Synthesis and characterization of nanocrystalline hexagonal boron carbo-nitride under high temperature and high pressure

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Abstract

A study of the synthesis of hexagonal boron carbo-nitride (h-BCN) compounds via a two-step high-temperature and high-pressure (HTHP) technique using melamine ($C_3N_6H_6$) and boron oxide (B_2O_3) as raw materials is presented. An amorphous BCN precursor was prepared at 1000 K under vacuum in a resistance furnace and then single-phase h-BCN nanocrystalline was synthesized at 1600 K and 5.1 GPa in a multi-anvil apparatus. X-ray diffraction (XRD) and transmission electron microscopy (TEM) indicated that the final products were pure h-BCN crystals with the lattice constants $a = 0.2510$ nm and $c = 0.6690$ nm. The average grain size was about 150 nm. X-ray photoelectron spectroscopy (XPS) results confirmed the occurrence of bonding between C–C, C–N, C–B and N–B atoms. Raman scattering analysis suggested that there were three strong Raman bands centered at 1359, 1596 and 1617 cm^{-1}, respectively. The band at 1617 cm^{-1} was considered to be consistent with the characteristic Raman peak of h-BCN.

1. Introduction

Diamond and c-BN are two representative superhard materials with a wide range of potential applications. Although diamond possesses the highest hardness, it is neither stable in the presence of oxygen, even at moderate temperatures, nor a suitable abrasive for machining ferrous alloys. The hardness of c-BN is only half that of diamond in spite of its higher thermal stability. Thus, great efforts have been devoted to the preparation of a new material

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which combines the advantages of the hardness of diamond and the thermal stability of c-BN. Conceivably, such a material may be found in the BCN family. In 1989, Liu *et al* theoretically proposed three structural models of BCN with first-principle calculations [1]. According to their investigations, cubic BCN was claimed to be a new superhard material possessing those properties. Furthermore, it was suggested that cubic BCN could be produced from hexagonal BCN using high-pressure and high-temperature techniques, in similar ways to diamond and c-BN.

Several methods for preparing BCN have been reported. Nitrification of solid-phase precursors at relatively high temperatures [2] has been tried in earlier times. However, the main problem preventing the BCN films from being obtained by that technique is that it is difficult to control their compositions accurately. In recent years, research on BCN thin-film synthesis concentrated on a variety of CVD processes [3, 4]. This method can produce BCN films with almost perfect chemical compositions, but the deposition rates are often low and sometimes the contents of BCN in the whole film are not high. Solid-phase pyrolysis techniques have also made a definite contribution to the field. In addition, ball milling [5, 6] techniques, in all probability, seem to obtain interesting results with higher practical values.

In this work, nanocrystalline h-BCN was prepared by an HTHP technique. The product was characterized by XRD, TEM, XPS and Raman scattering spectra.

2. Experimental details

We used B_2O_3 as the B source, and melamine ($C_3H_6N_6$) as the source of C and N. Powders of B_2O_3 and $C_3H_6N_6$ were mixed thoroughly in a ball mill. The mixed powders were pressed into columns and placed into a quartz tube. In order to react fully and eliminate the superfluous H and O, the sample was heated to 1000 K, maintaining it for 2 h under vacuum condition. Thus we obtained the high-purity BCN precursor. The chemical reaction of the mixture could be written as

$$B_2O_3 + C_3H_6N_6 \rightarrow BCN + H_2O.$$
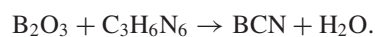
After the precursor underwent high-temperature high-pressure treatment at 5.1 GPa and 1600 K in a multi-anvil high-pressure apparatus for 20 min, the final product was obtained.

The structural analysis and bonding states of the samples were performed using XRD (Rigaku-Dmax-Ra, Cu Kα radiation $\lambda = 1.5418$ Å) and XPS (Thermo ECSALAB 250). The morphology and electron diffraction of the samples were carried out using TEM (HITACH H-8100). The vibrational properties of the samples were characterized by Raman scattering spectra (Renishaw spectroscopy).

