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On some alkali- and alkaline-earth-metal boron nitrides, unsaturated with boron

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Abstract

Three new lithium, magnesium and calcium boron nitrides, namely $Ca_6BN_5(L)$, $Mg_6BN_5(H)$ and $Li_3Mg_3B_2N_5(L)$, were synthesized using a metal nitride-boron nitride sintering technique at low (L) or high (H) pressures. All these new compounds are typical metal boron nitride powders and, like previously known Mg_3BN_3 , seem to have the N^{3-} anion in their structures. \bigcirc 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

Cubic boron nitride (c-BN), a super-hard synthetic compound with hardness standing next to diamond among all materials, is of a great importance as a highly effective abrasive material for making tools such as grinding wheels, slitting saws, turning tools, rock drills, etc. [1,2]. Moreover, compared with diamond, c-BN is particularly attractive because of its higher thermostability and lower solubility in ferrous systems. Most of the known common processes for producing c-BN from hexagonal boron nitride (h-BN) are based on high-pressure (HP) synthesis with alkali- or alkaline-earth-metal nitrides or boron nitrides acting as flux catalyst–solvents [1–10]. That is why the systems M_3^1N –BN, $M_3^1N_2$ –BN, $M_3^1(BN_2)_2$ –BN, etc. have been extensively studied.

However, in the literature to date there are many contradictions and discrepancies concerning various properties and composition of alkali- or alkaline-earthmetal boron nitrides. For example, at low pressure, magnesium boron nitride, as was found, has the composition Mg₃BN₃[11–13] rather than Mg₃(BN₂)₂. Then, the composition LiCaBN₂ was rather long referred to as lithium–calcium boron nitride [10,14]; however, later investigations have established that the true composition of the thus boron nitride is LiCa₄(BN₂)₃ [15–17].

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Finally, the structure of calcium boron nitride, $Ca_3(BN_2)_2$, was determined only rather recently [18,19], though the compound has been known since 1961, when Goubeau and Anselment carried out their first experiments in the system Ca_3N_2 -BN [20].

The purpose of the present study was to examine the possibility of formation of several new metal-boronnitrogen compounds with compositions, different from those known for the most popular systems M-B-N (M = Li, Mg, Ca), and to study the properties of these new boron nitrides at ambient and high pressures. We carried out atmospheric pressure and high temperature (APHT) experiments and high pressure and high temperature (HPHT) experiments using a wide variety of starting mixtures M_xN_y-BN. New metal-boron-nitrogen compounds (Table 1) were detected using X-ray diffraction (XRD) of our APHT and HPHT samples. Unfortunately, we could not obtain single crystals of these compounds, and this is the purpose for further study; however, the fact of the existence of these compounds will be of some interest for researchers in this area.

2. Experimental procedure

2.1. Starting materials

To study HPHT or APHT sintering reactions, commercially available h-BN and Li₃N powders and calcium

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Table	1			
Some	characteristics	of new	boron	nitrides

Composition	Pressure	Unit cell	Cell parameters (Å)	Density (g/cm ³)	Indexing reliability
Ca ₆ BN ₅	low	orthorhombic	a = 8.210(3) b = 9.217(4) c = 10.567(5)	$d_{exp} = 2.69(2)$ $d_{calc} = 2.67$	<i>M</i> (20)=15.0
Mg_6BN_5	high	hexagonal	a = 5.397(2) c = 10.585(5)	$d_{exp} = 2.88(5)$ $d_{calc} = 2.82$	M(20) = 15.3
$Li_3Mg_3B_2N_5$	low	tetragonal	a = 8.4987(25) c = 8.8964(32)	$d_{exp} = 1.90(2)$ $d_{calc} = 1.92$	M(20) = 12.6

and magnesium nitrides prepared from metals were used. We synthesized Mg_3N_2 and Ca_3N_2 by the reaction of metal and nitrogen gas. The oxygen content of the N_2 gas was less than 10 ppb. The Mg_3N_2 was prepared at 600°C for 2 h and subsequently at 700°C for 4 h. The Ca_3N_2 was prepared at 800°C for 1 h and subsequently at 900°C for 3 h. The LiMgN was obtained according to the method reported by Juza and Hund [21]. According to the powder XRD analysis, the recovered samples were pure Mg_3N_2 , Ca_3N_2 and LiMgN, except for very weak and broad diffraction peaks of $M_x(OH)_y$.

