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Synthesis of Cubic Boron Nitride at Low-Temperature and Low-Pressure Conditions

X. P. Hao,[†] D. L. Cui,*[,†] G. X. Shi,[†] Y. Q. Yin,[†] X. G. Xu,[†] J. Y. Wang,[†] M. H. Jiang,[†] X. W. Xu,[‡] Y. P. Li,[‡] and B. Q. Sun[§]

State Key Laboratory of Crystal Materials, Shandong University, Jinan 250100, People's Republic of China, Department of Inorganic Nonmetal Materials, Beijing Science and Technology University, Beijing 100083, People's Republic of China, and Key Laboratory of Semiconductor Superlattice Materials, Institute of Semiconductors, Chinese Academy of Science, Beijing 100800, People's Republic of China

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Introduction. Cubic boron nitride has been investigated extensively by many researchers because it is an important material that is widely used in cutting tools, grinding, and abrasive materials because of its supreme hardness, high thermal conductivity, and high-temperature stability.[1−5] Usually, cubic BN (cBN) is obtained from the conversion of hBN to cBN at high temperature (1200−2000 °C) and high pressure (2.5−7.5 GPa) in the presence of catalyst or solvent.[6] In addition, other methods have also been developed to prepare BN. Tadashi Endo et al.[7] obtained cBN by pyrolyzing $Ca_3B_2N_4$ at high pressure (4.4−6.5 GPa) and high temperature (1180−1800 °C). Hirano et al.[8] synthesized cBN at 1800 °C and 6.5 Gpa. On the basis of the theoretical calculation, V. L. Solozhenko[9] has proposed that the cubic phase of BN is stable at low temperature ($<$1300 K) and low pressure ($<$2 GPa). But this conclusion is challenged by many researchers. Our experimental results reported in this paper directly support this conclusion.

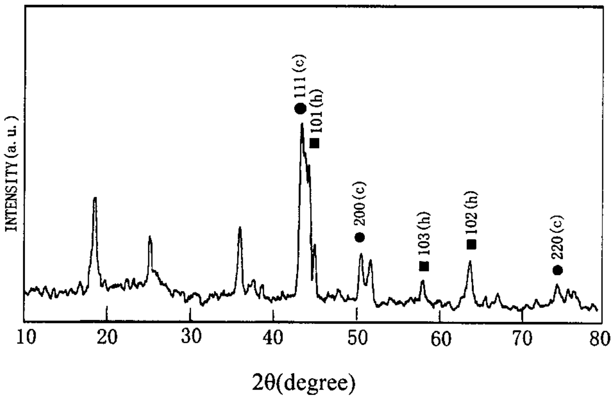

Figure 1. XRD pattern of BN nanocrystals synthesized at 480 °C.

On the other hand, there are few papers reported on the synthesis of BN nanocrystals. Hu et al.[10] prepared BN nanocrystals at 650 °C and 22 MPa. But the reaction

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* To whom correspondence should be addressed. Fax: 86-531-8564260. E-mail: dlcui@icm.sdu.edu.cn.

[†] Shandong University.

[‡] Beijing Science and Technology University.

[§] Chinese Academy of Science.

(1) Laurence, V.; Gerard, D.; Etoureau *J. Mater. Sci. Eng.* **1991**, *B10*, 149.

(2) Liouu, S. S.; Worrel, W. L. *Appl. Phys.* **1989**, *A49*, 25.

(3) Gameza, L. M.; Shipilo, V. B.; Savchuk, V. A. *Phys. Stat. Sol. (B)* **1996**, *198*, 559.

(4) Milan, H.; Tadao S. *J. Mater. Sci.* **1997**, *32*, 3293.

(5) Matsui, Y. *J. Cryst. Growth* **1984**, *66*, 243.

(6) Rao, L.; Kaner, R. B. *Inorg. Chem.* **1994**, *33*, 3210.

(7) Endo, T.; Fukunga O.; Iwata, M. *J. Mater. Sci.* **1981**, *16*, 2227.

(8) Hirano, S.; Yogo, T.; Asada, S.; Naka, S. *J. Am. Ceram. Soc.* **1989**, *72*, 68.

(9) Solozhenko, V. L. *Diamond Relat. Mater.* **1994**, *4*, 1.

(10) Hu, J. Q.; Lu, Q. Y.; Tang, K. B.; Yu, S. H.; Qian, Y. T.; Zhou, G. E.; Liu, X. M.; Wu, J. X. *J. Solid State Chem.* **1999**, *148*, 325.

