

Short Communications

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On the crystal structure of barium tetraborate, $\text{BaO}\cdot 4\text{B}_2\text{O}_3$. By J. KROGH-MOE, *Department of Chemistry, University of Trondheim, 7000 Trondheim, Norway* and M. IHARA, *Department of Ceramics, Kyoto Technical University, Kyoto, Japan*

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An approximate structure of barium tetraborate, $\text{BaO}\cdot 4\text{B}_2\text{O}_3$, has been determined from three-dimensional X-ray data. The structure contains two separate interlocking three-dimensional networks, each of which consists of alternating triborate and pentaborate groups as building blocks. This structure is quite similar to those found previously in other tetraborates.

Barium tetraborate, $\text{BaO}\cdot 4\text{B}_2\text{O}_3$, was first characterized by Levin & McMurdie (1949) who tabulated the X-ray powder pattern and some optical data for the compound. Levin & McMurdie stated that this phase 'appears as irregular grains, many of which are striated as in polysynthetic twinning and is uniaxial negative or biaxial negative with a small optic axial angle'. Krogh-Moe (1960) determined the following unit-cell dimensions from single-crystal Weissenberg photographs: $a=8\cdot 56$, $b=2\times 8\cdot 69$ (very weak doubling of b axis), $c=13\cdot 20$ Å. The Weissenberg photographs showed the phase to be probably orthorhombic, but with a pronounced pseudotetragonal symmetry (in agreement with the optical properties). The crystals investigated exhibited twinning (in which the a and b axes directions were interchanged).

With a structure determination in mind, efforts were made to find crystals free from twinning; the twinning causes an

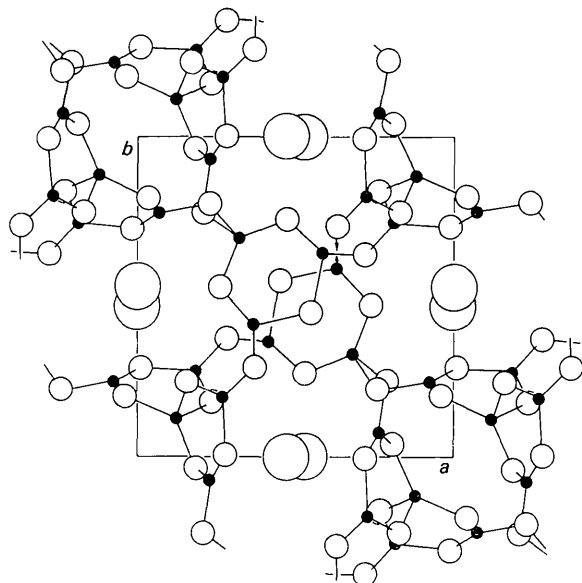


Fig. 1. Projection along the pseudotetragonal c axis of one of the twin networks in barium tetraborate. Small black circles represent boron, small open circles represent oxygen and large open circles represent barium. The pentaborate groups are at the corners and triborate groups at the centre of the unit cell.

overlap of different reflexions in certain regions of reciprocal space and this prevents the collection of an accurate set of intensity data. Since such crystals could not be found, however, a structure determination was carried out with crystals where one of the twins predominated. Most of the data originate from a crystal rotated about the b axis of the predominating twin, but exposures were obtained also for corresponding rotations about the a and c axes. Mo $K\alpha$ radiation with small crystals (0.01 cm diameter) was used. Intensities were estimated visually. No absorption corrections were made but rough corrections for the effect of overlapping twins were attempted; systematic errors in the data could not be avoided, however. Some 450 reflexions were recorded.

In the subsequent structure determination the very weak doubling of the b axis was disregarded. The c axis showed extinctions for $l=2n+1$ and the space group $P222_1$ was assumed. By refining the barium positions given by Krogh-Moe (1960) and subsequently calculating three-dimensional electron density maps with phase angles from the barium positions, a discernible structure emerged. The structure refined by least-squares in the space group $P222_1$ to an R value of 16.3. Inspection of the structure showed that it could be reasonably well described in the tetragonal space group $P4_122$ (or $P4_322$) which is a supergroup to $P222_1$. Refinement in the tetragonal space group led to an R value of 16.9%. Parameters from the latter refinement are reported in Table 1. (Positional parameters for the atoms O(1), B(1) and B(2) in special positions were not refined by least-squares.)

