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ON THE CRYSTAL STRUCTURE OF BARYLITE

RIASSUNTO. — La barylite è un silicato di formula chimica $BaBe_2Si_2O_7$, che cristallizza nel sistema rombico, gruppo spaziale $Pnma$. La cella elementare, i cui lati sono: $a = 9.79 \text{ \AA}$, $b = 11.65 \text{ \AA}$, $c = 4.63 \text{ \AA}$, contiene quattro delle unità stechiometriche sopra riportate.

La struttura cristallina di questo minerale è stata determinata da Abrashev, Ilyukhin e Belov nel 1964, basandosi su dati bidimensionali. Essa consiste di gruppi Si_2O_7 , collegati fra loro da tetraedri BeO_4 , in modo da formare un'impalcatura tridimensionale di tetraedri, nelle cavità della quale sono posti gli atomi di bario.

L'affermazione di Abrashev e Coll. che la barylite è fortemente piezoelettrica e la constatazione che le coordinate degli atomi pubblicate si discostano pochissimo da quelle di una struttura centrosimmetrica, hanno fatto ritenere utile un riesame della struttura basato su dati röntgenografici tridimensionali. E' risultato che la struttura proposta da Abrashev e Coll. è, nelle grandi linee, corretta, ma che i dati bidimensionali raccolti da questi Autori non hanno permesso loro di accorgersi che la posizione di alcuni atomi è notevolmente diversa. Poiché inoltre il test di piezoelettricità, eseguito sul campione da noi utilizzato, è stato negativo, il raffinamento è stato condotto nel gruppo spaziale $Pnma$. Il fattore di discordanza finale è 0.071.

Si confrontano i parametri finali ricavati da questa analisi con quelli degli Autori russi e si discutono criticamente le discordanze osservate.

Introduction.

Barylite $BaBe_2Si_2O_7$ has been recently studied from a structural point of view by Abrashev, Ilyukhin and Belov [1]. The interest of this laboratory in the field of silicates as well as some unsatisfactory statements found in the paper of Abrashev *et al.*, persuaded the authors of this work that a re-examination of the crystal structure of barylite was desirable. Furthermore, at least a refinement based on three-dimensional data was necessary in order to obtain more precise values of the bond distances and angles.

The following is a short outline of the crystal structure analysis made by the Russian Authors and of their results.

« A very marked piezoelectric effect, greater than that for quartz » led them to the adoption of the emihedral $Pn2_1a$ space group instead of the more obvious $Pnma$. The X-ray data used were $hk0$ and $0kl$ reflexions measured on MoK_α Weissenberg photographs. Patterson syntheses permitted to locate the Ba atoms and from successive Fourier syntheses the coordinates of all the remaining atoms but Be were obtained. The positions of Be were determined by means of a difference Patterson synthesis. The final reliability factors were $R_{hk0} = 11.4\%$ and $R_{0kl} = 11.7\%$. The coordinates of this acentric structure are shown in Table I, free of some evident misprints occurring in both the Russian and English version of the paper. As one can see these coordinates are very close to centrosymmetry. It should be not far from true to say that the differences from an actual centrosymmetry of these coordinates are of the same order of magnitude of the probable standard deviations (not given in the paper).

Experimental.

The sample of barylite used for this work has been kindly furnished by Prof. C. Frondel. A crystal fragment was chosen and reduced to a suitable spherical shape ($r = 0.018$ cm). Integrated Weissenberg photographs (rotation axis c , l from 0 to 4) were taken by using the CuK_α radiation and the multiple films technique. Of the about 640 reflexions present in the CuK_α limiting sphere, 562 were inspected (87%); 405 out of them were measured photometrically and 157 were either too faint to be conveniently measured or did not give any blackening on the films. The intensities were corrected for absorption ($\mu = 618$ cm^{-1}) using the curves for crystals of spherical shape published by Weber [2]. The lattice parameters measured on the rotating crystal and Weissenberg pictures are in good agreement with those published by Ito and Frondel [3] for synthetic barylite. So the following values quoted from these Authors were used:

$$a = 9.82, b = 11.67, c = 4.69 \text{ \AA}.$$

Also the correction for the incomplete $\alpha_1 - \alpha_2$ spot doubling was applied, taking into account the integration technique, which complicates the splitting effect for its diagonal direction with respect to the sides of the films.

