

Structural changes of wurtzite-type and zincblende-type boron nitrides by shock treatments

TAMOTSU AKASHI, HAN-RYONG PAK, AKIRA B. SAWAOKA*

Center for Explosives Technology Research, New Mexico Institute of Mining and Technology, Socorro, New Mexico 87801, USA

Wurtzite-type boron nitride (w-BN) and zincblende-type boron nitride (z-BN) powders were shock-treated in the pressure range of 60 to 200 GPa to clarify their polymorphic transformations. The recovered BN powders revealed the effects of the shock wave and residual temperature on phase transition of BN. W-BN was partly transformed to z-BN by shock compression at a pressure of about 100 GPa. At pressures greater than 100 GPa, portions of the w-BN and z-BN powders changed into the BN having a turbostratic structure. Subsequently, this form was crystallized to graphite-like BN (g-BN) and a new form of BN due to high residual temperatures. This new BN modification, probably stabilized by the high surface energy associated with its fine crystallite size of less than 50 nm, was identified as fcc structure with a lattice parameter of $a_0 = 0.8405$ nm. The transformation of z-BN to w-BN was not detected in this post-shock study, as was observed in static high pressure studies.

1. Introduction

Physical and chemical properties of boron nitride (BN) are very similar to those of carbon. Graphite-like form (g-BN), wurtzite-type form (w-BN), and zincblende-type form (z-BN) are known as polymorphs of BN, corresponding to graphite, hexagonal and cubic diamonds in the carbon system, respectively. Many studies have been made on the polymorphic transformation of BN by using static and dynamic high pressure techniques [1-4]. The transformation of g-BN to w-BN occurs at shock pressures above 12 GPa [4], and z-BN is formed from rhombohedral BN (r-BN) by shock compression in the pressure range of 40 to 100 GPa [5]. Z-BN is believed to be a stable phase of BN at high pressures from the comparison of theoretical densities of w-BN and z-BN; the density of zincblende-type structure is about 1% higher than that of wurtzite-type structure [6]. The transformation of low density phases of BN to denser forms by shock compression has been understood to proceed by a diffusionless process (martensitic transformation). This mechanism is the same as that reported on the transformation of graphite to hexagonal diamond under static high pressure [7]. The stacking sequence of atomic layers in starting BN materials is preserved during the transformation [5]. Johnson and Mitchell [8] studied the shock-induced transformation of g-BN to w-BN using a flash X-ray diffraction technique. They reported that this transformation occurred just behind the shock wave front at shock pressures of 24.5 GPa.

A few investigators reported that the transformation from g-BN to z-BN by shock loading took place

in the pressure range of 12 to 50 GPa [9, 10]. In their reports, however, there are some uncertainties in confirming z-BN in the recovered powders. The reports disagree with each other in regard to the relative concentration of w-BN and z-BN in the samples which were shock-treated under almost the same conditions. Two of the present authors investigated the transformation of g-BN under various shock conditions. However, the formation of z-BN from g-BN was not found in the recovered BN powders [6, 11, 12]. This result is consistent with that obtained by Johnson and Mitchell [8].

In the previous note [12], two of the present authors reported the structural changes of g-BN caused by multiple shock-treatments. G-BN was transformed to w-BN by single shock-compression, while z-BN was produced by multiple shock-treatments of g-BN. In the present work, structural changes of high density forms of BN (w-BN and z-BN) caused by shock treatments were studied to clarify the polymorphic transformation of BN. W-BN was transformed to z-BN by single shock-compression. A new BN modification and turbostratic BN were formed from w-BN and z-BN by shock treatments. Their formation mechanisms and the possibility of the formation of z-BN from g-BN by single shock-compression will be discussed.

2. Experimental procedure

Powders of w-BN and z-BN were used as starting materials, which were synthesized by a shock treatment and a static high pressure technique utilizing a catalyst, respectively. Average particle sizes and impurities of starting materials used are listed in Table

*On leave from the Research Laboratory of Engineering Materials, Tokyo Institute of Technology, Midori, Yokohama 227, Japan.

