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Synthesis of cubic boron nitride from rhombohedral form under high static pressure

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The cubic, zincblende-type boron nitride (z-BN) has been synthesized from the rhombohedral form (r-BN) under high static pressures greater than 6 GPa without any planned addition of catalysts. The process of forming z-BN has been delineated from isobaric and isothermal series of data. At 6 GPa, r-BN begins conversion to the graphite-type form (g-BN) upon heating to 600° C. This conversion terminates at 1200° C forming single-phase g-BN, which in turn transforms into z-BN at temperatures higher than 1300° C. The appearance of z-BN occurs at lower temperatures when the pressure is raised to 7 or 8 GPa. At pressures beyond 10 GPa the wurtzite-type form (w-BN) is observed between 400 and 1200° C, whereas z-BN is formed above 1000° C. The boundary of pressure–temperature conditions for synthesizing z-BN from r-BN runs through 6 GPa and 1300° C, and is located near to the lowest bound hitherto known for non-catalytic z-BN synthesis from g-BN.

1. Introduction

The cubic, zincblende form of boron nitride (z-BN) is very similar to diamond: with a high hardness [1] next to diamond as well as high thermal conductivity [2], z-BN is a material important for such industrial applications as cutting tools, abrasives, and electronic devices. The similarity is also envisaged in the phase relations of the two materials. The pressure–temperature conditions for synthesizing diamond and z-BN are close to each other in the catalytic processes under static compression [1, 2].

Without catalysts, however, the pressures needed for z-BN synthesis [3–9] are significantly lower than those for non-catalytic formation of diamond [10–18], and are in some cases nearer to those for catalytic z-BN synthesis. Such pressure conditions can be met only when either very finely grained graphite-type BN(g-BN) [3–5], amorphous BN(a-BN) [7], or turbostratic BN(t-BN) [9] is used for the starting material. Also, grinding g-BN powder has a marked effect in lowering the required pressure [8].

The wurtzite-type BN(w-BN) is predominantly synthesized from well-crystallized g-BN samples, [5, 19]. The conditions for this synthesis are a higher pressure and a much lower temperature than for z-BN synthesis. When g-BN is dynamically compressed, a prevalence of w-BN is observed in most cases [20–23].

It is obvious from these observations that, for non-catalytic synthesis of the dense forms of BN, the pressure–temperature conditions and the appearance of the forms are strongly governed by the nature of the starting materials and also the pressure environment. This can be qualitatively interpreted by the contribution of non-chemical terms, surface and strain energies for instance, to those non-equilibrium processes.

In this regard, the structure of starting BN is also of interest. The starting material for z-BN synthesis has so far been limited primarily to g-BN. The rhombohedral form of BN (r-BN) is expected readily to undergo conversion to z-BN because of the same periodicity in the stackings of crystallographic layers. In fact, shocked r-BN is directly converted into z-BN [24].

No report had been published on the static compression of r-BN until we succeeded in synthesizing z-BN from chemical vapour deposited r-BN. This paper describes the pressure–temperature conditions for the synthesis of z-BN from r-BN without planned addition of catalysts. We also report the sequences of conversion between various forms of BN, as viewed from isobaric or isothermal conditions.

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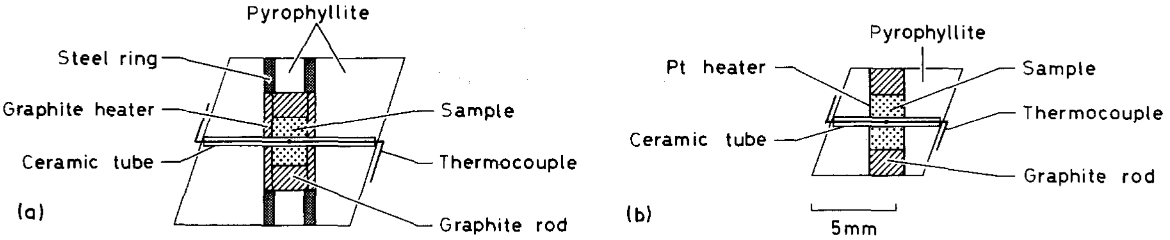

Figure 1 Cross-sections of octahedral sample cells: (a) cell for experiments below 8 GPa; (b) cell for experiments above 10 GPa.