We also synthesized Mg_3BN_3 , Li_3BN_2 and Ca₃(BN₂)₂. The Mg₃BN₃ was prepared by sintering of the mixture of Mg flakes and h-BN powder in the molar ratio 3:1 in a dry N₂ atmosphere by three-step reaction at 600°C for 1 h, at 650°C for 1 h and at 1150°C for 10 h. The recovered sample was reacted again at 1150°C for 4 h using crushed and remixed powder. The Li_3BN_2 was obtained from the equimolar mixture (1:1) of Li₃N and h-BN powders in an N₂ atmosphere at 600°C for 1 h and at 700°C for 3 h. The Ca₃(BN₂)₂ was prepared using a 1:2 molar mixture of Ca₃N₂ and h-BN in a dry N₂ atmosphere at 1100°C for 1 h and subsequently at 1150°C for 4 h. According to the powder XRD analysis, the recovered samples were pure Mg_3BN_3 , Li_3BN_2 and $Ca_3(BN_2)_2$, except for weak and broad peaks of $Mg(OH)_2$, LiOH or $Ca(OH)_2$.

All the mixtures were prepared in a dry N_2 or Ar atmosphere and were compacted into an Mo- or Ta-ampoule directly before HPHT experiments or into a stainless-steel container before APHT nitrogenation/sintering. The samples after APHT or HPHT treatment were immediately put under a protective film and then were examined by XRD analysis (Cu K α radiation). The pycnometric densities of newly obtained compounds were measured in CCl₄ and are listed in Table 1.

2.2. High pressure apparatus

The experiments under HP conditions were carried out using a toroid-type apparatus described in Refs.

[2,22]. The pressure generated in the cell ($V=0.08 \text{ cm}^3$) was calibrated using the known phase transitions of standard substances (Bi: 2.55 and 7.7 GPa; Yb: 4.0 GPa; PbTe: 5.0 GPa; Ba: 5.5 GPa) at room temperature. The pressure was therefore estimated to be accurate to within ± 0.3 GPa.

The temperature in the reaction cell was determined from the relation between the electric power supplied to the graphite heater and the temperature using a Pt– Pt13Rh thermocouple during a dummy run. No correction was made to allow for the thermocouple's electromotive force being a function of pressure. The cell assembly used is shown in Fig. 1. The pressure was first increased and then the temperature was increased. The temperature and the pressure were held for the desired time. After quenching, the run pressure was slowly released and the sample was recovered.

3. Results and discussion

3.1. Calcium boron nitride Ca_6BN_5

Owing to its rather wide use as a catalyst for producing c-BN, calcium boron nitride $Ca_3(BN_2)_2$ was considered as the only known compound in the system



Fig. 1. Scheme of a toroid-type apparatus in initial (a) and high-pressure (b) states: (1) binding steel rings; (2) tungsten carbide anvils; (3) catlinite toroid pressure medium; (4) graphite heater; (5) pyrophyllite disc; (6) sample in Mo- or Ta-ampoule.

Ca₃N₂–BN. We managed to obtain new calcium boron nitride, Ca₆BN₅, when we varied the initial molar ratio Ca₃N₂:h-BN and conditions of synthesis in a nitrogen atmosphere [Eq. (1)]. The optimum conditions found to obtain Ca₆BN₅ were molar ratio Ca₃N₂:h-BN=2:1 and reaction temperature between 950 and 980°C for no less than 3 h [23]. The color of the Ca₆BN₅ was dark-brown. The indexed data of this compound are listed in Tables 1 and 2.

$$2Ca_3N_2 + h - BN = Ca_6BN_5. \tag{1}$$

Observing a yellow-brown powder as a result of sintering of a mixture with an initial 1:1 molar ratio of Ca_3N_2 :h-BN, Goubeau and Anselment [20] assumed the reaction in Eq. (2) for this sample, though XRD peaks of Ca_3N_2 were not detected. Now we can assume that the reaction in Eq. (3) also could occur in that case.

