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On the choice of hexagonal boron nitride for high pressure phase transformation using the catalyst solvent process

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The degree of three-dimensional ordering, particle-size distribution and purity of two types of hexagonal boron nitride have been studied with a view to establish any possible correlation between these characteristics with the conversion of hexagonal form to cubic phase at high pressure and high temperature using magnesium as the catalyst solvent. The crystalline phases formed at high pressure and high temperature have been studied and the dependence of degree of graphitization of boron nitride and purity on the cubic boron nitride conversion discussed.

1. Introduction

The first high pressure phase transformation of hexagonal boron nitride to a hard denser phase of cubic boron nitride was achieved by Wentorf employing the catalyst solvent process with the use of magnesium [1, 2]. Later, a number of scientists succeeded in synthesizing CBN at high temperature and high pressure using the catalyst solvent process [3–8]. The catalyst solvents that were selected belonged to the series consisting of alkali and alkaline earth metals and their nitrides. Besides, other catalyst solvents such as Fe–Al and Ag–Cd alloys [9], water, urea and boric acid [10], and a mixture of ammonium fluoride and silicon [11] were also found to be effective for CBN conversion.

CBN can also be synthesized by direct transformation from HBN in a high temperature–high pressure environment. The first direct transformation of HBN–CBN was realized by Balchan and Drickamer [12] under static pressure. Subsequently, Bundy and Wentorf [13] and Corrigan and Bundy [14] studied the direct phase transformation of HBN to CBN in greater detail and obtained a comprehensive phase diagram for boron nitride. A shock-wave compression technique has also been adopted to synthesize CBN [15].

Ichinose *et al.* [16] investigated the effect of degree of crystallization, particle size and moisture in the starting material on the direct transformation of HBN to CBN. It was observed that the HBN of lower three-dimensional ordering and with smaller crystallite size transformed into CBN at much lower pressures than that observed for direct transformation by earlier workers. Endo and coworkers [8] studied the role of oxygen impurities present in the starting HBN in CBN conversion employing the catalyst solvent process with magnesium as the catalyst. It was concluded from this study that the presence of a high concentration (7.9 wt %) of oxygen tends to raise the lower temperature limit of CBN formation.

The present investigation is an attempt to understand the possible role of degree of crystallization, particle-size and impurity present in the starting HBN samples in CBN conversion involving the catalyst solvent process with magnesium as the catalyst. The starting materials have been characterized in respect of the degree of graphitization, crystallite-size distribution and purity. HBN samples so characterized were used in synthesizing CBN using magnesium as the catalyst solvent in high pressure–high temperature environment. The reaction products were also characterized for various crystalline phases formed during high temperature and high pressure reactions. The results of these investigations are described and discussed with respect to the characteristics of the starting HBN samples.

2. Experimental details

2.1. Samples

Two types of starting HBN have been used. The first was in powder form and was obtained from Union Carbide, USA (Grade HCP, high purity). The other starting HBN was in the form of a rod (6 mm diameter) and was obtained from Carborundum Co., (Combat Boron Nitride, Grade HP). For the sake of convenience the former type of HBN is labelled as type A and the latter as type B. Elemental magnesium (99.5% pure) obtained from Sarabhai Chemicals Ltd, Baroda, India was used as the catalyst solvent.

2.2. Techniques

Powder X-ray diffraction has been used to evaluate the degree of crystallization in HBN samples as well as to study the crystalline phases formed at high temperature and high pressure in the BN–Mg system. CuK_α has been used as the exploring beam.

Scanning electron microscopy (SEM) has been used

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to determine the particle-size distribution in the initial HBN samples of types A and B. Particle-size range of the synthesized CBN was also determined by SEM. JEOL JSM-35 CF and ISI-130 DS SEMs were used in secondary electron emission mode.

Electron spectroscopy for chemical analysis (ESCA) has been used to assess the purity in the HBN samples. A MgK_α (1253.6 eV) X-ray beam was used to excite ESCA spectra of the constituent elements in the HBN samples of types A and B. An ESCA assembly manufactured by Inficon–Leybold Heraeus was employed for this purpose. The operating conditions of the magnesium target were 11 kV and 36 mA. HBN samples of type A were prepared in the form of pellets for recording ESCA spectrum. The surfaces of both types A and B specimens were cleaned by using the argon ion sputtering technique in a ESCA vacuum chamber. A silver substrate was used as a sample holder to record the ESCA spectra.

