559(8), c 7.1569(9) Å, $Z=4$, groupe spatial $Pnma$, a été affinée par la méthode des moindres carrés à matrice entière jusqu'à un indice R de 0.0295 (indice pondéré $R_w=0.0474$) en utilisant 326 réflexions obtenues en radiation $\text{MoK}\alpha$ filtrée au Zr.

(Traduit par la Rédaction)

INTRODUCTION

The crystal structure of barite, BaSO_4 , was determined by James & Wood (1925) and has been refined by Sahl (1963) and Colville & Staudhammer (1967). Hawthorne & Ferguson (1975) have refined the structure of celestite using anisotropic thermal vibration parameters for all atoms, but Colville & Staudhammer (1967) and Sahl (1963) reported only isotropic parameters in their refinements of barite and anglesite respectively. In view of the significantly higher temperature factors obtained for the oxygen atoms which were constrained to lie on the mirror plane in all these studies, it was interesting to speculate whether these atoms do indeed occupy special positions, or whether they are disordered on either side of the symmetry plane. For these reasons, a three-dimensional refinement of barite was undertaken.

EXPERIMENTAL

Electron microprobe analyses of barite crystals from Mapimi, Durango, Mexico, confirmed that no elements other than Ba, S and O were

present in significant amounts. A cleavage fragment of this material was ground into an ellipsoid with semi-dimensions $0.083 \times 0.124 \times 0.162$ mm and mounted with the a axis parallel to the ϕ axis of a Picker card-controlled four-circle diffractometer after precession photography had confirmed the space group as $Pnma$ or $Pn2_1a$. The unit-cell parameters were refined by a least-squares method using the angular coordinates (measured at 21°C) of 24 accurately centered reflections in the range $2\theta=47-55^\circ$ using $\text{MoK}\alpha_1$ radiation ($\lambda=0.70930\text{Å}$). The results are a 8.8842(12), b 5.4559(8), c 7.1569(9) Å, V 346.9(1) Å³, and compare favorably with the values of Colville & Staudhammer (1967). X-ray intensity data were collected at 21°C using Zr-filtered $\text{MoK}\alpha$ radiation ($\lambda=0.71069\text{Å}$) and a 2θ scan rate of 2° per minute. Background intensities were estimated from 10-second stationary counts at both ends of each 3° scan. A total of 1326 reflections of the types hkl , $\bar{h}kl$, $hk\bar{l}$ and $h\bar{k}\bar{l}$ with $2\theta < 50^\circ$ was measured, using three reflections to monitor instrument and crystal stability at frequent intervals: these showed no significant change. The resultant data were corrected for background, Lorentz, polarization and absorption effects (for ellipsoidal crystal shape, $\mu=118.7\text{ cm}^{-1}$) and averaged (using weights based on inverse counting-statistic variances) to yield 326 unique structure factors. The internal consistency index $R_1 = \frac{\sum(I - \bar{I})}{\sum \bar{I}}$, where \bar{I} is the weighted average, was 3.2%.

Scattering factors for Ba, S and O (neutral atoms) were obtained from *International Tables for X-ray Crystallography* (1974) with real and imaginary anomalous dispersion components. Programs utilized for data reduction, refinement, and geometry calculations were local modifications of DATALIB, DATASORT, FOURIER, ORXFLS3, ORFFE3 and ORTEP2. All programs are included in the *World List of Crystallographic Computer Programs*. The atomic parameters of Colville & Staudhammer (1967) were refined in space group $Pnma$ by least-squares minimization of the function $\sum w(|F_o| - |F_c|)^2$ where $\bar{w} = 2\bar{I} / [\sigma_I^2 + (0.03\bar{I})^2]$ with σ_I derived

from counting and averaging statistics. Full-matrix refinement of all variables using an isotropic thermal model resulted in convergence at R and R_w indices of 0.056 and 0.093, respectively, where

$$R = \frac{\sum (|F_o| - |F_c|)/\sum |F_o|}{\sum |F_o|}; R_w = \frac{[\sum w (|F_o| - |F_c|)^2 / \sum w F_o^2]^{1/2}}{[\sum w F_o^2]^{1/2}}$$

