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Crystal data of two high pressure phases of SrB₂O₄. By P. D. DERNIER, *Bell Telephone Laboratories, Inc., Murray Hill, New Jersey, U.S.A.*

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SrB₂O₄(III) and SrB₂O₄(IV) are two high pressure phases of strontium metaborate. Polycrystalline SrB₂O₄(III) was prepared at 15 kbar and 600°C. It is orthorhombic, with $a = 12.426 \pm 0.002$, $b = 6.418 \pm 0.001$ and $c = 11.412 \pm 0.002$ Å, $Z = 12$, $d_c = 3.77$ g.cm⁻³, symmetry $Pna2_1$, and is isostructural with CaB₂O₄(III). SrB₂O₄(IV), formed at 20 kbar and 600°C, is cubic, with $a = 9.222 \pm 0.001$ Å, $Z = 12$, $d_c = 4.38$ g.cm⁻³, space group symmetry $Pa\bar{3}$, and is isostructural with CaB₂O₄(IV). In general the behavior of SrB₂O₄ under pressure is very similar to that of CaB₂O₄.

Introduction

This paper reports the synthesis and crystal data of two new high pressure phases of strontium metaborate. At atmospheric pressure SrB₂O₄ is isostructural with CaB₂O₄(I) (Block, Perloff & Weir, 1964). The latter compound is orthorhombic with all boron atoms triangularly coordinated and the calcium atoms surrounded by eight-oxygen polyhedra. Since the polymorphism of SrB₂O₄ is similar to that of CaB₂O₄, all modifications of SrB₂O₄ will be designated in the same fashion as their isostructural CaB₂O₄ counterparts. (Marezio, Remeika, & Dernier, 1969a).

Synthesis

The high pressure apparatus and experimental procedures were the same as has been previously described in the synthesis of the high pressure modifications of CaB₂O₄ (Marezio *et al.* 1969 *a, b*). However, the pressure and temperature conditions were significantly lower for each of the respective high pressure phases of SrB₂O₄. SrB₂O₄(III) was retained metastably after pressurizing SrB₂O₄(I) to 15 kbar and raising the temperature to 600°C for a one hour period. The synthesis of SrB₂O₄(IV) required a pressure of 20 kbar and a temperature of 600°C. Further increases of pressure above 40 kbar resulted in the decomposition of SrB₂O₄. One product of decomposition was

found to be SrB₄O₇ (Krogh-Moe, 1964), as identified by X-ray powder photographs and precession films.

Both SrB₂O₄(III) and SrB₂O₄(IV) could be reconverted to the low pressure starting material, SrB₂O₄(I), by annealing overnight at 750°C in air. X-ray powder films of the annealed SrB₂O₄ and unpressurized SrB₂O₄ were identical. In addition, single crystals of both high pressure modifications were grown at a pressure of 15 kbar and a temperature of 600°C with water as a solvent. The crystals were easily identified and separated under a crossed polarized field of light, since the crystals of SrB₂O₄(III) were birefringent whereas those of SrB₂O₄(IV) were isotropic. It should be noted that the presence of water apparently lowered the pressure range of stability of SrB₂O₄(IV). This phenomenon has been observed previously for several other systems but no *a priori* justification can be proposed at this time.

Crystal data

From precession photographs taken with Mo $K\alpha$ radiation SrB₂O₄(III) was found to be orthorhombic with systematic absences for $0kl$, $k+l=2n+1$, and for $h0l$, $h=2n+1$. These are identical with the conditions found for CaB₂O₄(III) (Marezio, Remeika & Dernier, 1969a). The correct space group for CaB₂O₄(III) was found to be $Pna2_1$ and it is highly probable that it is the same for SrB₂O₄(III). The lattice parameters for SrB₂O₄(III) were

determined from a powder film taken at room temperature and atmospheric pressure with a Norelco Camera of 114.6 cm diameter and Cr $K\alpha$ (2.2909 Å) radiation. The parameters were refined by the least-squares program of Mueller, Heaton & Miller (1960). The final refined parameters are $a=12.426\pm 0.002$, $b=6.418\pm 0.001$ and $c=11.412\pm 0.002$ Å. The calculated density based on 12 molecules per unit cell is 3.77 g.cm^{-3} . A comparison of observed and calculated interplanar spacings is given in Table 1.