A test for piezoelectricity gave negative results. We must say that the amount of crystal fragments we used was small. However we made the same test on a comparable amount of quartz crystal fragments: the piezoelectric effect was in this case unequivocally detected.

Crystal Structure Analysis.

An attempt to refine by means of the least-squares method the coordinates of Abrashev *et al.* with our experimental data was completely unsuccessful. The discrepancy factor did not decrease, the standard deviations of atomic coordinates were high and the temperature factors of several atoms became negative or extremely high. An examination of the observed and calculated structure factors showed that the greatest disagreement occurred for the reflexions with $h = 2n + 1$; more precisely the values of the calculated structure factors were too low. At this stage the three-dimensional Patterson synthesis was examined; the pseudo-acentric coordinates of Abrashev *et al.* seemed to be roughly consistent with it. A « spread-out » of some Patterson maxima in the direction of the c axis attracted our attention. In the $Pnma$ space group if an atom has a z -coordinate equal to $1/4$ its contribution to the structure factor of the reflexions with $h = 2n + 1$ is zero; obviously this limitation is effective also for the pseudo-acentric structure of the Russian Authors. In fact the Ba atoms are in this situation and the Patterson maxima are in perfect agreement with this assumption. Furthermore the position of Ba is centric also for the space group $Pn2_1a$.

On the basis of all these considerations several attempts were made to find an alternative structure that could justify better the « strong piezoelectric effect » than the pseudo-acentric one of Abrashev *et al.* All these attempts led to the more obvious centric structure. Several doubts remained on the z -coordinates of some atoms because just these coordinates determine the more or less good agreement of the structure factors of the reflexions with $h = 2n + 1$. In order to solve the question a three-dimensional Patterson synthesis using only this group of reflexions was computed. Also with these new informations we were not able to find a « truly » acentric structure. On the other hand from this Patterson synthesis clearly emerged that the z -coordinates of silicon, of berillium and of some oxygens were considerably different from those deduced by Abrashev *et al.* on the basis of the Patterson projections. We deduced a consistent set of centric coordinates (Table I)

TABLE I.

Left: final parameters resulting from this work; the numbers in parentheses are the standard deviations. Right: atomic coordinates of the work of Abrashev et al., corrected for some evident misprints and arranged in such a way to show the differences from centrosymmetry.

Atom	x/a	y/b	z/c	B	Atom	x/a	y/b	z/c
Ba	.1515 (2)	.7500	.2473 (6)	0.86(*)	Ba	.142	.750	.250
Si	.0886 (6)	.3779 (5)	.1930(14)	0.45(11)	Si(1)	.096	.380	.250
					Si(2)	-.100	-.375	-.250
O(1)	.4297(13)	.3845(11)	.2131(37)	0.73(24)	O(1)	.427	.397	.220
					O(5)	-.430	-.390	-.290
O(2)	.1861(15)	.4701(13)	.3579(33)	0.53(24)	O(6)	.185	.475	.405
					O(3)	-.181	-.470	-.452
O(3)	.1092(17)	.3873(14)	.8584(38)	1.27(30)	O(2)	.087	.385	.870
					O(7)	-.090	-.385	-.874
O(4)	.1431(18)	.2500	.2983(46)	0.09(29)	O(4)	.130	.250	.310
Be	.1624(29)	.5021(24)	.6988(71)	0.90(45)	Be(2)	.170	.505	.750
					Be(1)	-.175	-.499	-.750

(*) Ba was treated anisotropically in the least-squares refinement; the value of B listed in this Table is that of the equivalent isotropic temperature factor after Hamilton [6].

