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The crystallography of some M^{2+} borates.

By S. Block, A. Perloff and C. E. Weir, *National Bureau of Standards, Washington 25, D.C., U.S.A.*

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As part of a research program aimed at achieving a better understanding of the structural principles of borate crystals and glasses, crystallographic studies of anhydrous borates have been undertaken. Crystals of barium, strontium and a lead borate were prepared from the melt. The cell dimensions* and space group of the $MO.2B_2O_3$ types are:

$BaO.2B_2O_3$

$a = 10{\cdot}56 \pm 0{\cdot}01$ Å $\quad \beta = 104° 57' \pm 10'$
$b = 8{\cdot}20 \pm 0{\cdot}01 \quad$ S.G. $= P2_1/c$
$c = 13{\cdot}01 \pm 0{\cdot}01 \quad Z = 8$

This structure has been completed with partial three-dimensional data. The present reliability index $R = 0{\cdot}081$. As soon as the refinement is finished, complete details of the structure will be reported. The structure consists of a three-dimensional boron–oxygen network. Half of the borons are in threefold coordination and half are fourfold.

The network is composed of six-membered rings. The rings are of two types. One type is a single ring of the type found in $Cs_2O.3BaO_3$ (Krogh-Moe, 1960). To each of the outside oxygen atoms, a double ring of the type found in $K_2O.5B_2O_3$ (Krogh-Moe, 1959) is connected. The barium atoms are in channels parallel to the *b* axis in this network.

Table 1. *X-ray diffraction powder pattern for* $SrO.2B_2O_3$

d	I/I_0	*hkl*	*d*	I/I_0	*hkl*
5·3679 Å	20	020	1·6609 Å	<10	042
4·4357	<10	100	1·5542	<10	142
4·0970	30	110	1·5422	10	161
3·9413	30	011	1·5303	<10	202
3·0609	30	101	1·4712	<10	222
2·9424	20	111	1·4465	10	170
2·7801	50	130	1·4387	<10	071
2·7305	50	031	1·4254	10	320
2·6758	20	040	1·4063	<10	232
2·6580	100	121	1·3817	<10	311
2·2928	20	140	1·3647	<10	062
2·2139	30	200	1·3449	<10	103
2·1176	30	002	1·3389	<10	080
2·0464	10	220	1·3284	<10	242
2·0153	80	141	1·3124	<10	033
1·9693	20	022	1·3042	10	162
1·9620	20	201	1·1941	<10	172
1·9293	20	150	1·1783	<10	053
1·9113	10	051	1·1615	<10	262
1·8812	20	230	1·1450	<10	280
1·8426	<10	221	1·1317	<10	082
1·7852	<10	060	1·1290	<10	233
1·7190	10	231	1·1030	<10	410
1·7054	<10	240	1·0740	<10	163
1·6839	10	132	1·0108	10	1,10,1

The two compounds $SrO.2B_2O_3$ and $PbO.2B_2O_3$ are isomorphous with each other but not with $BaO.2B_2O_3$. The diffraction aspect is $Pn{*}{*}$ with $Z = 2$. This means that the M^{2+} and one oxygen are each in a special twofold position.

	$SrO.2B_2O_3$	$PbO.2B_2O_3$
$a =$	$4{\cdot}431 \pm 0{\cdot}004$ Å	$4{\cdot}457 \pm 0{\cdot}0004$ Å
$b =$	$10{\cdot}706 \pm 0{\cdot}010$	$10{\cdot}840 \pm 0{\cdot}010$
$c =$	$4{\cdot}237 \pm 0{\cdot}004$	$4{\cdot}244 \pm 0{\cdot}004$

These compounds have an unusually small volume per ion. Neglecting the boron, which can be considered as interstitial, the volume per ion is only 12·56 Å^3. The density of the strontium compound was determined from displacement of toluene to be 3·85, which is a minimum value. The X-ray density is 4·01. Other possible $SrO:B_2O_3$ ratios give calculated densities ranging from 2·01 to 3·72. Furthermore, as pointed out by C. R. Robbins (personal communication) of this laboratory the phase diagram of the $PbO.2B_2O_3$ (Geller & Bunting, 1937) also indicates this is a 1:2 compound. The powder patterns are presented in Tables 1 and 2. This structure pair is now under study.

The cell dimensions of $SrO.B_2O_3$ are:

$a = 6{\cdot}577 \pm 0{\cdot}007$ Å
$b = 12{\cdot}02 \pm 0{\cdot}01$
$c = 4{\cdot}329 \pm 0{\cdot}004$