Table 1. Powder pattern of $\text{SrB}_2\text{O}_4(\text{III})$

<i>hkl</i>	d_{obs}	d_{calc}	<i>I</i>
202		4.202	<i>m</i>
211	4.177	4.157	
212	3.509	3.516	<i>m</i>
311	3.325	3.329	<i>m</i>
113	3.163	3.164	<i>m</i>
120		3.107	<i>m</i>
400	3.092	3.107	
121		2.998	<i>s</i>
401	2.997	2.997	
004	2.849	2.853	<i>ms</i>
204	2.587	2.593	<i>m</i>
114	2.548	2.551	<i>m</i>
412	2.509	2.511	<i>m</i>
214	2.401	2.404	<i>w</i>
322		2.318	<i>w</i>
510	2.323	2.318	
205	2.140	2.142	<i>m</i>
115	2.116	2.119	<i>w</i>
404		2.101	<i>w</i>
124	2.089	2.101	
131		2.073	<i>w</i>
600	2.064	2.071	
224	2.005	2.017	<i>m</i>
231		1.992	<i>m</i>
414	1.992	1.997	
513	1.975	1.979	<i>m</i>
610	1.967	1.971	<i>m</i>
611	1.938	1.942	<i>w</i>
006	1.898	1.902	<i>ms</i>
331	1.876	1.875	<i>w</i>
133	1.843	1.844	<i>m</i>
206	1.816	1.819	<i>w</i>
514	1.796	1.799	<i>w</i>
613		1.750	<i>w</i>
216	1.749	1.750	
710	1.708	1.711	<i>w</i>
026	1.636	1.636	<i>w</i>
326	1.521	1.522	<i>w</i>
810	1.508	1.509	<i>w</i>
606	1.400	1.400	<i>wm</i>
517	1.333	1.333	<i>wm</i>
805	1.284	1.284	<i>m</i>
726	1.203	1.203	<i>m</i>
825	1.192	1.192	<i>m</i>
346	1.176	1.176	<i>m</i>

A powder film of $\text{SrB}_2\text{O}_4(\text{IV})$ taken with Cu $K\alpha$ (1.5418 Å) radiation at room temperature and atmospheric pressure, was indexed on a cubic cell with a lattice parameter of approximately 9.2 Å. From a comparison with a powder film of the cubic phase $\text{CaB}_2\text{O}_4(\text{IV})$ (Marezio, Remeika & Dernier 1969*b*) it appears that $\text{SrB}_2\text{O}_4(\text{IV})$ is isostructural with $\text{CaB}_2\text{O}_4(\text{IV})$. The powder data of the former compound are given in Table 2. The final refined lattice parameter for $\text{SrB}_2\text{O}_4(\text{IV})$ was $a=9.222\pm 0.001$ Å, as obtained by the previously mentioned least-squares program. The calcu-

lated density based on 12 molecules per unit cell is 4.38 g.cm^{-3} .

Table 2. Powder pattern of $\text{SrB}_2\text{O}_4(\text{IV})$

$h^2+k^2+l^2$	d_{obs}	d_{calc}	<i>I</i>
5	4.118	4.124	<i>m</i>
6	3.747	3.765	<i>wm</i>
8	3.249	3.261	<i>w</i>
9	3.074	3.074	<i>w</i>
11	2.774	2.781	<i>s</i>
12	2.658	2.662	<i>vw</i>
13	2.552	2.558	<i>m</i>
14	2.457	2.465	<i>m</i>
16	2.296	2.306	<i>w</i>
17	2.226	2.236	<i>w</i>
18			
19			
20	2.056	2.062	<i>m</i>
21	2.009	2.012	<i>ms</i>
22	1.959	1.966	<i>m</i>
24	1.877	1.882	<i>w</i>
27	1.771	1.775	<i>m</i>
29	1.709	1.713	<i>wm</i>
30	1.680	1.684	<i>m</i>
32	1.628	1.630	<i>m</i>
33			
34	1.579	1.581	<i>w</i>
35			
36	1.535	1.537	<i>wm</i>
38	1.494	1.496	<i>m</i>
40	1.456	1.458	<i>vw</i>
43	1.404	1.406	<i>m</i>
44	1.389	1.390	<i>vw</i>
45	1.373	1.375	<i>m</i>
46	1.359	1.360	<i>m</i>
48			
53	1.266	1.267	<i>m</i>
54	1.253	1.255	<i>m</i>
56	1.230	1.232	<i>m</i>
57			
59	1.199	1.201	<i>ms</i>
61	1.179	1.181	<i>wm</i>
62	1.170	1.171	<i>wm</i>
64	1.152	1.153	<i>w</i>
69	1.108	1.110	<i>w</i>
70	1.101	1.102	<i>w</i>
75	1.064	1.065	<i>m</i>
77	1.050	1.051	<i>w</i>
78	1.043	1.044	<i>w</i>
84	1.006	1.006	<i>w</i>
85	1.000	1.000	<i>w</i>
86	0.9933	0.9944	<i>wm</i>
91	0.9662	0.9667	<i>w</i>
94	0.9502	0.9512	<i>w</i>
96	0.9404	0.9412	<i>m</i>
101	0.9167	0.9176	<i>m</i>
104	0.9036	0.9043	<i>w</i>
107	0.8911	0.8915	<i>m</i>
109	0.8827	0.8833	<i>w</i>
110	0.8786	0.8793	<i>m</i>
116	0.8556	0.8562	<i>w</i>
117	0.8519	0.8526	<i>w</i>
118	0.8484	0.8490	<i>w</i>
123	0.8312	0.8315	<i>m</i>
125	0.8245	0.8249	<i>m</i>
126	0.8212	0.8216	<i>m</i>
128	0.8148	0.8151	<i>w</i>
133	0.7995	0.7997	<i>w</i>
134	0.7964	0.7967	<i>m</i>
136	0.7906	0.7908	<i>vw</i>
139	0.7821	0.7822	<i>m</i>
141	0.7766	0.7766	<i>m</i>

