

## B<sub>2</sub>CN COMPOUNDS PREPARED BY HIGH PRESSURE AND TEMPERATURE

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The B-C-N precursor was prepared by using boric acid and melamine as starting materials. The precursor powder and catalyst were mixed uniformly, and then loaded into a graphite capsule. The experiment was conducted at a pressure of 5.5 GPa and temperature of 1600°C for 15 min. The synthesized products are of different crystal structures when different catalysts were used. B-C-N compounds synthesized by using Ni and Fe catalysts are of hexagonal structure, but they have different lattice parameters. Using Ca<sub>3</sub>B<sub>2</sub>N<sub>4</sub> catalyst, the orthorhombic B<sub>2</sub>CN was obtained. The X-ray photoelectron spectra of the B-C-N compound indicate the presence of B-N, C-N, C-C, and B-C bonds, which suggests that boron, carbon, and nitrogen atoms all bond with one another. We found that B<sub>2</sub>CN compounds with different structures show different photoluminescence properties.

### 1. Introduction

The search of metastable phases in ternary B-C-N system is interesting from both a basic and a technological standpoint. On the one hand, the study of structures with hardness close or even higher than diamond is driven by scientific curiosity. On the other hand, there is a constant search for advanced materials capable of withstanding the technological requirements. Many researchers have speculated that alloys or compounds containing all three elements should be possible based on the similar sizes of atoms. The similarities of crystal structures between graphite and hexagonal boron nitride (h-BN) and also between diamond and cubic boron nitride (cBN) suggest the possibility of forming a solid solution or a new compound with these materials. Liu et al. [1] and Lambrecht et al. [2] calculated theoretically the electronic structure of the hexagonal BC<sub>2</sub>N and the cubic (BN)<sub>x</sub>C<sub>2(1-x)</sub> system.

Many attempts to synthesize B-C-N ternary phase have been made by chemical vapor deposition (CVD) [7-9], physical vapor deposition (PVD) [10-12], precursor pyrolysis [13, 14], and arc-discharge methods [15-17]. In most cases, it has been reported that only turbostratic B-C-N were obtained. Several studies attempting to synthesize cubic boron carbon nitride have employed high temperature-high pressure techniques [2-6]. The segregation into diamond and cubic boron nitride was observed, indicating that this phase is immiscible at equilibrium. Its synthesis will require a technique far removed from equilibrium. For example, Yao [19] et al. found a new tetragonal B-C-N crystal produced by annealing the amorphous BCN powders

under 4 GPa above 880 K. Using high-pressure and high-temperature methods, several efforts have been made [1-3, 14-17] to synthesize cubic B-C-N phases.

The ratio of B to N so far in both theoretical predicted and most synthesized B-C-N compounds is close to 1. When the ratio is far departed from 1, some new metastable BCN crystals might exist in the ternary B-C-N system.

In the present work, characterization on the B<sub>2</sub>CN crystals was performed to investigate the crystal structure and chemical bonding. The analysis was based on several characterization techniques. The surface morphology and internal structures were examined by scanning electron microscopy and transmission electron microscopy, respectively. Finally, micro-Raman spectroscopy was used to study the crystal quality and doping of the diamond particles.

### 2. Experimental

The B<sub>2</sub>CN precursor was prepared by a chemical method described in our previous work. The mixture of precursor powder and catalyst (Ca<sub>3</sub>B<sub>2</sub>N<sub>4</sub>, Ni or Fe) was pressed into a pellet, and then loaded into a graphite capsule. The experiment was performed at approximately 5.5 GPa and temperature of 1600°C for 15 min. The recovered sample was boiled in a solution of H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub> to remove the catalyst and clinging graphite.

The structural analyses of the samples were performed by an X-ray diffraction (XRD) with Cu K<sub>α</sub> radiation and by transmission electron microscopy (TEM, Hitachi H-9000). Fourier-transform infrared spectroscopy and X-ray photoelectron spectroscopy (XPS) were

employed to investigate the chemical bonding, especially in the characterization of the chemical bonding of the B<sub>2</sub>CN compounds. The

photoluminescence (PL) spectrum of the B-C-N powders was excited by a radiation of 302 nm wavelength from a xenon arc lamp.

