Segregative Crystallization of Several Diamond-like Phases from the Graphitic BC_2N without an Additive at 7.7 GPa

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A graphite relative of composition BC_2N has been subjected to high-pressure (7.7 GPa) and high-temperature (2000–2400 °C) conditions to explore the possibility for the formation of a cubic phase via direct transformation. Several cubic phases with a diamond-like structure were confirmed in the products above 2150 °C by the powder X-ray diffraction patterns. The deconvolution of the broad and partly split diffraction lines suggested that the products obtained at 2150–2300 °C consisted of cBN, “diamond” (containing minor amount of B and N), and a cubic B–C–N substance. At 2400 °C, however, the cubic products tended to segregate into two major phases assigned as cBN and “diamond”. This tendency was strongly supported by the microstructural and elemental observation of the products using a high-resolution scanning electron microscope and Auger electron spectroscopy. The present study concludes that not a cubic B–C–N compound but a mixture of cBN and diamond exists as the thermodynamically stable phases in the ternary system under the conditions employed.

Introduction

Carbon and boron nitride have the same type of polymorphs, hexagonal forms (graphite and hBN) and cubic ones (diamond and cBN). Hybrid compounds composed of three elements, boron, carbon, and nitrogen, are attractive, in expectation of intermediate or even superior properties in comparison with carbon and boron nitride. Cubic B–C–N compounds would be expected to be prepared by transformation from hexagonal B–C–N compounds under high-pressure and high-temperature (HP/HT) conditions, by analogy to the preparation of diamond and cBN from their hexagonal polymorphs.[1–3] But few studies have been reported in this field. Only one example has been published by Badzian[4] in which cubic B–C–N materials were synthesized at 14 GPa and 3300 K starting from the graphitic B–C–N obtained in the reaction between BCl_3, CH_4, NH_3, and H_2 gases.

Graphitic B–C–N compounds have been studied[5–20] from a variety of viewpoints such as semiconductor fabrication and intercalation. It is difficult, however, to prepare a reliable material, mainly due to the difficulty in distinguishing a B–C–N compound from a microcrystalline mixture of graphite and hBN. Recently, some materials have been reported to be B–C–N compounds by means of various characterization techniques such as XPS and EELS. One of them is the graphitic BC_2N synthesized in a reaction between BCl_3 and CH_3CN.[20,21]

We have previously carried out HP/HT experiments on the graphitic BC_2N with the expectation of a cubic B–C–N compound.[21] The BC_2N was compressed in the presence of cobalt metal, which is a solvent–catalyst for the transformation from graphite to diamond, under 5.5 GPa and 1400–1600 °C. The compression resulted in simultaneous crystallization of diamond and cBN instead of a cubic B–C–N crystal. The solvent–catalyst, cobalt metal, promoted the separation of C and B/N phases. This result suggests that a direct transformation without an additive may be required to obtain a cubic B–C–N substance, avoiding the phase separation. Recently, Kakudate et al.[22] have reported the formation of a cubic B–C–N substance starting from

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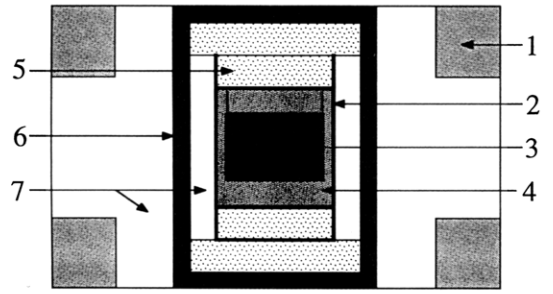

Figure 1. Sample assembly for the HP/HT treatments. 1, steel ring; 2, Mo foil; 3, sample (ground BC_2N); 4, Mo capsule; 5, NaCl + ZrO_2 (20 wt %) as a pressure medium; 6, graphite heater; 7, NaCl + ZrO_2 (10 wt %) as a pressure medium.

graphitic BC_2N under 30−40 GPa using a shock-wave compression, which also suggests that the direct transformation is effective.