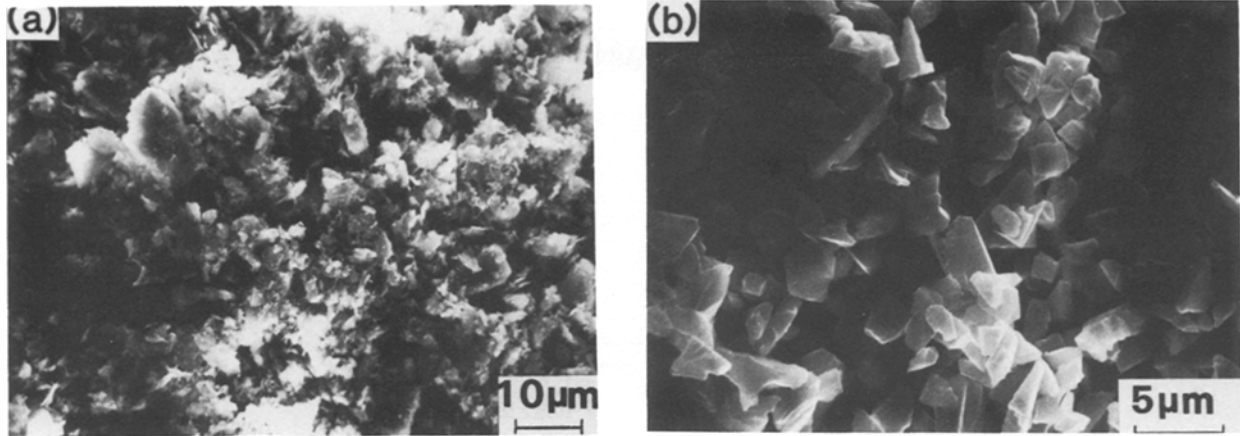


Figure 1 SEM photographs of starting (a) w-BN and (b) z-BN powders.

I. Scanning electron micrographs of the powders are shown in Fig. 1.

The BN powders and 150 to 300 mesh copper powders were mixed at a weight ratio of 5:95 with an alumina mortar and pestle. The mixtures were pressed into stainless steel capsules to form discs 5 mm thick and 12 mm in diameter with densities about 85% of the theoretical density. The discs were shock-compressed by using a mousetrap-type plane-wave generator and a momentum-trap recovery system [12]. Impact pressures induced in the stainless steel capsules were about 60 to 200 GPa for the impact velocities of 2.5 to 5.3 km sec⁻¹ employed in this experiment. These pressures were estimated from a one-dimensional impedance matching method [13]. Immediately after impact, the fixtures containing the capsules were driven into a water basin and quickly cooled before being recovered. Shock-treated specimens were carefully taken out of the capsules by using a lathe.

The recovered specimens thus obtained were immersed in a solution of HNO₃ and 3HCl for 24 h to dissolve the copper matrix. With this technique, the BN powders subjected to single shock-compression were obtained. For double shock-treatments of w-BN, the recovered BN powders, after the single shock treatment, were again mixed with the copper powders, formed into a disc, and shock-compressed by using a shock assembly identical to the first one.

Phases present in the recovered BN samples were examined by an X-ray diffractometer with nickel-filtered CuK α radiation. Lattice spacings were measured by using a silicon powder as an internal standard for the diffraction angle. The scanning speed was 0.125° min⁻¹ in 2 θ . Microstructures of the BN

specimens after shock treatments were examined by a Hitachi HU-200F transmission electron microscope (operated at 175 keV).

3. Results

3.1. Shock treatment of w-BN

X-ray diffraction patterns of the starting w-BN and shock-loaded powders are shown in Fig. 2, and the *d*-spacings of these BN samples are summarized in Table II.

A peak located at 43.4° in 2 θ , which seems to correspond to the (1 1 1) peak for z-BN, was detected in the X-ray diffraction pattern of the single shock-treated w-BN powder (at 100 GPa), Fig. 2b. A similar peak was observed in the X-ray diffraction pattern for the recovered BN powder after double shock-treatments (at 150 GPa and then 200 GPa), Fig. 2c. This peak had a sharp profile and relatively large diffraction intensity. Diffraction peaks of z-BN are located fairly close to those of copper in an X-ray diffraction pattern for

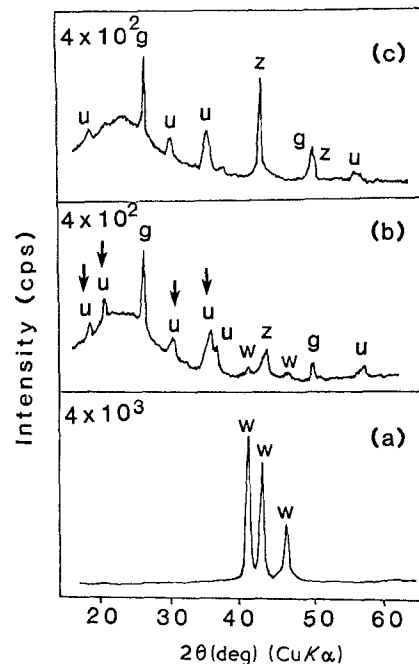


Figure 2 X-ray diffraction patterns of (a) original w-BN, (b) BN shocked at 100 GPa, and (c) BN double shocked at 150 and 200 GPa; g = graphite-like BN, w = wurtzite-type BN, z = zincblende-type BN, u = unknown.