which maintained the general features of the structure of the Russian Authors and at the same time gave a better agreement for the reflexions with $h = 2n + 1$. These coordinates were submitted to a centrosymmetrical least-squares refinement. The R factor dropped in few cycles to 0.09. A three-dimensional ΔF Fourier synthesis showed a marked anisotropy for Ba atom. Two successive least squares cycles carried out with anisotropical temperature factor for Ba lowered the R factor to 0.08. The application of the anomalous dispersion correction for barium ($\Delta f'$ and $\Delta f''$ given by Cromer [4]) and of the extinction correction (Zachariasen [5]) led, after two more least squares cycles, to a final discrepancy factor of 0.071. At this stage we were very puzzled; the centrosymmetrical crystal structure of a mineral which showed a «strong piezoelectric effect» gave a disagreement factor that can be considered quite satisfactory.

In Table I our final centric atomic coordinates are compared with the acentric ones of Abrashev *et al.* The analysis of the anisotropic thermal parameters of Ba is reported in Table II; their significance is lessened by the fact that not all the atoms were treated anisotropically and that the structure factors are scaled level by level.

TABLE II.

Analysis of the anisotropic thermal parameters.

(root mean square thermal vibration along the ellipsoid axes (Å), magnitudes of the principal axes (Å²) and angles (°) between the crystallographic axes and the principal axes of the vibration ellipsoid)

Atom	r.m.s.	B	Angles with respect to		
			a	b	c
Ba	0.12	1.08	95	90	5
	0.13	1.31	90	0	90
	0.05	0.20	5	90	85

In Table III the final observed and calculated structure factors are compared. The calculated structure factors are computed with the following formula, which takes into account the secondary extinction and the anomalous dispersion:

$$F_c = \frac{\sqrt{[\sum_i (f_i + \Delta f'_i) \cos \varphi_i]^2 + [\sum_i \Delta f''_i \cos \varphi_i]^2}}{(1 + \beta_{(2\theta)} g I_0)}$$

The final value of the extinction coefficient is $g = 3.17 \cdot 10^{-8}$; the terms due to the absorption were neglected in computing $\beta_{(2\theta)}$.

Discussion.

The structural model of barylite resulting from this work does not differ, in its general aspect, from that of Abrashev *et al.* The main feature of this silicate is the three-dimensional tetrahedral network built up by Si₂O₇ groups connected by chains of Be-tetrahedra (Fig. 1 and 2). However the differences in the z-coordinates of some atoms modify significantly the structural details.

TABLE III.

Structure factors of *Barylite*.

Reflexions marked with an asterisk were unobservably weak; in this case F_0 differs from 0.5 I_{min} .