In the present study, we examined the compression of the graphitic BC_2N without an additive under HP/HT conditions of 7.7 GPa and 2000−2400 °C for 15−60 min. We selected the static high-pressure method using a belt-type apparatus and an indirect heating method in order to employ a large amount of sample and a long reaction time under the conditions. The synthesis temperatures, up to 2400 °C, were decided within the thermodynamically stable region of diamond at the examined pressure.

Experimental Section

Preparation of the Graphitic BC_2N. The graphitic BC_2N was prepared by a vapor-phase reaction of BCl_3 and CH_3CN. The details of the method were described elsewhere.[21] The XRD pattern of the prepared BC_2N reveals a graphite-like turbostratic structure.

HP/HT Treatments on the Graphitic BC_2N. The graphitic BC_2N was ground and then annealed under a nitrogen gas flow at 1800 °C for 2 h in order to remove volatile components. Neither a compositional change nor disproportionation was observed by annealing up to this temperature as described previously.[21] The resulting powder was loaded in a molybdenum capsule at 600 MPa. The capsule was put into a molybdenum foil capsule in a pressure cell, as shown in Figure 1, which was set into a modified belt-type high-pressure apparatus with a bore diameter of 32 mm.[23]

The experiments were carried out under the conditions of 7.7 GPa and 2000−2400 °C for 15−60 min. After quenching, the pressure was reduced, and the sample was recovered.

The pressure was calibrated beforehand at room temperature using the known pressure-induced transitions of bismuth (2.55, 2.71, 7.7 GPa), thallium (3.67 GPa), and barium (5.5 GPa) using the resistance change of the metals. All experiments were carried out at the oil pressure detected at the pressure induced Bi III−V transition of 7.7 GPa. The temperature was estimated from the relationship between the electric power supplied to a heater and temperature which had been measured in advance up to 2200 °C using a W5%Re−W26%Re thermocouple. No correction was made for the pressure effect on the emf of the thermocouples.

Characterization. The recovered samples were identified by a powder X-ray diffraction (XRD). The XRD data were collected by a Phillips PW-1800 type X-ray diffractometer with Cu Kα radiation. A profile fitting was performed using the intermediate Lorentzian as a profile−shape function.[24] The lattice constant, the fractional yield and the full width at half-maximum (fwhm) of each phase were deduced on the basis of the fitting. The lattice constant was corrected using Si as an internal standard.

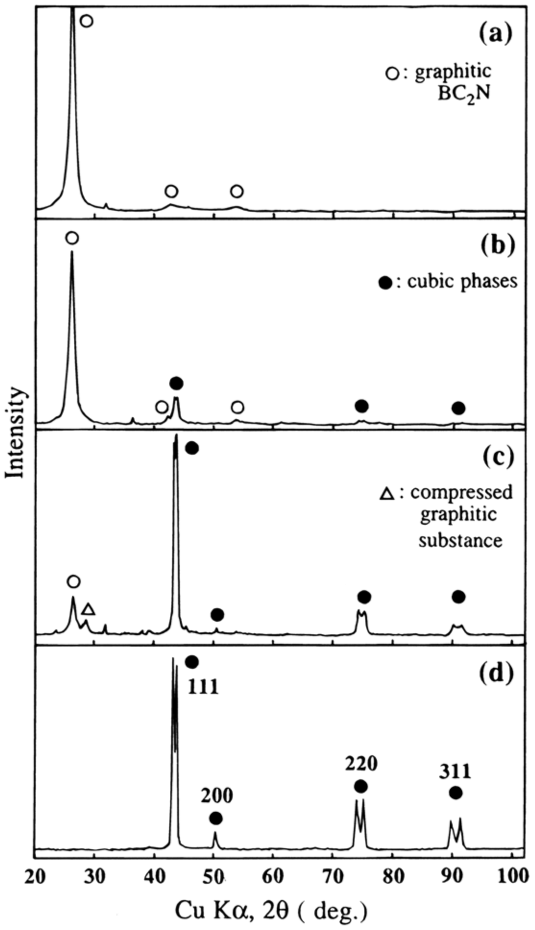

Figure 2. Powder XRD patterns of the sample obtained at 7.7 GPa and (a) 2000 °C, (b) 2150 °C, (c) 2300 °C, and (d) 2400 °C for 15 min.