TABLE I Average particle size and impurities of starting powder

	w-BN	z-BN
Average particle size (μ m)*	1 to 10	1 to 5
Impurities [†] (p.p.m.)	Si: 100 Fe, Ni: 50 Al: 10 Cu, Ca, Mg, Mn: 5	Fe: 100 to 1000 Ni, Cu: 10 to 100 Cr: 10 Ti, Ca, K, Al, Si: 5

*Obtained from SEM photographs.

[†]Emission spectrochemical analysis.

TABLE II *d*-spacings of original and shock-loaded w-BN

Original w-BN			Shock-loaded w-BN (100 GPa)			Shock-loaded w-BN (150 and 200 GPa)		
Form	<i>hkl</i>	<i>d</i> (obs) (nm)	Form	<i>hkl</i>	<i>d</i> (obs) (nm)	Form	<i>hkl</i>	<i>d</i> (obs) (nm)
Wur.	100	0.2210	N		0.482	N		0.482
Wur.	002	0.2111	N		0.425	Gra.	002	0.3346
Wur.	101	0.1957	Gra.	002	0.3351	N		0.2968
Wur.	102	0.1526	N		0.297	N		0.2535
Wur.	110	0.1275	N		0.253	Zin.	111	0.2081
Wur.	103	0.1186	Wur.	100	0.220	Zin.	200	0.181
			Zin.	111	0.208	Gra.	102	0.180
			Gra.	102	0.1818	Zin.	220	0.127

*Gra.: graphite-like, Wur.: wurtzite-type, Zin.: zinblende-type, N: new modification.

CuK α radiation. Since copper as a matrix of BN powders may penetrate into grain boundaries of BN particles and remain after the chemical treatments, copper contents in the shock-treated w-BN samples were examined by emission spectrochemical analysis. The copper contents in these samples were found to be less than 100 p.p.m., which were lower than the limit of detection by X-ray diffraction analysis. Therefore, the peaks mentioned above were identified as the (111) peak for z-BN.

The *d*-spacings of the (111) peak of the z-BN formed by single and double shock-treatments of the w-BN powders were 0.208 and 0.2081 nm, respectively. These values were about 0.5% smaller than that of statistically synthesized z-BN [2, 6, 14]. On the other hand, the *d*-spacings of the (002) diffraction of g-BN transformed from w-BN were 0.3351 and 0.3346 nm for single and double shock-treatments, respectively. These values were about 0.6% larger than that for well-annealed g-BN, reported by Pease [15].

Several unidentified peaks, and a broad peak ranging from 15 to 35° in 2 θ appeared in the X-ray diffraction patterns for single and double shock-treatments, Fig. 2b and c. These unknown peaks were located at almost the same diffraction angles as those obtained for multiple shock-treatments of g-BN powders in the previous work [12].

3.2. Shock treatment of z-BN

X-ray diffraction patterns for the starting z-BN and shock-loaded powders are shown in Fig. 3. The *d*-spacings of these BN samples are listed in Table III.

A trace of a broadening line ranging from 15 to 35° in 2 θ and an unknown peak, which corresponds to one of the unidentified peaks obtained for the shock-treated w-BN powders, were observed in the X-ray diffraction pattern for the shock-treated z-BN sample (at 60 GPa). In the shock-treated z-BN powders at 150 and 200 GPa, diffraction intensity of the broadening lines became strong and a part of the z-BN was changed into g-BN and unknown phases. The amounts of g-BN and unknown phases formed from z-BN increased with increasing shock pressure (corresponding to the increase in shock and residual temperatures), Fig. 3c and d. The diffraction patterns for the shock-treated z-BN powders exhibited slight line-broadening of the (111) peak of z-BN due to the shock compression, as compared to that of the starting powder. Changes in *d*-spacings of the (111) of z-BN before and after shock-treatments, however, were not evident within the experimental accuracy. Diffraction angles of unknown peaks, designated by a "u" in Fig. 3b, c and d, agreed within an accuracy of 0.2° in 2 θ with those of the unknown peaks obtained for the shock-treated w-BN powders (Fig. 2b and c). No transformation of z-BN to w-BN was detected in the pressure range employed in this experiment.

4. Discussion

4.1. Formation of turbostratic BN

The broadening line ranging from 15 to 35° in 2 θ obtained in the shock-treated w-BN and z-BN samples seem to correspond to a turbostratic boron nitride (t-BN) reported by Thomas *et al.* [16]. They examined

TABLE III *d*-spacings of original and shock-loaded z-BN

Original z-BN			Shock-loaded z-BN								
Form	<i>hkl</i>	<i>d</i> (obs) (nm)	(60 GPa)			(150 GPa)			(200 GPa)		
			Form	<i>hkl</i>	<i>d</i> (obs) (nm)	Form	<i>hkl</i>	<i>d</i> (obs) (nm)	Form	<i>hkl</i>	<i>d</i> (obs) (nm)
Zin.	111	0.2089	N		0.250	Gra.	002	0.3347	N		0.486
Zin.	200	0.1809	Zin.	111	0.2088	N		0.254	N		0.427
Zin.	220	0.1278	Zin.	200	0.1809	Zin.	111	0.2091	Gra.	002	0.3351
Zin.	311	0.1090	Zin.	220	0.1278	Zin.	200	0.181	N		0.296
			Zin.	311	0.1090	Zin.	220	0.127	N		0.253
						Zin.	311	0.109	N		0.246
									U		0.228
									Zin.	111	0.2089
									Zin.	200	0.181
									Gra.	102	0.181

Gra.: graphite-like, Wur.: wurtzite-type, Zin.: zinblende-type, N: new modification, U: unknown.