 $2Ca_{3}N_{2} + 2h-BN = Ca_{3}(BN_{2})_{2} + Ca_{3}N_{2}$ (2)

$$3Ca_{3}N_{2} + 3h-BN = Ca_{3}(BN_{2})_{2} + Ca_{6}BN_{5}.$$
 (3)

New calcium boron nitride Ca_6BN_5 had a much narrower temperature formation range compared with that of $Ca_3(BN_2)_2$ and tended to turn into the latter according to the reactions in Eq. (4) (at APHT) and

Table 2

XRD indexing results on new low pressure calcium boron nitride Ca_6BN_5 (orthorhombic crystal lattice with a=8.210(3) Å, b=9.217(4) Å, c=10.567(5) Å and Z=4)

$2\theta_{obs}$ (deg)	$d_{\mathrm{obs}}(\mathrm{\AA})$	I/I_0 (%)	$d_{\text{calc}}\left(\text{\AA}\right)$	hkl
9.60	9.215	5	9.214	010
10.77	8.216	8	8.212	100
12.74	6.948	2	6.943	011
14.45	6.129	3	6.130	110
20.01	4.438	3	4.443	102
21.63	4.109	9	4.106	200
25.19	3.535	4	3.534	211
25.65	3.473	2	3.473	022
27.47	3.247	5	3.241	202
29.05	3.074	6	3.071	030
30.30	2.950	3	2.950	031
31.10	2.876	12	2.877	130
32.72	2.737	33	2.737	300
33.52	2.673	85	2.673	203
35.74	2.512	100	2.514	104
36.99	2.430	7	2.430	302
40.00	2.2538	4	2.2514	041
42.06	2.1482	3	2.1498	322
44.07	2.0550	10	2.0529	400
49.36	1.8461	15	1.8465	421
51.54	1.7733	30	1.7732	151
54.20	1.6924	4	1.6926	116
57.90	1.5926	16	1.5941	216
59.35	1.5571	7	1.5575	045
61.43	1.5094	5	1.5095	007
			1.5100	160
62.45	1.4871	17	1.4868	154
62.70	1.4817	25	1.4810	306
64.42	1.4463	5	1.4483	530

Eq. (5) (at HPHT).

$$Ca_6BN_5 + 3h - BN = 2Ca_3(BN_2)_2$$
(4)

$$2Ca_6BN_5 = Ca_3(BN_2)_2 + 3Ca_3N_2.$$
 (5)

To confirm the presence of $(N=B=N)^{3-}$ linear anions in the crystalline structure of new boron nitride, its IR-spectrum was obtained (Fig. 2b). As one can see, in general features it is very similar to that of Mg₃BN₃(L) [11] (Fig. 2a).

It was interesting to examine the behavior of Ca_6BN_5 in h-BN \rightarrow c-BN catalytic transition and to compare it with those of Ca_3N_2 and $Ca_3(BN_2)_2$. For this purpose three mixtures of different catalysts with h-BN were prepared and then treated at HPHT conditions. All the mixtures were so calculated that the calcium content was the same (10 at.%) in each case. Thus the total charge composition was the same, namely $2Ca_3N_2+25h$ -BN; Ca_6BN_5+24h -BN and $2Ca_3(BN_2)_2$ + 21h-BN (which gave Ca:B:N=1/10:5/12:29/60 for each mixture). Such a ratio for prepared mixtures was selected for easy detection by XRD and correct comparison of all the products of the reactions considered.

As can be seen from Fig. 3, the minimum c-BN synthesis temperature for the Ca_6BN_5 -BN system is



Fig. 2. IR-spectra (transmittance against wave number) of (a) $Mg_3BN_3(L)$ [11], (b) Ca_6BN_5 and (c) $Li_3Mg_3B_2N_5$.