3. Results and discussion

3.1. Degree of graphitization in starting HBN

The degree of crystallization or three-dimensional ordering in HBN samples of types A and B was evaluated by adopting a method proposed by Thomas and coworkers [17] using powder X-ray diffractometry. The degree of graphitization in HBN is known to be influenced by the manifestation of (100), (101) and (102) lattice planes in the HBN lattice. The resolution of X-ray diffraction lines due to these lattice planes and their relative diffracted intensities are governed by the degree of three-dimensional atomic ordering in HBN. It was also observed that as the degree of crystallinity decreases the resolution of (100) and (102) reflections and the intensity of (102) diffraction line tend to diminish. Following these observations Thomas and coworkers [17] defined the degree of three-dimensional ordering in terms of the "graphitization-index" (GI) for HBN as

$$\mathrm{GI} = \frac{\mathrm{Area}[(100) + (101)]}{\mathrm{Area}[(102)]}$$

According to this definition a higher value of GI would mean less three-dimensional ordering in HBN and vice versa. Thomas *et al.* [17] obtained a GI value of 1.60 for the completely graphitized (crystallized) HBN and a value of about 50 as an upper limit for the least three dimensionally ordered HBN.

Fig. 1a and b show powder X-ray diffraction patterns depicting the (100), (101) and (102) reflections obtained for HBN samples of types A and B, respectively, using CuK_α as the exploring beam under identical experimental conditions. The integrated X-ray intensities for (100), (101) and (102) corresponding to these two patterns were determined with the aid of a computer attached to the powder X-ray diffractometer and the results are summarized in Table I.

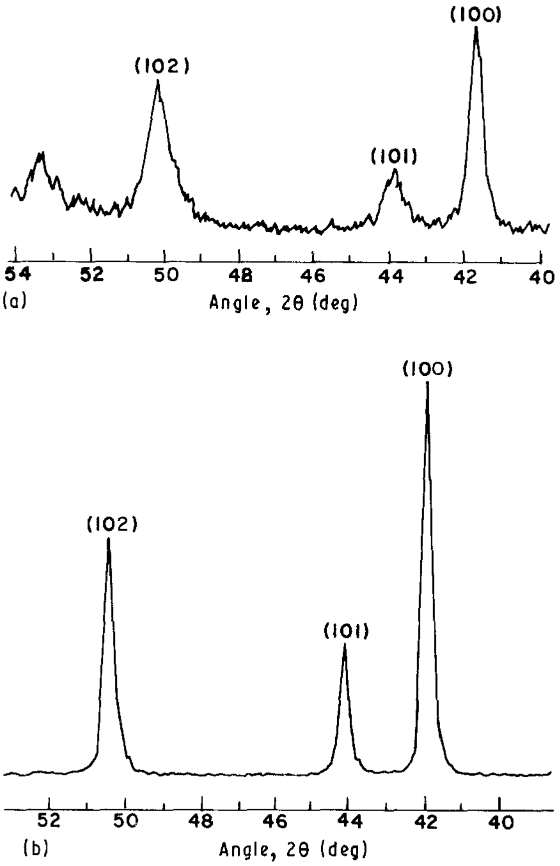

Figure 1 Powder X-ray diffraction pattern depicting (100), (101) and (102) reflections of HBN samples: (a) type A (b) type B.

TABLE I X-ray diffraction data for three-dimensional ordering for HBN samples

Sample	Lattice planes	Integrated intensity	GI
Type A	(100)	2642	1.68
	(101)	1755	
	(102)	2604	
Type B	(100)	14761	
	(101)	6102	1.79
	(102)	11656	

It can be seen from Fig. 1 and Table I that these samples are highly crystallized, with GI values of 1.68 and 1.79 for HBN samples of types A and B, respectively. It can, therefore, be concluded that as far as the degree of three-dimensional ordering is concerned there is not much difference between type A and B specimens.