For microscopic observations of the compressed products, the unreacted graphitic material in the recovered sample was removed by a hot mixture of H_2SO_4 and HNO_3. The samples recovered from the 2300 °C experiment were broken into pieces by the acid treatment. As the samples from the 2400 °C experiment were not broken during the acid treatment, they were fractured into small pieces before the treatment. The microscopic textures and the compositional distribution in the products were examined using a Hitachi S-900 type high-resolution scanning electron microscope (HRSEM) and a Perkin-Elmer PHI 670 type Auger electron spectrometer (AES), respectively.

Results

Temperature Dependence of the Transformation of the Graphitic BC_2N. Figure 2 shows the XRD patterns of the samples treated at 7.7 GPa and 2000−2400 °C for 15 min. The pattern of the sample obtained at 2000 °C was virtually identical with that of the starting graphitic BC_2N. When the temperature was increased to 2150 °C and above, new diffraction peaks appeared in angular regions where (111), (200), (220), (311), (400), and (331) reflections for diamond and cBN occur. The XRD results definitely demonstrate that the graphitic BC_2N was transformed directly to diamond-like cubic phases without an additive. The yield of the cubic products increased as the synthesis temperature increased to 2400 °C where the starting graphitic BC_2N was totally converted.

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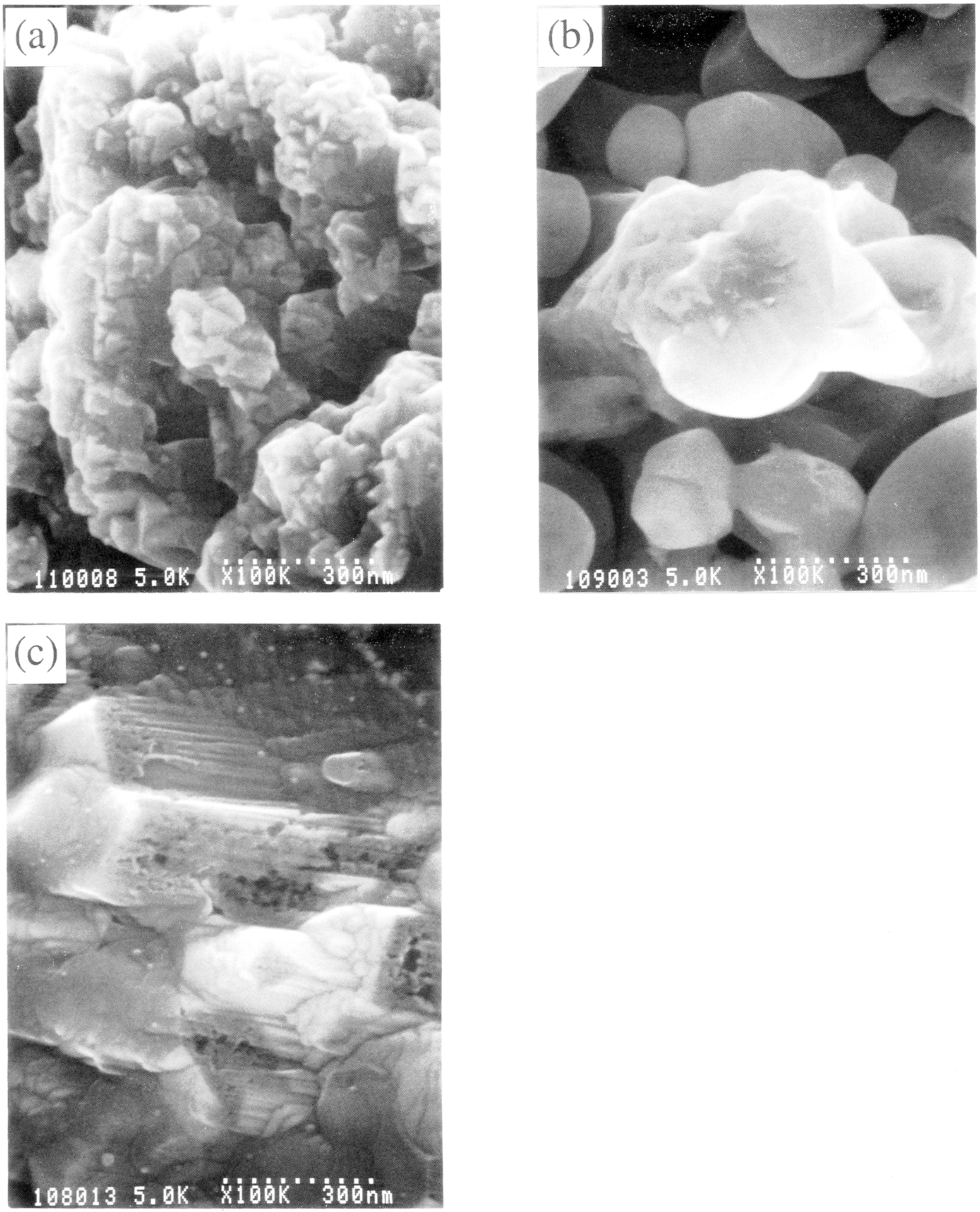