Temperature factors were converted to anisotropic of the form

$$\exp \left[- \sum_{i=1}^3 \sum_{j=1}^3 \beta_{ij} h_i h_j \right]$$

A correction was made for isotropic extinction as defined and scaled by Coppens & Hamilton (1970). Refinement of all variables using all the data resulted in convergence at $R=0.032$ and $R_w=0.063$ with 76 intensities affected more than 5% by the extinction-parameter value of 0.23(4). At this stage it became clear that the rather high values obtained for R_w (relative to R) and the extinction parameter were a function of disproportionately large weights given to the biggest structure factors. Attempts were made to optimize the weighting scheme via the "instrument" parameter (originally set = 0.03), but it was discovered that the best results (both in terms of parameter *e.s.d.*'s and R indices) were obtained when unit weights were used. In fact, no parameter changed by more than 2σ in this process, but the values for R and R_w dropped to 0.0295 and 0.0474, respectively. Moreover, the number of reflections affected more than 5% by the new extinction parameter value of 0.16(2) dropped to 59. The major peaks in a difference Fourier synthesis (of maximum density $1.8e\text{\AA}^{-3}$, or somewhat less than 10% of an O atom peak), were in the immediate environment of the Ba atom and probably represent residual ionization and/or absorption effects. The complete set of observed and calculated structure factors is available, at a nominal charge, from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Canada,

Table 2. MAGNITUDES AND ORIENTATIONS OF THE PRINCIPAL AXES OF THERMAL ELLIPSOIDS IN BARITE.

Atom	Axis	R.m.s. displacement \AA	$\pm\alpha$	Angle in degrees to	
				$\pm b$	$\pm c$
Ba	1	0.093(3)	36(9)	90	54(9)
	2	0.102(3)	54(9)	90	144(9)
	3	0.114(3)	90	0	90
S	1	0.089(9)	112(24)	90	22(24)
	2	0.105(8)	158(24)	0	112(24)
	3	0.114(7)	90	0	90
O(1)	1	0.10(3)	15(13)	90	104(13)
	2	0.16(2)	90	180	90
	3	0.17(2)	75(13)	90	15(13)
O(2)	1	0.11(2)	71(15)	90	19(15)
	2	0.17(2)	90	180	90
	3	0.17(2)	19(15)	90	109(15)
O(3)	1	0.10(2)	52(56)	135(18)	111(82)
	2	0.11(1)	119(65)	89(62)	151(67)
	3	0.14(1)	52(20)	45(18)	110(22)

K1A OS2. Atomic coordinates and thermal parameters are given in Table 1. The r.m.s. components of thermal displacement, and thermal ellipsoid orientations appear in Table 2.

DISCUSSION

The barite structure is shown in Figure 1 and the bonding geometry is listed in Table 3. The results are statistically identical to those of Colville & Staudhammer (1967). (Note, however, that there is a typographical error in the z-coordinate of O(3) in Table 1 of the earlier paper: the value should be 0.3109). Details of the barite structure-type have been described elsewhere (Bragg & Claringbull 1965).

Both the Ba and S polyhedra in barite show distortions that are very similar to those described for the isostructural minerals celestite (Hawthorne & Ferguson 1975) and anglesite (Sahl 1963). In all three species, the (equivalent) isotropic thermal parameters of O(1) and O(2), both of which lie on the mirror plane, are significantly higher than that of O(3), in the general

Table 1. FRACTIONAL ATOMIC COORDINATES AND TEMPERATURE FACTOR COEFFICIENTS FOR BARITE*

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	B_{equiv}
Ba	0.1845(1)	1/4	0.1585(1)	23(1)	86(4)	38(2)	0	-3(1)	0	0.84(4)
S	0.4373(4)	3/4	0.1913(5)	26(4)	87(11)	33(6)	0	3(4)	0	0.84(13)
O(1)	0.5890(12)	3/4	0.1066(16)	29(13)	174(39)	111(22)	0	15(14)	0	1.8(4)
O(2)	0.3183(13)	3/4	0.0518(15)	70(16)	197(41)	54(19)	0	-17(15)	0	1.9(5)
O(3)	0.4204(8)	0.9700(13)	0.3116(9)	35(9)	97(23)	48(11)	15(12)	-3(8)	-11(14)	1.1(3)