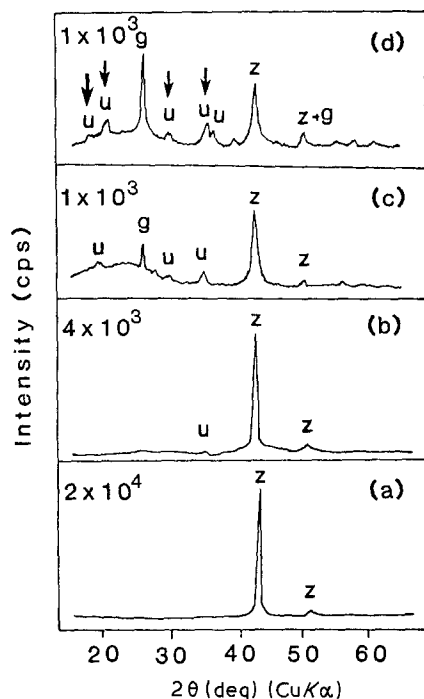


Figure 3 X-ray diffraction patterns of (a) original z-BN, (b) BN shocked at 60 GPa, (c) BN shocked at 150 GPa, and (d) BN shocked at 200 GPa; g = graphite-like BN, w = wurtzite-type BN, z = zincblende-type BN, u = unknown.

BN powders synthesized from fused urea–boric acid and ammonia and reported two diffuse diffraction lines for t-BN. One is a line in the range of 20 to 30° in 2θ for the (002) diffraction for $\text{CuK}\alpha$ radiation and the other is a weak line in the range of 40 to 45° in 2θ for the (10) diffraction. The above-mentioned broadening lines obtained in the present work suggest that the formation of t-BN by shock loading was related to the presence of high density form, w-BN or z-BN, in starting materials. Although it is uncertain whether or not w-BN is stable in pressure and temperature regions of its formation, z-BN is a stable phase of BN under the shock-compression conditions employed in this experiment. It is, therefore, unlikely that t-BN was produced directly from z-BN during shock compression.

The stability of z-BN at high temperatures seems to depend upon its crystallite size analogously to the graphitization of diamond. The dependence of grain size on the graphitization of diamond was examined by Akaishi *et al.* [17]. They reported that fined grained diamonds (0 to 1 μm size) were easily transformed to graphite by heat treatment at 1400°C in vacuum, while little graphitization of coarse grained diamonds (5 to 12 μm size) was detected. Furthermore, the introduction of a large number of defects into a crystal seems to make the crystal structure unstable and results in an amorphous structure [18]. It is, therefore, probable that fine z-BN crystallites resulting from the comminution of z-BN grains by a passage of the shock wave were transformed to a BN with an amorphous-like structure after release of the shock pressure due to the large strain energy in the crystal structure. On the other hand, the thermal stability of shock-synthesized w-BN is considerably lower than that of z-BN. This w-BN is easily converted into g-BN by heat treatment

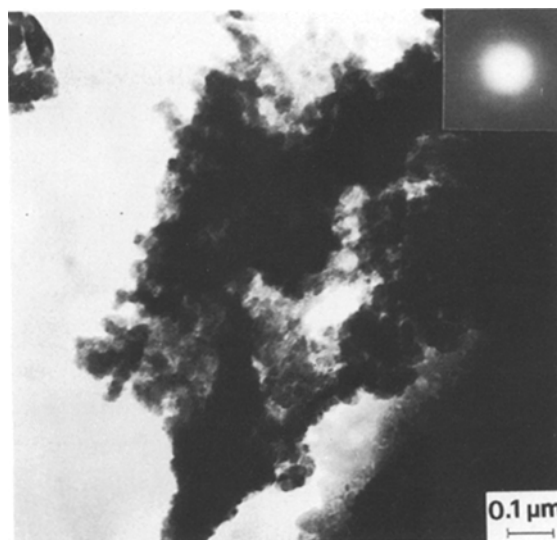


Figure 4 Transmission electron micrograph of turbostratic BN in the recovered BN after single shock-compression of w-BN at 100 GPa.

above 600°C under atmospheric pressure [19]. This is probably due to the large lattice strain in the crystal structure and its fine crystallite size of about 30 nm [20]. Therefore, fine crystallites in w-BN powder after a passage of the shock wave seem to be transformed more easily to the amorphous-like form of BN than those of z-BN. X-ray diffraction of the shock-treated w-BN that those of z-BN. X-ray diffraction of the shock-treated w-BN and z-BN powders show that a part of the amorphous form was crystallized to t-BN and g-BN from high residual temperatures. It is, therefore, concluded that the t-BN was produced during the process of the crystallization of the amorphous form of BN to g-BN and unknown phases.