Table I

Diffraction angles 2θ, interplanar spacings, and Miller indices for the orthorhombic B<sub>2</sub>CN phase

No	2θ	sin <sup>2</sup> θ	sin <sup>2</sup> θ <sub>i</sub> /sin <sup>2</sup> θ <sub>1</sub>	d (nm)	h	k	l	I(%)
1	18.60	0.0261	1	0.47665	1	0	0	4
2	26.68	0.0532	2	0.33385	1	1	0	100
3	30.92			0.28897	1	0	1	<1
4	31.14			0.28698	0	1	1	<1
5	36.54			0.24571	1	1	1	1
6	37.44	0.1030	4	0.24001	2	2	0	1
7	42.48	0.1312	5	0.21262	2	1	1	1
8	43.76			0.20670	1	2	0	1
9	45.74			0.19820	2	0	1	<1
10	50.04			0.18213	0	0	2	1
11	54.60			0.16794	0	1	2	1
12	55.02	0.2104	8	0.16671	2	2	2	11
13	57.38			0.16045	1	1	2	<1
14	61.72	0.2631	10	0.15017	3	1	1	1
15	64.88			0.14360	3	0	1	1
16	64.88			0.14037	0	3	1	1
17	69.82			0.13459	2	1	3	<1
18	73.94			0.12808	2	3	0	<1
19	77.84			0.12261	2	2	2	<1
20	79.10			0.12097	0	0	3	<1
21	80.98			0.11863	4	0	0	<1
22	82.08			0.11731	1	0	3	<1
23	84.08			0.11503	3	1	2	<1
24	84.78			0.11425	1	3	2	<1
25	86.98	0.4736	18	0.11192	3	3	3	<1
26	87.84			0.11104	4	0	1	1
27	90.46			0.10850	4	1	1	<1
28	93.02			0.10617	3	2	2	<1
29	95.16			0.10434	4	2	0	<1
30	95.56			0.10320	2	4	0	<1
31	116.82			0.09043	0	0	4	1

### 3. Results and Discussion

Different structures of B<sub>2</sub>CN crystals can be obtained by the HP/HT treatment when different catalysts are used. The three B<sub>2</sub>CN crystals obtained by same precursor under 5.5 GPa and 1600°C show different morphologies. Fig.1 shows the scanning electron micrograph (SEM) images of the B<sub>2</sub>CN compounds.

X-ray diffraction (XRD) spectra of the three B<sub>2</sub>CN crystals synthesized using different catalysts are shown in Fig.2. In order to determine their crystal structures, we performed selected area electron diffraction (SAD) for the three B-C-N powders. We calculated the series of d spacings and angles. The results calculated

from XRD data and the SAD patterns indicate that hexagonal B<sub>2</sub>CN crystals were prepared using Fe or Ni catalysts, but they have different lattice parameters. The lattice parameters of hexagonal B<sub>2</sub>CN(I) (using Fe catalyst) are: a=0.442 nm, c=0.670 nm; and those for hexagonal B<sub>2</sub>CN(II) (using Ni catalyst) are a=0.238 nm, c=0.335nm. The orthorhombic B<sub>2</sub>CN crystal can be obtained when Ca<sub>3</sub>B<sub>2</sub>N<sub>4</sub> catalyst was used. Its lattice parameters are a=0.4776 nm, b=0.4585 nm and c=0.3629 nm.

X-ray photoelectron spectroscopy and infrared spectra are the two common means for characterization of the chemical bond states of the B-C-N powders.



Fig. 1. Morphologies of  $B_2CN$  crystals synthesized by turbostratic  $B_2CN$  precursor and (a) Ni, (b) Fe, (c)  $Ca_3B_2N_4$  catalysts after HPHT treatment at 5.5GPa, 1600°C for 15 min

There is not significant different among the spectra of the three  $BC_2N$  crystals. Fig.3 shows the XPS spectra of B 1s, N 1s and C 1s for a

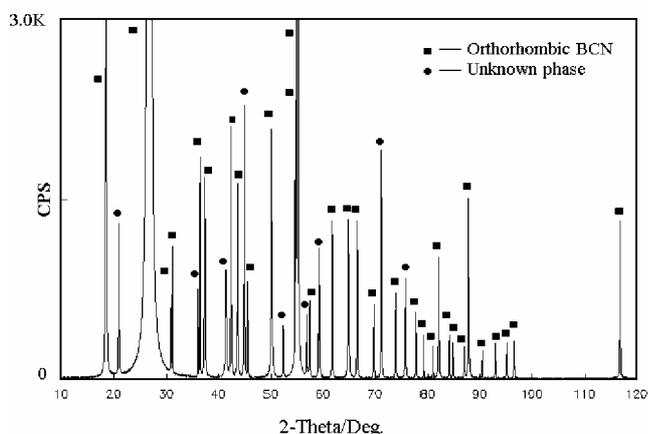
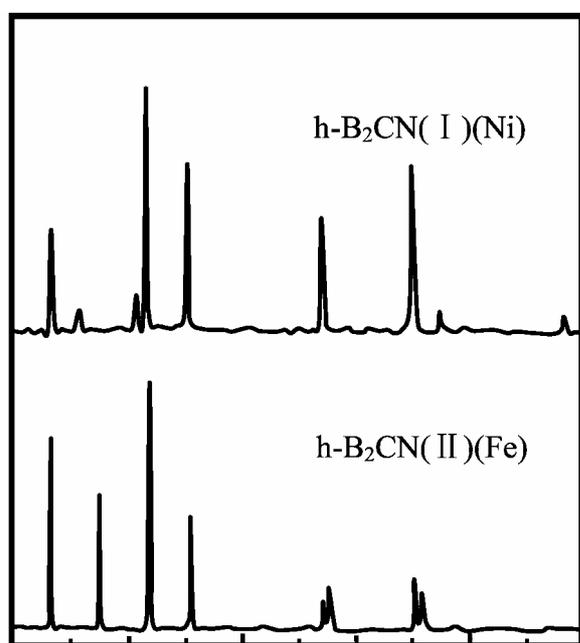