Table 3. *Polymorphism of SrB₂O₄ and CaB₂O₄*

Phase	Approximate range of stability*		Density (g.cm ⁻³)		Symmetry	Lattice parameters (Å)	
	SrB ₂ O ₄	CaB ₂ O ₄	SrB ₂ O ₄	CaB ₂ O ₄		SrB ₂ O ₄	CaB ₂ O ₄
I	0-8 kbar	0-12 kbar	3.33	2.70	Orthorhombic	a = 6.589 b = 12.018 c = 4.337	a = 6.214 b = 11.604 c = 4.285
II	-	12-15 kbar	—	2.89	Orthorhombic	— — —	a = 8.369 b = 13.816 c = 5.007
III	8-15 kbar	15-25 kbar	3.77	3.05	Orthorhombic	a = 12.426 b = 6.418 c = 11.412	a = 11.380 b = 6.382 c = 11.304
IV	15-40 kbar	25-40 kbar	4.38	3.43	Cubic	a = 9.222	a = 9.008

* Temperature = 600°C for SrB₂O₄ and 900°C for CaB₂O₄.

Discussion

For ease of comparison between the SrB₂O₄ and CaB₂O₄ polymorphic series, crystal data and pressure ranges of stability are given in Table 3, and a plot of densities *versus* fraction of tetrahedral boron can be found in Fig. 1. It can be seen from Table 3 as well as from Fig. 1 that the behavior of SrB₂O₄ under pressure is very similar to that of CaB₂O₄.

One notable difference in the two polymorphic series is that an expected phase of SrB₂O₄ is missing, namely, SrB₂O₄(II). It could be predicted from the data in Table 3 that this phase should exist at 6-8 kbar and 600°C. By further extrapolation of densities (see Fig. 1) and analogy to CaB₂O₄(II) (Zachariasen, 1967) one would expect this modification to be orthorhombic with a density of 3.6 g.cm⁻³, a unit-cell volume of 650 Å³, and very roughly, lattice parameters a = 8.9, b = 14.3, and c = 5.1 Å. However, after considerable experimentation not a trace of SrB₂O₄(II) could be detected in any of the X-ray powder films of the high pressure samples. It should be noted that CaB₂O₄(II) was never obtained in the pure state from high pressure experiments at these laboratories. Instead, CaB₂O₄(II) was always found as a mixture with CaB₂O₄(I) or CaB₂O₄(III). It seems reasonable to expect the pressure range of stability for SrB₂O₄(II) to be narrower than CaB₂O₄(II). From Table

3 and from the known coordination changes for CaB₂O₄ the implication is that the energy associated with the transition I → II should be about the same for both compounds since only the boron coordination is changing. However, for the transition II → III both cation coordinations are increasing and the energy required for this transition should be less for SrB₂O₄ than for CaB₂O₄.

In general it can be seen from Table 3 that considerably less energy is required, for each of the respective transitions, for SrB₂O₄ than for CaB₂O₄. Less energy is necessary to increase the strontium coordination than the calcium coordination since Sr is larger than Ca in ionic radius and is more easily accommodated in a larger lattice site. One would expect even lower energies for similar transitions for BaB₂O₄. However, preliminary experiments with BaB₂O₄ show that high pressure phases of this compound are not isostructural with any of the SrB₂O₄ phases.

Finally, a comparison of lattice parameters between isostructural compounds in Table 3 shows that for phase III a unique distortion of the unit cell occurs when strontium is substituted for calcium. Whereas the lattice parameters a₀ for SrB₂O₄(III) is 9.2% larger than the corresponding parameter of CaB₂O₄(III), the lattice parameters b₀ and c₀ are only 0.6% and 1.0% larger respectively. It is difficult to explain this unidirectional expansion without a knowledge of the structural details of SrB₂O₄(III). Nevertheless, it can be speculated that second-nearest neighbor interactions in CaB₂O₄(III) could become first-nearest neighbor interactions in SrB₂O₄(III).

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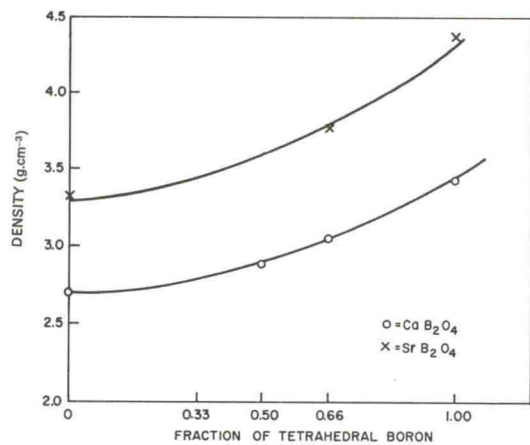


Fig. 1.