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Synthesis of Nanocrystalline Boron Nitride by Combustion Process*

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Abstract—Nanocrystalline boron nitride powders were synthesized by combustion process using urea as a fuel. Experiments were carried out by heating boric acid and urea in an N_2 atmosphere at 850°C. Boric acid was used as a source of boron while urea, as a source of nitrogen. The reactions were carried out in an autoclave with provisions for purging with nitrogen gas. The samples were characterized by powder X-ray diffraction, Fourier transform IR spectroscopy (FT-IR), FT-Raman spectroscopy, UV-VIS spectroscopy, and SEM.

Keywords: combustion synthesis, hexagonal boron nitride, FT-IR, FT-Raman, UV-VIS spectroscopy, SEM.

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INTRODUCTION

Hexagonal boron nitride (h-BN) is often referred to as "white graphite" because it is a lubricious material with the same platy hexagonal structure as carbon graphite. Unlike graphite, BN is an insulator. It offers very high thermal conductivity, good thermal shock resistance, extreme hardness, chemical inertness, high mechanical strength, low density, high melting point, corrosion/oxidation resistance, and transparency [1–3]. Due to these advantageous properties, BN becomes an important industrial material. It has potential applications in refractory, lubricating, protective, and optical coatings, electrical insulators, cutting tools, grinding and abrasive materials, advanced ceramic composites and mold release liners, electronic devices, electrical insulators, etc. [4–7].

Boron nitride nanotubes were synthesized by thermal heating chemical vapor deposition (TH-CVD) using trimethyl borate and nitrogen gas [8]. Nanocrystalline boron nitride was synthesized by the reaction of sodium borohydride with sodium azide [9]. Hexagonal boron nitride nanoropes synthesized by reaction of KBH_4 with NH_4Cl using $COCl_2$ as a catalst [10]. Cubic BN (c-BN) crystals were prepared by a low-pressure benzene thermal synthesis using BCl_3 and Li_3N [11]. BN nanotubes and nanowires were prepared by heating H_3BO_3 with MWCNT and Fe_2O_3 in an NH_3 atmosphere [12, 13]. Tubular form of BN was produced by heating a mixture of B and Fe_2O_3 in a flow of ammonia gas [14]. Room-temperature synthesis has been tried on the preparation of hollow sphere of BN by using BBr_3 and $NaNH_2$ as raw materials [15]. BN nanotubes and nanocrystals were prepared by an extended vapor-liquid-solid method [16]. Nanocage- [17] and nanocapsule-like BN powders [18] were prepared using the single source precursor method and arc melting method. In all these experimental methods, the reaction time and temperature are important in synthesizing boron nitride. However from a commercial point of view, these methods have certain limitations to produce BN in an economical way. Presently, there has been a concerted effort by several researches on the preparation of boron nitride by low-temperature synthesis process. In view of that, we made an attempt to synthesize this compound at low temperatures using a short-term process and low-cost raw materials.

In this communication, we report on the combustion synthesis process as a simple and convenient chemical route to prepare crystalline boron nitride [19].

EXPERIMENTAL

Experiments were performed by using mix 1 and mix 2 (characterized in Table 1) as starting mixtures. All the reactants were of commercial grade purity.

* The article is published in the original.

Boric acid acted as a source of boron while urea, as a source of nitrogen and reaction heat. For the synthesis of boron nitride, required quantities of reactants were individually taken in an alumina crucible and then placed in an inconel autoclave. The reactor was placed in an electrically heated furnace. The reactor had provisions for purging with nitrogen gas and a ventilator for exhaust gases. Nitrogen gas was purged and the reaction was carried out in a controlled atmospheric conditions. The reaction temperature was 850°C and the duration of the reaction was 3 h. Voluminous gases were evolved during the reaction.

The resultant foamy product was removed from the alumina crucible and washed with triple distilled water. A white crystalline solid was obtained which was again thoroughly washed with acetone to remove surface impurities. Then it was dried at 60°C using a vacuum oven. The dried product was examined for its crystallinity using powder X-ray diffraction technique using a PANALYTICAL model X PERPRO apparatus [Cu-K_α radiation (2.2 kW), $2\theta = 10–70°$]. FT-IR and FT-Raman spectra (in KBr discs) were recorded with a thermo Nicolet model 670 spectrophotometer (NEXUS) within the range 600–4000 cm^{-1}. UV-VIS spectra were recorded using a VARIAN CARY 500 scan spectrophotometer.