Fig. 2. X-ray diffraction (XRD) patterns of the three  $B_2CN$  crystals synthesized using different catalysts

typical  $B_2CN$  sample. It can be seen that the binding energies of B 1s, N 1s and C 1s are 190.3, 398.4 and 284.4 eV, respectively. The results are consistent with the reported data: 189.5, 398.7 and 284.4 eV [15]. The full width at half maximum FWHM of B 1s, N 1s and C 1s peaks are 2.5, 2.4 and 3.8 eV, respectively. The broad FWHM suggests that there is more than one type of bonding scheme for B, C and N atoms. As shown in Fig.3a, the deconvolution of B 1s spectrum gives two peaks centered at 190.0 and 191.0 eV. It was reported that the binding energies of B 1s are 188.4 eV and 189.4 eV for  $BC_4$  and  $BC_{3,4}$ , respectively [16], and 191.0 eV for h-BN [17]. Therefore, the resolved two peaks of the B 1s spectrum can be attributed to B-C and B-N bonding. In Fig.3b, the results of the deconvolution show the presence of three types of N chemical states, centered at 397.3, 398.2 and 399.4 eV. They can be reasonably assigned to the C-B-N, N-B and N-C bonding [17,18]. The deconvolution of the C 1s spectrum gives also three peaks centered at 283.6, 284.4 and 285.7 eV. The deconvolution peaks possibly result from the contribution of C-B-N, C-C and C-N bonding.

The XPS spectra of the B-C-N powder indicate the presence of B-N, C-N, C-C, B-C bonds, which suggests that all boron, carbon, and nitrogen atoms bond with one another and that the B-C-N crystal is a compound in which the three kinds of atoms are mixed atomically.

Watanabe et al. examined the band gap of a layered  $BC_2N$  compound by means of scanning tunnel microscopy (STM). They indicate that the layered  $BC_2N$  is a semiconductor with a band gap of about 2 eV. Figure 4 show the typical PL spectra of the orthorhombic (a) and hexagonal (b)  $B_2CN$  powders measured at room temperature. The PL peak energy of the orthorhombic  $B_2CN$  centered