Fig. 4 shows a typical particle morphology and diffraction pattern for t-BN found in the w-BN powder shock-treated at 100 GPa. This diffraction pattern is similar to that of a turbostratic graphite [21]. Turbostratic BN particles are composed of loose clusters consisting of fine grains under about 10 nm in size. The particle morphology of t-BN produced from the z-BN powders shocked at 150 and 200 GPa was almost the same as that of t-BN in the shocked w-BN powder. Transmission electron microscopy and electron diffraction analysis of the shock-treated w-BN and z-BN powders, except for the z-BN powder shocked at 60 GPa, revealed that the predominant phase in the recovered BN powders was t-BN. This may be caused by rapid cooling due to the high thermal conductivity of the copper matrix after release of the shock pressure.

4.2. New modification of BN

Effects of shock wave on the crystallization of t-BN powder were studied by Batsanov *et al.* [3]. They reported that the crystallinity of t-BN increased with increasing shock pressure and that a small amount of more or less perfect crystals with a density of 2.55 g cm^{-3} was produced from t-BN by shock compression. These crystals, which exhibit an X-ray diffraction pattern different from those of the previously-

TABLE IV X-ray diffraction pattern for new BN modification (fcc lattice, $a_0 = 0.8405$ nm)

hkl	d (obs) (nm)	d (calc) (nm)	I (obs)
111	0.4854	0.4852	weak
200	0.433	0.4202	trace
220	0.2973	0.2971	middle
311	0.2536	0.2534	strong
222	—	0.2426	—
400	—	0.2101	—
331	—	0.1928	—
420	—	0.1879	—
422	0.1716	0.1715	weak
333, 511	0.1618	0.1617	middle
440	—	0.1485	—
531	—	0.1420	—

known forms of BN, was named E-BN. They measured a refractive index and a density of the E-BN crystal. However, a crystal structure of the new BN modification was not clearly identified.

Some peaks indicated by arrows in Figs 2 and 3 agree within an accuracy of 0.5° in 2θ (for $\text{CuK}\alpha$ radiation) with those of E-BN reported by Batsanov *et al.* [3]. Furthermore, the d -spacings of the unknown peaks indicated by a “u” in Figs 2 and 3 seem to imply that the structure has a fcc symmetry with a lattice parameter of $a_0 = 0.8405$ nm. The d -spacings measured and calculated based on the fcc structure for the new modification of BN are listed in Table IV along with the observed relative intensities. The agreement between measured and calculated d -values is very good. Therefore, one of the unknown phases obtained in the shocked w-BN and z-BN powders can be identified as E-BN having an fcc structure. The molecular number in a unit cell of this crystal should be 38, assuming that a density of E-BN is 2.55 g cm^{-3} .

Batsanov *et al.* [3] regarded the crystallization and formation of E-BN from t-BN as an effect of shock wave. If E-BN is formed from the t-BN by shock wave, the results of the shock-treated w-BN and z-BN

powders obtained in the present experiment should imply that the new modification was produced from w-BN or z-BN during shock compression, because no t-BN was contained in the starting materials. This is inconsistent with the fact that z-BN is a stable phase under the shock conditions employed in this experiment. Therefore, from the results of both Batsanov *et al.* [3] and the present work, it is reasonably concluded that E-BN was crystallized from t-BN due to high residual temperatures after release of the shock pressure.

Fig. 5a shows a transmission electron micrograph of the shocked z-BN powder at a pressure of 200 GPa and its diffraction pattern. This pattern is composed of two crystal structures; one is for z-BN and the other is for E-BN. The microstructure consisting of z-BN and the E-BN is complicated, as compared to that of t-BN shown in Fig. 4. Fig. 5b is a dark field image produced with one of the strong diffraction spots of the E-BN in Fig. 5a. This image reveals that crystallite size of the new modification is under 50 nm.

Thomas *et al.* [16] reported that no transformation from t-BN took place by heat treatment up to 2000°C in nitrogen atmosphere. The residual temperature in BN particles was estimated for a pressure of 100 GPa and was approximately 1500°C [22]. It is interesting to note that t-BN produced by shock treatment from high density forms was easily transformed to E-BN, which is a metastable phase. The E-BN obtained in this experiment with its fine crystallite size of less than 50 nm. Therefore, when surface energy is decreased by grain growth at high residual temperatures, the E-BN is possibly transformed to g-BN. Stabilization of metastable phases due to the high surface energy was reported in the polymorphic transformations of TiO_2 and ZrO_2 [23, 24].