* β_{ij} thermal parameters $\times 10^4$. The value for B_{equiv} was calculated using the method of Hamilton (1959).

positions (Table 1). Part of this disparity may be ascribed to differences among the environments of the anions. All three atoms are coordinated on one side by the other atoms of the sulfate group ($S+3O$) and are bonded to an additional three barium atoms on the other side. However, for O(1) and O(2), only one barium atom lies within a radius of 3.0\AA (with $\angle S-O-Ba = 161^\circ$ and 134° respectively) whereas for O(3), all three occur within a distance of 2.91\AA (with $\angle S-O(3)-Ba = 101$ to 114°). In addition, the relatively large intermediate axis of thermal displacement for both O(1) and O(2) is oriented perpendicular to the mirror plane (*i.e.* parallel to the b axis) and it was considered that this may reflect slight disorder of the atoms from their ideal positions, thereby increasing the magnitude of their apparent thermal vibration. Indeed, the confinement of the O(2) atom to a position on the mirror plane may also explain

why the S-O(2) distance is shorter than the other bonds in the sulfate tetrahedron (Table 3). However, attempts to refine "split-atom" models for O(1) and O(2) in space group $Pnma$, and also a refinement of the structure in the alternative space group $Pn2_1a$, produced neither an improvement in the R -index nor a significant departure of the atoms from their positions on the mirror plane. It is therefore concluded that the bond-length and bond-angle distortions in the symmetry-constrained model are valid within the experimental limits imposed by the presence of the "heavy" Ba atom. Even when the bond lengths in the sulfate group are corrected for thermal motion using the "riding" and "independent" approximations (Busing & Levy 1964), the S-O(2) distance remains considerably shorter than the other S-O bonds.

In an attempt to rationalize the tetrahedral bond-length variations in more than 50 accurate-

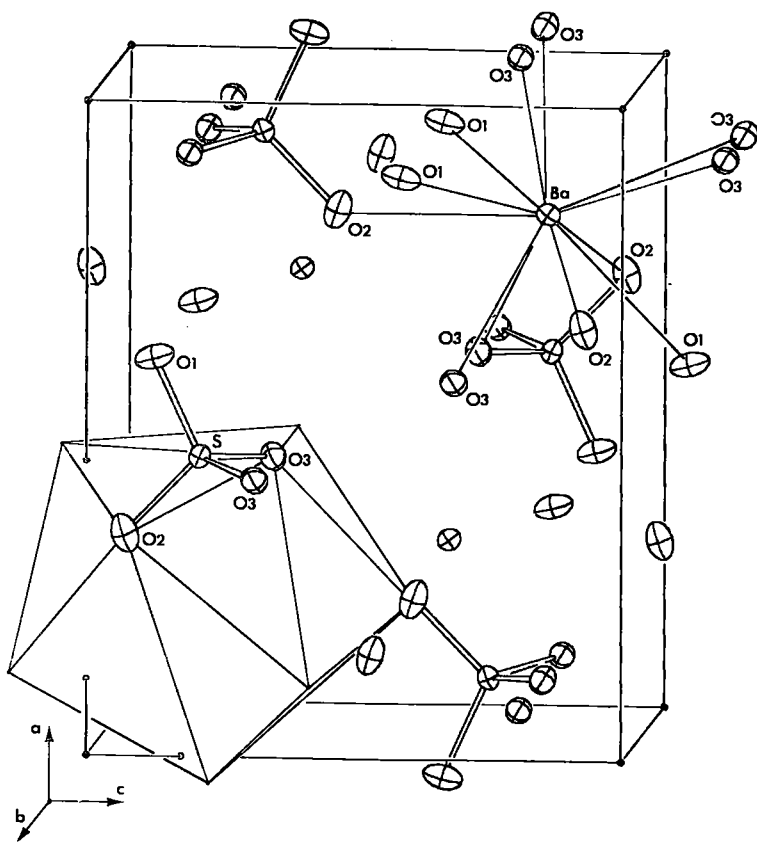


FIG. 1. Unit-cell diagram of the barite crystal structure. Thermal ellipsoids for all atoms represent 50% probability surfaces. Sulfur-oxygen interactions within the SO_4 groups are indicated by conical bonds. The coordination sphere surrounding one of the Ba atoms is indicated by line bonds, and for another by an opaque polyhedron.