3.2. Particle-size distribution in the starting HBN samples

Particle-size distribution analysis of HBN samples of types A and B was carried out in detail using SEM. For this purpose a large number of SEM micrographs of both types of specimen were recorded in the secondary electron emission mode with 0° tilt. Fig. 2a and b show typical SEM micrographs obtained for samples of types A and B, respectively. Particle-size distribution of boron nitride (BN) grains in types A and B was obtained manually from magnified SEM photographs. For the evaluation of particle size the maximum value of the edge-to-edge length of the grain was

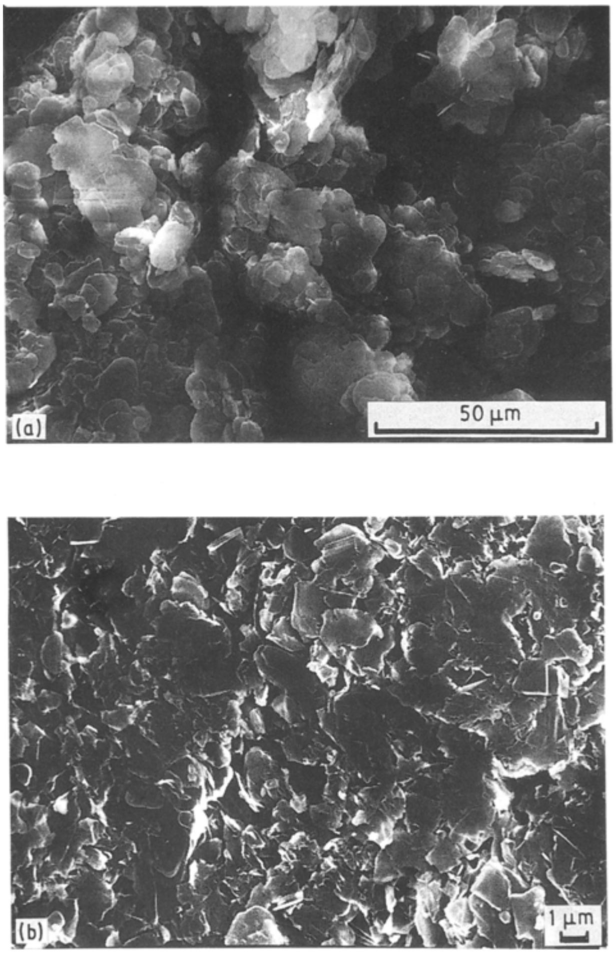

Figure 2 Typical SEM micrographs of HBN samples: (a) type A (b) type B.

TABLE II Particle-size distribution of BN grains in samples of types A and B

Sample of type	% of particles	Particle size (μm)
A	10	5.0
	30	6.25
	26	7.50
	4	8.75
	12	10.00
	4	11.25
	14	12.00
B	4	0.6
	6	0.8
	38	1.0
	10	1.2
	26	1.6
	14	2.0

taken as a measure of particle size. Table II shows the result of particle-size distribution analysis made on HBN samples of types A and B. This table shows the percentage distribution of particles having a particular value of particle size in type A and B specimens. It can be seen in Table II that BN grains in type A specimen lie in the range of 5 to 12 μm, with 60% of the particles having a range of 6 to 9 μm. For type B specimen, a particle-size range of 0 to 2 μm for BN grains was obtained, with 48% of the particles having a particle size of about 1 μm.

3.3. ESCA characterization of the starting HBN

The starting HBN samples of types A and B were characterized for purity using ESCA. The surface of the specimens was cleaned by argon ion sputtering for 1 h in three steps, each lasting for 20 min, and the corresponding ESCA spectra were recorded. Initially the spectra for both the specimens showed an intense $1S_{1/2}$ peak in their kinetic energy ESCA spectra due to carbon, whose height was considerably reduced after cleaning the surface for 20 min. Further cleaning did not, however, yield any reduction in either $ClS_{1/2}$ or $OlS_{1/2}$ spectra. Fig. 3a and b show the kinetic energy ESCA spectra obtained for HBN samples of types A and B, respectively, after 1 h argon ion sputtering. The ESCA spectra observed in Fig. 3 have been marked with each photo-emission line of the constituent elements along with the kinetic energy of the emitted electrons. It can be seen that some of the Auger lines are also observed, however, some of the silver lines are also seen in Fig. 3. This is due to the sputtered silver atoms from the probe holder being deposited on the sample surface during the argon ion sputtering process.

