

Rapid quench formation of E-BN from shocked turbostratic BN precursors

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Ambient pressure phases of BN are known as hexagonal BN(h-BN), rhombohedral BN(r-BN) and turbostratic BN(t-BN). In these BNs, hexagonal networks of B and N are stacked along the c-axis. In h-BN, the stacking sequence is twofold (ABAB...), while in r-BN there is threefold stacking (ABCABC...). In t-BN the layers are stacked irregularly, which is different from h-BN and r-BN. From shock compression recovery experiments, it has been found that h-BN and r-BN convert to high pressure phase, wurzite BN(w-BN) and cubic BN(c-BN) [1–3]. From their structure relationship these transformations involve a diffusionless process (martensitic transformation). Contrary to the transformations of h-BN and r-BN, t-BN has no structural correspondence to w-BN or c-BN and converts through a compression diffusion process [4]. In addition to these BN phases, E-BN was found during investigation of a t-BN explosion experiment [5]. Akashi *et al.* [6] also reported that fcc-type BN with lattice constant of 0.8405 nm found in post-shocked w-BN and c-BN, which is quite similar to E-BN. It is not always formed in shock compression of t-BN [4] and the conditions of E-BN formation have not yet been clarified.

We examined the formation condition of E-BN using two kinds of BN precursors which were prepared via B–C–N compounds [7]. The first one was synthesized from a mixture of B₂O₃, urea, and saccharose by reaction at 240 °C and heating at 1500 °C in N₂ atmosphere. Elements analysis revealed that this product, sample I, contains large amounts of carbon (50–70 wt%) and oxygen (6–18 wt%) in addition to boron and nitrogen. The second one was further heated at 2200 °C in N₂ atmosphere. Carbon and oxygen are removed to the level of about 1 wt% by this treatment. This product is termed sample II. These starting materials were investigated by X-ray diffraction (XRD) techniques to be turbostratic and were powdered and mixed with Cu powders (about 3–5 wt% t-BN). The powders were put into stainless steel (SUS 304) containers, and pressed at 40–100 kg/cm². The density of the sample, calculated from the volume and mass, ranges between 3.7 and 6.0 g/cm³. A second Cu pressed disc 1.5 mm thick was situated behind the sample to absorb the reflected shocks from the bottom of the sample. We employed two ways of

packing the sample to investigate the effect of differences in quenching rates. These types are schematically shown in Fig. 1 as types A and B. In A, the sample space of the container is entirely filled with mixture and Cu, but in B a space about 1.5 mm thick is open behind the Cu within the container. The change of temperature within the sample is schematically shown in Fig. 2.

Shock-recovery experiments were carried out by a propellant gun [8]. The impact velocity of the flyer (SUS304) was measured with a magnetoflyer method [8]. The pressure within the sample is estimated based on the free surface velocity approximation and the impedance match method. The initial pressure is calculated using the Hugoniot data of porous copper [9], whose density is assumed to be equal to that of the pressed mixture. Shock temperature of the sample is estimated based on that of porous copper [10].

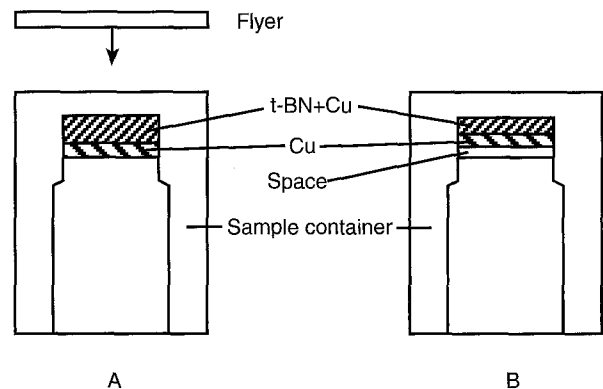


Figure 1 Two types of sample packing in the shock-recovery container. Note that there is a space behind the pressed mixture and copper in Type B.

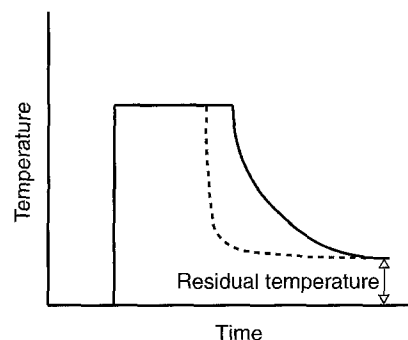


Figure 2 Schematic representations of the time dependence of temperature profile attained by the two types of sample packing A (—) and B (---) in shock recovery containers as shown in Fig. 1.

