American Mineralogist, Volume 62, pages 167–169, 1977

Barylite, $BaBe_2Si_2O_7$: its space group and crystal structure

P. D. Robinson and J. H. Fang

Department of Geology, Southern Illinois University
Carbondale, Illinois 62907

Abstract

The barylite structure can be refined to an *R* index of 0.060 in the orthorhombic centrosymmetric space group *Pnma*, despite the fact that the structure is intrinsically non-centrosymmetric as disclosed by a second harmonic generation (SHG) test. Refinement in the non-centrosymmetric space group $Pn2_1a$ yielded no significant changes in positional parameters, possibly because of the dominant role of the centrosymmetrically arranged Ba atoms in the scattering. The F_0 and ΔF maps provided no clues as to the source of the acentric distribution of structure factors. We therefore suggest that a sensitive physical test, such as SHG, be routinely performed before a crystal structure is accepted as centrosymmetric.

Introduction

A crystal structure for barylite ($BaBe_2Si_2O_7$) was first proposed by Abrashev *et al.* (1964). They report that barylite exhibits strong piezoelectricity and, therefore, must belong to the noncentrosymmetric space group $Pn2_1a$, despite the fact that the structure is very nearly centrosymmetric. However, their results were based on 2-dimensional film data which led to a relatively high *R*-index (11.7%) and, as was later discovered, several incorrect *z* coordinates.

Thus, Cannillo *et al.* (1969) initiated a reexamination of the structure to confirm (or refute) the somewhat questionable results of the Russian workers. Their attempt to refine the Russian coordinates, using their own 3-dimensional Weissenberg photographic data, met with failure because of the incorrect *z* coordinates mentioned above. Interestingly, they could detect *no* piezoelectricity. However, they state that "the amount of crystal fragments used (for the piezoelectric test) was small." They ultimately solved the structure by use of Patterson synthesis and refined it to an anisotropic *R*-index of 0.071 in the centrosymmetric space group *Pnma*.

However, a question remained as to the space group of barylite, particularly in light of the conflicting piezoelectric results. Thus, we have undertaken this study in an attempt to resolve the problem.

Data collection and reduction

A few transparant cleavage fragments from a large (45 × 23 × 15 mm) barylite crystal, found in an amazonite pocket in Park County, Colorado, was kindly supplied by John S. White, Jr., of the Smithsonian Institution (specimen no. USNM 123956). The sample has been confirmed as barylite by X-ray powder diffraction, optical properties, cleavage, and electron microprobe analysis (Arem, 1972). The unit cell parameters, from precession photographs, are a = 9.82(1)Å, b = 11.67(1)Å, c = 4.69(1)Å, Z = 4 and space group *Pnma* or $Pn2_1a$.

The crystal used for data collection was a transparent rectangular tablet of dimensions 0.20 × 0.09 × 0.05 mm. The shortest dimension corresponds to the *a* axis, about which the crystal was rotated during the intensity-gathering process. A total of 2670 raw intensities were collected with a computer controlled Buerger-Supper equi-inclination goniometer and Zr filtered Mo$K\alpha$ radiation; 1045 reflections were considered "observed" after passing the $\{I - B \geq 4\sqrt{I + B}\}$ test (where I = total counts accumulated during the scan and B = total background). Scan speed was varied directly with peak intensity (1°/min–15°/min) in order to minimize variations in counting statistics.

All data were corrected for Lp and absorption (μ = 80.82 cm^{-1}) using the ACACA program of Prewitt (Wuensch and Prewitt, 1965).