Figure 3. High-resolution scanning electron micrographs for the cubic products obtained at 7.7 GPa and (a) 2300 °C for 15 min, (b) 2400 °C for 15 min, and (c) 2400 °C for 60 min.

The diffraction peaks assignable to the cubic products were rather broad for a single reflection and were split, indicating multicomponent nature. The peak splitting increased with the temperature and finally, at 2400 °C, appeared to indicate the presence of two principal cubic phases. The detailed identification of the cubic phases will be described in the discussion section.

The weak peak at around a 2θ of 28.8° in Figure 2c may be attributable to a compressed graphitic substance.[25] This peak did not disappear by an acid treatment to remove the starting graphitic BC_2N, which

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[25] (25) In the direct transformation from graphite to diamond and from hBN to cBN, the compressed graphite and hBN are often formed giving a characteristic reflection of about 3.1 Å.[26,27]

suggests that the substance was trapped in the cubic crystals or at the grain boundaries of the crystals. The compressed graphitic substance disappeared at 2400 °C. In the direct transformation from hBN to cBN, the compressed hBN disappears in a higher temperature region, and the obtained cBN is, under such conditions, sintered tightly.[28] The compressed hBN is transformed to cBN at the higher temperature where the B/N atoms can diffuse sufficiently fast to become sintered. In the present study, the absence of the compressed graphitic substance in the sample prepared at 2400 °C may be ascribed to a similar reason; vigorous diffusion of B, C, and N atoms at this temperature.

Morphology of the Cubic Crystals Formed from the Graphitic BC_2N. Figure 3 shows the morphology of the cubic crystals. The product obtained at 2300 °C for 15 min was an aggregate of crystals of 20−30 nm in diameter. With increase of the temperature to 2400 °C (duration 15 min), the aggregation grew into the independent grains of dimension 100−300 nm. Lengthening of the reaction time to 60 min combined the grains, which made it difficult to distinguish individual crystallites.

Elemental Distribution of B, C, and N in the Cubic Crystals. Figure 4 displays the AES micrographs of the cubic products obtained at 2300 °C for 15 min. In Figure 4a, the distribution of carbon and boron was generally homogeneous within the size of the beam spot (about 10−20 nm) except for a heterogeneous distribution in a limited area. That of carbon and nitrogen was also similar, as is shown in Figure 4b. The elemental segregation to B/N and C became predominant for the cubic products at 2400 °C as exemplified by Figure 5. The location where boron is enriched corresponds to that for nitrogen. This suggests that the segregative crystallization took place under the present HP/HT conditions.