In the present study an attempt has been made to compute the atomic concentration of the different elements observed in samples of types A and B in their ESCA spectra. For this purpose, only the ESCA component of the spectra has been used. The area of the different lines has been determined and with the use of the sensitivity factor of the corresponding elements the atomic concentrations were determined. A sensitivity factor of 0.13, 0.42, 0.25 and 0.66 for B, N, C and O has been used, respectively [18]. The atomic concentrations have been calculated from the following expression:

$$\text{Atomic percentage} = \frac{(\text{Area}[\text{ESCA line}] \times \text{Sensitivity}) \times 100}{\sum_i (\text{Area}[\text{ESCA line}] \times \text{Sensitivity})_i}$$

Table III shows the atomic percentage of B, N, C and O obtained for HBN samples of types A and B. It can be seen that oxygen is present in these samples in quite appreciable amounts, type A sample showing a larger concentration (51.4 at %) than type B (37.7 at %). The atomic concentrations determined in this manner represent the approximate concentration of different elements present on the surface. The actual bulk composition of elements may still be different. Although a more accurate analysis is possible using neutron activation analysis, for the purpose of this study which mainly concerns the affect of the relative concentration of oxygen, the present analysis appears to be adequate.

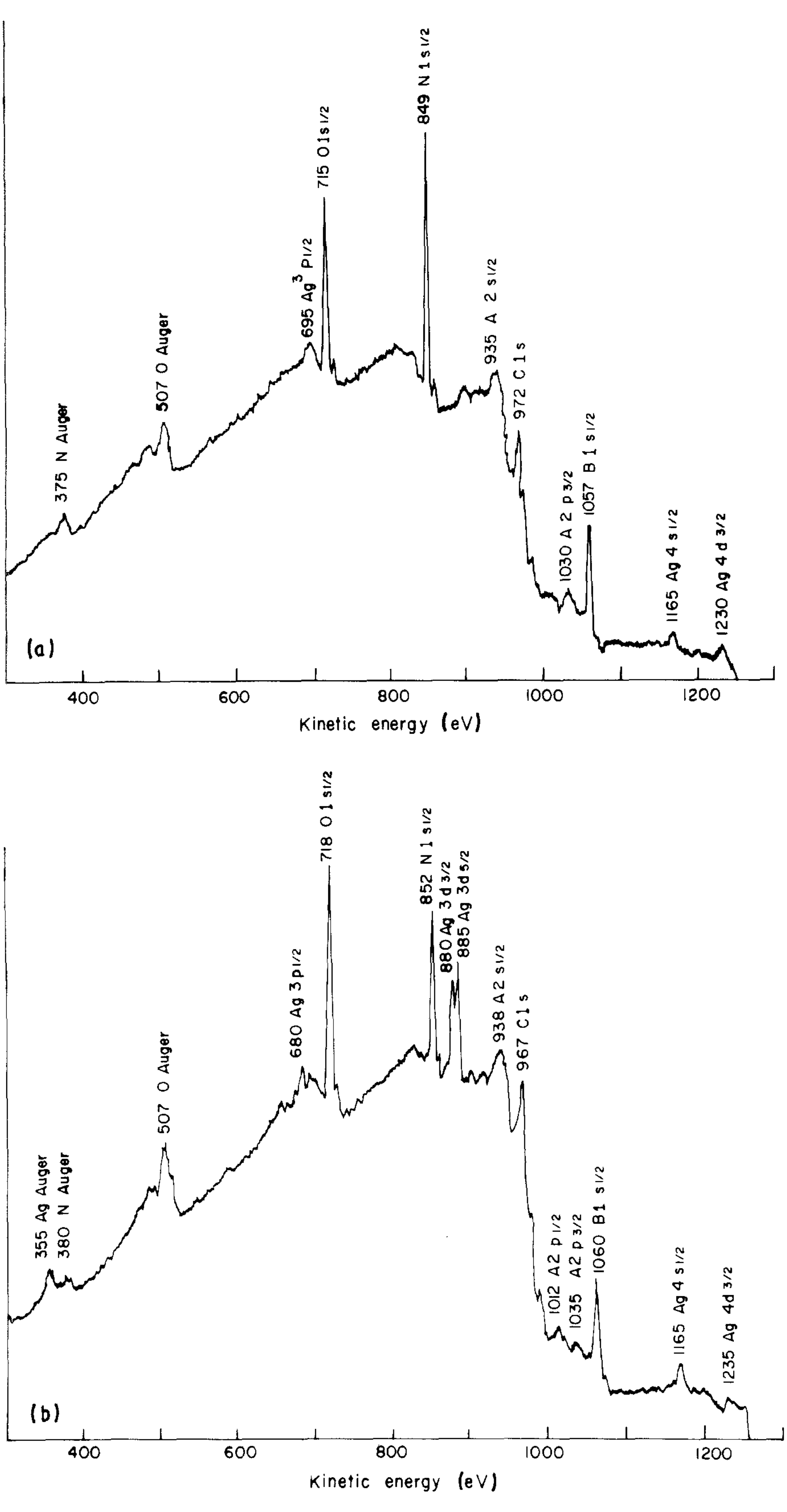

Figure 3 ESCA spectra (kinetic energy) of HBN samples: (a) type A (b) type B

TABLE III Atomic percentage of elements present in HBN samples

	Atomic %			
HBN	B	N	O	C
Type A	8.1	32.7	51.4	7.8
Type B	6.96	48.7	37.7	6.6

3.4. CBN conversion

HBN samples of types A and B, whose characterization results regarding three-dimensional ordering, particle-size distribution and purity have been described in Sections 3.1, 3.2 and 3.3 were used as the starting material for high pressure phase transformation into CBN using magnesium as the catalyst solvent. The pressure and temperature were optimized for maximum CBN conversion in both cases. The maximum conversion was achieved at 5.8 GPa and 1450 °C. Fig. 4a and b show SEM micrographs for CBN crystals synthesized from types A and B HBN, respectively. The CBN crystals are predominantly of the shapeless variety in both cases. Intertwinning and clustering among crystals have also been observed. The size of the crystals is found to lie in 10 to 50 μm range.