h	k	l	FO	FO*	10FC	10FC*	
0	2	1284	1891	-1392	2322	0	
0	4	822	828	764	319	0	
0	6	1588	1713	-1730	-304	0	
0	8	2256	2481	2515	284	0	
0	10	798	784	-759	277	0	
0	12	605	330	221	284	0	
0	14	1023	1042	-1023	-207	0	
0	16	883	880	829	312	0	
0	18	1777	1723	-1693	-107	0	
0	20	2366	2350	2304	207	0	
0	22	1307	1294	-1271	-208	0	
0	24	1744	1580	-1550	-126	0	
0	26	2862	2823	2789	278	0	
0	28	483	482	473	85	0	
0	30	1118	1128	-1129	-224	0	
0	32	1448	1429	-1407	-276	0	
0	34	192	188	133	68	0	
0	36	2828	2844	-2807	-259	0	
0	38	1730	1514	-1168	-203	0	
0	40	2447	2305	2295	236	0	
0	42	4	990	882	841	199	0
0	44	702	691	-643	-249	0	
0	46	1782	1832	-1822	-188	0	
0	48	1118	1274	1255	237	0	
0	50	1680	1534	1341	161	0	
0	52	1334	1348	-1350	-221	0	
0	54	196	595	-569	-167	0	
0	56	197	621	-593	-203	0	
0	58	11	458	445	415	112	0
0	60	12	646	617	-573	-183	0
0	62	1238	1206	-1244	-278	0	
0	64	1672	1663	1641	161	0	
0	66	8	678	663	643	161	0
0	68	8	678	678	678	274	0
0	70	1	1460	1388	-1375	-175	0
0	72	1	1375	1082	-1021	-271	0
0	74	3	1692	1617	1602	172	0
0	76	3	1692	1688	-1699	-185	0
0	78	3	1608	1638	-1651	-207	0
0	80	6	1006	1022	-1005	-216	0
0	82	8	606	600	622	325	0
0	84	8	1021	1002	-957	-144	0
0	86	10	808	801	-808	-285	0
0	88	11	548	508	488	133	0
0	90	12	3006	3128	-3115	-286	0
0	92	13	412	402	392	316	0
0	94	10	229	119	-192	-75	0
0	96	1	1780	1558	-1525	-241	0
0	98	2	730	606	-599	-76	0
0	100	3	798	706	-658	-305	0
0	102	3	798	706	-658	-305	0
0	104	3	798	706	-658	-305	0
0	106	3	798	706	-658	-305	0
0	108	3	798	706	-658	-305	0
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0	168	3	798	706	-658	-305	0
0	170	3	798	706	-658	-305	0
0	172	3	798	706	-658	-305	0
0	174	3	798	706	-658	-305	0
0	176	3	798	706	-658	-305	0
0	178	3	798	706	-658	-305	0
0	180	3	798	706	-658	-305	0
0	182	3	798	706	-658	-305	0
0	184	3	798	706	-658	-305	0
0	186	3	798	706	-658	-305	0
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0	194	3	798	706	-658	-305	0
0	196	3	798	706	-658	-305	0
0	198	3	798	706	-658	-305	0
0	200	3	798	706	-658	-305	0
0	202	3	798	706	-658	-305	0
0	204	3	798	706	-658	-305	0
0	206	3	798	706	-658	-305	0
0	208	3	798	706	-658	-305	0
0	210	3	798	706	-658	-305	0
0	212	3	798	706	-658	-305	0
0	214	3	798	706	-658	-305	0
0	216	3	798	706	-658	-305	0
0	218	3	798	706	-658	-305	0
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0	234	3	798	706	-658	-305	0
0	236	3	798	706	-658	-305	0
0	238	3	798	706	-658	-305	0
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0	242	3	798	706	-658	-305	0
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0	252	3	798	706	-658	-305	0
0	254	3	798	706	-658	-305	0
0	256	3	798	706	-658	-305	0
0	258	3	798	706	-658	-305	0
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0	264	3	798	706	-658	-305	0
0	266	3	798	706	-658	-305	0
0	268	3	798	706	-658	-305	0
0	270	3	798	706	-658	-305	0
0	272	3	798	706	-658	-305	0
0	274	3	798	706	-658	-305	0
0	276	3	798	706	-658	-305	0
0	278	3	798	706	-658	-305	0
0	280	3	798	706	-658	-305	0
0	282	3	798	706	-658	-305	0
0	284	3	798	706	-658	-305	0
0	286	3	798	706	-658	-305	0
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0	290	3	798	706	-658	-305	0
0	292	3	798	706	-658	-305	0
0	294	3	798	706	-658	-305	0
0	296	3	798	706	-658	-305	0
0	298	3	798	706	-658	-305	0
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0	310	3	798	706	-658	-305	0
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0	316	3	798	706	-658	-305	0
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0	324	3	798	706	-658	-305	0
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0	328	3	798	706	-658	-305	0
0	330	3	798	706	-658	-305	0
0	332	3	798	706	-658	-305	0
0	334	3	798	706	-658	-305	0
0	336	3	798	706	-658	-305	0
0	338	3	798	706	-658	-305	0
0	340	3	798	706	-658	-305	0
0	342	3	798	706	-658	-305	0
0	344	3	798	706	-658	-305	0
0	346	3	798	706	-658	-305	0
0	348	3	798	706	-658	-305	0
0	350	3	798	706	-658	-305	0
0	352	3	798	706	-658	-305	0
0	354	3	798	706	-658	-305	0
0	356	3	798	706	-658	-305	0
0	358	3	798	706	-658	-305	0
0	360	3	798	706	-658	-305	0
0	362	3	798	706	-658	-305	0
0	364	3	798	706	-658	-305	0
0	366	3	798	706	-658	-305	0
0	368	3	798	706	-658	-305	0
0	370	3	798	706	-658	-305	0
0	372	3	798	706	-658	-3	

