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# The thermal expansion of a highly crystalline hexagonal BC<sub>2</sub>N compound synthesized under high temperature and pressure

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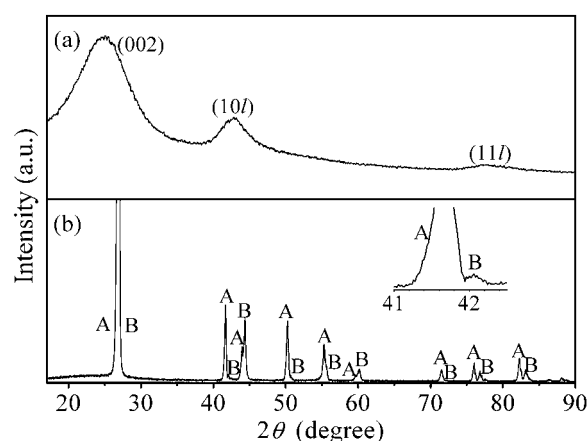
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## Abstract

The thermal expansion has been investigated for a highly crystalline hexagonal BC<sub>2</sub>N compound synthesized by the compression of a turbostratic B–C–N precursor with iron catalyst at the high temperature of 1500 °C and the high pressure of 5.5 GPa. The thermal expansion in the *c* direction is large and linear with an expansion coefficient of  $35.86 \times 10^{-6} \text{ K}^{-1}$  up to 1000 °C, while in the basal plane, the *a* dimension displays a slight linear contraction up to 750 °C with a contraction coefficient of  $-8.76 \times 10^{-7} \text{ K}^{-1}$ , but above 750 °C a linear expansion is observed with a larger expansion coefficient of  $1.52 \times 10^{-6} \text{ K}^{-1}$ .

In the past few decades, the B–C–N compounds have attracted significant interests due to their expected intermediate or even superior properties in comparison to carbon and boron nitrides [1–6]. The cubic B–C–N compounds should exhibit excellent mechanical properties [5–7]. On the other hand, the hexagonal B–C–N phases are expected to have semiconducting properties with various band gap energies by controlling their compositions and structures [8, 9]. In the B–C–N ternary systems, the stoichiometric graphite-like BC<sub>2</sub>N (g-BC<sub>2</sub>N) compound has been paid more attention. Some theoretical studies were carried out on the structural stability [8–10], electronic [8, 9], and vibrational [11, 12] properties of the g-BC<sub>2</sub>N compound. In experimental studies, some g-BC<sub>2</sub>N samples were synthesized using various methods, such as the chemical vapour deposition (CVD) [13], solid-phase pyrolysis [14], and mechanical milling with h-BN and graphite as starting materials [15]. So far, the obtained samples are of amorphous, turbostratic structure or are poorly crystalline. Due to the structural similarity in the three phases of hexagonal BCN, graphite and BN, it is difficult to say if the prepared poorly crystalline sample has a single phase or multiple phases. Based

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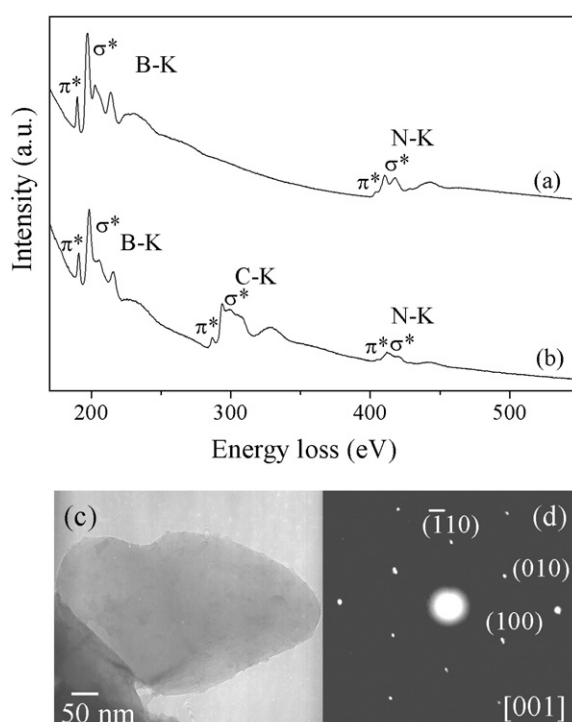
**Figure 1.** The XRD spectra of the B–C–N precursor (a) and the sample (b) prepared at 5.5 GPa and 1500 °C with the iron catalyst. The letters A and B label the two sets of peaks corresponding to the two different phases.

on the assumption that the sample is single phase, the determination of the lattice constants and compositions of the prepared samples just from the x-ray diffraction (XRD) may not be reliable. The measured properties of the hexagonal BCN are not very convincing, either. Thus, it is necessary to prepare highly crystalline hexagonal BC<sub>2</sub>N (h-BC<sub>2</sub>N) compound for determining its structure as well as its properties.

