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A REFINEMENT OF THE STRUCTURE OF BARITE

ALAN A. COLVILLE, *Department of Geology, California State College at Los Angeles, Los Angeles, California.*

AND

KARL STAUDHAMMER, *TRW Systems, Redondo Beach, California.*

INTRODUCTION

The structure of barite ($BaSO_4$) was first determined by James and Wood (1925) who also showed that celestite ($SrSO_4$) and anglesite ($PbSO_4$) are isostructural. Recently Sahl (1963) completed the structure of anglesite and refined the atomic coordinates of barite (using precession film techniques and *hk*O and *h*O*l* sections) in order to make a comparison of the two structures.

A three-dimensional refinement of the structure of barite was undertaken to obtain precise information on the atomic coordinates, thermal parameters, and interatomic distances and angles so that the coordination geometry of the barium and sulfur atoms could be well delineated. We also were interested in this structure because it would give us an opportunity to study the effects of the heavy barium atom on the results of the analysis.

The specimen selected was a transparent, colorless crystal from the Cow Green Mine, Teesdale, Durham, England. Electron probe microanalysis showed 0.18 weight percent Sr. and no Ca, Fe, or Pb at the 0.01-percent level. The unit-cell dimensions were determined by least-squares refinement of the powder diffraction pattern using a computer program by Burnham (1962). The following are the results of this refinement and a comparison of the cell parameters with those of a synthetic barite determined by Swanson *et al.*, (1954).

TABLE 1

Barite: Atomic coordinates and thermal parameters

Atom	Coordinates (Fractions of cell edge)			Isotropic Temp. Factor
	x	*y*	*z*	*B* (A^2)
Barium	0.1846[1]	1/4	.1581[1]	0.68[02]
Sulfur	.4370[2]	3/4	.1914[3]	0.37[04]
Oxygen (1)	.5878[6]	3/4	.1062[10]	1.56[15]
Oxygen (2)	.3192[6]	3/4	.0515[10]	1.63[15]
Oxygen (3)	.4186[4]	0.9702[5]	.3190[7]	0.85[09]

Barite: Cow Green Mine	*Barite: synthetic*
a 8.884[4] A	8.878 A
b 5.458[3] A	5.450 A
c 7.153[3] A	7.152 A
V 346.9[2] A³	346.1 A³

A small cleavage fragment, with dimensions $0.1\times0.1\times0.2$ was mounted on the elongate *c*-axis. A series of precession and Weissenberg