2. Experimental procedure

2.1. Preparation of r-BN

Our r-BN was prepared by chemical vapour deposition (CVD) technique [25]. In brief, r-BN was deposited on to a graphite heater from a gaseous mixture of BCl_3-NH_3-H_2 at a pressure of 665 Pa and at temperatures from 1500 to 1600° C. The lattice parameters of the deposited r-BN, as determined from X-ray diffraction analysis, were $a = 1.003 \pm 0.002$ nm and $c = 0.2506 \pm 0.0004$ nm, in agreement with earlier reports [26, 27]. Either pieces cleft from as-deposited plates or powders pulverized from the plates were subjected to high-pressure experiments.

2.2. High-pressure experiments

Pressure was generated in an octahedral-anvil type device [28, 29]. The pressure was known from calibrations using fixed points [30, 31]. The sample to be studied was enclosed in the centre of an octahedral shaped cell made of pyrophyllite. Two types of sample cell were employed (Fig. 1): the larger cell, Fig. 1a, was used primarily for experiments below 8 GPa; the smaller cell, Fig. 1b, was for pressures higher than 10 GPa. Fig. 1 basically shows configurations for the study of a powder sample. For studying as-deposited plates, the powder sample near the centre was replaced by layers of r-BN plates.

High pressure was first generated at room temperature. High temperature was then attained at a fixed pressure by passing an alternating current through the graphite tube in Fig. 1a or the platinum tube in Fig. 1b. The temperature was measured by a Pt–Pt/Rh (13%) thermocouple. The duration at high temperature was in most cases 10 min. After cooling the sample by switching off the current while under pressure, the pressure was released to recover the sample.

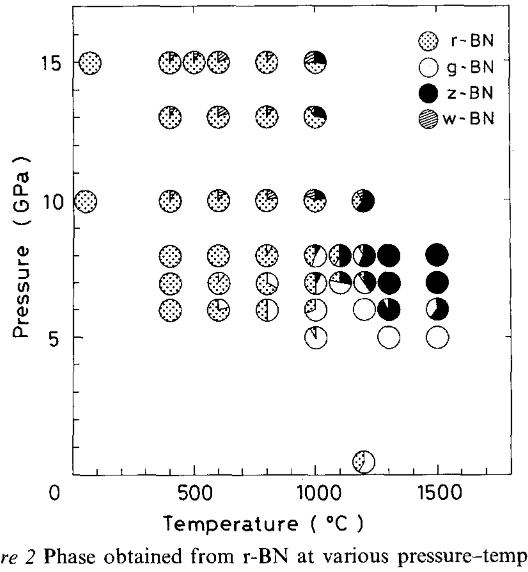

Figure 2 Phase obtained from r-BN at various pressure–temperature conditions after 10 min duration.

2.3. Analysis

The samples recovered were subjected to powder X-ray diffraction. In the case of as-deposited plates, they were X-rayed as-recovered, i.e. without pulverizing. In this case a micro-focused X-ray beam was impinged upon the sample perpendicular to the plate and the diffracted X-rays were analysed by a position sensitive detector. For samples recovered in forms of sintered compacts, Vickers-micro hardness was measured at room temperature.

3. Results

3.1. Conversion diagram

Fig. 2 gives plots of pressure–temperature conditions and the phases present in the recovered samples after a duration of 10 min at each point. The starting samples were all powdered r-BN. The amount of each phase was estimated from the intensities of characteristic peaks in the powder X-ray diffraction patterns. A disturbance of g-BN (0 0 2) reflection with r-BN (0 0 3) reflection occurs at an angle 26.7° for Cu*Kα* radiation. This causes ambiguity in estimating the relative amount of g-BN and r-BN.

In Fig. 2, all the known phases of BN are seen, but their appearance depends on the pressure–temperature conditions. Essentially, r-BN persists at lower pressures and temperatures. Also at lower pressures but at higher temperatures, g-BN formed from r-BN is prevalent. At pressures higher than 10 GPa, w-BN is present although the amount is small. Above 6 GPa z-BN is predominant at temperatures higher than 1200° C. The formation of z-BN occurs through different paths, as will be reported in the following sections.