3. Results and discussion

Figure 1(a) shows the XRD pattern of the BCN precursor prepared at 1000 K in the vacuum chamber. The XRD pattern exhibits characteristic peaks at 26.2°, 42.2°, 44.4° and 77.2°, respectively. However, the broadness of the peaks indicates that the precursor is, to some extent, in a disordered state. Figure 1(b) shows the XRD pattern of the final product obtained at 5.1 GPa and 1600 K. The behaviors of amorphous phases disappear and sharp peaks of well-crystallized crystals emerge. The characteristic peaks are at 26.7°, 41.6°, 43.9°, 50.2°, 55.2°, 75.9° and 82.2°, respectively. These results are in good agreement with the corresponding *d* values of h-BCN compound reported in the literature [7, 8]. Thus, this indicates that the BCN precursor experienced a transition from the amorphous phase to a single-phase highly crystalline h-BCN (PDF#351292) compound with lattice constants $a = 0.2510$ nm and $c = 0.6690$ nm.
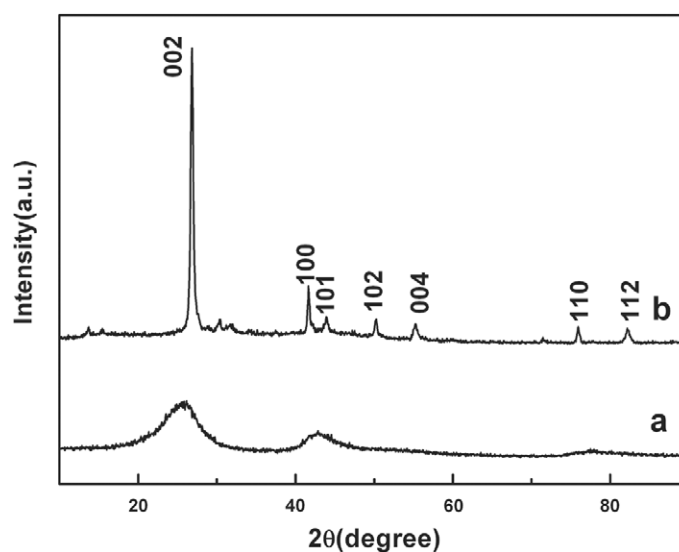
Figure 1. (a) XRD pattern of the B–C–N precursor; (b) XRD pattern of the precursor heat-treated under high pressure.

Table 1. XPS parameters of the sample.

Name	Start BE	Peak BE	End BE	FWHM (eV)	At.%
C 1s	290.7	284.68	282.35	1.94	36.91
N 1s	401.55	398.03	395.9	1.72	13.71
O 1s	537	533.2	529.05	2.92	12.08
B 1s	193.35	190.21	188.15	1.76	37.3

　　　Figure 2 shows the TEM morphology and the selected area electron diffraction (SAED) pattern of the final product. From figure 3, we can observe the morphology and size of the samples. The result indicates that most of these crystals are about 150 nm in size. We use selected area electron diffraction to measure and calculate the d values of the samples. The result is in good agreement with our XRD studies. Thus, this suggests that the samples are nanocrystalline h-BCN.

　　　In order to determine the bonding energy of the product, XPS analysis was carried out. The XPS analysis data of the samples are listed in table 1. This shows the full width at half-maximum (FWHM) and the atom ratio of the samples. Figure 3 shows the survey scan XPS spectrum. The XPS spectrum indicates the presence of B, C, N and a small amount of O due to the surface absorption and oxidation. Therefore, this suggests that the samples are pure BCN compounds.