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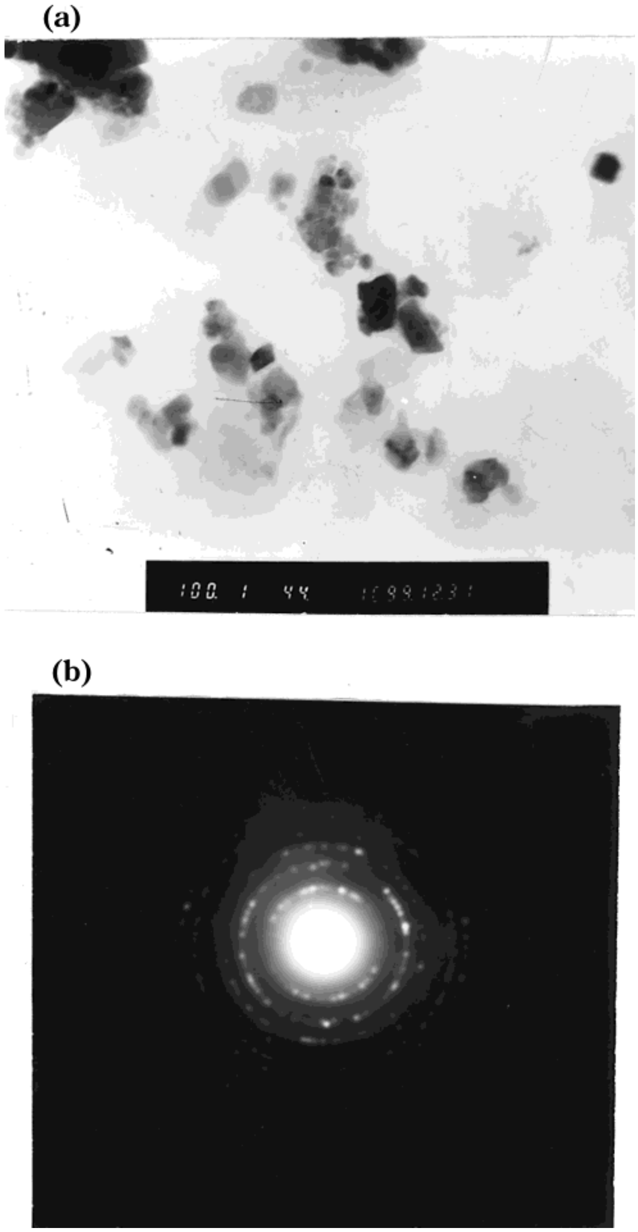

Figure 2. Morphology (a) and electron diffraction patterns (b) of cBN prepared at 480 °C.

temperature is too high and a large amount of hydrogen is produced during the reaction process. These disadvantages make this method have almost no value in application.

Here, we have obtained a BN nanocrystals sample with cubic BN phase as the dominant phase at low temperature and low pressure for the first time.

Experimental Section. BN nanocrystals were synthesized in an autoclave with benzene as solvent. The reaction may be expressed as

$$BBr_3 + Li_3N = BN + 3LiBr$$

The experimental procedures were as follows: first, BBr_3 was dissolved into benzene and then Li_3N powder was added to the solution and stirred simultaneously for 30 min. Finally, the mixed solution was transferred into a stainless steel autoclave and sealed. The whole manipulation process was carried out in a N_2-flowing glovebox. The reaction temperature was 480 °C and reaction time was 8−12 h. When the reaction finished, the resultant product was filtered with water and then dried in a vacuum at 80 °C for 2−3 h.

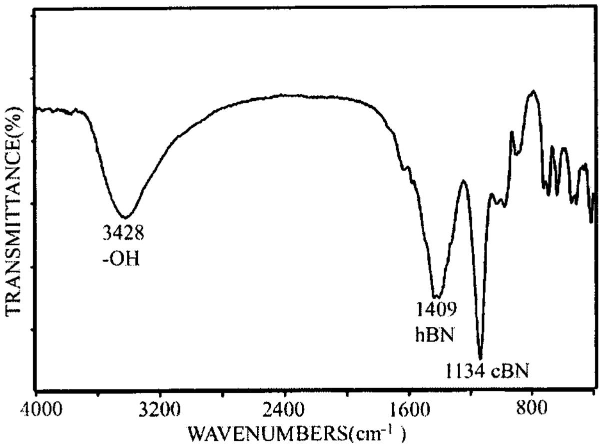

Figure 3. FTIR spectra of BN nanocrystals. The broadening of the peaks at 1409 and 1134 cm^{-1} can be explained as follows: the amount of dangling bonds at the surface of BN nanocrystals increased rapidly with the decrease of BN particles size. As a result, instead of a single vibration mode in BN nanocrystals, there did exist a very wide region distribution of the vibration modes.

X-ray powder diffraction pattern was obtained on a Rigaku D max-γ A X-ray diffractometer with Ni-filtered Cu Kα radiation ($V = 50$ kV, $I = 100$ mA) with a scanning speed of 4°/min. Fourier transformation infrared spectroscopy (FTIR) measurement was carried out using a Nicolet FTIR760 infrared spectrometer. BN nanocrystals were mixed with KBr and ground thoroughly, and then they were pressed into pellets for characterization. The morphology of nanocrystalline BN was observed with a Hitachi H-800 transmission electron microscopy (TEM). The accelerating voltage was 200 kV and the magnification ratio was 150 K. XPS measurement was carried out on an ESCALAB 2200-XL X-ray photoelectron spectrometer for the surface elemental analysis of BN nanocrystlas. The X-ray source is Al Kα radiation, and the measurement was carried out in a vacuum of $1-3 \times 10^{-8}$ Torr.