Fig. 5a shows a powder X-ray diffraction pattern for the reaction mixture obtained from type A HBN as the starting material. The diffraction line observed at $2\theta = 44^\circ$ ($d = 0.2058$ nm) corresponds to CBN. The diffractogram also shows the presence of HBN with its (002), (100) and (102) diffraction lines at $2\theta = 26.8^\circ$, 42.5° and 49.4°, respectively. The other crystalline phases that are present in the reaction product obtained from type A HBN are Mg, MgO and Mg_3N_2, MgB_6 and MgB_{12}. The different reflections corresponding to these phases are marked in Fig. 5a with 2θ and d values, however, few weak diffraction lines observed at lower 2θ values could not be identified.

Fig. 5b depicts the X-ray diffractogram of the reaction product obtained from HBN of type B. The different X-ray diffraction lines observed in Fig. 5b are labelled along with their 2θ, d values and the corresponding crystalline phases. The phases are: HBN, CBN, Mg, MgO and Mg_3N_2. No borides of magnesium have been observed in this case. The absence of borides is being studied in greater detail and will be reported subsequently.

The present investigation shows that even though the graphitization index i.e. the degree of three-dimensional ordering (GI = 1.7) was nearly the same for type A and B HBN starting materials. CBN conversion was found to be drastically different in the two cases. For HBN samples of type A, the yield was more than 70% by weight, whereas in case of type B the yield did not exceed 25%. The explanation for the large difference in the yield in the two cases does not appear to have its origin in the characteristics of the starting materials, because the degree of three-dimensional ordering and the impurity level in types A and B HBN are essentially of the same order. The increased CBN conversion in the case of type A HBN is presumably due to the fact that the solid state reaction at high pressure and high temperature is nearly complete because of the homogeneous mixing of the starting HBN powder (type A) and magnesium. The homogeneously mixed starting material being in powder form, provides an increased effective surface area for the solid state reaction resulting in better percentage conversion, however, since the type B HBN was in the form of a solid rod and the catalyst solvent (magnesium) was put on its surface only, the solid state reaction could have taken place only at the boundary and within a thin section of the HBN rod yielding a lower CBN conversion.