Table 2. *X-ray diffraction powder pattern for* $PbO.2B_2O_3$

d	I/I_0	*hkl*	*d*	I/I_0	*hkl*
5·4201 Å	70	020	1·5953 Å	<10	241
4·4578	10	100	1·5570	20	161
4·1200	70	110	1·5363	<10	202
3·9516	80	011	1·5212	<10	212
3·0742	50	101	1·4788	10	222
2·9568	20	111	1·4627	10	170
2·8081	70	130	1·4592	10	251
2·7526	70	031	1·4359	20	152
2·7120	20	040	1·4137	<10	232
2·6742	100	121	1·4029	10	260
2·3457	<10	131	1·3906	10	311
2·3166	10	140	1·3757	<10	062
2·2291	20	200	1·3575	<10	321
2·1831	10	210	1·3372	<10	242
2·1233	20	002	1·3175	<10	033
2·0615	10	220	1·3083	10	123
2·0329	60	141	1·2399	<10	181
1·9754	30	022	1·2180	<10	271
1·9497	20	150	1·2045	<10	172
1·9414	20	211	1·1872	<10	322 213
1·9301	20	051	1·1580	<10	280
1·8960	10	230	1·1422	<10	082
1·8863	40	112	1·1341	<10	233
1·8538	10	221	1·0808	<10	163
1·8070	20	060	1·0567	<10	421
1·7717	<10	151	1·0460	<10	253
1·7311	20	231	1·0276	<10	114
1·7214	<10	240	1·0199	<10	313
1·6929	20	132			
1·6709	10	042			

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* The uncertainties quoted on all the cell dimensions are estimates based on past experience with the camera and measuring device used. In the authors' opinion a conservative estimate of error will be obtained if these uncertainties are treated as standard deviations.

The extinctions indicate space group *Pnca* and thus this compound is isostructural with $CaO.B_2O_3$ (Marezio, Plettinger & Zachariasen, 1963). Here the boron network consists of chains of triangularly coordinated boron groups.

$BaO.B_2O_3$ appears to have two polymorphic forms. At the moment, data are available only for the high-temperature form, which is rhombohedral. The cell dimensions referred to the hexagonal axis are $a=b=7{\cdot}23\pm0{\cdot}01$, $c=39{\cdot}17\pm0{\cdot}04$ Å. There is a marked halving of the c axis. The space group is either $R3c$ or $R\bar{3}c$.

The cell dimensions of all these crystals were obtained on a precession camera with Mo $K\alpha$ radiation $=0{\cdot}7107$ Å. The data for the structure determination of $BaO.2B_2O_3$ were obtained with an integrating Weissenberg camera, with Mo $K\alpha$ radiation. The powder patterns were obtained with a diffractometer and Cu $K\alpha$ radiation.

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Van der Waals radius and closest crystalline packing in the large spherical molecule, tetrakis(trimethylsilyl)methane.

By R. L. MERKER and M. J. SCOTT, *Mellon Institute*,* *Pittsburgh* 13, *Pennsylvania, U.S.A.*

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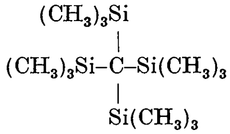
The synthesis of tetrakis(trimethylsilyl)methane recently accomplished in this laboratory will be the subject of a future publication. This large and spherically symmetrical molecule (the carbon analog of which has never been reported) possesses a surface comprised of twelve geometrically equivalent methyl groups:



$$\begin{array}{c} (CH_3)_3Si \\ | \\ (CH_3)_3Si\text{–}C\text{–}Si(CH_3)_3 \\ | \\ Si(CH_3)_3 \end{array}$$

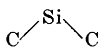
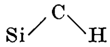
It is a crystalline material which appears from visual observations to undergo a phase transition to another solid form at about 195–210 °C. Under atmospheric conditions sublimation occurs without true melting. Such behavior appears analogous to that of many spherically symmetrical molecules in which free rotation of the molecule within the crystal lattice can readily occur (Pauling, 1930; 1945, p. 375).

X-ray powder data have shown tetrakis(trimethylsilyl)-methane to be face-centered cubic with $a=12{\cdot}96\pm0{\cdot}08$ Å. The calculated density for $Z=4$ was found to be $0{\cdot}929$ g.cm^{-3} which is in good agreement with the observed value of $0{\cdot}9113$ g.cm^{-3}.

From the X-ray data, assuming that the molecules behave as rigid spheres without interpenetration, the molecular radius (r_1), which is the sum of the average distance from the center of the central carbon atom to the center of a hydrogen atom (r_2) and the van der Waals radius (r_3)† between this hydrogen and a peripheral hydrogen atom of a neighboring molecule, was calculated to be 4·58 Å.

From the bond angles and bond distances in tetramethylsilane tabulated in Table 1, the average distance (r_2) from the center of the central carbon atom to the center of a peripheral hydrogen atom was determined to be 3·53 Å.

Table 1. *Bond distances and angles in* $(CH_3)_4Si$

Bond distances		
Si–C	$1{\cdot}888\pm0{\cdot}02$ Å	(Sheehan & Schomaker, 1952)
C–H	$1{\cdot}10\ \pm0{\cdot}05$ Å	
Bond angles		
	109°	(Pauling, 1945, p. 85)
	110 ± 3°	(Sheehan & Schomaker, 1952)

From this the van der Waals radius (r_3) was calculated to be 1·05 Å, the distance between hydrogen nuclei being 2·10 Å. This compares favorably with van der Waals radii determined for crystalline methane (1·002 Å) and ethane (1·165 Å) from X-ray analysis (Mack, 1932) and with the mean value of the intermolecular hydrogen radius ($1{\cdot}17\pm0{\cdot}02$ Å) determined from later work with well defined structures containing the C–H bond (Kitaigorodskii, 1961).

The authors are indebted to S. S. Pollack and G. S. Smith of Mellon Institute for the X-ray powder data.

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† Actually r_3 represents one half the distance between spheres of radius r_2. To a first approximation this is one half the distance between hydrogen nuclei or van der Waals radius.