RESULTS AND DISCUSSION

Figure 1 shows the X-ray diffraction patterns of the samples synthesized from mix 1 (a) and mix 2 (b). In Fig. 1a, the peaks at 40 and 54° can be indexed as the (100) and (004) diffractions of hexagonal BN (h-BN). In Fig. 1b, the peaks at 26, 41, and 53° correspond to the (002), (100), and (004) diffractions of h-BN, respectively.

Lattice parameters of the product were determined using the following expression:

$$\frac{1}{d^2} = \frac{4}{3}\frac{h^2 + hk + k^2}{a^2} + \frac{1}{c^2},$$

where d is the density, a and c are lattice parameters, and h, k, l the Miller indices.

The size L of product crystallites was determined using the Debye-Scherrer formula as given below:

$$l = \frac{0.94\lambda}{\beta\cos\theta},$$

where $\beta = \Delta/2$ (Δ is the full width at half maximum for a given diffraction peak) and $\theta = 1/2\ 2\theta$.

Thus obtained lattice constants and the crystallite size of h-BN crystals are collected in Table 2. The crystallite size L is seen to vary between 18 to 58 nm depending on the concentration of the reactants used. Our lattice constants (a = 2.584 Å, c = 6.743 Å for mix 1 and a = 2.520 Å, c = 6.762 Å for mix 2) are in good agreement with the reported values of a = 2.57 Å and c = 6.70 Å (JCPDS card # 34-0421). No evidence for the presence of impurities (such as B, B_2O_3) can be inferred from the XRD patterns. The width of the XRD peaks suggests that the grain size of the samples is on a nanometer scale.

Table 1. Starting mixtures used in experiments

	Reactants	Reactants ratio
Mix 1	Boric acid + urea	1 : 1
Mix 2	Boric acid + urea	1 : 2

Table 2. Lattice constants (a, c) and the size (L) of h-BN crystallites formed in mixtures 1 and 2

	a, Å	c, Å	L, nm
Mix 1	2.584	6.743	18
Mix 2	2.520	6.762	58

Figure 2 shows the FT-IR spectra of h-BN prepared from mix 1 (a) and mix 2 (b). The absorption bands at

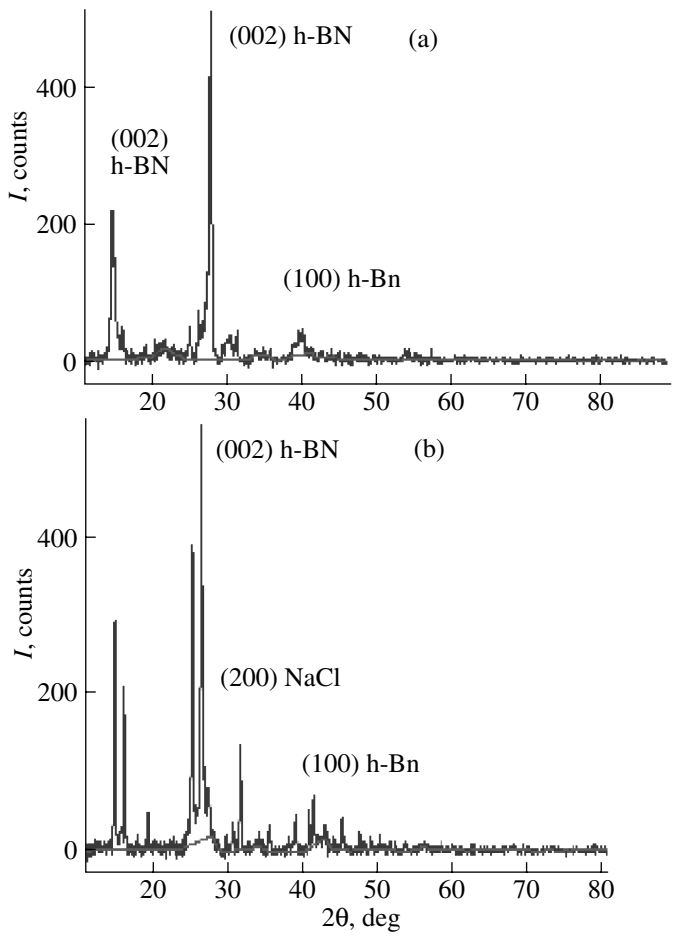

Fig. 1. (a) XRD patterns of Products Prepared from mix 1 (a) and mix 2 (b).