Ichinose *et al.* [16], in a direct conversion of HBN to CBN, observed that HBN of lower structural ordering (higher GI) and smaller particle size can be converted at lower pressures (6.8 GPa) and vice versa, bringing the pressure down to less than 70% of that required otherwise for direct conversion. In the catalyst solvent process Fukunaga *et al.* [7] using the BN–Mg, BN–Li_3N and BN–Mg_3N_2 system studied the growth *P–T* regions employing a large variety of starting HBN obtained from different sources. In this study [7], however, any possible relationship between the three-dimensional ordering in the starting HBN with CBN yield or lowering of pressure required for CBN conversion was not discussed. Endo *et al.* [8] studied CBN conversion employing the catalyst-solvent process (BN–Mg) in which two types of starting HBN, namely R-type and N1 type, with GI values of 1.56 and 1.39, respectively, were used. CBN conversion was studied from 6 to 8 GPa and at different temperatures. No specific mention about any possible role of three-dimensional ordering in HBN structure was made. In the present case, HBN samples of types A and B with GI value of 1.68 and 1.79, respectively (Sec. 3.1) were used for CBN conversion. As described earlier (Section 3.4) a CBN conversion of more than 70 wt % was achieved from type A HBN at fairly moderate *P–T* values (5.8 GPa, 1450 °C). The present results indicate that in the catalyst solvent process the role of three-dimensional ordering in the starting HBN has no significant effect on CBN conversion with respect to yield or lowering of pressure. This observation can be understood in the following way.

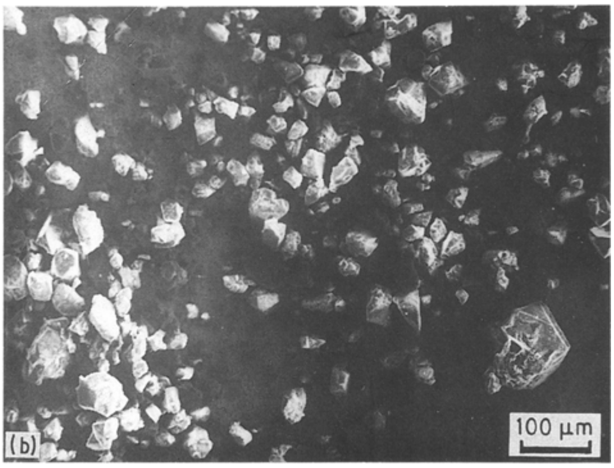

Figure 4 SEM micrographs of CBN crystals synthesized by using HBN samples of (a) type A, (b) type B.

