Journal of Solid State Chemistry 184 (2011) 2902–2908

Contents lists available at SciVerse ScienceDirect

Journal of Solid State Chemistry

journal homepage: www.elsevier.com/locate/jssc

Synthetic approaches to borocarbonitrides, BC_xN ($x=1$–2)

Nitesh Kumar, