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Synthesis and Characterization of Nanocrystalline Boron Nitride

Jun-Qing Hu, Qing-Yi Lu, Kai-Bin Tang,[1] Shu-Hong Yu, Yi-Tai Qian,[1] Gui-En Zhou, Xian-Ming Liu, and Jian-Xin Wu

Structure Research Laboratory and Department of Chemistry, University of Science and Technology of China, Hefei, 230026, P.R. China

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Nanocrystalline boron nitride (BN) with a whisker-like morphology has been synthesized from the reaction of KBH_4 and NH_4Cl at a temperature of 650°C and a pressure of about 22 MPa. The pressure is much lower than that of previous routes and the yield of nanocrystalline BN reached 70%. X-ray powder diffraction pattern indicated the coexistence of two structures of BN: hexagonal and cubic. Fourier transformation infrared spectroscopy was used to distinguish the sp^2-bonded hexagonal and sp^3-bonded cubic phase. X-ray photoelectron spectra analysis gave the average composition of $B_{1.01}N$. © 1999 Academic Press

Key Words: **nanocrystalline; boron nitride; synthesis; characterization.**

INTRODUCTION

Boron nitride, BN, is an important material due to its high temperature stability, low dielectric constant, large thermal conductivity, high mechanical strength, hardness, corrosion resistance, and oxidation resistance. It has great potential applications in refractory, lubricants, electrical insulators, cutting tools, grinding, and abrasive materials (1–4).

Traditionally, hexagonal BN (hBN) has been prepared by the classical high-temperature synthesis routes (5), such as the direct combination of boron with nitrogen (6) (>1200°C) and carbothermic reduction of boric oxide (>1800°C) (7, 8). Usually, cubic BN (cBN) is obtained from the conversion of hBN to cBN at high pressures (2.5–7.5 GPa) and high temperatures (1200–2000°C) in the presence of a catalyst or solvent (9–11). In addition, other methods have been developed to prepare BN. Hirano *et al.* (12) pyrolyzed $(HBNH)_3$ at constant pressure (100 MPa) and 250–700°C and obtained cBN by the resulting pyrolysis at 1800°C and 6.5 GPa. Yogo *et al.* (13) reported that pyrolysis of an adduct $Al(BH_4)_3 \cdot 4NH_3$ at 600°C and <5.0 GPa led to a mixture of hBN and AlN, and that cBN was formed at 900–1000°C and 5–7 GPa. Recently, Rao *et al.* (14) and Solozhenko *et al.* (15) selected a self-propagating route to obtain mainly crystalline hBN powders from the reaction of MBF_4 (M = K, Na), Li_3N, and NaN_3. Prior to our work, solid state reactions of MBH_4 (M = K, Na) and NH_4Cl at 750–1000°C under nitrogen were also reported; however, these routes only produced amorphous or rhombohedral BN rather than crystalline hBN or cBN (16, 17).

Herein, the coexistence of nanocrystalline hBN and cBN via the reaction of KBH_4 and NH_4Cl at a temperature of 650°C and a pressure of 22 MPa is reported. The synthetic reaction was carried out in an autoclave and can be represented by

$$KBH_4 + NH_4Cl \rightarrow BN + KCl + 4H_2. \quad [1]$$

EXPERIMENTAL

All manipulations were carried out in an N_2-flowing glove box. In a typical experiment procedure, analytical grade KBH_4 (0.02 mol) and excess NH_4Cl (0.05 mol) were put into a titanium alloy autoclave of 50 ml capacity. The autoclave was sealed and maintained at 650°C for 2 h and then allowed to cool to room temperature in furnace. The product was collected and washed with distilled water several times and dried in vacuum at 100°C for 1 h. White powders were obtained.

X-ray powder diffraction (XRD) pattern was carried out on a Rigaku Dmax-γA X-ray diffractometer with Cu$K\alpha$ radiation (λ = 1.54178 Å). The morphology of nanocrystalline BN was observed from transmission electron microscopy (TEM) images taken with a Hitachi H-800 transmission electron microscope. Fourier transformation infrared spectroscopy (FTIR) spectra were obtained using a Shimadzu IR-400 spectrometer by using the KBr pressed disks. X-ray photoelectron spectra (XPS) were recorded on a VGESCALAB MKII X-ray photoelectron spectrometer, using nonmonochromatized Mg$K\alpha$ X rays as the excitation source. *Caution*: The synthetic reaction produces large quantities of H_2. A high overpressure resistant autoclave

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[1] To whom all correspondence should be addressed.

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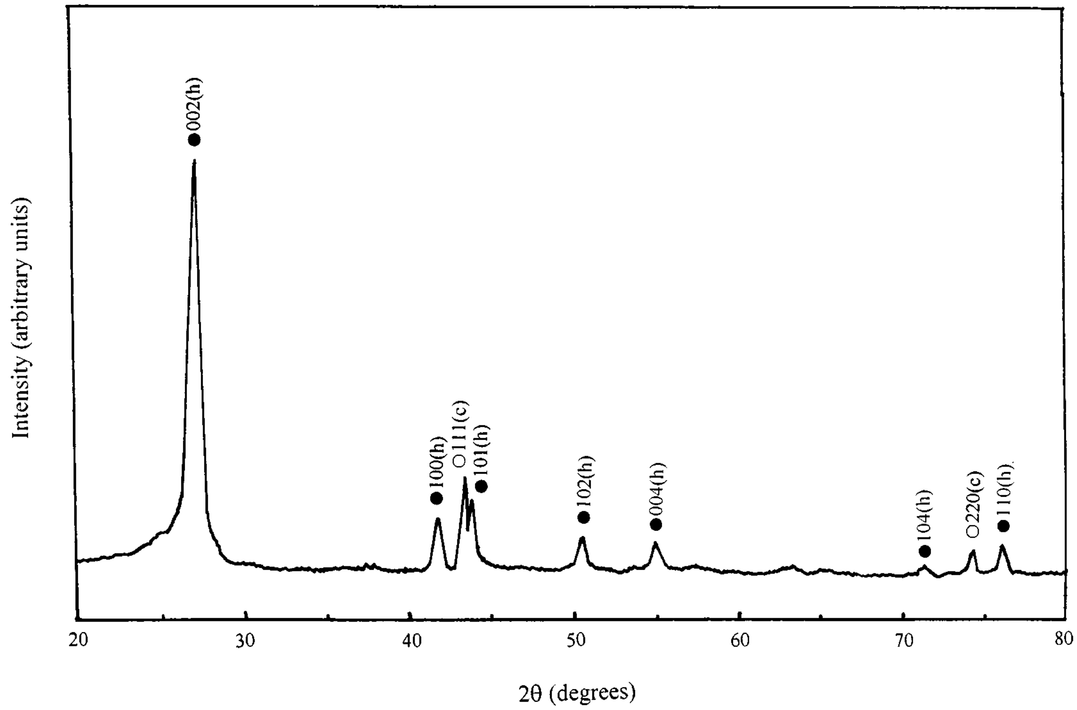

FIG. 1. XRD pattern of nanocrystalline BN.

should be used to minimize the risk of pressure explosions and the reaction should be carried out behind a safety screen. When the autoclave is cooled to room temperature, the relief valve should be carefully opened to conduct the produced H_2 out of the autoclave slowly.

RESULTS AND DISCUSSION

Figure 1 shows the XRD pattern of the sample. All reflections marked with dots can be indexed as hBN with lattice constants $a = 2.4975$, $c = 6.6841$ Å, which are near the reported values ($a = 2.5044$, $c = 6.6562$ Å) (18). The other reflections, (1 1 1) and (2 2 0), marked with circles can be indexed as cBN with lattice constant $a = 3.6156$ Å, which is also close to the reported data ($a = 3.6162$ Å) (19). No impurities such as B_2O_3 were detected by the XRD. The broadening nature of the XRD peaks indicated that the grain sizes of the samples are on a nanometer scale. The average particle size was about 15 nm by the Scherrer formula.

Figure 2 shows that the BN powders consisted of whisker-like particles with an average size of 250 × 10 nm.

FTIR was used to distinguish the sp^2 hexagonal and sp^3 cubic phase. Figure 3 shows the FTIR spectra of the sample. Two strong characteristic peaks located at 1386.64 and 809.21 cm^{-1} are identified with the TO modes of the sp^2-bonded hBN and a weak peak near 1078 cm^{-1} is attributed to the TO mode of the sp^3-bonded cBN, which are in accordance with the reported values (20).

Further evidence for the formation of BN can be obtained from the XPS of the sample. In Figure 4, the binding energies near the 190.35 eV for B1s and 398.20 eV for N1s

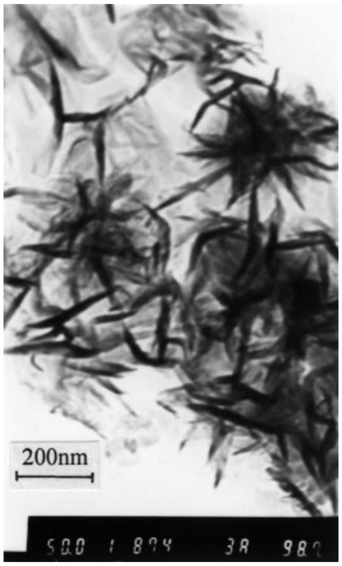

FIG. 2. TEM image of nanocrystalline BN.

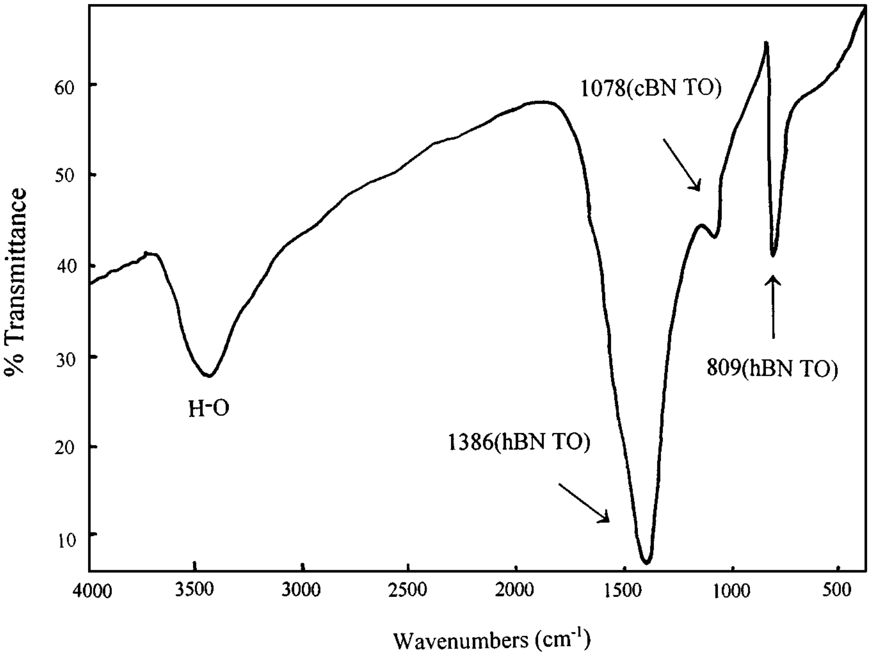

FIG. 3. FTIR spectra of nanocrystalline BN.

level are in good agreement with values in the published literature (21). The quantification of peaks confirmed that the atomic ratio of B : N was 1.01 : 1. The difference in bonding energies between the atoms in hBN (sp^2) and cBN (sp^3) appears to be that hBN has a π plasmon loss peak at approximately 9 eV away from the B1s and N1s peaks (20). Figure 4 shows that a feature of the π plasmon loss peak for both B1s and N1s is present, in accordance with the previous reports (22). This result, together with the infrared absorption data shown in Figure 3, confirmed that the sample mainly consisted of sp^2-bonded hBN.

The influences of reaction temperature, time, and the amount of reactant NH_4Cl on the formation of BN were investigated. The XRD patterns confirmed that the reflections for the cBN phase were not detected when the temperature was lower than 600°C. We believe that it might be caused by the broadened nature of the reflections and the poorer crystallinity of the products. When the temperature was higher than 630°C, the crystallinity increased and the reflections for the cBN phase were more evident. A treatment time in a range of 2–10 h at 650°C did not have obvious effects on the crystallinity and the content of cBN in the product. However, as the amount of NH_4Cl increased, the content of cBN increased. It is believed that the increasing pressure in the autoclave from the decomposition of the excess of NH_4Cl may be beneficial to the formation of cBN.

The possible formation mechanism of BN was proposed. In the present route, with the temperature increasing ($>340°C$), the mixture of NH_4Cl and KBH_4 began to occur in the decomposition reactions as expressed in Eqs. [2] and [3]. The produced NH_3, HCl, BH_3, and KH will react further and produce $NH_3 \cdot BH_3$ (18), H_2, and KCl as expressed in Eq. [4].

$$NH_4Cl \rightarrow NH_3 + HCl \qquad [2]$$

$$KBH_4 \rightarrow BH_3 + KH \qquad [3]$$

$$NH_3 + HCl + BH_3 + KH \rightarrow NH_3 \cdot BH_3 + H_2 + KCl \qquad [4]$$

With the processing temperature up to 650°C, intermediate $NH_3 \cdot BH_3$ could subsequently pyrolyze to lose hydrogen and form BN in the presence of KCl. The newly formed BN may be amorphous. According to the free energy calculations ($\Delta G_f^0 = -65.56$ kcalmol^{-1}, $\Delta H_f^0 = -35.68$ kcalmol^{-1}) (23), the reaction of NH_4Cl and KBH_4 is exothermic; the heat generated in this process resulted in a high temperature but short-lived molten KCl flux (KCl: the m.p. of 711°C) (23). It is probable that hBN crystallized by the heat remaining in the KCl flux. Cubic BN crystals are generally obtained by a nucleation and growth process in which hBN is dissolved in a solvent at higher pressure (24). In our route, the short-lived high-temperature KCl flux could have acted as a solvent for the recrystallization of hBN into cBN. A higher pressure of about 22 MPa (estimated by the ideal gas law), coming from by-product H_2 and the decomposed NH_3, HCl gases would promote the crystallization of cBN. Meanwhile, at higher pressure, the presence of a

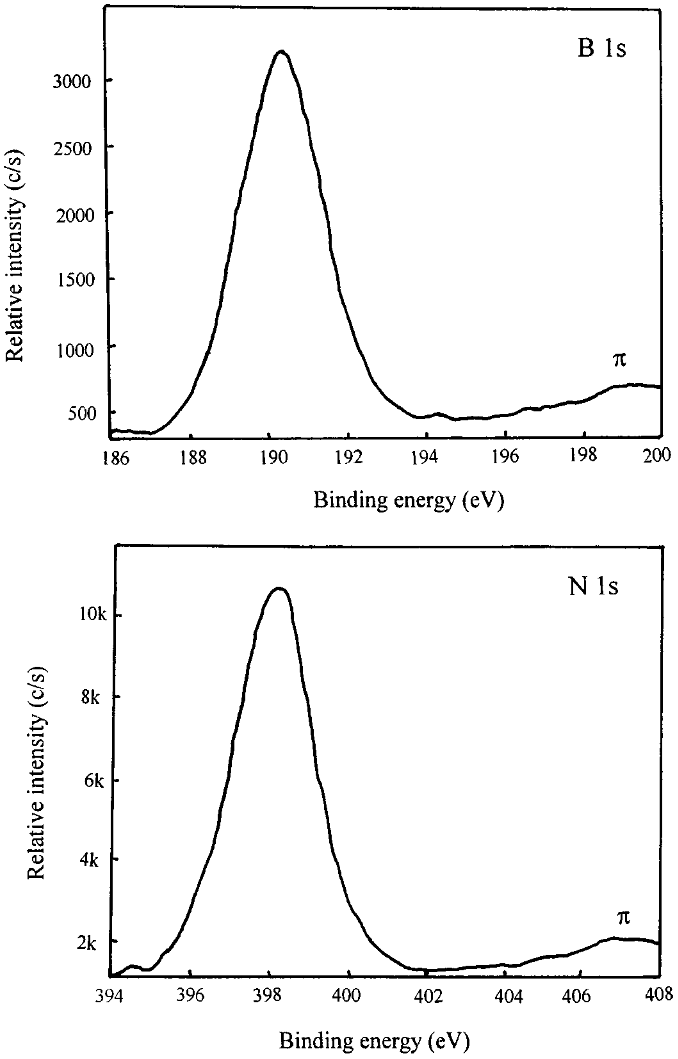

FIG. 4. XPS spectra of nanocrystalline BN (π:π plasmon loss peak).

monovalent anion Cl^{-1} may play an important role in the formation of cBN, which could coordinate with B atoms on the hBN surface causing it to undergo a structural change (19, 25). Owing to the short-lived high temperature, the solubility of the KCl flux was small and only a small fraction of hBN was converted into cBN.

CONCLUSION

In summary, nanocrystalline BN was successfully synthesized using KBH_4 and NH_4Cl as the reactants at a temperature of 650°C and a pressure of 22 MPa. The pressure is much lower than that of previous routes and the yield of nanocrystalline BN reached 70%. The coexistence of hBN and cBN was characterized with XRD, TEM, FTIR, and XPS. The lattice constants of hBN with $a = 2.4975$, $c = 6.6841$ Å and cBN with $a = 3.6156$ Å were consistent with the literature. XPS analysis gave the chemical formula $B_{1.01}N$. The influences of the temperature, time, and amount of reactant NH_4Cl on the formation of nanocrystalline BN were studied.

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