Refinement and space group determination

We began by refining the Canillo *et al.* coordinates in *Pnma*, using the RFINE full-matrix least-squares program of Finger (1969). No problems were encountered, and the structure refined smoothly to an *R*

TABLE 1. Atomic coordinates and temperature factors for barylite*

Atom	Equi-point	x RF**	x CNR**	y RF	y CNR	z RF	z CNR	B(Å^2) RF	B(Å^2) CNR
Ba	4c	.15158(8)	.1515(2)	3/4	3/4	.2470(3)	.2473(6)	0.79(1)+	0.86+
Be	8d	.161(1)	.162(3)	.502(1)	.502(2)	.703(2)	.699(7)	0.6(1)	0.90(45)
Si	8d	.0885(3)	.0886(6)	.3779(2)	.3779(5)	.1995(5)	.1930(14)	0.50(3)	0.45(11)
O(1)	8d	.4291(6)	.4297(13)	.3846(5)	.3845(11)	.2175(14)	.2131(37)	0.63(7)	0.73(24)
O(2)	8d	.1874(6)	.1861(15)	.4712(5)	.4701(13)	.3558(14)	.3579(33)	0.51(6)	0.53(24)
O(3)	8d	.1072(7)	.1092(17)	.3868(6)	.3873(14)	.8592(14)	.8584(38)	0.74(8)	1.27(30)
O(4)	4c	.1454(9)	.1431(18)	1/4	1/4	.2958(16)	.2983(46)	0.50(9)	0.09(29)

*Parenthesized figures represent the estimated standard deviation (esd) in terms of least units cited for the value to their immediate left.

**RF refers to the coordinates of Robinson and Fang while CNR refers to the coordinates of Cannillo, Negro and Rossi.

+The equivalent isotropic temperature factor calculated from the anisotropic.

index of 0.060 with Ba anisotropic and all other atoms isotropic.

At this point we asked Dr. Joseph D. Dougherty, of North American Philips Corporation, to run a second harmonic generation (SHG) test, using the laser instrument which Philips Laboratories has developed. The theoretical basis for this method, stated very briefly, is as follows: When a light wave passes through a non-centrosymmetric crystal, the electric field associated with the wave induces a polarization at twice the incident frequency. If this signal (second harmonic) is detected, the crystal must be non-centrosymmetric, since the second harmonic coefficients form a third-rank tensor which is subject to the same symmetry constraints as the piezoelectric tensor. The analyzer developed by Philips Laboratories can detect second harmonic generation at levels 1/1000 of that generated in a quartz standard (Dougherty and Kurtz, 1975). The second harmonic analyzer (SHA) is capable of handling single crystals up to 15 mm in diameter with a thickness of 4 mm or less, and powder samples in quantities of 3–10 milligrams. However, the SHA instrument is capable of detecting less than 50 micrograms of quartz in an index-matching liquid. In the case of barylite, one thin rectangular cleavage fragment (largest dimension slightly over 1 mm) was immersed in an index-matching liquid and run on the SHA. According to Dr. Dougherty, "The second harmonic tests on the barylite crystals indicate that these crystals are definitely non-centrosymmetric." He further stated that "the signals are very strong." Somewhat puzzled, we proceeded to refine the structure in the non-centrosymmetric $Pn2_1a$. During the refinement, the atoms related by the "pseudo" center of symmetry were not simultaneously varied, in order to avoid the problem of high correlation coefficients. This refinement produced the same atomic coordinates (within the standard deviations) as did the centrosymmetric refinement and the R index remained at 0.060. As a final check, both F_0 and ΔF maps were computed using centrosymmetric atomic positions. No spurious peaks or irregular electron-cloud distributions were found. Thus we were unable to detect the source of the acentric distribution of F's from our X-ray data, despite the fact that barylite is undeniably non-centrosymmetric.

