TECHNICAL PHYSICS

MAGNESIUM BORIDES PREPARED UNDER SUPERHIGH-PRESSURE CONDITIONS

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During the synthesis of cubic boron nitride under superhigh-pressure (40–70 kbar) conditions and at high temperatures (1500-2200°K) from the system components Mg–B–N, magnesium borides are obtained as by-products [1], and these were used as the objects for our investigations.

According to the chemical analyses done by M. V. Kharitonova, these borides have the compositions corresponding to the formulas for magnesium diboride and hexaboride (Table 3). Magnesium borides are generally synthesized from a mixture of metallic magnesium and boron at atmospheric pressure in a hydrogen medium; the products obtained by this method are in the form of dark-brown dispersed powders, the particle size of which does not exceed 0.005 mm [2].

The magnesium borides obtained by us under superhigh-pressure conditions are usually well crystallized. Magnesium diboride is in the form of reddish-yellow platelets, the size of which, depending on the experiment, varies between 0.1 and 1.4 mm. Magnesium hexaboride crystallizes in the form of light-green isometric grains, whose size ranges from 0.02–0.04 to 0.1 mm.

The magnesium diboride and hexaboride which were separated from the products of the synthesis were subjected to x-ray diffraction and microscopic analyses, and their chemical stability and microhardness were determined.

The results of the x-ray diffraction analysis of magnesium diboride by the Debye method are shown in Table 1.

The calculation of identity periods from the 210 and 211 lines showed that a = 3.083 Å and c = 3.523 Å; according to data of [2], a = 3.083 Å and c = 3.521 Å. Thus, within the accuracy of the measurements, our data for d, a, and c are in good agreement with those of [2]. Consequently, the structure of magnesium diboride prepared by the superhigh-pressure technique does not differ from that of magnesium diboride synthesized under normal conditions.

TABLE 1. X-Ray Diffraction Characteristics of Magnesium Diboride, Obtained from a Debye Pattern Using Co Kα Radiation

Line No.	hkl	Our data		Data of [2], Fe Kα	
		I	d, Å*	I	d, Å*
1	001	–	–	< 5	3.54
2	100	m.s	2.671	25	2.673
3	101	v.v.s	2.123	100	2.126
4	002	m	1.763	10	1.760
5	110	s	1.542	30	1.542
6	102	m.w	1.466	10	1.469
7	111	w	1.414	5	1.412
8	200	w	1.335	5	1.337
9	201	s	1.251	20	1.2488
10	112	s	1.158	25	1.1596
11	103	m.s	1.073	15	1.0738
12	202	v.w	1.062	5	1.0638
13	210	m.w	1.009	10	1.0099
14	211	v.s	0.970		

*Calculated by us from kX in Å by multiplying by 1.00202.
Notation: v.v.s., very very strong; v.s., very strong; s., strong; m.s., medium strong; m., medium, m.w., medium weak; w., weak; v.w., very weak.

Results of the x-ray diffraction study of magnesium hexaboride (Table 2) showed that most of the d values are close to the corresponding values for magnesium boride (phase A) synthesized under atmospheric pressure [2]. It must be mentioned that several lines which were given for phase A [2] were not present on our Debye patterns, namely:

TABLE 2. X-Ray Diffraction Characteristics of Magnesium Hexaboride, Obtained from a Debye Pattern Using Ni Kα Radiation

Line No.	Magnesium hexaboride (our data)		Phase of A of [2], Fe Kα		Line No.	Magnesium hexaboride (our data)		Phase of A of [2], Fe Kα	
	I	d, Å	I	d, Å*		I	d, Å	I	d, Å*
1	m.s	4.15	v.w	4.18	26	v.w	1.400	w	1.392
2	m.w	3.75	w	3.79	27			v.w	1.346
3	m	3.32			28	s	1.341	s	1.324
4	w	3.06	w	3.09	29	m	1.307	s	1.313
5	s	2.75	w	2.73	30	m.w	1.296	w	1.303
6	m.s	2.54	v.s	2.53	31	s	1.274	w	1.273
7	v.v.s	2.32	s	2.32	32			w	1.263
8			m	2.26	33	v.v.v.w	1.254	w	1.256
9	v.s	2.21	m	2.20	34	v.v.v.w	1.214	w	1.221
10	v.w	2.15	m	2.16	35	v.v.v.w	1.200	v.w	1.205
11	s	2.07	v.w	2.05	36	m.w	1.168	m	1.168
12			m	2.01	37	v.w	1.158	w	1.160
13	v.v.v.w	1.979	s	1.96	38	v.v.v.w	1.140	m	1.146
14	v.v.v.w	1.892	w	1.89	39	w	1.118	w	1.125
15			m	1.86	40	m	1.104	m	1.100
16	m	1.835	m	1.83	41	m.s	1.090	m	1.083
17	m	1.768	w	1.76	42	v.w	1.069	s	1.070
18	m	1.727	w	1.71	43			w	1.063
19	w	1.670	w	1.69	44			s	1.050
20	m	1.641	s	1.63	45			m	1.047
21			v.w	1.60	46	m.d	1.035	s	1.028
22	v.v.v.w	1.576	w	1.58	47	m.s	1.021	w	1.018
23	v.v.v.w	1.53	s	1.53	48	m.s	1.001		
24	v.v.w	1.454	m	1.454					
25	m.s	1.430	m						

*Calculated by us from kX in Å by multiplying by 1.00202.