4.3. Formation of z-BN

The transformation of w-BN to z-BN was detected in the shock-treated w-BN powder (at a pressure

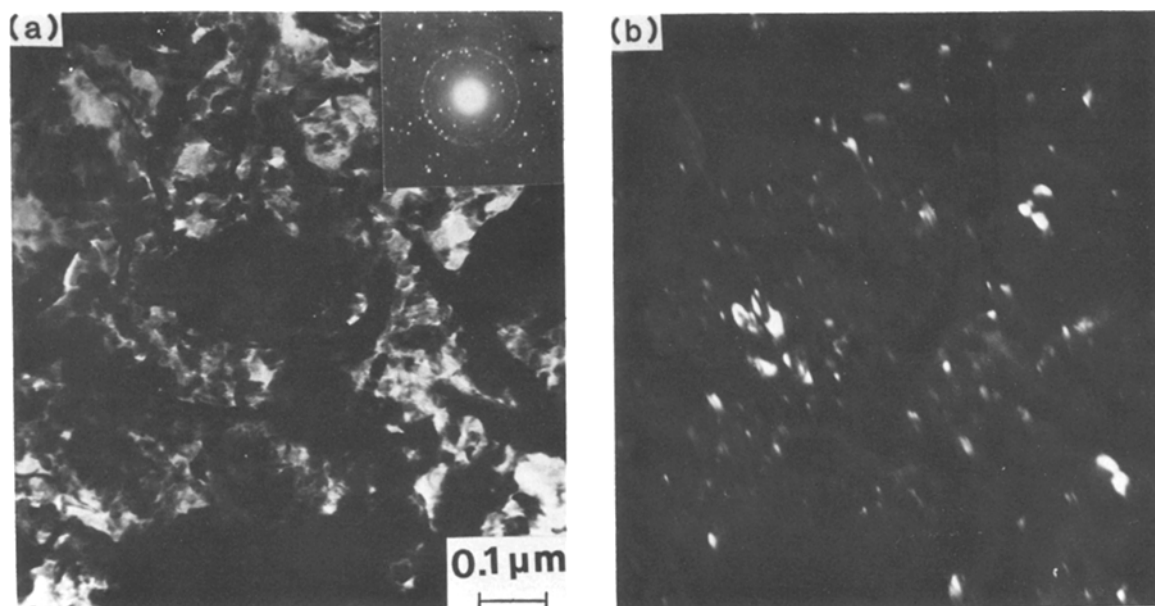


Figure 5 Transmission electron micrographs of the recovered BN after shock compression of z-BN at 200 GPa; (a) bright-field image and its diffraction pattern, (b) dark-field image obtained using the diffraction spot of the new BN modification.

of 100 GPa). This suggests that the transformation from g-BN to z-BN induced by multiple shock-compressions, observed in the previous work [12], was related to the presence of w-BN transformed from g-BN by the first shock-treatment. By the comparison of the two structures, w-BN and z-BN, one can find that the (001) planes of the wurtzite-type lattice are identical to the (111) planes of the zincblende-type lattice and they consist of similar tetrahedron with sp^3 hybrid bonds. It is, therefore, assumed that the energy difference between the wurtzite-type and zincblende-type structures is very small. Thus, the stacking defects in the wurtzite-type structure seem to act as two-dimensional seeds for the formation of the zincblende-type structure. By taking the above consideration into account, the process of the transformation from g-BN to z-BN by the multiple shock-treatments can be explained as follows. The crystal structure of w-BN, which was transformed from g-BN by the first shock-compression, contained large numbers of structural defects. Such defects were additionally introduced into the w-BN structure by the second shock-compression, mainly at the shock wave front, producing large numbers of two-dimensional seeds for the z-BN formation. These seeds grew rapidly at high shock temperatures and became large enough to be detected by X-ray diffraction after the third shock-compression. In the present single shock-treatment of the w-BN powder at a high shock pressure, it seems that large numbers of seeds for the z-BN formation were created at the shock wave front and grew rapidly at a high temperature during the shock compression.

The results obtained in the double-shocked w-BN powder (at pressures of 150 and 200 GPa) suggest another formation process of z-BN by shock loading. The BN powder recovered after the single shock-treatment of the w-BN powder (at 150 GPa) was found to consist of g-BN, t-BN, E-BN and a trace of w-BN and z-BN. Further formation of z-BN by the second shock-compression (at 200 GPa), therefore, suggests that the t-BN and/or the E-BN were transformed to z-BN by the shock compression. Sato [25] carried out shock-compression experiments of a t-BN powder and reported that a part of t-BN was transformed to z-BN at shock pressures of 40 to 100 GPa. It is, therefore, certain that the t-BN was transformed to z-BN by the second shock-compression at 200 GPa. T-BN is considered to have a layered structure partially similar to g-BN and to rhombohedral BN (r-BN). Thus, it is no wonder from the results reported that a part of t-BN is converted into both w-BN and z-BN by shock compression. In the present post-shock study, however, no formation of w-BN from t-BN was detected, as was reported by Sato [25]. This is probably due to the low thermal stability of w-BN after release of the shock pressure. T-BN may have transformed to both w-BN and z-BN during the second shock-compression, but transformed w-BN crystallites seem to be completely changed into an amorphous form and then crystallized to t-BN and g-BN due to the high residual temperature. This interpretation is supported by the fact that w-BN transformed from the g-BN by the second shock compression was also

