Short Communications

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The beryllium-boron system.*

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The existence of beryllium–boron phases with compositions near Be_2B, BeB_2 and BeB_6 was reported by Markovskii, Kondrashev & Kaputovskaia (1955), hereafter referred to as M.K.K. A fourth phase, beryllium-rich, was observed, but its composition was not established. Markovskii, Kondrashev & Goryacheva (1955) found that Be_2B has the CaF_2 structure with $a = 4{\cdot}670$ Å. In addition to verifying these results, we have prepared and studied single crystals of BeB_2 and 'BeB_6', and we have obtained a powder pattern of the beryllium-rich phase.

Samples of the beryllium borides were prepared by sintering pressed powdered mixtures of the elements in BeO crucibles under an argon atmosphere. Homogenization was carried out at 1400 to 1600 °C. The amorphous boron used contained 96% boron and about 3% oxygen, with less than 1% metallic impurities. Spectroscopic analysis of the beryllium metal showed 0·1 to 0·2% each of Si, Fe, Mn, Mg, and Al, and trace amounts of Cr and Cu.

The powder patterns were photographed with Cu $K\alpha$ radiation ($\lambda = 1{\cdot}5418$ Å). Intensities were estimated visually by comparison with a standard scale. The increased complexity of our powder patterns over those published diagrammatically by M.K.K. may be due to our higher sintering temperatures.

'Be_6B'

Characterization of this material is still incomplete; no chemical analyses have been performed, nor were single crystals obtained. Maximum relative intensity of the powder diffraction lines of this phase was achieved with an initial Be:B ratio of about 6:1. The first 25 lines of this pattern are listed in Table 1. Pure beryllium accounts for several of the intense lines, and some Be_2B is also present.

Table 1. *Powder pattern of* 'Be_6B'

I	*d*	*I*	*d*
5	3·51 Å	5	1·762 Å
20	3·32	70	1·732 (*b*)
45	3·03	5	1·683
5	2·68 (*c*)	100	1·671
15	2·43	5	1·647 (*c*)
5	2·386	5	1·597
85	2·346 (*c*)	10	1·560
10	2·253	5	1·521
10	2·186 (*a*)	15	1·472
10	2·045 (*a*)	35	1·438
40	1·979 (*b*)	5	1·416
5	1·912	5	1·384
15	1·791 (*b*)		

(*a*) = broad lines. (*b*) = Be lines. (*c*) = Be_2B lines.

Be_2B

Our powder pattern of Be_2B is listed in Table 2; a few additional lines due to 'Be_6B' are not included. This pattern gave $a = 4{\cdot}663$ Å.

Table 2. *Powder pattern of* Be_2B

I	*d*	*hkl*	*I*	*d*	*hkl*
60	2·69 Å	111	10	1·070 Å	331
25	2·335	200	5	1·043	420
100	1·648	220	60	0·953	422
15	1·407	311	20	0·898	511
10	1·347	222	30	0·824	440
30	1·166	400	20	0·788	531

BeB_2

Chemical analysis of material prepared with the initial Be:B ratio approximately 1:2 gave $29{\cdot}3 \pm 0{\cdot}2$% Be, weighed as BeO, and $70{\cdot}8 \pm 0{\cdot}5$% B, titrated as boric acid. The presence of about 1% BeO in the sample, as indicated by the powder pattern, is within the limits of the accuracy of the analysis. The stoichiometry computed from these figures is $BeB_{2{\cdot}01 \pm 0{\cdot}03}$.

Single crystals were selected from samples of crushed BeB_2, and oscillation and Weissenberg photographs taken with Cu $K\alpha$ radiation ($\lambda = 1{\cdot}5418$ Å) showed a hexagonal unit cell with

$$a = 9{\cdot}79 \pm 0{\cdot}02,\ c = 9{\cdot}55 \pm 0{\cdot}02 \text{ Å}.$$

The Laue symmetry is $P6/mmm$, and there are no systematic extinctions. The density of a powdered sample, measured by pycnometer, was 2·42 g.cm.$^{-3}$; however, flotation tests on individual fragments showed a variation from 2·32 to 2·48 g.cm.$^{-3}$. The density reported by M.K.K. was 2·35 g.cm.$^{-3}$. This density range indicates 36 to 38 BeB_2 groups per unit cell.

The intensities of 361 independent reflections, of which 103 were too weak to be observed, were measured visually on multiple-film Weissenberg exposures taken with Cu $K\alpha$ radiation. The statistical distribution of intensities (Howells, Phillips & Rogers, 1950) was hypercentric (Lipson & Woolfson, 1952) with no appreciable difference between the distributions for the three-dimensional data and for the projections. The probable space

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group is therefore $P6/mmm$. Efforts to interpret the three-dimensional Patterson function have so far been unsuccessful. We plan to extend the quantity and quality of the data by counter techniques.