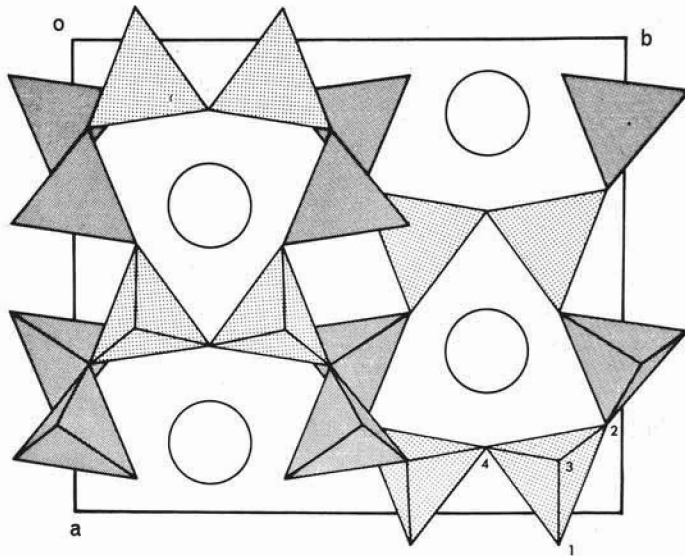


Fig. 1. — Schematic drawing of the crystal structure of barylite projected along [001]. The large circles represent barium atoms; the Si-tetrahedra are dotted, the Be-tetrahedra are dashed. The numbers are referred to the four independent oxygen atoms.

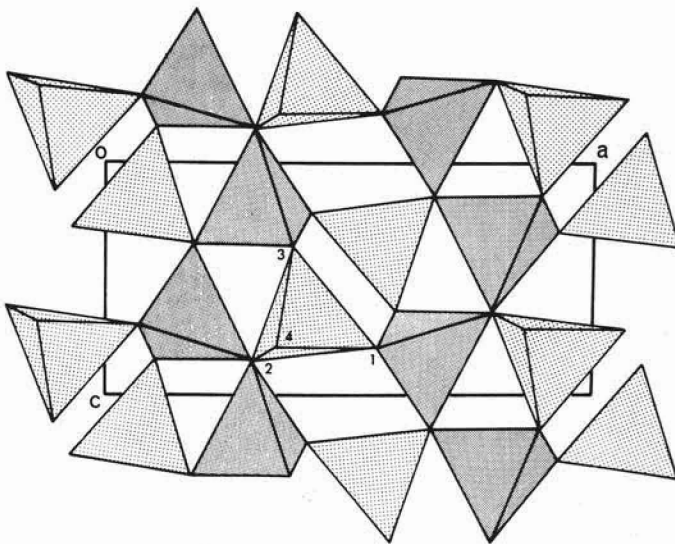


Fig. 2. — Partial projection ($1/4 < y < 3/4$) of the crystal structure of barylite. Barium atoms are omitted in order to show clearly the chains of Be-tetrahedra and their connections with the Si-tetrahedra (for *legenda* see Fig. 1).

The interatomic distances and angles from our work are listed in Table IV. Those computed from the coordinates of Abrashev *et al.* are given in Table V and are surprisingly quite different from the distances published by the same Authors in Table 3 of their paper. From the comparison of Table IV with Table V the differences between the sets of coordinates are evident in their effects on the bond distances and angles of the tetrahedra. Following our set of coordinates barium has a nine-fold coordination forming a sort of cube with a centered face. The twelve-fold coordination of barium proposed by the Russian Authors is not achieved not only because some Ba-O distances are too great, but also because some oxygens are screened and their negative charge cannot reach barium.

TABLE IV.