Fig. 3. c-BN growth region in the systems Ca_3N_2 -BN (1), Ca_6BN_5 -BN (2) and $Ca_3B_2N_4$ -BN (3); c-BN exists in the region above each curve; Eqn.: c-BN–h-BN equilibrium line.

higher than that for the Ca_3N_2 -BN system, and that for the $Ca_3(BN_2)_2$ -BN system is the lowest. An explanation of this fact may be the following. As is agreed, the process of c-BN formation in the system Ca-B-N is connected with the preliminary formation of $Ca_3(BN_2)_2$. Then, using the volume changes of the reactions in Eqs. (6) and (7), it is possible to assume that the reaction in Eq. (7) is more preferable under HP conditions than is the reaction in Eq. (6). Hence the reaction in Eq. (7) may require a lower temperature than the reaction in Eq. (6) at the same pressure.

$$Ca_6BN_5 + 3h-BN = 2Ca_3(BN_2)_2 (\Delta V/V = +2.71\%)$$
 (6)

$$Ca_3N_2 + 2h-BN = Ca_3(BN_2)_2 (\Delta V/V = -0.02\%).$$
 (7)

In addition it should be noted that after HPHT treatment for more than 3 min all three systems mentioned above revealed almost the same XRD patterns $[Ca_3(BN_2)_2, h-BN \text{ and/or c-BN}]$. Thus, the role of Ca_6BN_5 in $h-BN \rightarrow c-BN$ transformation, apparently, is limited only to the role of intermediate compound in $Ca_3(BN_2)_2$ formation [Eq. (6)].

3.2. Magnesium boron nitride Mg_6BN_5

The system Mg_3N_2 -BN has been repeatedly studied [5-9,11-13,24]. It was established that the only compound forming at AP was magnesium boron nitride $Mg_3BN_3(L)$ [11-13]. When heated at HP of more than 2.0 GPa, $Mg_3BN_3(L)$ was shown to undergo transformation into its HP modification, $Mg_3BN_3(H)$ [12,13,24,25]. As to HP conditions, numerous sources reported at least one more boron nitride phase. The composition, XRD characteristics, and stability field of this phase (or phases) are widely discussed.

Nakano et al. [24] have already reported that in the course of their experiments in the system Mg_3N_2 -BN a new X-phase was detected. They obtained the X-phase

at 4.0 GPa and 1300°C for 15 min and at the molar ratio Mg₃N₂:BN from 2:1 to 1:1 (from Mg₆BN₅ to Mg₃BN₃); they determined its composition as slightly Mg₃N₂-rich Mg₃BN₃. Then they investigated the relation between c-BN formation and the X-phase stability and concluded that the X-phase observed from the quenched products was unstable when surrounded by h-BN. No evidence of decomposition of the X-phase to form c-BN was observed. As XRD data show (with some correlation), the same X-phase was earlier assigned by Hohlfeld [9] as Mg₃BN₃(H), by Elyutin et al. [7] as β -Mg₃BP₂N₄ and then by Gladkaya et al. [26] as Mg₃BN₃(H) too.

At first, we observed the appearance of the X-phase when we tried to obtain a HP magnesium boron nitride modification of composition $Mg_3(BN_2)_2$ and hence treated the mixtures Mg_3N_2+2h -BN or Mg_3BN_3+h -BN at various HPHT conditions. Then we could detect the X-phase at HP from 1.5 to 5.0 GPa and HT near 1100°C. However, it was obvious that the samples investigated contained, except X-phase, significant amounts of other phases, mostly h-BN and Mg_3BN_3 [27].

Sufficient purity of this compound was attained only at 1.5 GPa and a charge composition close to $Mg_3B_2N_4$ [27]. The substance thus obtained was almost free from Mg_3BN_3 admixture, but contained some quantities of unreacted h-BN and Mg_3N_2 , judging from XRD data. The attempts to obtain a sample of better purity by increasing the run time or by varying the initial charge composition or synthesis conditions were unsuccessful.