TABLE 2. Selected interatomic distances and angles for barylite*

Tetrahedral coordination around Si and Be

	RF**	CNR**		RF	CNR
Si-O(3)	1.610(6)Å	1.59(2)Å	O(3)-Si-O(1)	110.3(4)°	113.7(9)°
Si-O(1)	1.615(6)	1.60(2)	O(3)-Si-O(2)	109.5(4)	109.6(9)
Si-O(2)	1.633(6)	1.65(2)	O(3)-Si-O(4)	106.9(4)	107.9(9)
Si-O(4)	1.656(4)	1.67(1)	O(1)-Si-O(2)	115.8(4)	114.2(8)
			O(1)-Si-O(4)	107.7(4)	106.3(9)
			O(2)-Si-O(4)	106.1(4)	104.4(9)
MEAN	1.628Å	1.63Å	MEAN	109.4°	109.4°
Be-O(1)	1.59(1)Å	1.60(3)Å	O(1)-Be-O(3)	119.3(7)°	118.7(2)°
Be-O(3)	1.62(1)	1.62(3)	O(1)-Be-O(2)	108.6(7)	107.8(2)
Be-O(2)	1.68(1)	1.66(4)	O(1)-Be-O(2)	107.7(6)	108.6(2)
Be-O(2)	1.69(1)	1.70(3)	O(3)-Be-O(2)	104.5(7)	103.7(2)
			O(3)-Be-O(2)	108.0(7)	107.7(2)
			O(2)-Be-O(2)	108.4(6)	110.1(2)
MEAN	1.64Å	1.64Å	MEAN	109.4°	109.4°

Coordination around Ba

	RF	CNR
Ba-O(1)	2.822(7)Åx2	2.80(2)Å
Ba-O(3)	2.905(7)x2	2.89(2)
Ba-O(4)	2.907(7)	2.92(2)
Ba-O(1)	3.043(7)x2	3.06(2)
Ba-O(3)	3.042(7)x2	3.06(2)
MEAN	2.948Å	2.95Å

*Parenthesized figures represent the estimated standard deviation in terms of least units cited for the value to their immediate left.

**RF refers to the results of Robinson and Fang while CNR refers to the work of Cannillo, Negro and Rossi.

Table 1 lists the positional and thermal parameters (in space group *Pnma*), and Table 2 presents selected interatomic distances and angles. The left columns in these tables give our results while, for comparative purposes, the right columns list the values reported by Cannillo *et al.* (1969). Adequate crystal-structure illustrations are presented by Cannillo *et al.*, and are omitted here.

Conclusions

(1) Barylite is non-centrosymmetric based on the SHG test.

(2) The non-centrosymmetric barylite structure can be refined to an *R* index of 0.060 in the centrosymmetric space group *Pnma* by standard least-squares techniques.

(3) One possible explanation for the successful refinement in space group *Pnma* is the dominance of X-ray scattering by centrosymmetrically located heavy atoms (Ba in this structure).

(4) A satisfactory, centrosymmetric refinement is not conclusive evidence of centrosymmetry. A sensitive physical test, such as SHG, should be routinely performed.

Acknowledgments

We wish to thank Dr. Joseph P. Dougherty for performing the SHG test and for several hours of enlightening conversations regarding the SHG technique. We also thank the Smithsonian Institution for providing the barylite sample.

References

Abrashev, K. K., V. V. Ilyukhin and N. V. Belov (1964) Crystal structure of barylite, $BaBe_2Si_2O_7$. *Kristallografiya,* **9,** 816. English translation (1965): Soviet Physics-Crystallography, **9,** No. 6, 691–699.

Arem, Joel E. (1972) What's new in minerals? *Mineral. Rec.* **3,** 131–133.

Cannillo, E., A. Dal Negro and G. Rossi (1969) On the crystal structure of barylite. *Rend. Soc. Ital. Mineral Petrol.* **26,** 2–12.

Dougherty, J. P. and S. K. Kurtz (1975) *A second harmonic analyzer for the detection of non-centrosymmetry.* Technical Report No. 273, Program 301, 41 pages, Philips Laboratories, Briarcliff Manor, N.Y.

Finger, L. W. (1969) The crystal structure and cation distribution of a grunerite. *Mineral. Soc. Am. Spec. Pap.* **2,** 95–100.

Wuensch, B. J. and C. T. Prewitt (1965) Corrections for X-ray absorption by a crystal of arbitrary shape. *Z. Kristallogr.* **122,** 24–59.

Manuscript received, February 6, 1976; accepted for publication, July 2, 1976.