In this paper, we have reported the synthesis of a highly crystalline h-BC<sub>2</sub>N compound by the compression of a precursor (prepared by a chemical process) with iron catalyst at the high temperature of 1500 °C and the high pressure of 5.5 GPa. The structure and composition of the synthesized h-BC<sub>2</sub>N compound have been confirmed unambiguously by measurements of XRD, electron energy loss spectroscopy (EELS), transmission electron microscopy (TEM), and selected-area electron diffraction (SAED). The thermal expansion of the synthesized h-BC<sub>2</sub>N crystal has been investigated by high-temperature XRD.

Melamine and boric acid were used as the starting materials for the preparation of the B–C–N precursor. Melamine and boric acid in a weight ratio of 2:1 were first dissolved completely in boiling water, and the solution was then dried at 150 °C. Finally, the obtained white porous solid was annealed at 1500 °C for 30 min in a nitrogen gas flow. After cooling down to room temperature in the nitrogen atmosphere, the B–C–N precursor was obtained. Figure 1(a) shows the XRD spectrum for the B–C–N precursor. The observed three broad peaks are typical for the turbostratic structure, corresponding to the (002), (10 $l$ ) and (11 $l$ ) planes, respectively, as shown in figure 1(a).

The B–C–N precursor with the iron catalyst was compressed at the high temperature of 1500 °C and the high pressure of 5.5 GPa for 20 min. The recovered sample after the high-temperature and high-pressure (HTHP) treatment was washed by hot hydrochloric acid and distilled water sequentially, then was dried in a baker at 150 °C for 5 h. Figure 1(b) gives the XRD spectrum of the sample obtained after the HTHP treatment. Two distinct sets of diffraction peaks are observed, which is especially obvious in the high-angle range. In the low-angle range, after amplification of the peaks, as shown in the inset of figure 1(b), two peaks can be still observed clearly. The two distinct sets of peaks, as shown in figure 1(b), correspond to two different hexagonal phases, which are labelled as phase A and phase B, respectively, as shown in figure 1(b). The lattice constants of the two phases are determined to

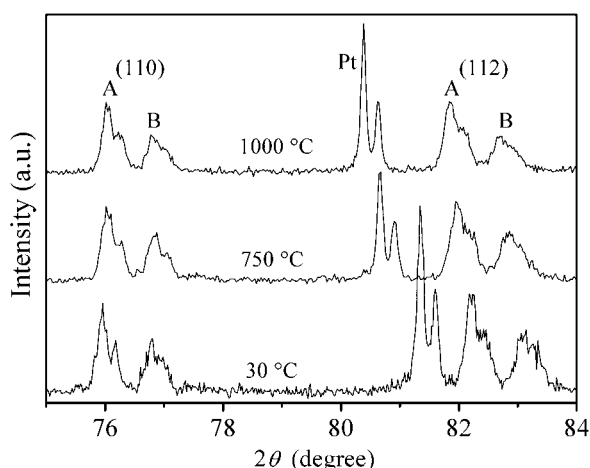


**Figure 2.** The typical EELS spectra for h-BN (a) and h-BC<sub>2</sub>N (b) particles in the sample prepared at 5.5 GPa and 1500 °C, the TEM image (c) and the SAED pattern (d) for a typical h-BC<sub>2</sub>N particle.

be  $a = 0.2504$  nm,  $c = 0.6661$  nm (phase A) and  $a = 0.2486$  nm,  $c = 0.6637$  nm (phase B) from the XRD data. The lattice constants of phase A are in good agreement with those of h-BN ( $a = 0.2504$  nm,  $c = 0.6656$  nm, ICDD card No.: 34-421). The lattice constant  $a$  of phase B lies between graphite ( $a = 0.2470$  nm,  $c = 0.6724$  nm, ICDD card No.: 41-1487) and h-BN, and the  $c$  value is smaller than those of graphite and h-BN. Thus, phase A should be the h-BN, and phase B is likely to be a hexagonal compound composed of boron, carbon and nitrogen elements.

In order to confirm unambiguously the structures and chemical compositions of the two hexagonal phases observed in the XRD spectrum, TEM and parallel EELS measurements have been performed on a series of synthesized crystalline particles selected randomly from the sample. After analyses of the EELS measurements, only two kinds of particles were observed among the investigated particles: one is found to be h-BN, and the other is h-BC<sub>2</sub>N, which are shown in figures 2(a) and (b). The TEM image and the SAED pattern for a typical h-BC<sub>2</sub>N crystalline particle are shown in figures 2(c) and (d), respectively. The TEM image displays a sheet-like morphology with a size of about 300–500 nm. In the SAED pattern, the sharp spots and their six-fold symmetric arrangement indicate that the particle is a single crystal with hexagonal structure. The  $d$ -spacing value calculated from the SAED pattern is consistent with that obtained from the XRD data.