Notation: v.v.s., very very strong; v.s., very strong; s., strong; m.s., medium strong; m., medium; m.d., medium diffused; m.w., medium weak; v.w., very weak; v.v.w., very very weak; v.v.v.w., very very very weak.

TABLE 3. Some Properties of Magnesium Boride, Prepared under Superhigh-Pressure Conditions

Properties	Magnesium diboride	Magnesium hexaboride
Chemical composition	53% Mg, 47% B	27.4-26.6% Mg; 72.6-73.4% B
Syngony	Hexagonal	Rhombic
Crystal habit	Lamellar	Isometric
Color	Goldish-yellow	Light-green
Degree of transparency	Nontransparent	Transparent
Luster	Metallic	Diamond-like
Light refringence N_m	Not determined	2.8
In polished section:		
Color	Goldish-yellow	White
Reflectivity	High	High
Bireflection	High; coloration: ε, orange-gold; ω, pinkish	Low
Color anisotropy effect	In bright-azure and yellowish tints	Is not present
Microhardness H_V, kg/mm^2	1260	3500
Chemical stability	Soluble in acidic and alkali solutions	Insoluble in acidic and alkali solutions Is oxidized by water vapor at 800°C with the formation of 3 MgO · B_2O_3, pseudomorphically replacing MgB_6 grains

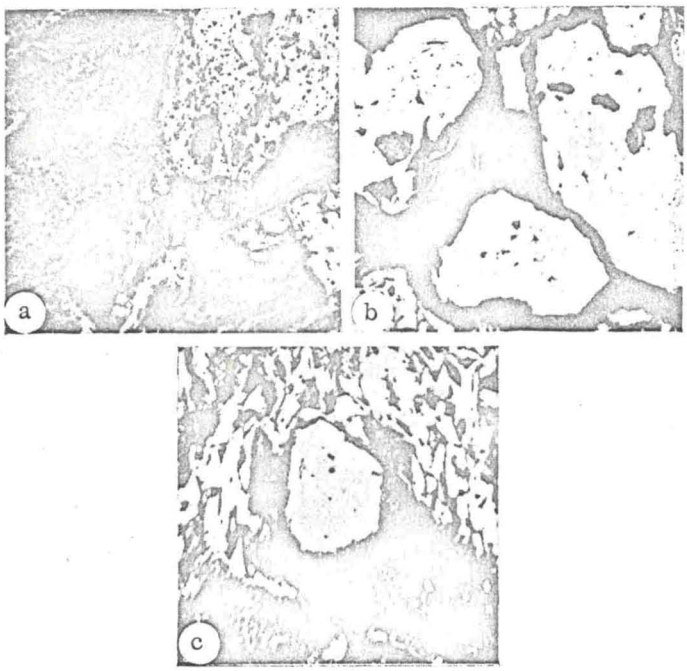

Fig. 1. Magnesium borides, at × 200. a) Magnesium diboride, reflected and polarized light; b) magnesium hexaboride, reflected light; c) isomorphous crystal of magnesium hexaboride and thin magnesium diboride platelets, reflected light.

medium at 2.26, medium at 2.01, medium at 1.86, very weak at 1.60, very weak at 1.346, weak at 1.263, weak at 1.063, strong at 1.050, and medium at 1.047 Å. The intensities of many of the lines do not agree. In particular, a number of lines of the A phase have higher relative intensities than those obtained from our Debye patterns. All these differences can, apparently, be explained not only by the peculiarities of crystallization under pressure, but also by the fact that the material which was named phase A by the authors of [2], and presumably considered by them to be magnesium hexaboride, is actually not single-phase.

Microscopic investigation of magnesium borides prepared by the superhigh-pressure technique was done by observation under a binocular, by the immersion method and by examination of polished sections; characteristic polished sections of magnesium borides are shown in Figs. 1a and 1b. In these polished sections the formation of magnesia as a result of the pyrolysis of magnesium diboride (Fig. 1c) was also observed.

Results of the microscopic investigation and the determination of some properties of magnesium borides prepared under superhigh-pressure conditions and at high temperatures are shown in Table 3.

Thus, the present work showed that under superhigh-pressure conditions favorable conditions are created for the synthesis of well-crystallized magnesium borides of stoichiometric composition. It seems expedient to try to synthesize other magnesium borides, which, as is known, cannot be prepared in pure form by the conventional method [2, 3], in order to define more precisely their chemical composition, crystal structure, and properties.

LITERATURE CITED

1. N. E. Filonenko, V. I. Ivanov, M. I. Sokhor, and L. I. Fel'dgun, Transactions of the All-Union Scientific-Research Institute of Abrasives and Polishing, No. 2 (1966).
2. L. Ya. Markovskii, Yu. D. Kondarshev, and G. V. Kaputovskaya, ZhOKh, 25, 87, No. 3 (1955).
3. Duhart, Ann. Chem., 7, Nos. 5-6 (1962).