transformed to t-BN and g-BN. On the other hand, the transformation of the E-BN to z-BN was not confirmed in the present experiment because the E-BN coexisted with t-BN, which was transformed to z-BN. Batsanov *et al.* [3] regarded the formation of E-BN from t-BN as one step in the shock-induced transformation of g-BN to z-BN since the density of the E-BN is between those of g-BN and z-BN. However, this interpretation is uncertain because the E-BN was formed from t-BN not during shock compression but after release of the shock pressure as mentioned before. In order to discuss a possibility of the formation of z-BN from E-BN by shock loading, detailed crystallographic data of the E-BN structure, especially on an atomic arrangement of boron and nitrogen in this crystal, are required.

Two of the present authors [6, 11, 12] concluded from the experimental results of g-BN powders shock-treated under various shock conditions that g-BN could be transformed to w-BN, but not to z-BN. However, the transformation of w-BN to z-BN by shock compression found in the present work suggests a possibility of synthesizing z-BN by single shock-compression of g-BN.

According to the results by Johnson and Mitchell [8], the transformation of g-BN to w-BN occurs just behind the shock wave front at shock pressures above 25.4 GPa. Two-dimensional seeds for the z-BN formation should be simultaneously created in the transformed w-BN structure accompanied by the introduction of a large number of defects into the w-BN crystal. Thus, when the shock temperature is sufficiently high, seeds for the z-BN formation might be able to grow rapidly during single shock-compression. High shock temperatures, however, usually give rise to high residual temperatures in conventional shock-compression techniques, resulting in the reverse-transformation of z-BN to low density forms such as t-BN and g-BN. Therefore, the grain growth of seeds for the z-BN formation after passage of a shock wave front is limited and controlled by optimum shock temperature and duration of shock pressure. The limited grain size is considered to be in the range of 10 nm from the crystallite size of shock synthesized diamonds [26]. The thermal stability of z-BN grains after release of shock pressure depends strongly upon its crystallite size as mentioned before. Therefore, shock and residual temperatures have opposite effects on the synthesis of z-BN by shock compression.

The transformation of g-BN to z-BN has not been recognized in our past shock experiments and can be explained as follows. In shock treatments of g-BN powders accompanied by high shock temperatures, z-BN seeds grew rapidly during shock compression, but they are mostly reversely transformed to low density forms due to high residual temperatures. At low shock temperatures, on the other hand, z-BN crystallites produced during shock-loading were extremely small and easily reverse-transformed to low density forms even at low residual temperatures. If the temperatures in BN particles during and after shock compression could be independently controlled, z-BN would be able to be synthesized from g-BN by single shock-treatment.

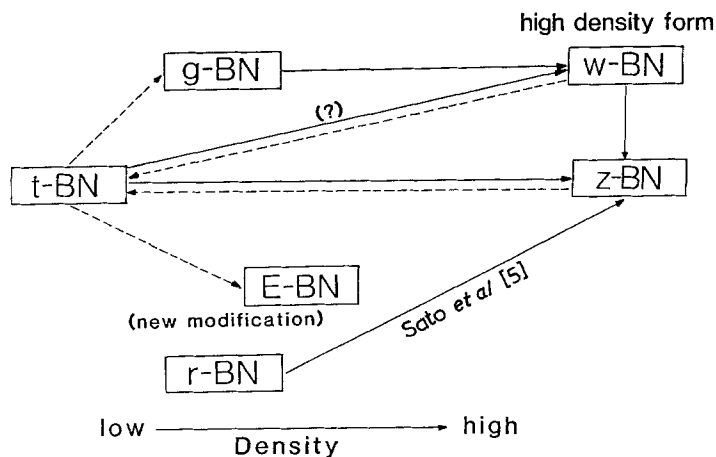


Figure 6 Polymorphic transformation of BN induced by shock treatments; (—) transformations induced by shock wave, (---) structural changes due to the residual temperature.

5. Summary

In this post-shock study on the BN powders, the recovered powders revealed the effects of the shock wave and residual temperature on phase transformation of BN. The polymorphic transformation of BN caused by shock treatments is summarized schematically in Fig. 6, including the results reported [5, 12, 25]. The solid and dotted lines in this figure, respectively, indicate the transformations induced by the shock wave and the structural changes due to the residual temperature. The transformation of E-BN to z-BN is not clear in this experiment.