From XRD, TEM, EELS and SAED measurements, it can be concluded unambiguously that the synthesized sample after the HTHP treatment is composed of the h-BC<sub>2</sub>N and h-BN phases. The in-plane lattice constant  $a = 0.2486$  nm of h-BC<sub>2</sub>N is comparable to the

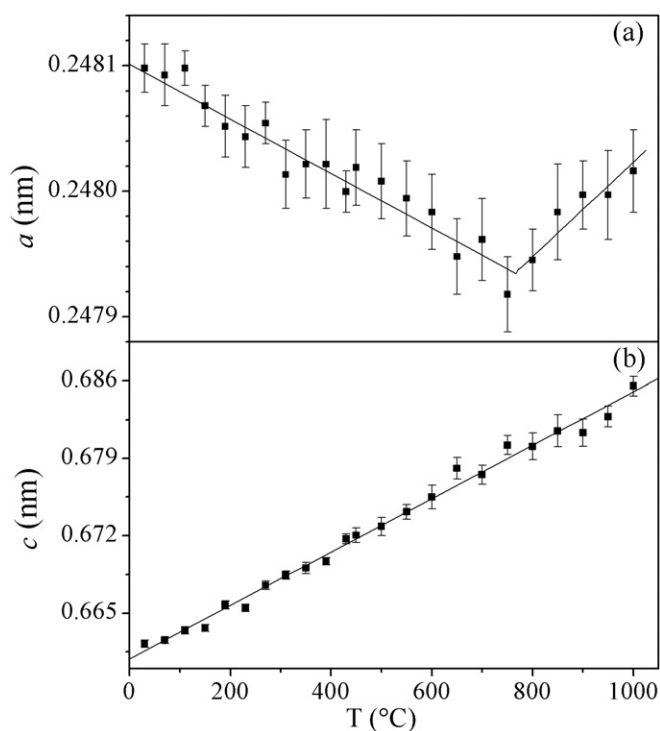


**Figure 3.** The high-temperature XRD spectra for the sample prepared at 5.5 GPa and 1500 °C with iron catalyst at three typical temperatures 30, 750 and 1000 °C. A and B represent the (110) and (112) peaks from the h-BN and h-BC<sub>2</sub>N compounds, respectively. The Pt peaks arise from the platinum holder.

previous experimental result ( $a = 0.2475$  nm) [16] and in good agreement with the average (0.2487 nm) of the values of graphite ( $a = 0.2470$  nm) and h-BN ( $a = 0.2504$  nm) expected from Vegard's law. However, the lattice constant  $c = 0.6637$  nm of the h-BC<sub>2</sub>N is smaller than those of graphite ( $c = 0.6724$  nm) and h-BN ( $c = 0.6656$  nm), and the previous experimental results for h-BC<sub>2</sub>N [4, 16, 17]. It does not follow Vegard's law, probably due to the different stacking model from those of graphite and h-BN. For our synthesized h-BC<sub>2</sub>N compound, it is crystallized much better than the previous ones, which is possibly the reason why our  $c$  value is smaller. The smaller interlayer distance also indicates that the synthesized h-BC<sub>2</sub>N compound is not a mechanical mixture of graphite and h-BN.

It is very difficult to synthesize the B–C–N phase with high purity. Generally, the synthesized sample is a mixture of the B–C–N phase and the h-BN (and/or graphite) phase. In the previous synthesis of the h-BC<sub>2</sub>N compound [18], it is hard to distinguish the B–C–N phase from a mixture of the B–C–N and h-BN (and/or graphite) phases in the XRD spectra, especially when the crystallization of the B–C–N phase is poor, because their diffraction peaks are broad and overlap with each other. However, in our synthesis of the h-BC<sub>2</sub>N compound after HTHP treatment with the assistance of iron, in spite of the existence of mixed h-BC<sub>2</sub>N and h-BN phases in our sample, the peaks corresponding to the two phases are separated completely in the XRD spectra, as shown in figure 1(b). Hence, this makes it possible to determine the thermal expansion of the h-BC<sub>2</sub>N compound using the high-temperature XRD diffraction.