As soon as calcium boron nitride Ca_6BN_5 [23] had been prepared, we supposed the same composition for the X-phase, too. Thus the sample (a) from Fig. 4, almost clean from all impurities and containing a little of h-BN and MgO, was obtained after double treatment of the initial mixture $2Mg_3N_2$ +h-BN at 2.0 GPa and $1600^{\circ}C$ for 1 h [28]. When heated in nitrogen atmosphere up to $600^{\circ}C$, the sample (a) remained unchanged, but at 900°C it decomposed to yield sample (b) (Fig. 4). The amounts of MgO and h-BN in both samples remained almost the same. This is why we could assume the composition Mg_6BN_5 for the X-phase and the reaction in Eq. (8) (at HT and in an N₂ atmosphere) for samples (a) and (b) to explain these results:

$$Mg_6BN_5 + xMgO + yh-BN = Mg_3BN_3(L)$$

+ Mg_3N_2 + xMgO + yh-BN. (8)

As was found in our studies elsewhere [27,28], the formation of almost single-phase Mg_6BN_5 sample (or former X-phase [24]) was possible only in a very narrow pressure range near 2.0 GPa. At lower pressure the formation of the $Mg_3BN_3(L)$ occurred, and at increased pressure the formation of the $Mg_3BN_3(H)$, together with the Mg_6BN_5 , was observed, and the concentration



Fig. 4. XRD patterns of twice treated at 2.0 GPa and 1600°C mixture $2Mg_3N_2 \cdot BN$ before (a) and after (b) heating in a nitrogen atmosphere at 900°C; (\bigcirc): h-BN; (\diamondsuit): Mg_6BN_5 ; (\blacksquare): MgO; (\bigtriangledown): $Mg_3BN_3(L)$; (\triangle): Mg_3N_2 .

of the $Mg_3BN_3(H)$ increased with the pressure increase. The novel compound Mg_6BN_5 was a brick-red powder that gradually reacted with water vapor in the air. When the XRD pattern of Mg_6BN_5 was indexed, hexagonal symmetry with the unit cell parameters shown in Table 1 was assumed (see Table 3). As the Mg_6BN_5 is unstable at HP above 5.0 GPa, its role in catalytic h-BN \rightarrow c-BN transformation, apparently, can be limited only to $Mg_3BN_3(H)$ formation [reaction in Eq. (9)]:

$$Mg_6BN_5 + h-BN = 2Mg_3BN_3(H).$$
 (9)

3.3. Lithium–magnesium boron nitride $Li_3Mg_3B_2N_5$

Data for complex lithium-magnesium boron nitride have not been presented in the literature. The previously sintered mixture of Li:Mg:B:N=1:1:1:2 composition was successfully used for production of harder c-BN crystals compared with those produced with the same previously non-treated mixture as a catalyst [10]. The author, probably, observed two or more phase patterns after sintering of the above mixture, and that is why did not report the formation of a new lithium-magnesium boron nitride.

As a result of our studies in the system $Li_3N-Mg_3N_2-BN$, we synthesized a new complex boron nitride of composition $Li_3Mg_3B_2N_5$ by sintering of different initial components in inert gas atmosphere

Table 3

XRD indexing results on new high pressure magnesium boron nitride Mg_6BN_5 (hexagonal crystal lattice with a=5.397(2) Å, c=10.585(5) Å and Z=2)

