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Crystal data of two high pressure phases of SrB_2O_4. By P. D. Dernier, *Bell Telephone Laboratories, Inc., Murray Hill, New Jersey, U.S.A.*

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SrB_2O_4(III) and SrB_2O_4(IV) are two high pressure phases of strontium metaborate. Polycrystalline SrB_2O_4(III) was prepared at 15 kbar and 600 °C. It is orthorhombic, with $a=12{\cdot}426\pm0{\cdot}002$, $b=6{\cdot}418\pm0{\cdot}001$ and $c=11{\cdot}412\pm0{\cdot}002$ Å, $Z=12$, $d_c=3{\cdot}77$ g.cm^{-3}, symmetry $Pna2_1$, and is isostructural with CaB_2O_4(III). SrB_2O_4(IV), formed at 20 kbar and 600 °C, is cubic, with $a=9{\cdot}222\pm0{\cdot}001$ Å, $Z=12$, $d_c=4{\cdot}38$ g.cm^{-3}, space group symmetry $Pa3$, and is isostructural with CaB_2O_4(IV). In general the behavior of SrB_2O_4 under pressure is very similar to that of CaB_2O_4.

Introduction

This paper reports the synthesis and crystal data of two new high pressure phases of strontium metaborate. At atmospheric pressure SrB_2O_4 is isostructural with CaB_2O_4(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 SrB_2O_4 is similar to that of CaB_2O_4, all modifications of SrB_2O_4 will be designated in the same fashion as their isostructural CaB_2O_4 counterparts. (Marezio, Remeika, & Dernier, 1969*a*).

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 CaB_2O_4 (Marezio *et al.* 1969 *a*, *b*). However, the pressure and temperature conditions were significantly lower for each of the respective high pressure phases of SrB_2O_4. SrB_2O_4(III) was retained metastably after pressurizing SrB_2O_4(I) to 15 kbar and raising the temperature to 600 °C for a one hour period. The synthesis of SrB_2O_4(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 SrB_2O_4. One product of decomposition was found to be SrB_4O_7 (Krogh-Moe, 1964), as identified by X-ray powder photographs and precession films.

Both SrB_2O_4(III) and SrB_2O_4(IV) could be reconverted to the low pressure starting material, SrB_2O_4(I), by annealing overnight at 750 °C in air. X-ray powder films of the annealed SrB_2O_4 and unpressurized SrB_2O_4 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 SrB_2O_4(III) were birefringent whereas those of SrB_2O_4(IV) were isotropic. It should be noted that the presence of water apparently lowered the pressure range of stability of SrB_2O_4(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 SrB_2O_4(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 CaB_2O_4(III) (Marezio, Remeika & Dernier, 1969*a*). The correct space group for CaB_2O_4(III) was found to be $Pna2_1$ and it is highly probable that it is the same for SrB_2O_4(III). The lattice parameters for SrB_2O_4(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 $a=12·426\pm0·002$, $b=6·418\pm0·001$ and $c=11·412\pm0·002$ 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* SrB_2O_4(III)

hkl	d_{obs}	d_{calc}	*I*
202	4·177	4·202	*m*
211		4·157	
212	3·509	3·516	*m*
311	3·325	3·329	*m*
113	3·163	3·164	*m*
120	3·092	3·107	*m*
400		3·107	
121	2·997	2·998	*s*
401		2·997	
004	2·849	2·853	*ms*
204	2·587	2·593	*m*
114	2·548	2·551	*m*
412	2·509	2·511	*m*
214	2·401	2·404	*w*
322	2·323	2·318	*w*
510		2·318	
205	2·140	2·142	*m*
115	2·116	2·119	*w*
404	2·089	2·101	*w*
124		2·101	
131	2·064	2·073	*w*
600		2·071	
224	2·005	2·017	*m*
231	1·992	1·992	*m*
414		1·997	
513	1·975	1·979	*m*
610	1·967	1·971	*m*
611	1·938	1·942	*w*
006	1·898	1·902	*ms*
331	1·876	1·875	*w*
133	1·843	1·844	*m*
206	1·816	1·819	*w*
514	1·796	1·799	*w*
613	1·749	1·750	*w*
216		1·750	
710	1·708	1·711	*w*
026	1·636	1·636	*w*
326	1·521	1·522	*w*
810	1·508	1·509	*w*
606	1·400	1·400	*wm*
517	1·333	1·333	*wm*
805	1·284	1·284	*w*
726	1·203	1·203	*m*
825	1·192	1·192	*m*
346	1·176	1·176	*m*

A powder film of SrB_2O_4(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 CaB_2O_4(IV) (Marezio, Remeika & Dernier 1969*b*) it appears that SrB_2O_4(IV) is isostructural with CaB_2O_4(IV). The powder data of the former compound are given in Table 2. The final refined lattice parameter for SrB_2O_4(IV) was $a=9·222\pm0·001$ Å, as obtained by the previously mentioned least-squares program. The calculated density based on 12 molecules per unit cell is 4·38 g.cm^{-3}.

Table 2. *Powder pattern of* SrB_2O_4(IV)

$h^2+k^2+l^2$	d_{obs}	d_{calc}	*I*
5	4·118	4·124	*m*
6	3·747	3·765	*wm*
8	3·249	3·261	*w*
9	3·074	3·074	*w*
11	2·774	2·781	*s*
12	2·658	2·662	*vw*
13	2·552	2·558	*m*
14	2·457	2·465	*m*
16	2·296	2·306	*w*
17	2·226	2·236	*w*
18			
19			
20	2·056	2·062	*m*
21	2·009	2·012	*ms*
22	1·959	1·966	*m*
24	1·877	1·882	*w*
27	1·771	1·775	*m*
29	1·709	1·713	*wm*
30	1·680	1·684	*m*
32	1·628	1·630	*m*
33			
34	1·579	1·581	*w*
35			
36	1·535	1·537	*wm*
38	1·494	1·496	*m*
40	1·456	1·458	*vw*
43	1·404	1·406	*m*
44	1·389	1·390	*vw*
45	1·373	1·375	*m*
46	1·359	1·360	*m*
48			
53	1·266	1·267	*m*
54	1·253	1·255	*m*
56	1·230	1·232	*m*
57			
59	1·199	1·201	*ms*
61	1·179	1·181	*wm*
62	1·170	1·171	*wm*
64	1·152	1·153	*w*
69	1·108	1·110	*w*
70	1·101	1·102	*w*
75	1·064	1·065	*m*
77	1·050	1·051	*w*
78	1·043	1·044	*w*
84	1·006	1·006	*w*
85	1·000	1·000	*w*
86	0·9933	0·9944	*wm*
91	0·9662	0·9667	*w*
94	0·9502	0·9512	*w*
96	0·9404	0·9412	*m*
101	0·9167	0·9176	*m*
104	0·9036	0·9043	*w*
107	0·8911	0·8915	*m*
109	0·8827	0·8833	*w*
110	0·8786	0·8793	*m*
116	0·8556	0·8562	*w*
117	0·8519	0·8526	*w*
118	0·8484	0·8490	*w*
123	0·8312	0·8315	*m*
125	0·8245	0·8249	*m*
126	0·8212	0·8216	*m*
128	0·8148	0·8151	*w*
133	0·7995	0·7997	*w*
134	0·7964	0·7967	*m*
136	0·7906	0·7908	*vw*
139	0·7821	0·7822	*m*
141	0·7766	0·7766	*m*