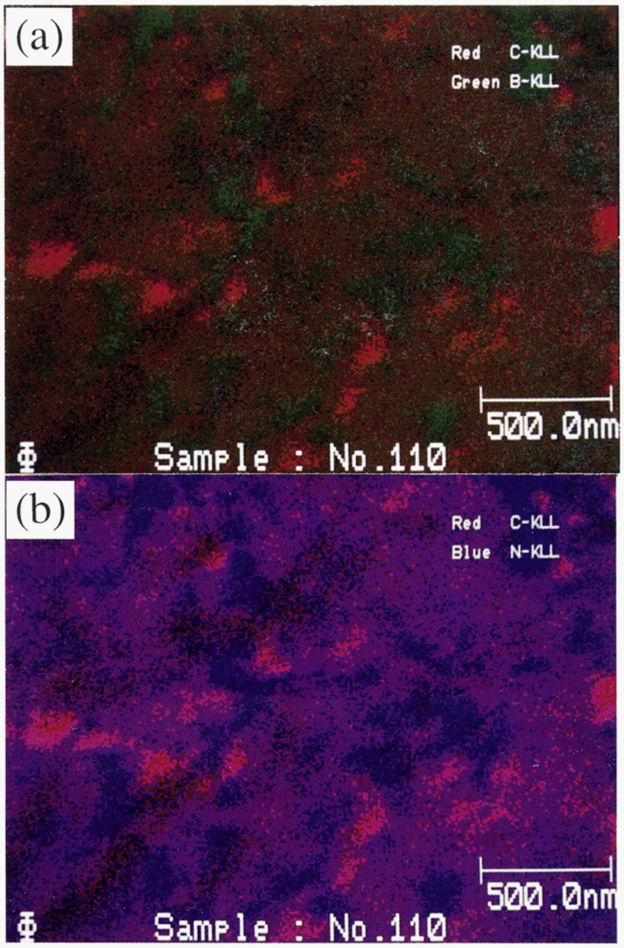

Figure 4. Auger electron spectroscope photographs for the cubic products obtained at 7.7 GPa and 2300 °C for 15 min: (a) mapping for atomic distribution of carbon and boron; (b) mapping for carbon and nitrogen in the same view. A red dot corresponds to carbon, a green to boron, and a blue to nitrogen.

Discussion

The graphitic BC_2N was successfully transformed to cubic phases without an additive at 7.7 GPa. The formation pressure is much lower than that reported by Badzian (14 GPa)[4] or Kakudate et al. (30−40 GPa).[22] In the present study, the extension of the reaction time effectively made the formation pressure lower. The transformation of the graphitic BC_2N at 7.7 GPa and above 2150 °C might reflect its intermediate properties between those of hBN and graphite. Under the present conditions, hBN transforms to cBN easily but graphite does not to diamond without a solvent−catalyst.

As pointed out above, the XRD patterns of the products suggested the presence of several cubic phases. The AES data also revealed a heterogeneous elemental distribution, especially at the higher temperatures, indicative of segregative crystallization. Therefore, it is important to make an accurate identification of the cubic products using a deconvolution for the XRD data. Figures 6, parts a and b, show the results of the profile fitting by assuming two and three components, respectively, for the (111) peak for the sample obtained at 2300 °C for 15 min. A sum of three curves successfully fitted the profile, whereas two curves did not. The other peaks, except for the (200) line, were also satisfactorily fitted by assuming three components. These data strongly suggest that the compressed products include three different cubic phases rather than two phases. We name these phases A, B, and C in order of the 2θ value as shown in Figure 6b. Although a question may be raised regarding the existence of a B phase, this phase was confirmed more obviously in other preparations, as is shown in Figure 6c. The deconvolution procedure for the products obtained at 2400 °C indicated a phase separation to two major components, A and C phases, although the B phase still persisted. Only the (200) peak could be fitted by assuming one component. The lattice constant, calculated from the (200) peak, equals that of the A phase. The (200) reflection was absent for the B and C phase.