　　　Figure 4 shows the deconvoluted B 1s, C 1s, N 1s and O ls spectra. As can be seen from figure 4(a), the full width at half-maximum (FWHM) spectrum is 1.76 eV and 0.92 eV for the B 1s and the BN, respectively [9]. The wide peak is evidence that there are at least two types of bonding for the B atoms. The deconvolution of the B 1s spectrum gives three peaks centered at 190.1, 191.2 and 193.1 eV, respectively. The peak at 191.3 eV is for h-BN. The chemical shift toward lower energy is ascribed to the contribution of B–C bonding, for the electro-negativity of C atoms is lower than that of N atoms. The bonding energy of B–C in $BC_{3,4}$ is 189.4 eV [9], implying that the 190.1 eV for our samples is for B–C bonding. However, 193.1 eV for B 1s is very close to that of B_2O_3 (194 eV), which may be due to electron radiation from the B 1s core
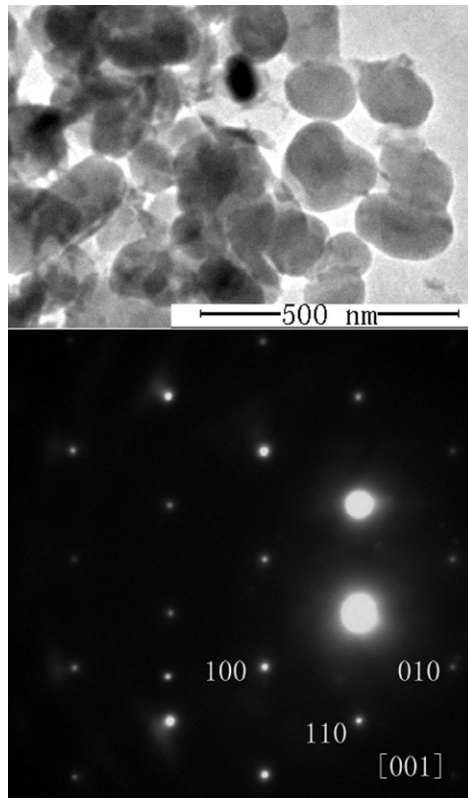
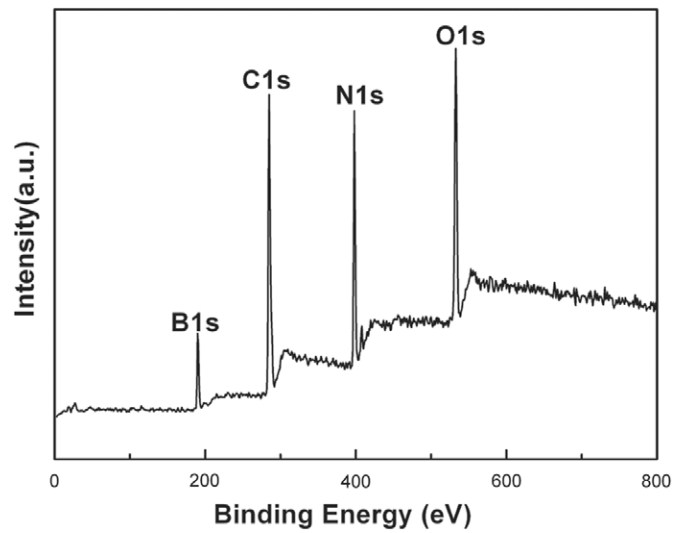**Figure 2.** TEM and SAED pattern of the hexagonal BCN.

Figure 3. XPS survey spectra of the sample.

level in B–O bonding. The small amount of B_2O_3 may be due to the fact that B is very easily oxidized, which is in accord with the above conclusions.
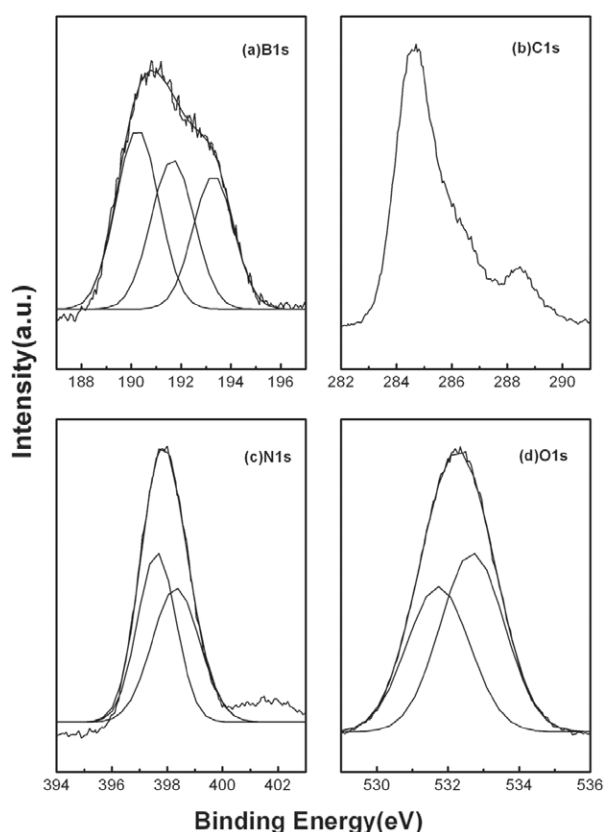
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Figure 4. B 1s (a), C 1s (b), N 1s (c) and O 1s (d) core-level XPS spectra and their deconvoluted components.