From Fig. 2, a boundary can be derived for pressure–temperature conditions to synthesize z-BN. For approximately 50% z-BN, a conversion boundary is given by line D in Fig. 3. Also given in Fig. 3 for comparison are boundaries for synthesizing z-BN from a-BN (line A; [7]), from t-BN (line B; [9]), from incompletely crystallized g-BN (line C; [4]), and from well-crystallized g-BN (line E; [32]). The boundaries are apart from the thermodynamic equilibrium line [33] because all are obtained simply from conversion to z-BN, without undergoing reconversion. Line D for r-BN to z-BN

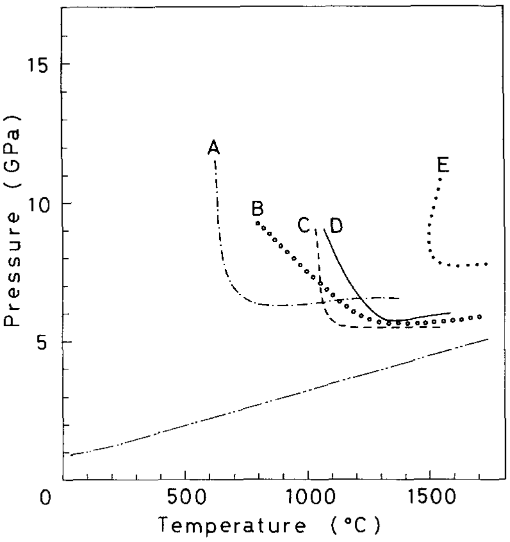

Figure 3 Pressure–temperature boundaries for synthesizing z-BN from various forms of BN. Line A from a-BN [7]; line B from t-BN [9]; line C from incompletely crystallized g-BN [4]; line D from r-BN (present study); line E from well-crystallized g-BN [32]. (- - -) Thermodynamic calculation for equilibrium between g-BN and z-BN [33].

conversion is located near to line C, the lowest bound known for non-catalytic g-BN to z-BN conversion [4].

3.2. Results from the 6 GPa isobar

Fig. 4 shows X-ray diffraction patterns of the samples recovered from 6 GPa. The starting sample was powdered r-BN. The pattern at 400° C is substantially the same as that observed at ambient conditions. At 800° C a weak peak from g-BN (1 0 0) reflection appears at an angle 41.7°. The stronger reflection, g-BN (0 0 2), is disturbed with the r-BN (0 0 3) reflection, however.

At 1200° C the sample turns into g-BN single phase (see also Fig. 2). All the peaks in the diffraction pattern (Fig. 4) are unequivocally interpreted by the reflections from g-BN. This g-BN is, in turn, converted into z-BN at 1300° C (Fig. 2), but z-BN thus formed is reconverted in part to g-BN at 1500° C (Figs 2 and 4) due to its approach to the thermodynamic equilibrium line (see Fig. 3). From as-deposited r-BN plates, g-BN single phase was also obtained under the same conditions (6 GPa, 1200° C) as for powdered r-BN.

From these observations a sequence of the conversion between the BN phases upon heating at 6 GPa is viewed as r-BN → g-BN → z-BN. A similar sequence is observed at 7 and 8 GPa, with behaviour to some extent different from that at 6 GPa: z-BN starts to appear at lower temperature, 1000° C (Fig. 2); no g-BN single phase appears (Fig. 2); a path opens for r-BN to transform directly into z-BN as evidenced in Fig. 2 by the relative amounts of phases between 1100 and 1300° C.

3.3. Results from the 10 GPa isobar

Fig. 5 shows X-ray diffraction patterns of the samples started with powdered r-BN and recovered from 10 GPa. The diffraction pattern at 25° C is basically the same as that under ambient conditions, except for the disappearance of the r-BN (1 0 2) reflection from an angle 45.6°. As the temperature is elevated, the r-BN (0 0 3) peak becomes weakened and broadened, but still persists at 1200° C.