Figure 7 shows the lattice constants obtained by averaging the deconvolution results on the (111), (200), (220), and (311) peaks in Figure 2b−d. The lattice constant of the A phase was equal to that of cBN within the experimental error independent of the synthesis temperature. The lattice constant of the B phase takes an intermediate value between diamond and cBN. The phase is most likely to be a cubic substance composed of three elements, boron, carbon, and nitrogen. The composition of the B-phase was implied to be between BC_2N and BC_4N by the lattice constant assuming

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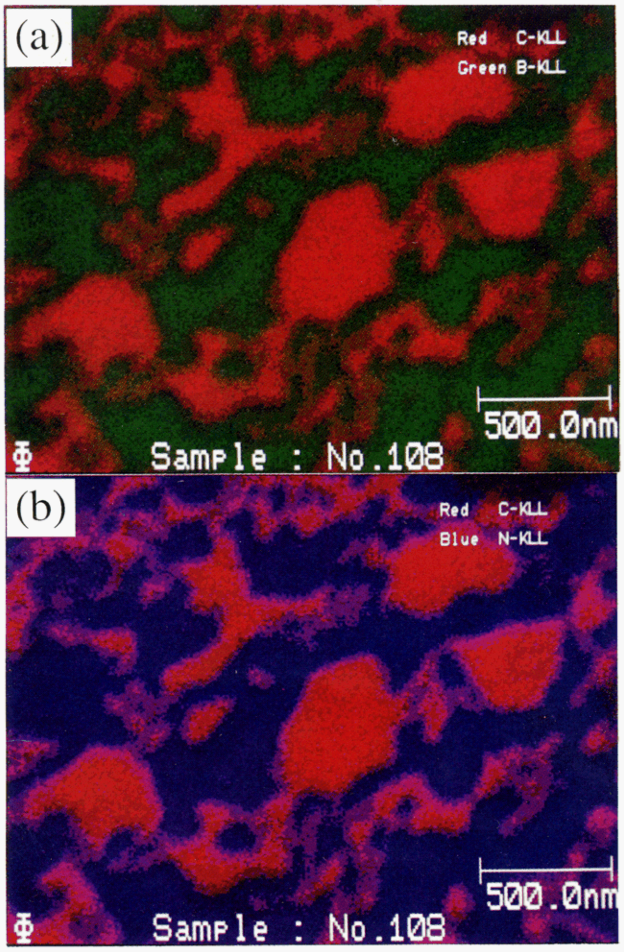

Figure 5. Auger electron spectroscope photographs for the cubic products obtained at 7.7 GPa and 2400 °C for 60 min: (a) mapping for atomic distribution of carbon and boron; (b) mapping for carbon and nitrogen in the same view. A red dot corresponds to carbon, a green to boron, and a blue to nitrogen.

Vegard's law holds between cBN and diamond. The lattice constant of the C phase is slightly larger than that of diamond, and it approaches that of diamond with increasing temperature. These deconvolution data suggest that the compressed product consisted of cBN (A phase), a cubic B−C−N (B phase) and "diamond" containing minor amount of B and N (C phase). The presence of the (200) reflection for the A phase and its extinction for the C phase also support these phase assignments. The absence of the (200) line for the B phase indicates a disordered arrangement of B, C, and N atoms in the diamond-like structure.

The fractional yield deduced by the deconvolution suggests that the graphitic BC_2N tends to segregate to cBN and diamond especially at high temperature. This is consistent with the AES data; the domains of carbon and boron/nitrogen became separate for the cubic products prepared at 2400 °C.

The temperature of 2400 °C may be just sufficient to activate the diffusion, which brings about the segregation to cBN and diamond as the thermodynamically stable phases. Actually, as pointed out above, the disappearance of the compressed graphitic residue at this temperature strongly suggested an appreciable atomic diffusion. Table 1 gives the average crystal sizes calculated from the fwhm value of the deconvolution using Scherrer's equation. The table indicates the rapid growth of cBN and diamond at 2400 °C, also suggesting fast atomic diffusion at this temperature. These crystal dimensions are generally consistent with the grain size observed using the HRSEM and AES.