Table 3. BARITE INTERATOMIC DISTANCES AND ANGLES*

SO ₄ tetrahedron		Ba polyhedron	
S-O(2)	1.454(11)Å	Ba-O(1) ^{iv}	2.765(11)Å
O(1)	1.478(11)	O(3) ^{iii,2}	2.808(7)
O(3) ⁱ ×2	1.485(7)	O(2) ^{iv}	2.815(11)
mean	1.476(8)	O(3) ^v ×2	2.815(7)
O(2)-O(1)	2.436(16)	O(3) ^v ×2	2.911(7)
O(3)×2	2.392(11)	O(2)×2	3.072(5)
O(1)-O(3)×2	2.416(12)	O(1) ^{iii,2} ×2	3.315(7)
O(3)-O(3) ⁱ	2.400(14)	mean	2.952(7)
mean	2.409(9)	S-O bond lengths corrected for thermal vibration†:	
O(2)-S-O(1)	112.4(7)°	riding	independent
O(3)×2	109.0(4)	S-O(2)	1.466(12)
O(1)-S-O(3)×2	109.3(4)	O(1)	1.489(11)
O(3)-S-O(3) ⁱ	107.9(5)	O(3)×2	1.488(7)
mean	109.5(4)	mean	1.483(9)
			1.497(10)

*Symmetry transformations for atoms outside the asymmetric unit:

- i. $x, 1+1/2-y, z$ iv. $1/2-x, 1-y, 1/2+z$
 ii. $1-x, y-1/2, -z$ v. $1/2-x, 1-y, z-1/2$
 iii. $x-1/2, 1+1/2-y, 1/2-z$

ly refined sulfate compounds (representing 248 individual S-O bonds), Louisnathan *et al.* (1977) were able to account for more than 90% of the variation in S-O bond lengths from a consideration of the average of the three valence angles common to each bond. The algorithm presented therein accurately predicts the S-O(2) and S-O(3) bond lengths in barite ($\Delta=+0.002\text{\AA}$), but suggests a shorter value for the length of S-O(1) (1.452Å). In fact, the mean valence angle common to the S-O(1) bond need only decrease by 1.3° in order for the calculated bond length to correspond to the observed value. However, the changes in atomic position necessary to effect bond-angle changes of this magnitude lie well within the rather large r.m.s. thermal displacements of the O(1) and O(2) atoms and it is to be expected that they would not be detected in a "split atom" or lower-symmetry refinement. For comparison, the extended electrostatic valence rule proposed by Baur (1970) predicts that all three S-O bonds should have the same length (1.45Å) since all have the same coordination and therefore the same sum of bond strengths.

The Ba atom is surrounded by a very irregular array of twelve O atoms at distances from 2.8 to 3.3Å (Fig. 1). Hawthorne & Ferguson (1975) were able to show that all twelve Sr-O interactions are significant from a consideration of the band-strength sums in celestite. Similar calculations for the Ba polyhedron in barite tend to indicate that all twelve bonds are also significant for this structure although, as frequently

found in Ba compounds (Brown & Wu 1976), the sums are relatively poor. The bond angles also show a wide variation (45-163°) and it is clear that the Ba atom environment is largely determined by the bonding requirements of its seven neighboring sulfate groups. However, the deviation of the O-S-O valence angles from the ideal tetrahedral value, with concomitant variations in the S-O bond lengths (and vice versa), indicates that the sulfate groups are in turn measurably influenced by the bonding requirements of the surrounding Ba atoms.

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