Table 1. Atomic positional and temperature parameters

	x	y	z	B
Ba	0	0.4718	0	1.8 Å ²
O(1)	0.450	0.550	0.125	0.9
O(2)	0.278	0.370	0.159	1.0
O(3)	0.763	0.212	0.219	1.2
O(4)	0.529	0.261	0.136	1.3
O(5)	0.237	0.169	0.292	1.5
O(6)	0.965	0.189	0.345	4.4
O(7)	0.011	0.284	0.192	2.6
B(1)	0.680	0.320	0.125	0.5
B(2)	0.120	0.120	0.375	5.4
B(3)	0.412	0.368	0.142	0.8
B(4)	0.185	0.272	0.219	3.1
B(5)	0.927	0.238	0.250	3.9

The rather high R values are believed to be due to the systematic errors known to affect the observed intensities. The available experimental data are not considered good enough to sustain a more accurate structure determination than the tetragonal approximation reported here. The main features of the structure, however, are probably correct. Like the previously studied tetraborate structures, $\text{Ag}_2\text{O} \cdot 4\text{B}_2\text{O}_3$ (Krogh-Moe, 1965a) and $\text{Na}_2\text{O} \cdot 4\text{B}_2\text{O}_3$ (Hyman, Perloff, Mauer & Block, 1967), the $\text{BaO} \cdot 4\text{B}_2\text{O}_3$ structure consists of two separate interlocking three-dimensional infinite networks, each of which is built up from alternating triborate and pentaborate groups. Triborate groups are linked only to pentaborate groups as in the sodium tetraborate (whereas the group sequence is different in the silver tetraborate). Fig. 1 shows one of the twin networks in a projection along the c axis.

Bond lengths are fairly inaccurate, ranging for instance from 1.1 to 1.7 Å for the individual boron–oxygen bonds. The average boron–oxygen bond length of 1.46 Å is in better agreement with the expected values, however. The average bond length in each boron–oxygen polyhedron shows less scatter, ranging from 1.56 to 1.33 Å (the tetrahedral bond length averages being larger than the triangular). With the systematic errors in mind, no significance should be attached to the details of the structure, such as bond lengths (or the distortions of the triborate and pentaborate groups).

Further support for the above structure proposal was obtained from infrared spectroscopy. The infrared spectrum of crystalline barium tetraborate is fairly similar to that of crystalline silver tetraborate, as shown in Fig. 2. Krogh-Moe

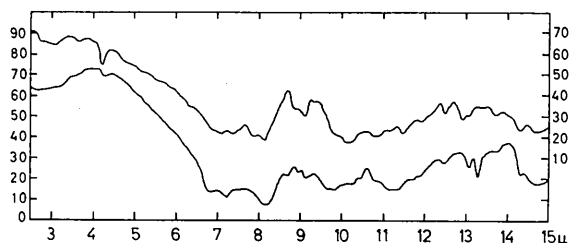


Fig. 2. Infrared spectra, in the range from 2.5 to 15 microns, of crystalline barium tetraborate (upper curve) and crystalline silver tetraborate (lower curve). The transmission percentages to the right refer to the upper curve. The spectra were obtained with KBr discs.

(1965b) has previously demonstrated that the infrared spectra of silver tetraborate and sodium tetraborate look much alike. The infrared spectra therefore confirm the close structural relationship of barium tetraborate with the silver and sodium tetraborates.

References

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Korrekturen zu den Angaben 'Untergruppen' in den Raumgruppen der Internationalen Tabellen zur Bestimmung von Kristallstrukturen (1935), Band 1. Corrections to the sections 'Untergruppen' of the space groups in Internationale Tabellen zur Bestimmung von Kristallstrukturen (1935), Vol. 1. Von E. ASCHER, *Battelle Institute, Advanced Studies Center, 7, route de Drize, 1227 Carouge, Genève, Schweiz*, und V. GRAMLICH* und H. WONDRAUSCHEK, *Mineralogisches Institut der Universität (Technische Hochschule), 75 Karlsruhe, Kaiserstrasse 12, Deutschland*

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1935 erschien der erste Band der *Internationalen Tabellen zur Bestimmung von Kristallstrukturen*. Die Beschreibung der Raumgruppen in diesem Band enthält unter der Überschrift 'Untergruppen' Angaben über gewisse Untergruppen der Raumgruppen. Die Tabellen enthalten verschiedene Irrtümer (Koptsik (1966) übernahm diese Angaben mit nur wenigen Korrekturen), die im folgenden korrigiert werden sollen. Man beachte:

1. Nur die 'zellengleichen' Untergruppen (in denen alle Translationen der Ausgangsraumgruppe erhalten bleiben) sind in Band I von 1935 aufgeführt.

2. Die Hermann–Mauguin Symbole von 1935 stimmen nicht in allen Fällen mit den Symbolen der *International*

Vol. 1 of *Internationale Tabellen zur Bestimmung von Kristallstrukturen* was published in 1935. In this Volume the description of the space groups includes some remarks on certain subgroups of the space groups under the headings 'Untergruppen'. Koptsik (1966) reproduced these data with partial corrections only. Several errors have been found and are corrected in the following. Please note:

(i) Only the 'zellengleiche' subgroups (in which all translations of the original space group are retained) are given in the volume.

(ii) The Hermann–Mauguin symbols of 1935 do not always agree with the symbols given in *International Tables*

* Gegenwärtige Anschrift: Institut f. Kristallographie und Petrographie der ETH, 8006 Zürich, Sonneggstrasse 5, Schweiz.