Figure 3 shows the XRD spectra at three typical temperatures. With an increase in temperature, the peak positions corresponding to the (112) plane are shifted largely toward the low-angle range, while the peak positions corresponding to the (110) plane are shifted very slightly toward the high-angle range below 750 °C, but above 750 °C they are shifted very slightly toward the low-angle range, and the shift is much less obvious. The temperature-dependent lattice constants  $a$  and  $c$  for h-BC<sub>2</sub>N are determined from the XRD spectra, which are shown in figures 3(a), and (b). For the lattice constant  $a$  of h-BC<sub>2</sub>N, as shown in figure 4(a), the  $a$  dimension shows a slight linear contraction, with a contraction coefficient of  $-8.76 \times 10^{-7} \text{ K}^{-1}$ , up to the temperature 750 °C. However, above 750 °C, a linear expansion,



**Figure 4.** The temperature dependences of the lattice constants for the h-BC<sub>2</sub>N compound. The solid lines are fittings to the experimental data. (a) The  $a$  dimension shows a slight linear contraction up to a temperature of 750 °C and linear expansion above 750 °C. (b) In the  $c$  direction, h-BC<sub>2</sub>N presents a large linear expansion up to 1000 °C.

with an expansion coefficient of  $1.52 \times 10^{-6} \text{ K}^{-1}$ , is observed. As to the  $c$  direction, h-BC<sub>2</sub>N presents a large linear expansion up to 1000 °C. For h-BC<sub>2</sub>N, the  $c$  expansion coefficient is found to be  $35.86 \times 10^{-6} \text{ K}^{-1}$ . The thermal expansion behaviour of h-BC<sub>2</sub>N is similar to that of graphite, for which the  $a$  dimension shows a contraction below about 400 °C and an expansion above this temperature, while the  $c$  direction shows a large expansion [19].

Thermal contraction has been observed or anticipated in many materials, especially in low-dimensional solids. Some layered compounds [20–23] demonstrate complicated thermal expansion behaviour in the layer dimension. With an increase in temperature, the layer dimension shows a thermal contraction in the low-temperature range, while at high temperature it presents a thermal expansion. According to the well-known Grüneisen theory of thermal expansion, the thermal expansion behaviour of hexagonal layer crystal is concerned with the Grüneisen parameters  $\gamma_a$  (in the basal plane) and  $\gamma_c$  (perpendicular to the basal plane). For graphite-like layer crystals, the in-plane negative thermal expansion is attributed to the negative Grüneisen parameter  $\gamma_a$ , which is deduced from the transversal acoustic modes with atomic vibrations parallel to the  $c$  axis [20]. At low temperature, only the transversal acoustic modes (the lowest-frequency modes) will be first excited, which results in a lattice stretched in the  $c$  direction. Due to the Poisson effect, the bending of the plane sheet causes thermal contraction in the  $a$  dimension [20, 21]. With a temperature increase, high-frequency longitudinal and transverse modes with atomic vibrations in the plane will be excited, and then a positive Grüneisen parameter  $\gamma_a$  can be obtained, leading to thermal expansion in the  $a$  dimension.

Due to the strong covalent bonds within the basal layers and weak van der Waals coupling between the layers, the Poisson contraction in the  $c$  axis can be neglected when the basal plane expands. The Grüneisen parameter  $\gamma_c$  is typically positive and large, and then the thermal expansion coefficient in the  $c$  axis is positive and large in the entire temperature range.

In conclusion, a highly crystalline h-BC<sub>2</sub>N compound was obtained by the application of high temperature and high pressure (1500 °C, 5.5 GPa) to a turbostratic precursor (prepared by a chemical process) with iron catalyst. The lattice constants of h-BC<sub>2</sub>N are determined to be  $a = 0.2486$  nm and  $c = 0.6637$  nm. The measurement of the thermal expansion for h-BC<sub>2</sub>N has been performed using high-temperature x-ray diffraction. In the  $a$  dimension, a slight linear contraction up to a temperature of 750 °C and a linear expansion above this temperature up to 1000 °C have been observed. The contraction and expansion coefficients are found to be  $-8.76 \times 10^{-7} \text{ K}^{-1}$  and  $1.52 \times 10^{-6} \text{ K}^{-1}$ , respectively. In the  $c$  direction, the h-BC<sub>2</sub>N presents a large linear expansion up to 1000 °C, with an expansion coefficient of  $35.86 \times 10^{-6} \text{ K}^{-1}$ . The temperature dependence of the thermal expansion in the  $a$  dimension is determined from the Grüneisen parameter  $\gamma_a$ . In the low-temperature range, transversal acoustic modes (the lowest-frequency modes) are first excited and dominate, giving rise to the negative value of  $\gamma_a$  and then the thermal contraction in the  $a$  dimension, while in the high-temperature range, high-frequency longitudinal and transverse modes with atomic vibrations in the plane are excited, leading to a positive Grüneisen parameter  $\gamma_a$  and then the thermal expansion in the  $a$  dimension.

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