In figure 4(b), the deconvolution of the C 1s spectrum gives two peaks centered at 284.7 and 288.3 eV. The FWHM is 1.94 eV for C 1s and 0.35 eV for graphite powders [9]. Therefore, this suggests that there are at least two types of bonding for C atoms. The binding energy of C–C (285 eV) in graphite is used as the calibration standard. Another peak (288.3 eV) is very close to the C 1s of the C–N bond in many compounds [10], which may be due to the C 1s core-level electron radiation of the C–N bond.

In figure 4(c), the FWHM for N 1s is 1.72 eV, while that for BN powders is 0.88 eV [9]. The results of the deconvolution indicate that there are two types of N chemical states in the powders, and the peaks are centered at 397.6 and 398.3 eV. The N 1s peak of h-BN is 398.3 eV. The peak at 397.6 eV may be brought on by the N 1s core-level electron radiation of the B–C–N bond.

In figure 4(d), the FWHM for O 1s is 2.22 eV. The deconvolution of the O 1s gives a peak at 532.4 eV. The peak is very close to the O 1s peak of B_2O_3. So, it may be due to the existence of a small amount of B_2O_3, which is in accord with the above XPS spectra of B 1s.

Figure 5 shows that the Raman scattering bands of the BCN samples are at 1359, 1596 and 1617 cm^{-1}. In order to confirm the bonding of B–C, C–C, B–N and N–C in the high-pressure product, the Raman scattering spectra are compared with those of pure graphite and h-BN. The peak at 1359 cm^{-1} is in accord with that of h-BN, implying that there is a B–N bond in the sample. Also, the peak at 1596 cm^{-1} is similar to that of graphite (1588 cm^{-1}), showing the existence of a C–C bond. There is no Raman peak at 1617 cm^{-1} in pure graphite and h-BN.
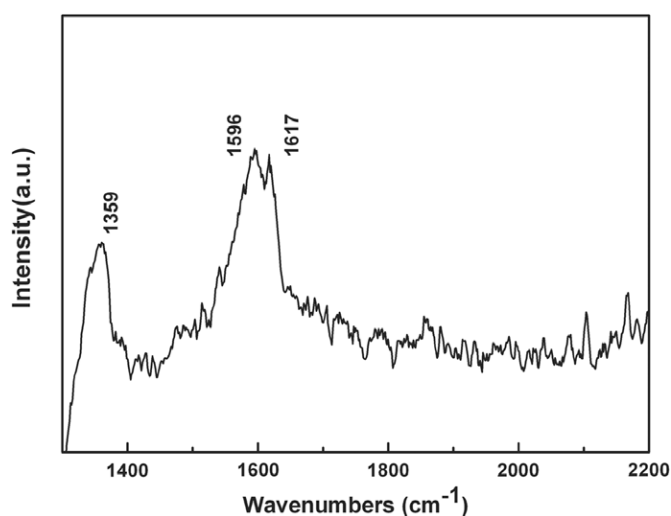
Figure 5. Raman spectra of the sample.

It has been reported [8] that an increase in the degree of doping causes the peak for graphite at 1580 cm^{-1} to shift towards higher wavenumber. Thus, the Raman peak at 1617 cm^{-1} is considered to be the characteristic peak of h-BCN compound. From the above investigations and analyses, the Raman peak at 1617 cm^{-1} is an important symbol for the formation of h-BCN.

4. Conclusion

An amorphous BCN precursor has been synthesized by chemical reaction at 1000 K under vacuum using $C_3N_6H_6$ and B_2O_3 as raw materials. The BCN precursor experienced a transition from the amorphous state to single-phase nanocrystalline h-BCN after annealing at 1600 K and 5.1 GPa for 20 min. It was determined that the lattice constants of the h-BCN are $a = 0.2510$ nm and $c = 0.6690$ nm. XPS analysis indicates that there are C–N, C–B, B–N, C–C and C–B–N bonds in the final product. Raman scattering peaks of the BCN samples appear at about 1359, 1596 and 1617 cm^{-1}, respectively. Furthermore, the Raman peak at 1617 cm^{-1} is considered to be the characteristic peak and an important symbol for the formation of h-BCN.

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