W-BN was transformed to z-BN by single shock-treatment. This suggested a possibility of the formation of z-BN from g-BN by single shock-compression. Portions of the wurtzite-type and zincblende-type structures subjected to intense shock wave were changed into turbostratic structure and subsequently crystallized to g-BN and E-BN from high residual temperatures. The E-BN was identified as a fcc structure with a lattice parameter of $a_0 = 0.8405$ nm. The transformation from z-BN to w-BN was not detected in this post-shock study, as was observed in static high pressure studies.

Acknowledgements

The authors would like to express sincere thanks to Dr S. Saito, President, Technological University of Nagaoka for encouragement of this study for several years and Dr T. Utsunomiya of Tokyo Institute of Technology for his performing emission spectrochemical analysis. They are also grateful to Mr M. Araki of Nippon Oil & Fats Co. Ltd. for providing the shock-synthesized w-BN and the opportunity to perform shock treatments. The research was in part supported by the State of New Mexico through the Center for Explosives Technology Research for New Mexico Institute for Mining and Technology.

References

1. R. H. WENTORF Jr, *J. Chem. Phys.* **26** (1957) 957.
2. F. P. BUNDY and R. H. WENTORF Jr, *ibid.* **38** (1963) 1144.
3. S. S. BATANOV, G. E. BLOKHINA and A. A. DERIBAS, *J. Struct. Chem.* **7** (1965) 209.

4. G. A. ADADUROV, Z. G. ALIEV, L. O. ATOVMYAN, T. V. BAVINA, YU. G. BOROD'KO, O. N. BREUSOV, A. N. DREMIA, A. KH. MURANEVICH and S. V. PERSHIN, *Soviet Phys. Dokl.* **12** (1967) 173.
5. T. SATO, T. ISHII and N. SETAKA, *J. Amer. Ceram. Soc.* **65** (1982) c-162.
6. T. SOMA, A. SAWAOKA and S. SAITO, *Mater. Res. Bull.* **9** (1974) 755.
7. F. P. BUNDY and J. S. KASPER, *J. Chem. Phys.* **46** (1967) 3437.
8. Q. JOHNSON and A. C. MITCHELL, *Phys. Rev. Lett.* **29** (1972) 1369.
9. N. L. COLEBURN and J. W. FORBES, *J. Chem. Phys.* **48** (1968) 555.
10. I. N. DULIN, L. V. AL'TSHULER, V. YA. VASHCHENKO and V. N. ZUBAREV, *Soviet Phys. Solid State* **11** (1969) 1016.
11. A. SAWAOKA, T. SOMA and S. SAITO, *Jpn. J. Appl. Phys.* **13** (1974) 891.
12. T. AKASHI, A. SAWAOKA, S. SAITO and M. ARAKI, *ibid.* **15** (1976) 891.
13. L. V. AL'TSHULER, *Soviet Phys. Uspekhi* **8** (1965) 52.
14. R. C. DeVRIES, General Electric Report, No. 72-CRD178, June (1972).
15. R. S. PEASE, *Acta. Crystallogr.* **5** (1952) 356.
16. J. THOMAS Jr, N. E. WESTON and T. E. O'CONNOR, *J. Amer. Chem. Soc.* **24** (1963) 4619.
17. M. AKAISHI, H. KANDA, Y. SATO, N. SETAKA, T. OHSAWA and O. FUKUNAGA, *J. Mater. Sci.* **17** (1982) 193.
18. T. G. BURTON, *Trans. Inst. Chem. Eng.* **44** (1966) T37.
19. H. HIRAOKA, O. FUKUNAGA and M. IWATA, *J. Ceram. Soc. Jpn.* **84** (1976) 163.
20. A. V. KURDYMOV, N. F. OSTROVSKAYA, A. N. PILYAKEVICH and I. N. FRANTSEVICH, *Sov. Phys. Dokl.* **18** (1973) 268.
21. J. KLEIMAN, N. M. SALANSKY and R. B. HEIMANN, *J. Mater. Sci. Lett.* **3** (1984) 117.
22. T. SOMA, A. SAWAOKA and S. SAITO, in Proceedings of the 4th International Conference on High Pressure, edited by J. Osugi (Physico-chemical Society, Kyoto, 1975) p. 446.
23. Y. SUWA, M. INAGAKI and S. NAKA, *J. Mater. Sci.* **19** (1984) 1397.
24. R. C. GARVIE, *J. Phys. Chem.* **69** (1965) 1238.
25. T. SATO, Report of National Institute for Research in Inorganic Materials, No. 27 (1981) p. 30.
26. L. F. TRUEB, *J. Appl. Phys.* **42** (1971) 503.

Received 30 December 1985
and accepted 11 February 1986