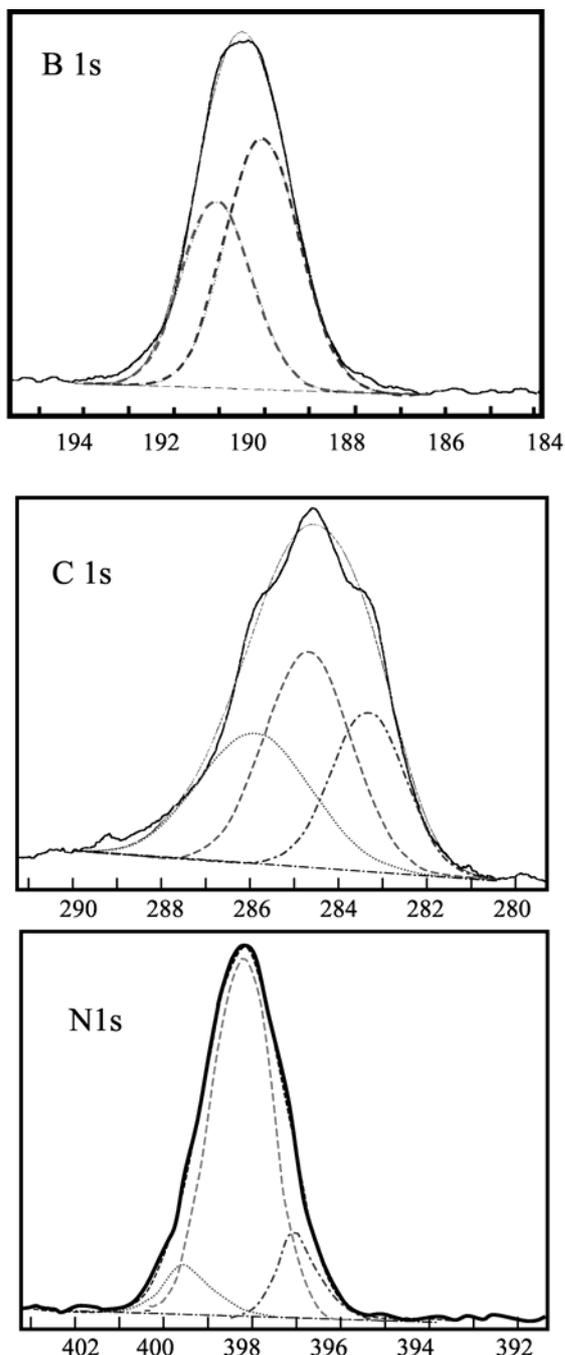


Fig.3. XPS spectra of B 1s, N 1s and C 1s for a typical B<sub>2</sub>CN sample

at 374 nm (Fig.4a), corresponding to 3.2 eV, is similar to that of wurtzite-GaN [20]. There are five peaks in the PL spectra of hexagonal B<sub>2</sub>CN synthesized with Fe catalyst (Fig.4b). The three main peaks centered from 361 to 410 nm show a broaden luminescence area of this material. In addition, the result indicates that the crystal

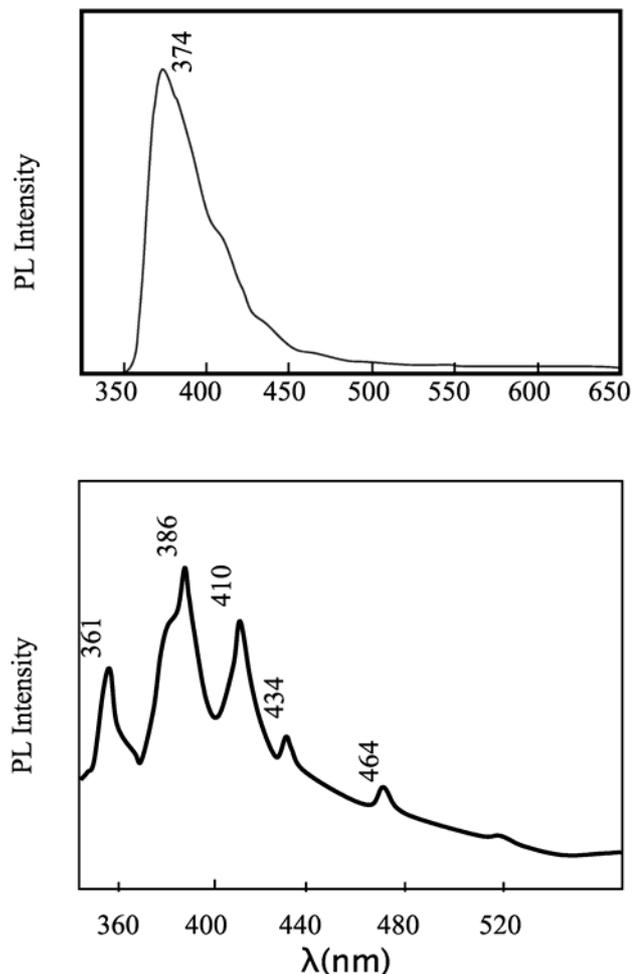


Fig.4. Room temperature photoluminescence spectra of the orthorhombic B<sub>2</sub>CN powders (a) and hexagonal B<sub>2</sub>CN powders (b)

structure and composition of B-C-N compounds have great effects on their PL properties.

#### 4. Conclusion

The synthesized products were characterized by X-ray diffraction and selected area electron diffraction. The lattice parameters of hexagonal B<sub>2</sub>CN(I) are:  $a=0.442$  nm,  $c=0.670$  nm; those for hexagonal B<sub>2</sub>CN(II) are  $a=0.238$  nm,  $c=0.335$ nm; And those for orthorhombic B<sub>2</sub>CN crystal are  $a=0.4776$  nm,  $b=0.4585$  nm and  $c=0.3629$  nm.

The X-ray photoelectron spectra of the B-C-N compound indicate the presence of B-N, C-N, C-C, and B-C bonds, which suggests that boron, carbon, and nitrogen atoms all bond with one another and that the B-C-N crystal is a compound in which the three kinds of atoms are mixed atomically.

The photoluminescence spectrum of hexagonal B-C-N powder measured at room temperature features a broad peak centered at 374 nm, corresponding to the band-edge emission of h-B-C-N, and is similar to that of w-GaN.

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