The presence of w-BN is found at 400° C as perceivable from the w-BN (1 0 0) peak at 40.8°. The intensity of this peak remains virtually unaltered when the temperature is raised further past 800 to 1000° C, but is slightly decreased at 1200° C. At 1000° C, z-BN (1 1 1) appears at 43.1° and this peak remarkably grows at 1200° C. Because the amounts of r-BN and w-BN are both correspondingly decreased, the formation of z-BN is attributed to conversion from both r-BN and w-BN.

These observations at 10 GPa provide us with elucidation of BN conversion upon heating: r-BN → w-BN → z-BN, taking place concurrently with

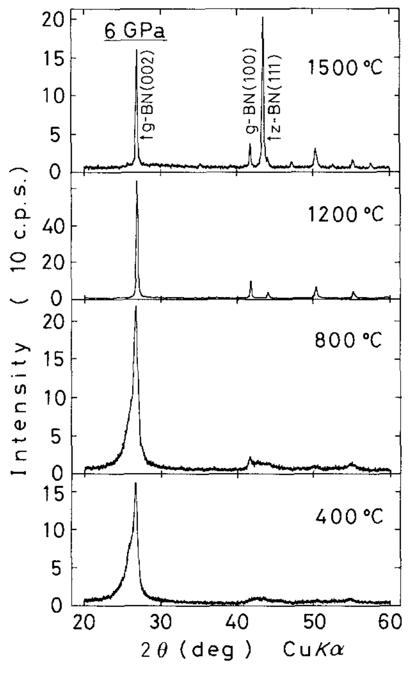

Figure 4 X-ray diffraction patterns of recovered samples started from r-BN powder and compressed to 6 GPa.

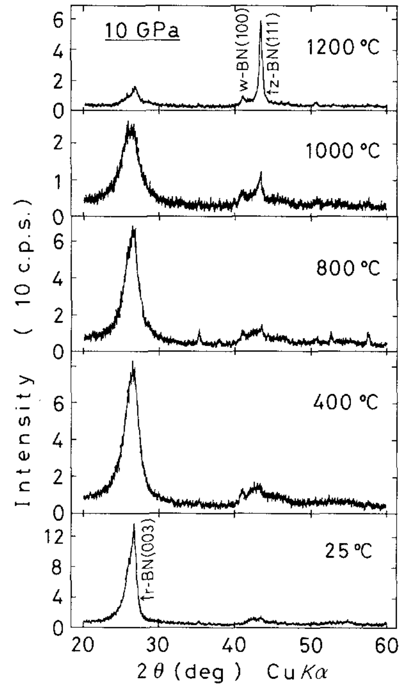

Figure 5 X-ray diffraction patterns of recovered samples started from r-BN powder and compressed to 10 GPa.

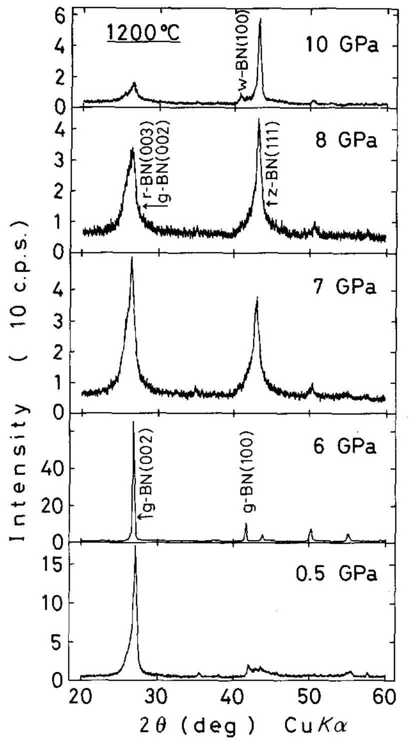

Figure 6 Isothermal 1200° C series of X-ray diffraction patterns for recovered samples started from r-BN powder.

r-BN → z-BN. This latter conversion, is more obvious at higher pressures, 13 and 15 GPa (Fig. 2). No g-BN appears at pressures greater than 10 GPa.

3.4. Results from the 1200° C isotherm

Fig. 6 gives X-ray diffraction patterns of the samples recovered from various pressures at 1200° C. The pattern at 0.5 GPa is made up of reflections from r-BN and g-BN. At 6 GPa, single-phase g-BN is formed without the presence of any other phases. As the pressure is increased to 7 or 8 GPa, z-BN and r-BN are formed. On further increasing the pressure to 10 GPa, w-BN appears and the reflections from z-BN increase whereas those from r-BN remain unchanged.