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Recovered samples were immersed in acid to remove Cu and steel and the residues were subjected to X-ray diffraction (XRD) measurement to identify and characterize the phases. The experimental conditions and results are summarized in Table I. In runs of type A, little change has been observed in recovered samples of the starting material I under a pressure of 5–12 GPa. Above 20 GPa it was not possible to recover samples of starting material I. Post-shock sample II contains w-BN and c-BN above 12 GPa. There were also small changes in the value of L_c calculated from FWHM of the (0 0 2) peak of the turbostratic graphite structure after shock loading. The L_c value corresponds to the size of crystallites along the c-axis. In runs of type B, the starting material II did not display any significant change. However, the recovered samples #411, #432 and #433 from starting material I indicates a series of new X-ray diffraction peaks as shown in Fig. 3. Shock pressures are 10–12 GPa and there remains the space after the shock treatment (about 0.2 mm as a result of compression). The peaks are indexed with an fcc structure, which corresponds to the E-BN previously reported. D-values from run 411 are listed in Table II, together with previous data [6]. Our D-values are slightly smaller than reference data [6], and consequently a axis length (0.8313 nm) calculated from the D-values is slightly smaller than the reference value (0.8405 nm) [6]. From the present results, the formation of E-BN is recognized only from starting material I and from the type B assembly.

E-BN is recovered from the starting material containing not only boron and nitrogen but also carbon and oxygen. This may suggest that E-BN is not pure BN and displays a compositional range in B–N–C–O.

Only in type B is E-BN recovered, not in type A. The reason for this is considered to be as follows: a compression process of type A is exactly the same as that of type B. However, the compression would persist as a result of shock reflections within sample type A. In type A the loaded pressure is released by the rarefaction wave originated from the flyer,

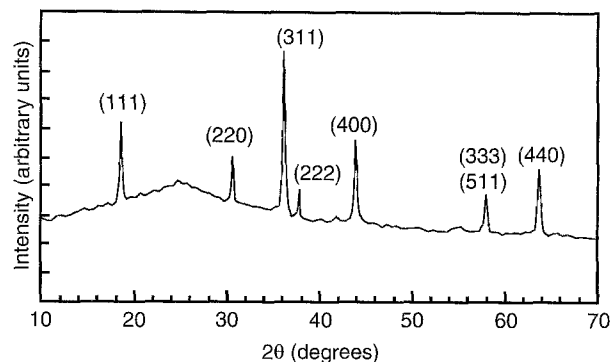


Figure 3 X-ray diffraction pattern of the post-shock sample 411. Peaks with index are from E-BN diffractions. Measured d -values are given in Table II.

TABLE II X-ray diffraction pattern of sample 411

Index (hkl)	d (observed) (nm)	d (calculated) (nm)	d_{E-BN} (reference [6]) (nm)
(111)	0.4811	0.4800	0.4854 (weak)
(200)	—	0.4157	0.433 (trace)
(220)	0.2942	0.2939	0.2973 (middle)
(311)	0.2506	0.2506	0.2536 (strong)
(222)	0.2400	0.2400	—
(400)	0.2077	0.2078	—
(422)	—	0.1697	0.1716 (weak)
(333)(511)	0.1599	0.1600	0.1618 (middle)
(440)	0.1468	0.1470	—

$$a_0 = 0.8313 \text{ nm}; a_{0(\text{ref})} = 0.8405 \text{ nm}$$

whereas in type B, because of the presence of the space, it is released sharply by the arrival of the shock wave on the bottom of the sample. On the release process as illustrated in Fig. 2, the pressure or temperature drops relatively slowly in type A, but very rapidly in type B. The space behind the sample in type B can result in rapid and efficient quenching of the shock-loaded, hot sample.

Therefore the rapid quenching must be one of the main reasons for the recovery of shock-formed E-BN. E-BN is considered as a metastable, high-temperature phase and E-BN converts back to t-BN so fast that E-BN can be recovered only in the case that the quench rate is rapid enough.

TABLE I Experimental results on shock treatments of BN precursors

Run No.	Density (g/cm ³)	Starting* sample	Sample Packing type	V_{imp} (km/sec)	Pressure (GPa)	Shock temp. (K)	Phases identified ($L_c(0\ 0\ 2)(\text{nm})$)**
423	3.95	I	A	1.09	5.7	2500	t-BN(0.8)
424	3.73	I	A	1.17	5.8	2500	t-BN(1.1)
419	4.77	I	A	1.25	10.1	2000	t-BN(1.33)
432	4.76	I	B	1.31	10.9	2000	t-BN(1.4), E-BN
433	4.60	I	B	1.35	10.9	2300	t-BN(1.1), E-BN
420	4.80	I	A	1.33	11.3	2000	t-BN(1.53)
412	4.86	I	A	1.33	11.6	2000	t-BN(1.76)
411	4.92	I	B	1.37	12.3	2000	E-BN, t-BN(0.8)
428	5.52	I	A	1.85	22.8	2500	capsule broken
427	5.67	I	A	1.96	25.8	2500	capsule broken
436	4.39	II	B	1.3	9.5	2500	t-BN
437	4.32	II	B	1.41	10.6	2700	t-BN
389	5.39	II	A	1.27	12.4	1600	t-BN, c-BN
368	6.03	II	A	1.60	20.4	1800	t-BN, c-BN, w-BN

*Characters I and II indicate samples containing large amounts of O and C, respectively (see text).

** L_c values of starting materials I are 1.54 ± 0.03 nm.

The space behind the sample in the container results in the rapid quench and there is a possibility that this technique can be applied for synthesis of new materials which require high quenching rates.

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