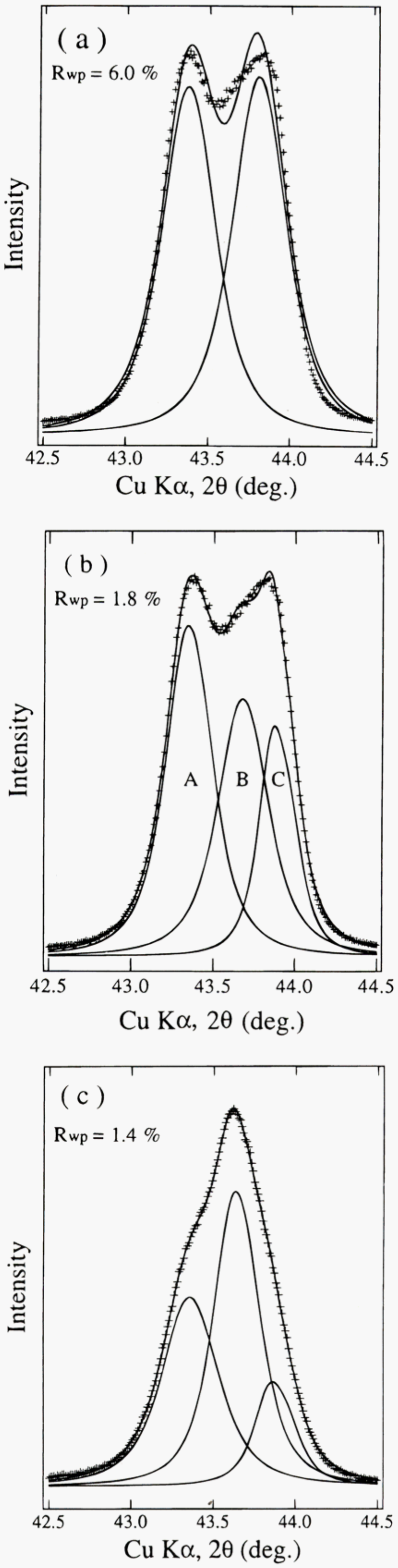

Figure 6. Profile fitting with (a) two and (b) three curves for the (111) XRD pattern of the cubic phases obtained at 7.7 GPa and 2300 °C for 15 min and (c) for another sample obtained at 2300 °C. The plus (+) reveals an observed datum, and the solid line is a curve calculated for the fitting. The R_{wp} is the weighted residual error for the fitting. Symbols A, B, and C reveal A, B, and C phases, respectively.

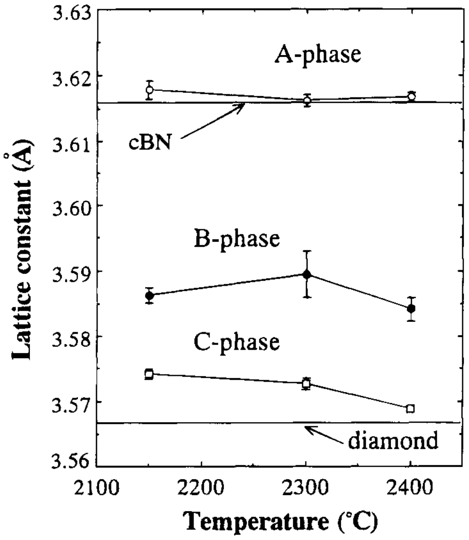

Figure 7. Lattice constants calculated from the profile fitting for the cubic products obtained at 7.7 GPa and various temperatures for 15 min. Lattice parameters of cBN and diamond are quoted from JCPDS cards.[31]

Table 1. Average Crystallite Sizes (nm) of the Cubic Products Deduced from the Profile Functions of the XRD Patterns Using Scherrer's Equation[a]

	phase		
temp (°C)	A	B	C
2150	21 (2)	19 (9)	41 (12)
2300	24 (4)	19 (7)	37 (9)
2400	40 (7)	18 (4)	86 (20)

[a] The products were obtained at 7.7 GPa for 15 min. The values in the parenthesis reveals the standard errors of the each average sizes.