$2\theta_{obs}$ (deg)	$d_{\mathrm{obs}}(\mathrm{\AA})$	I/I_0 (%)	d_{calc} (Å)	hkl
16.70	5.304	3	5.293	002
18.95	4.679	22	4.674	100
25.35	3.511	43	3.504	102
33.15	2.700	18	2.699	110
33.85	2.646	21	2.646	004
34.25	2.616	28	2.615	111
37.30	2.409	14	2.404	112
38.50	2.336	21	2.337	200
39.05	2.305	12	2.303	104
42.10	2.145	100	2.144	113
48.10	1.890	32	1.889	114
51.80	1.764	13	1.764	006
52.15	1.752	32	1.752	204
52.40	1.7447	36	1.7426	211
55.05	1.6668	26	1.6657	115
58.40	1.5789	3	1.5797	213
59.30	1.5571	21	1.5581	300
62.80	1.4785	2	1.4767	116
69.20	1.3565	3	1.3564	215
70.25	1.3388	3	1.3385	221
71.25	1.3225	9	1.3231	008
73.00	1.2950	3	1.2964	310
73.55	1.2867	10	1.2868	311
75.35	1.2603	5	1.2603	223
78.60	1.2162	6	1.2169	313
80.90	1.1873	2	1.1880	118
82.40	1.1694	3	1.1686	400
82.85	1.16423	6	1.16421	314
83.95	1.15175	5	1.151 42	208
84.20	1.14897	5	1.148 81	217
85.15	1.138 56	2	1.13787	225
88.40	1.110490	4	1.105 58	315

[29,30]. The novel compound was from light- to darkgray powder and relatively stable in the air. It was obtained at 950–1000°C for at least 2–4 h according to the reactions in Eqs. (10)–(14). The sinter obtained was usually ground in a dry glove box and then repeatedly treated to provide the most complete reaction. The most preferable ways to obtain the most pure product were found to be presented by the reactions in Eqs. (11), (13) and (14). The XRD powder data of the new compound were successfully enough indexed in the tetragonal unit cell (see Tables 1 and 4).

$$Li_3N + Mg_3N_2 + 2h - BN = Li_3Mg_3B_2N_5$$
 (10)

 $Li_3BN_2 + Mg_3BN_3 = Li_3Mg_3B_2N_5$ (11)

$$Li_3BN_2 + Mg_3N_2 + h-BN = Li_3Mg_3B_2N_5$$
 (12)

$$Li_3N + Mg_3BN_3 + h - BN = Li_3Mg_3B_2N_5$$
 (13)

$$3\operatorname{LiMgN} + 2h \cdot BN = \operatorname{Li}_{3} Mg_{3}B_{2}N_{5}.$$
 (14)

To confirm the presence of $(N=B=N)^{3-}$ linear anions in the crystal structure of the compound, its IR-spectrum was obtained (Fig. 2c).

Table 4

XRD indexing results on new low pressure lithium–magnesium boron nitride $Li_3Mg_3B_2N_5$ (tetragonal crystal lattice with a=8.4987(25) Å, c=8.8964(32) Å and Z=4)

$2\theta_{\rm obs}$ (deg)	$d_{\mathrm{obs}}(\mathrm{\AA})$	I/I_0 (%)	$d_{\text{calc}}\left(\text{\AA}\right)$	hkl
19.95	4.451 40	51	4.448 07	002
20.90	4.250 96	40	4.250 69	200
25.47	3.497 04	100	3.496 05	211
31.43	2.846 30	14	2.847 55	221
31.59	2.832 50	14	2.833 79	300
38.56	2.335 01	9	2.338 25	213
39.16	2.300 25	53	2.300 79	312
47.48	1.91496	37	1.91768	402
47.84	1.901 23	37	1.90097	420
52.27	1.749 98	21	1.749 55	304
			1.748 02	422
52.35	1.748 11	21	1.748 02	422
			1.749 55	304
53.51	1.71231	15	1.713 64	314
54.93	1.671 53	13	1.670 05	431
58.45	1.57901	3	1.578 67	520
62.41	1.48791	16	1.487 74	522
			1.488 69	334
63.76	1.459 73	5	1.460 64	106
			1.45797	530
64.47	1.445 35	4	1.445 04	424
69.80	1.347 34	13	1.347 04	415
72.85	1.298 38	6	1.298 32	316
			1.29901	425
73.59	1.28713	4	1.287 33	524
			1.28672	622
79.53	1.205 15	4	1.205 32	217
			1.203 77	416
84.11	1.15081	11	1.15040	624
98.44	1.018 03	2	1.01794	437
109.72	0.94273	6	0.943 32	833