Results and Discussion. Figure 1 shows the X-ray diffraction pattern of BN nanocrystals synthesized at 480 °C. All reflections marked with dots can be indexed as cBN with a lattice constant $a = 3.606$ Å, which is close to the reported data ($a = 3.6162$ Å).[11] The reflections marked with squares can be indexed as hBN with lattice constants $a = 2.4967$ and $c = 6.6342$, which are near the reported values ($a = 2.5044$ and $c = 6.6562$).[12] The other reflections can be indexed as the oBN[13] (orthorhombic phase prepared by shock-wave compression, with $a = 0.86$ nm, $b = 0.774$ nm, and $c = 6.35$ nm). No impurities such as B_2O_3 were detected by the XRD. The broadening nature of the XRD peaks indicates that the grain size of the samples are on a nanometer scale. The full width at half-maximum (FWHM) of the (111) peak of cBN is 0.6°, and the average size of the particles can be estimated from the Scherrer equation to be about 25 nm.

$$D_{hkl} = k\lambda/\beta_{hkl}{}^{*}\cos\theta_{hkl}$$

where D_{hkl} is the particle size perpendicular to the

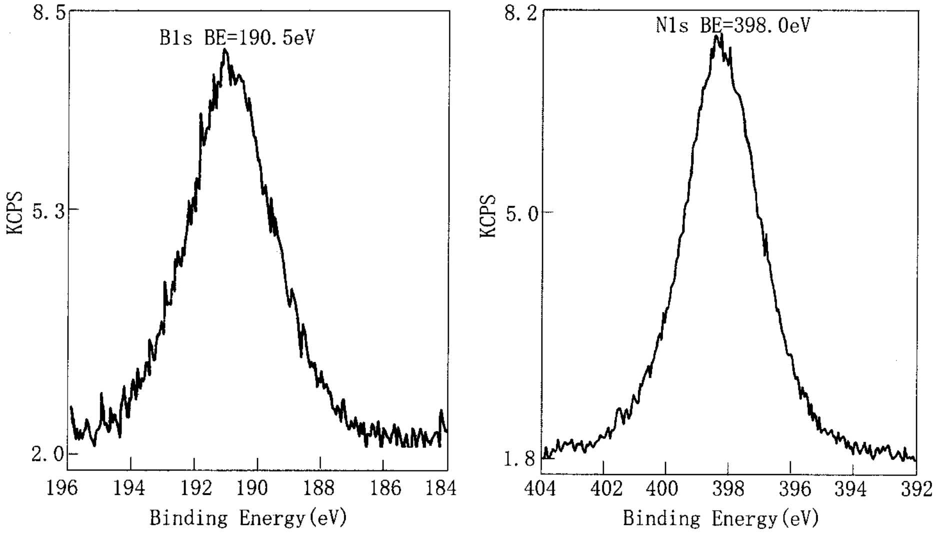

Figure 4. XPS spectrum of BN nanocrystals.

normal line of (*hkl*) plane, *k* is a constant (it is 0.9), β_{hkl} is the full width at half-maximum of the (*hkl*) diffraction peak, θ_{hkl} is the Bragg angle of (*hkl*) peak, and λ is the wavelength of X-ray.

Figure 2a shows the morphology of some cBN nanocrystals synthesized at 480 °C. It can be seen obviously that many particles are in nearly cuboidal shape and the average size is about 30 nm. The selected-area electron diffraction pattern of this sample is shown in Figure 2b. The innermost ring corresponds to the (111) diffraction of cBN, and the *d* value deducted from this figure agreed well with that of the XRD pattern, so it can be indexed as cBN.

FTIR was used to distinguish the sp^2 hexagonal and sp^3 cubic phase. Figure 3 shows the FTIR spectra of the sample. The peaks located at 1403 cm^{-1} can be attributed to hexagonal BN, while the one at 1134 cm^{-1} to cubic BN.[14] The peak at 3428 cm^{-1} can be attributed to the moisture absorbed on the surface of the BN nanocrystals. From the fact that the absorption peaks at 1403 cm^{-1} are much broader than those at 1134 cm^{-1}, we can come to such a conclusion that there are fewer hBN than cBN. Besides, they are all strong, and this means that the hexagonal BN and cubic BN are the dominant phases in the sample.

The XPS analysis of the sample is shown in Figure 4. The quantitative analysis of the B_{1s} and N_{1s} peaks indicates that the ratio of B to N is near 1.1:1, from which we can conclude that the sample is BN.

Conclusion. In conclusion, cBN nanocrystals have been successfully prepared by the benzene thermal synthesis method using BBr_3 and Li_3N as the reactants at a temperature of 480 °C, and the cubic BN is the dominant phase. The temperature is much lower than that of previous routes. The lattice constant of cBN with $a = 3.606$ Å are consistence with those in the literature.

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(11) JCPDS. No. 25−1032.

(12) JCPDS. No. 34−421.

(13) Gasgnier, M.; Szwarc, H.; Ribez, A. *J. Mater. Sci.* **2000**, *35*, 3003.

(14) Mirkarimi, P. B.; McCarty, K. F.; Medlin, D. *Mater. Sci. Eng.* **1997**, *R21* (2), 47.