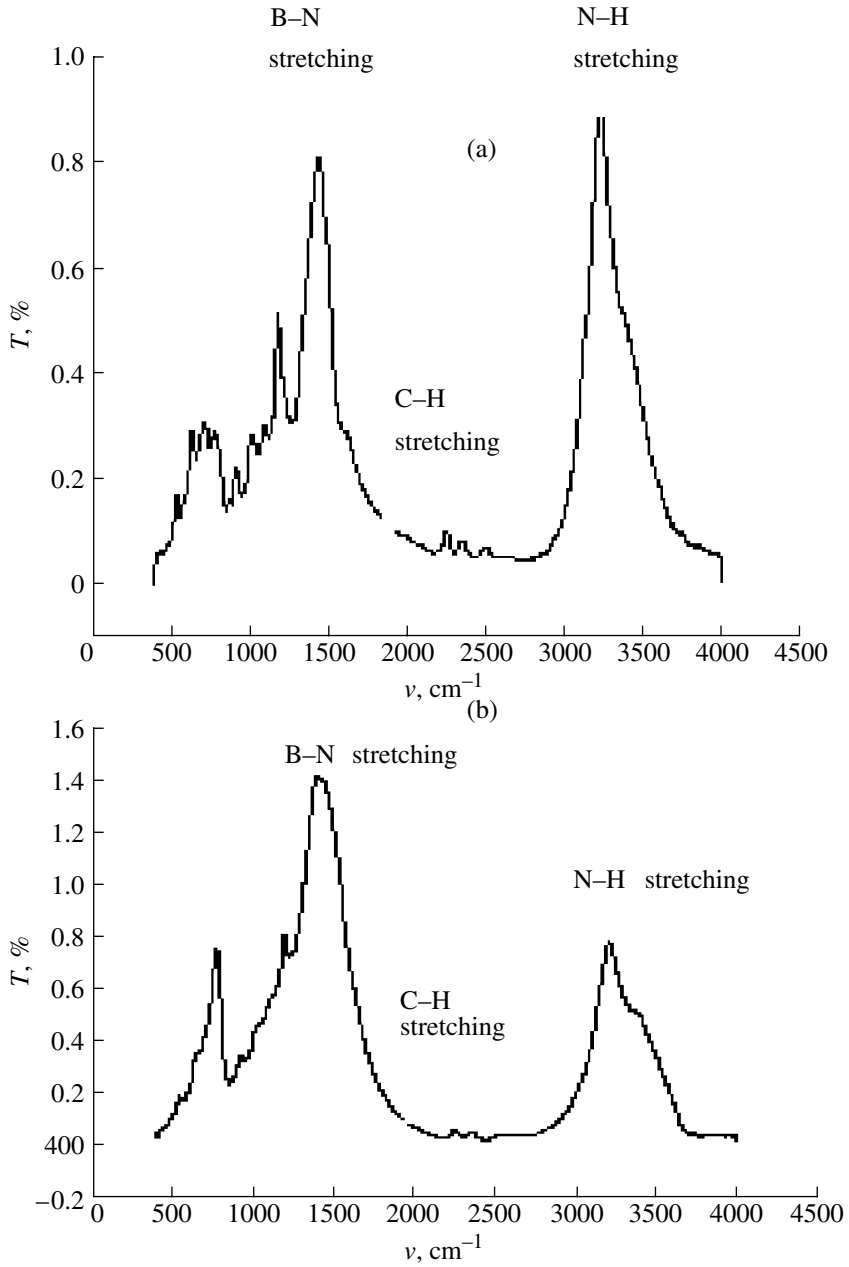

Fig. 2. FT-IR spectra of h-BN prepared from mix 1 (a) and mix 2 (b).

Table 3. Assignments of IR bands

	Characteristic peaks of h-BN, cm^{-1}	Characteristic peaks of N-H stretching, cm^{-1}
Mix 1	731	3218
	1457	
Mix 2	779	3217
	1407	

1457 and 1407 cm^{-1} can be attributed (see Table 3) to the B–N stretching modes while those at 731 and 779 cm^{-1}, to the B–N–B bending vibrations. The broad absorption bands peaked at 3218 and 3217 cm^{-1} are mainly due to the overlapping of the stretching vibrations of hydroxyl, water, and C–H groups.