Interatomic distances (Å) and angles (°) and their standard deviations (in parentheses).

A sign ' is used to distinguish equivalent atoms. The distances preceded by one asterisk occur twice.

Atoms	Bond lengths	Atoms	Bond angles
Si —O(2)	1.65(2)	O(2)—Si—O(3)	109.6 (9)
—O(3)	1.59(2)	O(2)—Si—O(4)	104.4 (9)
—O(4)	1.67(1)	O(2)—Si—O(1)	114.2 (8)
—O(1)	1.60(2)	O(3)—Si—O(4)	107.9 (9)
		O(3)—Si—O(1)	113.7 (9)
		O(4)—Si—O(1)	106.3 (9)
Be —O(3)'	1.62(3)	O(3)'—Be—O(2)	107.7(1.8)
—O(2)	1.66(4)	O(3)'—Be—O(1)	118.7(1.9)
—O(1)	1.60(3)	O(3)'—Be—O(2)	103.7(1.9)
—O(2)'	1.70(3)	O(2)—Be—O(1)	107.8(1.9)
		O(2)—Be—O(2)	110.1(1.8)
		O(1)—Be—O(2)	108.6(1.9)
Ba —O(1)	*2.80(2)	Si—O(4)—Si'	127.5(1.2)
—O(3)'	*2.89(2)	Be—O(2)—Be'	120.3(1.7)
—O(4)	2.92(2)		
—O(1)'	*3.06(2)		
—O(3)	*3.06(2)		
—O(2)	*3.25(2)		

Several other interesting considerations about the structure of barylite are made in the final part of the cited paper. Now we can only make some conclusive remarks about this puzzling silicate: 1) we did not detect piezoelectricity in barylite, but we did not exclude it 'a priori'; 2) our opinion is that the «acentric» structure proposed by Abrashev *et al.* does not give an acceptable account of «the strong piezoelectric effect»; 3) we cannot say that barylite is without any doubt centrosymmetric. Our centric structure is at least more acceptable than that of the cited Authors because it has a better discrepancy factor, better bond distances and angles and is based on three-dimensional data; 4) it is possible that two 'forms' of barylite exist.

TABLE V.

Interatomic distances for the Si and Be tetrahedra computed from the atomic coordinates published by Abrashev et al.

Atoms	Bond lengths	Atoms	Bond lengths
Si(1)—O(1)	1.67	Be(1)—O(3)	1.42
—O(2)	1.76	—O(1)	1.58
—O(4)	1.57	—O(7)	1.67
—O(6)	1.58	—O(6)	1.58
Si(2)—O(3)	1.65	Be(2)—O(2)	1.71
—O(4)	1.51	—O(5)	1.58
—O(5)	1.68	—O(3)	1.76
—O(7)	1.75	—O(6)	1.64

Abrashev *et al.* write: «In the first stage of the X-ray structure analysis we were hindered by the lack of single crystals due to the characteristic and uniform polysynthetic twinning of the mineral on (010). No less than 450 Laue photographs of the available specimen were necessary in order to find a crystal fragment which did not give diffuse reflexions or double (sometimes four- or fivefold) reflexions». The first crystal fragment we picked up and reduced to a spherical shape was a single crystal fragment. In effect the sample sent us by Prof. Frondel was formed by a 'granular' barylite (mixed with calcite) and by a 'layered' barylite (with calcite). X-rays powder

photographs did not show any difference between the fractions, but it is possible that one was twinned and the other untwinned. In any way, owing to the errors in the cited paper, it is impossible to know whether some structural differences correspond to the observed morphological differences; 5) the fact that the Russian Authors based their structure analysis only on $0kl$ and $hk0$ reflexions prevented them from getting valuable informations on some z coordinates. This one is another significant example of the mistakes which can be made in solving crystal structures only with bi-dimensional data.

Aknowledgements. — We are much indebted to Prof. C. Frondel who sent us a fine sample of barylite.

Centro Nazionale di Cristallografia del C.N.R., presso l'Istituto di Mineralogia dell'Università di Pavia. - Novembre 1969.

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