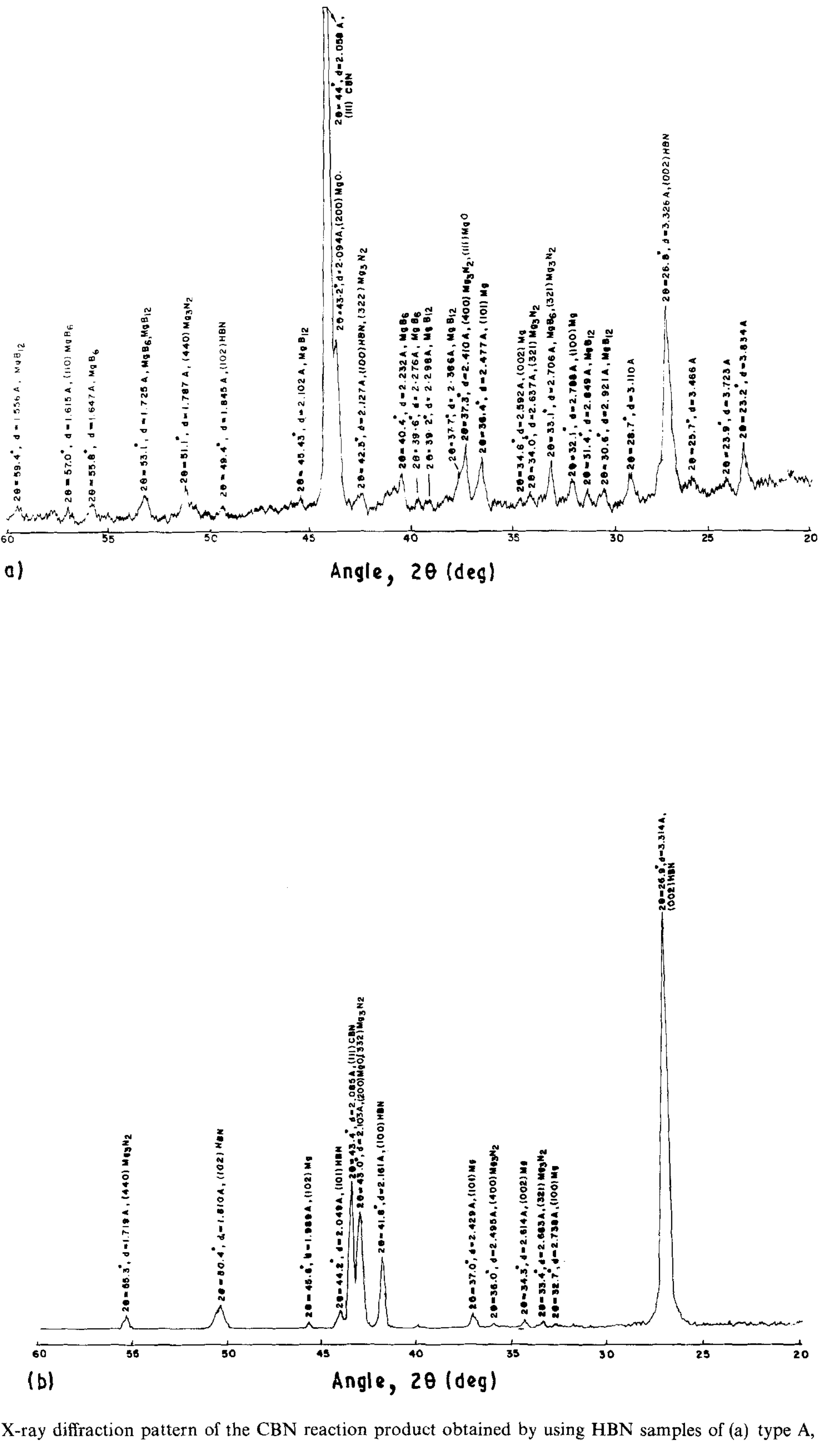

Figure 5 Powder X-ray diffraction pattern of the CBN reaction product obtained by using HBN samples of (a) type A, (b) type B.

In a direct transformation of HBN to CBN, starting with a lower degree of crystallization in HBN may facilitate breaking of bonds in the hexagonal structure under the influence of high pressure, whereas much greater pressure would be required for breaking the bonds to "pucker" them into a diamond structure in the case of highly crystallized (GI = 1.6) HBN, on the other hand, in case of the catalyst solvent process, since CBN growth is achieved through dissolution and precipitation (chemical process), the degree of three-dimensional ordering in the structure of HBN may not play a major role in CBN conversion.

The role of oxygen present in the starting HBN in CBN conversion using magnesium as the catalyst solvent is not clearly understood. It may be mentioned that although HBN of type A contained a higher concentration of oxygen, the yield obtained in CBN conversion was quite high (70 wt %) even at moderate

P–T conditions (5800 MPa, 1450 °C). In the case of type B HBN no good CBN conversion was obtained even though the oxygen concentration in this case too was comparable to that of type A (about 40 at %). Low conversion in type B specimen, as already explained earlier, is, however, due to inhomogeneous mixing of HBN and magnesium, resulting in a poor chemical reaction. There have been a number of attempts to understand the effect of oxide impurity present in the starting HBN in CBN conversion. Fukunaga *et al.* [7] used several different starting HBN samples having varying degrees of oxide impurities at fixed P–T conditions in CBN stable region of P–T diagram for CBN synthesis. They found that the amount of MgO formed decreased with increasing the purity of the starting HBN. In another series of experiments to establish that the oxide impurity in the starting material was responsible for the formation of MgO, they wrapped the reactants in zirconium foil and then treated them to high P–T conditions. Since the zirconium acted as an oxygen getter, they found that no MgO was formed. It was suggested, therefore, that the content of oxide impurity plays a minor role in determining the growth region of CBN [7].