The present results indicate that not the cubic B–C–N compound but cBN and diamond exist as the thermodynamically stable phases in the boron–carbon–nitrogen ternary system under the present conditions. Lambrecht et al.[29] have calculated the free energies of the system based on some structural models and discussed the miscibility gap between cBN and diamond. According to their study, there is only very limited mutual solubility in the solid state. The present experimental results are compatible with the predictions based on the thermodynamic calculations. On the other hand, Kakudate et al.[22] have claimed a synthesis of a single phase of cubic B–C–N substance from the graphitic BC$_2$N by a shock-wave compression. Badzian[4] has also reported cubic B–C–N synthesized by using direct heating of a short duration, below 3 min, or flash heating with which the electric power is directly supplied to the starting graphitic B–C–N material. The transformation in a short duration may restrict the diffusion of B, C, and N atoms which, in turn, may suppress the phase separation producing the cubic B–C–N substances although they were not well-crystallized.

The fractional yield of cBN was higher than that of "diamond" over the range of temperatures studied. Furthermore, "diamond" crystallized at lower temperature may contain a minor amount of B and N. Higher temperature was needed to precipitate purer "diamond". These phenomena may be associated with the facts that the similar compression under the present HP/HT conditions does not facilitate the direct transformation from graphite to diamond but does from hBN to cBN. Actually, when a 1/1 mechanical mixture of graphite and hBN was subjected to 7.7 GPa and 2200–2400 °C for comparison, the XRD pattern of the recovered sample revealed a mere mixture of graphite and cBN. This datum definitely shows that the graphitic BC$_2$N is a genuine B–C–N compound and not a microcrystalline mixture of graphite and hBN.

The direct transformation from graphite to diamond requires much higher pressure and temperature conditions, at least above 10 GPa and 3000 K.[30] Therefore, the noncatalytic formation of diamond at a low pressure of 7.7 GPa found here is of great interest. It is ascribed to the starting material, the graphitic BC$_2$N. There are two possible mechanisms for the formation of diamond from the graphitic BC$_2$N. The selective crystallization of BN from the graphitic BC$_2$N network may construct the remaining carbon as diamond, the thermodynamically stable phase under the conditions, rather than graphite. Another possible route to diamond is via the cubic B–C–N whose carbon is already sp^3 hybridized.

Conclusions

The graphitic BC$_2$N was subjected to HP/HT conditions of 7.7 GPa and 2000–2400 °C for 15–60 min using a static high pressure and an indirect heating technique. No additive or solvent was used. Our conclusions are as follows:

(1) The graphitic BC$_2$N was directly transformed to cubic phases above 2150 °C and completely at 2400 °C. The formation pressure of 7.7 GPa is much lower than that by a shock-wave compression reported previously.

(2) The compressed products consisted of different three components, cBN, "diamond" including minor amount of B and N, and a cubic B–C–N substance. With increasing temperature, the "diamond" phase approached pure carbon in composition and the cubic B–C–N was decomposed, which suggests a phase separation to cBN and diamond. The crystallization of diamond without an additive at a pressure as low as 7.7 GPa was accomplished for the first time.

(3) The phase separation to cBN and diamond as well as noticeable growth of their crystallite dimensions was confirmed using an HRSEM and an AES technique. This suggests that not the cubic B–C–N compound but the mixture of cBN and diamond was thermodynamically stable under the present conditions. This result agrees with the thermodynamic calculation by Lambrecht et al.

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(31) Diamond: $a = 3.5667$ Å (JCPDS No. 6-0675). cBN: $a = 3.6158$ Å (JCPDS No. 35-1365).