Figure 2 shows the reflectance spectra of both the samples. Using this spectrum, we calculated the energy band gap by plotting the graph E (eV) vs. $\{\ln[h\nu(R_{max} - R_{min})/(R - R_{min})]\}^2$. Here R_{max} and R_{min} are the maximum and minimum reflectance in the reflectance spectrum, respectively, and R is the running energy of

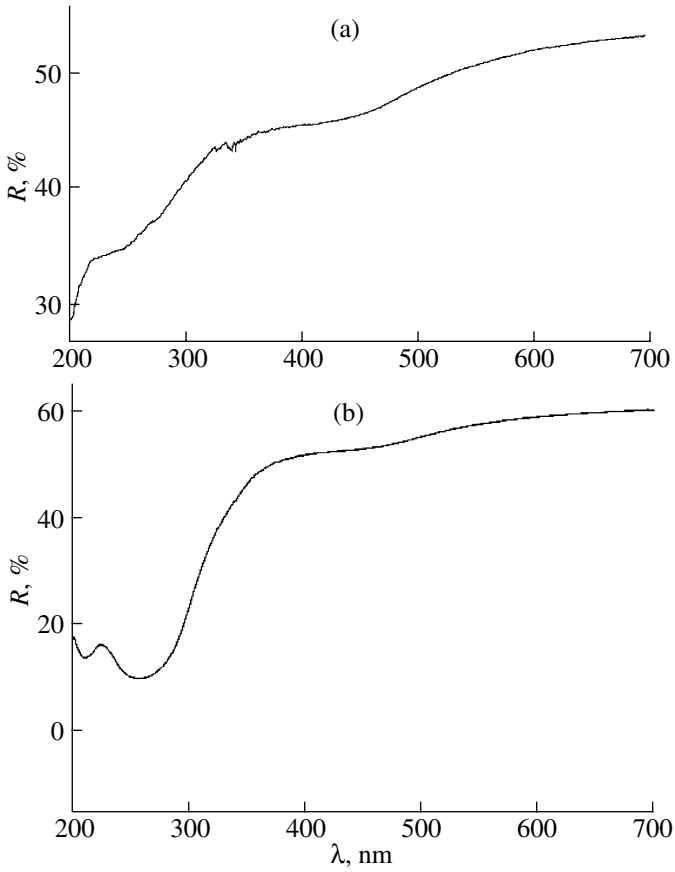

Fig. 3. Reflectance spectra of h-BN prepared from mix 1 (a) and mix 2 (b).

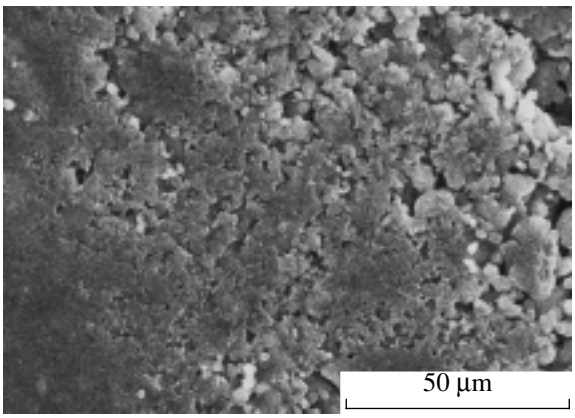

Fig. 4. SEM image of synthesized boron nitride.

photons. The plot was found to be linear. Its extrapolation to $\{\ln[h\nu(R_{max} - R_{min})/(R - R_{min})]\}^2 = 0$ gave a value of the direct band gap of about 5.5 eV, which also confirms the formation of homogenous products in our experiments.

The SEM image in Fig. 3 depicts an uneven distribution of product particles due to aggregation over a wide area. The product consists of large faceted particles with small incrustations on the surface. The presence of large faceted particles and the aggregation is due to the absorption of moisture by the product surface.

CONCLUSIONS

It has been demonstrated that nanocrystalline hexagonal boron nitride can be synthesized using simple, commercially available chemicals, such as boric acid and urea, by combustion process. The purity of the product is found to be as good as in other synthetic methods.

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