In another investigation by Endo *et al.* [8], two HBN starting samples (R type and N type) with nearly the same graphitization index and with 1.9 and 7.9 wt % of oxygen concentration, respectively, were used to study the effect of oxygen impurities on the CBN growth. It was suggested that the CBN precipitates from an intermediate compound $Mg_3B_2N_4$ in the CBN stable region. The oxygen impurities present, e.g. B_2O_3 react with $Mg_3B_2N_4$ forming MgO or $Mg_2(BO_3)_2$. In this process thus, BN instead of precipitating in the cubic form is consumed otherwise. They deduced that the lower temperature limit of CBN formation shifts towards higher temperature by 300 °C in N1 type HBN [8]. The present results on the CBN conversion using HBN samples with high oxygen concentration (Type A) show that a high conversion of CBN is achieved even at temperatures as low as 1450 °C at 5800 MPa. It appears that oxygen impurity in starting HBN samples has no significant effect on CBN conversion.

4. Conclusions

The present investigations on the CBN synthesis using the catalyst solvent process with magnesium as the catalyst, shows that starting HBN when used in powder form, yields better CBN conversion. The role of degree of crystallization in the starting HBN on the CBN conversion using the catalyst solvent process has been discussed for the first time. It has been found that this does not affect the minimum P–T conditions required for CBN conversion contrary to the case of direct transformation of HBN–CBN. The amount of oxygen present in the starting HBN samples does not adversely influence the yield of CBN in the HBN–CBN transformation.

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References

1. R. H. WENTORF, JR., *J. Chem. Phys.* **26** (1957) 956.
2. *Idem., ibid.* **34** (1961) 809.
3. *Idem.*, in Progress in Very High Pressure Research, Proceedings of an International Conference, New York, June 13–14, 1960. edited by F. P. Bundy, W. R. Hibbard, Jr and H. M. Strong, (John Wiley, New York, 1961) p. 82.
4. K. KUDAKA, H. KONNO and T. MATOBA, *Kogyo-Kagaku Zasshi* (*J. Chem., Soc. Japan, Ind. Chem. Section*) **69** (1966) 365.
5. M. USHIO, H. SAITO and S. NAGANO, *ibid.*, **74** (1971) 598.
6. R. C. DeVRIES and J. F. FLEISCHER, *J. Cryst. Growth* **13/14** (1972) 88.
7. O. FUKUNAGA, T. SATO, M. IWATA and H. HIRAOKA, Proceedings of the 4th International Conference on High Pressure, Kyoto, Japan (1974) p. 454.
8. T. ENDO, O. FUKUNAGA and M. IWATA, *J. Mater. Sci.* **14** (1979) 1375.
9. H. SAITO, M. USHIO and S. NAGANO, *Yogyo Kyokai Shi.* **74** (1970) 7.
10. T. KOBAYASHI, *J. Chem. Phys.* **70** (1979) 5898.
11. S. DeFORREST, PhD Thesis, Brigham Young University, USA (1965).
12. A. S. BALCHAN and H. G. DRICKAMER, *Rev. Sci. Instrum.* **32** (1961) 308.
13. F. P. BUNDY and R. H. WENTORF, JR. *J. Chem. Phys.* **38** (1963) 1144.
14. F. R. CORRIGAN and F. P. BUNDY, *ibid.* **63** (1975) 3812.
15. N. L. COLEBURN and J. W. FORBES, *J. Chem. Phys.* **48** (1968) 555.
16. K. ICHINOSE, M. WAKATSUKI, T. AOKI and Y. MAEDA, Proceedings of the Fourth International Conference on High Pressure, Kyoto, Japan (1974) p. 436.
17. J. THOMAS, JR., N. E. WESTON and T.E. O'CONNER, *J. Amer. Chem. Soc.* **84** (1963) 4619.
18. D. BRIGGS and M. P. SEAH (eds), "Practical Surface Analysis by Auger and Photoelectron Spectroscopy", (Wiley, Chichester, 1983)

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