Thus the conversion of r-BN on application of pressure at 1200° C is r-BN → g-BN occurring below 6 GPa, followed by g-BN → z-BN or g-BN → w-BN and also by g-BN → r-BN reconversion at higher pressures. Similar sequences can be observed for the pressure-induced conversion at 1000° C (see Fig. 2).

3.5. Sintered compacts

Some of the samples after high pressure–high temperature treatment were recovered as well sintered compacts. The sintering had been spontaneously achieved during conversion of r-BN to z-BN occurring in parallel with g-BN to z-BN conversion. This is referred to as reaction sintering. Fig. 7 shows a scanning electron micrograph of the fracture surface of a sintered compact obtained at 7 GPa and 1500° C. Grains ranging in size from 100 to 800 nm are bonded to each other. Intragranular rather than intergranular fracture is perceivable.

After being polished, the sintered compact was subjected to Vickers microhardness testing. The weights indented upon the sample were between 1.96 and 4.9 N. Typical examples of the hardness, H_V, ranged from 33.3 to 75.4 (51.2 on average) GPa. This hardness is compared with other compacts also obtained by reaction sintering: Knoop hardness, H_K = 10 to 80 (typically 60 to 70) GPa for compacts obtained from g-BN to z-BN conversion [3]; H_K = 46 to 80 GPa for sintered bodies from t-BN to z-BN conversion [6]; $H_v \simeq 76$ GPa for compacts of z-BN converted from w-BN, mixed with residual w-BN [34]; H_v = 16 to 42 GPa for compacts obtained from a-BN to z-BN conversion [32].

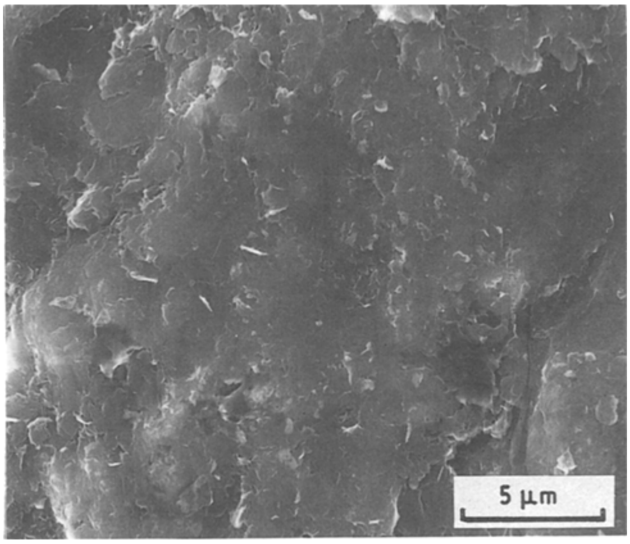

Figure 7 Scanning electron micrograph of the fractured surface of a compact sintered at 7 GPa and 1500° C.

4. Discussion

This study has revealed that z-BN can be formed from r-BN by high static pressure–high temperature treatment. The formation of z-BN occurs via three different paths: (i) r-BN → z-BN; (ii) r-BN → g-BN → z-BN; and (iii) r-BN → w-BN → z-BN. In addition to the anticipated conversion, path (i), conversions via paths (ii) and (iii) take place under static compression, differently from the results of dynamic compression [24]. From the isobaric viewpoint, path (ii) is obvious at 6 GPa, and this becomes concurrent with path (i) at 7 and 8 GPa. Paths (i) and (iii) are observed at pressures between 10 and 15 GPa.

The direct r-BN to z-BN conversion, path (i), is not so drastic as expected from the possible diffusionless mechanism arising from the same periodicity of atomic packings in the two forms. Rather, path (ii) is clearer as demonstrated by the conversion sequence at 6 GPa. The conversion of r-BN to g-BN requires rotation of a part of the layers by 60° plus glide of layers relative to each other, yet is readily achieved upon heating r-BN at pressures below 8 GPa.