Table 3. *Powder pattern of* BeB_2

I	d	$hk\cdot l$	I	d	$hk\cdot l$
75	9·5 Å	00·1	40	2·339 Å	31·0 (*b*)
55	8·5	10·0	15	2·287	31·1, 10·4
25	6·38	10·1	10	2·260	21·3
15	4·91	11·0	25	2·188	(*b*)
65	4·36	11·1	40	2·142	11·4
20	4·24	20·0	5	2·083	(*c*)
10	4·17	10·2	40	2·060	(*b*)
50	3·87	20·1	15	2·024	(*c*)
25	3·49	(*c*)	10	1·948	32·0
10	3·37	(*c*)	5	1·894	31·3
25	3·20	00·3, 31·0	5	1·862	21·0, 10·5
10	3·04	21·1	30	1·820	21·1, 30·4 (*a*)
50	2·98	10·3	10	1·762	40·3
25	2·83	30·0	25	1·742	20·5
35	2·71	30·1	30	1·694	50·0
100	2·66	21·2	60	1·661	32·3
75	2·54	20·3	75	1·631	33·0
50	2·45	22·0	40	1·598	00·6, 50·2 (*b*)
10	2·385	22·1, 00·4 (*a*)	50	1·582	30·5

(*a*) = broad lines. (*b*) = BeO. (*c*) = unidentified impurity.

Table 3 lists the first 38 lines observed on the powder pattern of BeB_2. Besides BeB_2 and BeO, this pattern shows a trace of an unidenfitied impurity.

'BeB_6'

Chemical analysis of material prepared with the initial Be:B atomic ratio 1:6 gave $12{\cdot}8 \pm 0{\cdot}2\%$ Be, $86{\cdot}3 \pm 0{\cdot}5\%$ B. These data suggest a phase $BeB_{5{\cdot}88 \pm 0{\cdot}25}$ containing $1{\cdot}5 \pm 1{\cdot}1\%$ BeO.

A single crystal of this brick-red phase was selected from crushed material and examined by oscillation and Weissenberg methods. A tetragonal unit cell, nearly identical with that of AlB_{12} (Halla & Weil, 1939), was found. Using the AlB_{12} dimensions

$$a = 10{\cdot}16,\ c = 14{\cdot}28 \text{ Å}$$

(Kohn, Katz & Giardini, 1958), 28 BeB_6 groups per unit cell give a calculated density of 2·33 g.cm.$^{-3}$. The density measured by pycnometer is 2·35 g.cm.$^{-3}$, and that reported by M.K.K. is 2·33 g.cm.$^{-3}$.

As in the case of AlB_{12}, the diffraction symmetry and systematic extinctions are characteristic of space groups $P4_32_12$ and $P4_12_12$. Comparison of single crystal photographs shows a general similarity in the intensities in the two materials; however, pronounced differences in individual reflections are frequently apparent.

A tetragonal polymorph of elemental boron dimensionally resembling AlB_{12} has been reported by Talley, LaPlaca & Post (1960). When melted and subsequently cooled, this polymorph transforms to β-rhombohedral boron; the only apparent change when a sample of 'BeB_6' was melted (at 2300 °C.) and cooled was the appearance on the powder patterns of three weak lines at 3·70, 3·36, and 3·06 Å.

The first 32 lines of a typical powder pattern of 'BeB_6' are listed in Table 4.

Table 4. *Powder patterns of* 'BeB_6'

I	d	hkl	I	d	hkl
15	8·3 Å	101	5	3·06 Å	302
15	7·2	110	20	2·93	312
80	6·42	111	5	2·80	214, 320
10	5·81	102	55	2·76	105, 303, 321
80	5·08	112, 200	40	2·66	115, 313
5	4·77	201	15	2·61	322 (*a*)
10	4·54	210	20	2·53	224, 400
100	4·32	103, 211	15	2·49	205, 401
90	4·14	202	35	2·46	304, 410
40	3·96	113	35	2·422	215, 323, 411
55	3·84	212	15	2·390	314, 402, 330
10	3·58	004, 220	45	2·332	412 (*b*)
5	3·46	203, 221	20	2·247	225, 403 (*a*), 421
20	3·29	213, 301	35	2·187	305 (*b*), 413
5	3·21	114, 222, 310	10	2·161	206, 422
20	3·13	311	50	2·058	423 (*b*)

(*a*) = broad. (*b*) = BeO.

Further studies, of compositions richer in boron, are planned. Our present data do not exclude the possibility that BeB_6 represents the low-boron side of a homogeneity range that extends to pure boron, the presence of beryllium preventing the high temperature transition to β-rhombohedral boron.

References

Halla, F. & Weil, R. (1939). *Z. Kristallogr.* **101**, 435.

Howells, E. R., Phillips, D. C. & Rogers, D. (1950). *Acta Cryst.* **3**, 210.

Kohn, J. A., Katz, G. & Giardini, A. A. (1958). *Z. Kristallogr.* **111**, 1.

Lipson, H. & Woolfson, M. M. (1952). *Acta Cryst.* **5**, 680.

Markovskii, L. Y., Kondrashev, Y. D. & Goryacheva, I. A. (1955). *Dokl. Akad. Nauk S.S.S.R.* **101**, 97.

Markovskii, L. Y., Kondrashev, Y. D. & Kaputovskaia, G. V. (1955). *Zhur. Obshchei Khim.* **25**, 1045.

Talley, C. P., LaPlaca, S. & Post, B. (1960). *Acta Cryst.* **13**, 271.