3.4. N^{3-} -containing boron nitrides

IR-spectra of alkali- and alkaline-earth-metal boron nitrides have not been studied extensively, but vibration

spectra of $(N=B=N)^{3-}$ anions have been discussed quite extensively [5,11,20,31]. The most complete picture of such spectra for Li₃BN₂, Ca₃(BN₂)₂ and Ba₃(BN₂)₂ was given by Somer [31]. In the present work we did not aim to study IR-spectra of our new boron nitrides in detail. We intended only to confirm the fact of the presence of $(N=B=N)^{3-}$ anions in their structures (and, consequently, the presence of N³⁻ anions). Therefore, our investigations were limited only to registering of spectra and also their comparison with those previously known from the literature, mainly of Refs. [11,31] (Fig. 2 and Table 5). In Table 5 our data are compared with those from Ref. [31]; the absorption of unreacted h-BN and of OH groups [from M_x(OH)_y] in our samples is comparable to those for Mg₃BN₃(L) [11].

Hiraguchi and coworkers [11,25] have shown earlier that the crystal structure of magnesium boron nitride, Mg₃BN₃, in its low- (L) and high-pressure (H) phases can be described as an ionic crystal formally composed of the molecular anions $(N=B=N)^{3-}$, the cations Mg²⁺ and the anions N³⁻. Thus magnesium boron nitride, Mg₃BN₃, became the first representative of the group of alkali- and alkaline-earth-metal boron nitrides that, owing to presence of the N³⁻ anions in their crystalline structure, could be called 'unsaturated with boron'. Formally these metal boron nitrides can be considered as a transition state between metal nitrides, M¹₃N, M¹₃N₂ and M¹M¹N, and so-called 'saturated with boron' boron nitrides, M¹₃BN₂, M¹₃(BN₂)₂ and M¹_xM¹_y(BN₂)_z.

In this work we have presented three new alkalineearth-metal and complex alkali–alkaline-earth-metal boron nitrides that on account of their crystal structure, namely the presence of both $(N=B=N)^{3-}$ anions and N^{3-} anions, can be considered as new members of the group mentioned above.

The following representative of this group could

Table 5

Assignment of frequencies (cm^{-1}) in IR-spectra of new Ca_6BN_5 and $Li_3Mg_3B_2N_5$ boron nitrides (present work) and their comparison with the data by Somer [31] for Li_3BN_2 , $Ca_3B_2N_4$ and $Ba_3B_2N_4$

Compound	$\nu_2(\Sigma_u), (^{10}B)$	$v_2(\Sigma_u), (^{11}B)$	$v_3(\Pi_u), ({}^{10}B)$	$v_3(\Pi_u), (^{11}B)$	h-BN	ОН
Ca ₆ BN ₅	1770 ^a	1700	_	580 ^b 610 ^b	1384	3640
$Li_3Mg_3B_2N_5$	1735	1685	640	-	1490	3670 ^k
1 . DN [21]	1750	1 (75		615		
$L1_3BN_2[31]$	1750	16/5	_	575	_	-
Ca ₃ B ₂ N ₄ [31]	1760	1680	625	582 607	_	-
Ba ₃ B ₂ N ₄ [31]	1705	1630	625	580 608	_	_

^a Weak absorption.

^b Very weak absorption.



Fig. 5. XRD pattern of sintered mixture $Ca_3N_2 \cdot 2BN$ (1150°C, 3 h) showing 'formation' of possible calcium boron nitride Ca_3BN_3 ; (\Box): CaO; (\bigcirc): h-BN.

become calcium boron nitride with possible composition Ca_3BN_3 . Until now there has been no information concerning the existence of such a boron nitride. As yet we have not managed to prepare it, but several of our samples have given XRD patterns (Fig. 5) that can be interpreted as the possible formation of Ca_3BN_3 with cubic body-centered crystal structure [Eq. (15)]:

$$2Ca_3N_2 + 4h-BN = Ca_3(BN_2)_2 + Ca_3BN_3 + h-BN.$$
 (15)

However, this assumption still has no strict confirmation, and thus the question of the existence of Ca_3BN_3 remains open.

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