For r-BN to w-BN conversion, g-BN could be expected as an intermediate, because g-BN can in turn be readily converted into w-BN by a diffusionless mechanism [19, 35]. However, no g-BN appears upon heating r-BN at pressures higher than 10 GPa. Instead, only direct conversion of r-BN into w-BN occurs at temperatures between 400 and 800° C. This direct conversion involves the approach of layers and reconstruction of bonds, and hence would seem to be difficult to achieve, but nevertheless is done so rather easily.

Synthesis of w-BN from g-BN was first reported by Bundy and Wentorf [36]. Later, static compression studies showed that w-BN can specifically be formed from well-crystallized g-BN at pressures higher than 10 GPa [5, 6, 19, 32], or at 6 GPa [9]. Also a-BN can form w-BN under very limited pressure–temperature conditions [7]. Consequently, this is the first time that w-BN has been reported to be synthesized from r-BN. By dynamic compression, r-BN is converted only to z-BN [24]. It should be noted that these w-BN syntheses have all been achieved without the presence of catalysts. In Fig. 2, w-BN is observed at pressures above 10 GPa and at temperatures between 400 and 1200° C. These conditions are similar to those for w-BN synthesis from g-BN [5, 6, 19, 32, 36]. The conversion of w-BN into z-BN at higher temperatures is in accord with earlier studies [6, 32, 37].

In Fig. 3, line D from this study is located in proximity to line C, which was obtained from incompletely crystallized g-BN [4] and has been the lowest bound for non-catalytic g-BN to z-BN conversion. The incompletely crystallized g-BN was specified [4] in terms of the graphitization index (GI) [38] as infinite. At the opposite extremity, well-crystallized g-BN has a GI of approximately 1.7. This g-BN has yielded line E in Fig. 3 for conversion to z-BN [32]. It is apparent from the locations of lines C and E that a smaller GI pushes the boundary for g-BN to z-BN conversion towards a higher pressure–temperature regime. Because line D in the lower pressure part primarily represents conversion of g-BN into z-BN, specification of g-BN converted from r-BN is needed for discussion of lines C, D, and E. The g-BN single phase obtained at 6 GPa and 1200° C is, as seen from Figs 4 and 6, well crystallized and has a GI of 1.4. If GI for g-BN governs the location of the boundary for conversion to z-BN, then line D should approach line E, obtained from g-BN with similar GI. However, line D runs nearer to line C. This implies that the relative ease for g-BN to z-BN conversion is not simply governed by the GI of the starting g-BN.

The conversions exhibited here by r-BN under static compression are, to a great extent, facilitated by temperature simply because, for instance, r-BN remains unaltered at room temperature by 15 GPa compression but, on the other hand, is converted to w-BN on heating to 400° C above 10 GPa. It is seen from Fig. 2 that 15 GPa compression is insufficient for r-BN to be converted into z-BN via a diffusionless mechanism. This is different from the findings that 10 GPa compression at room temperature can convert g-BN into w-BN [19, 32, 36]. The g-BN to w-BN conversion occurs through a diffusionless mechanism as noted earlier [19, 35]. Further compression beyond 15 GPa may induce conversion of r-BN directly into z-BN at room temperature. *In situ* x-ray diffraction analysis up to the sub-megabar region is under study.

5. Conclusion

High static pressure–high temperature treatment of chemical vapour deposited r-BN can form z-BN at 6 GPa and above 1300° C, at 1000° C and above 7 GPa, or at higher regime. A boundary line for the z-BN formation runs in proximity to the lowest bound hitherto known for the synthesis of z-BN from g-BN.

Combination of data from isobaric and isothermal series of experiments delineates that z-BN is formed either directly from r-BN, or indirectly via g-BN or w-BN. The conversion of r-BN into g-BN is drastic and the resultant single-phase g-BN is highly crystallized in terms of GI. Surprisingly, this g-BN transforms into z-BN at pressure–temperature conditions much lower than that simply expected from the value of GI.

Polycrystalline compacts can be obtained through spontaneous sintering which occurs during the formation of z-BN. A Vickers microhardness higher than 75 GPa has been recorded. This comprises upper bounds for the hardness of sintered polycrystalline z-BN.

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