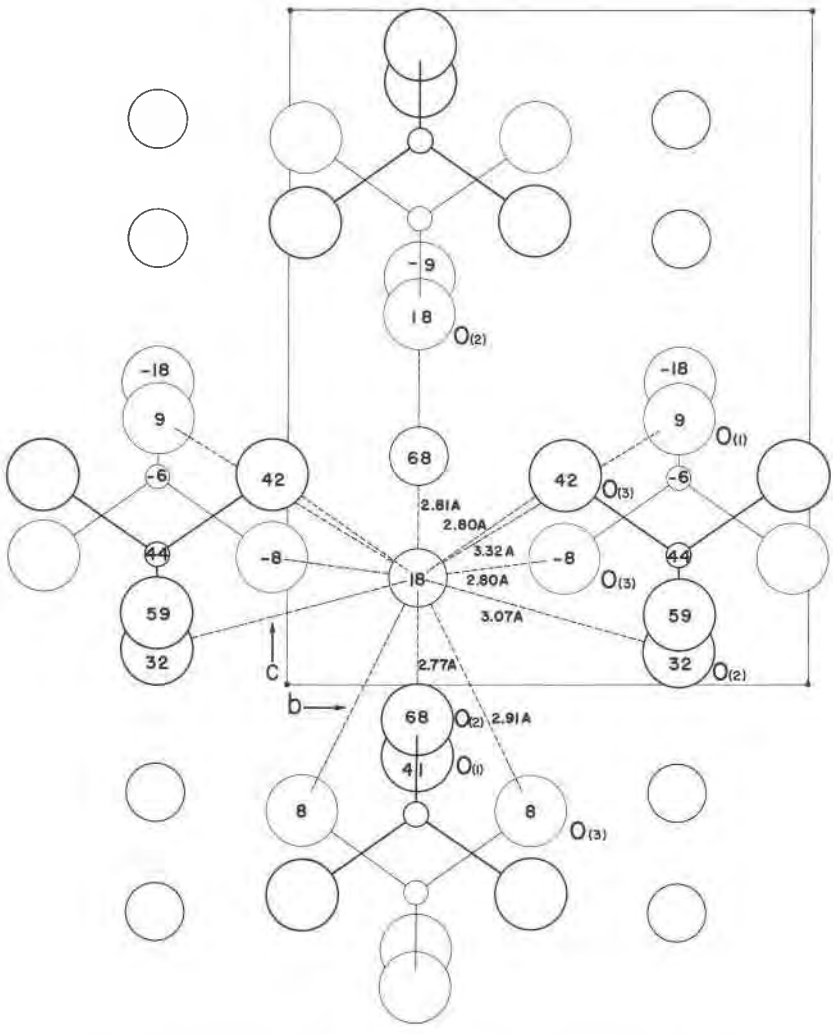

FIG. 1. Barite structure on [100] showing coordination of the barium atom.

photographs were taken; no deviation from the accepted space group *Pnma* was noted.

Intensity Measurement and Refinement

A total of 400 reflections, *hk*O-*hk*5, were measured using an equi-inclination single-crystal diffractometer, a scintillation counter and chart recording. Integrated intensities were corrected for the Lorentz and polarization factors. Absorption effects were corrected by treating the crystal as a cylinder and using the absorption formula of J. H. Van den Hende, Esso Research Co., Pearl River, N.Y. and the correction tables computed by Bond (1959) for an $\mu_1 R = 0.60$.

A full-matrix least-squares refinement was carried out with one scale factor and 16 atomic parameters varied. The computer program used was ORFLS written by Busing *et al.*, (1962). The final agreement factor was $R = 0.051$. The atomic coordinates and the thermal parameters are presented in Table 1. Interatomic distances and angles were computed using ORFFE (Busing *et al.*, (1964). The errors were computed from the correlation matrix and include the effect of errors in the cell parameters. It should be pointed out that the errors in the sulfur-oxygen and oxygen-oxygen distances are approximately twice those of the barium-oxygen distances because of the effect of the relatively large scattering factor of the barium atom on the intensities.

Discussion of the Structure

The main details of the structure are illustrated in Figure 1. Other views of the structure have been compiled by Deer *et al.*, (1962). In the

Table 2

Barite: Interatomic distances and angles

Sulfur-Oxygen distances (A)

S-O(1)	1.472[7]	(×1)
-O(2)	1.448[7]	(×1)
-O(3)	1.484[5]	(×2)
Mean	1.472[3]	

Oxygen-Oxygen Tetrahedral distances (A)

O(1)-O(2)	2.418[7]	(×1)
O(1)-O(3)	2.418[7]	(×2)
O(2)-O(3)	2.381[8]	(×2)
O(3)-O(3)	2.404[7]	(×1)
Mean	2.403[3]	

Barium-Oxygen distances (A)

Nearest neighbors

Ba-O(1)-1	2.768[4]	(×1)
-O(2)-2	2.814[6]	(×1)
-O(3)-2	2.802[4]	(×2)
-O(3)-3	2.802[4]	(×2)

Next neighbors

Ba-O(3)-1	2.908[5]	(×2)
-O(2)-1	3.075[3]	(×2)
-O(1)-2	3.321[4]	(×2)

Oxygen-Sulfur-Oxygen angles (degrees)

O(1)-S-O(2)	111.8[5]	(×1)
O(1)-S-O(3)	109.8[3]	(×2)
O(2)-S-O(3)	108.6[3]	(×2)
O(3)-S-O(3)	108.2[3]	(×1)
Mean	109.5[2]	

sulfur-oxygen tetrahedron, the y-coordinates of S, O(1), and O(2) are fixed by the mirror plane at either $\frac{1}{4}$ or $\frac{3}{4}$; whereas, O(3) is in a general position on either side of the plane. The mean interatomic distance for this tetrahedron is 1.472(3) Å (see Table 2): the average bond angle is 109.5(2) degrees. Barium is in a special position at $(x, \frac{1}{4}, z)$ and $(x, \frac{3}{4}, z)$ and is surrounded by a total of 12 oxygen atoms; however, in view of the range of interatomic distances, we have arbitrarily grouped six oxygen atoms as nearest neighbors. These have a mean distance of 2.80 Å. The other six oxygen atoms are in pairs at progressively longer distances.

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CALZIRTITE FROM CARBONATITES OF NORTHERN SIBERIA

A. G. BULAKH, G. F. ANASTASENKO, L. M. DAKHIYA, *Departments of Mineralogy and Geochemistry, Leningrad State University Leningrad, U.S.S.R.*

INTRODUCTION

Calzirtite, a complex oxide of calcium, zirconium, and titanium, is one the rare accessory minerals of carbonatites and alkaline rocks. In 1956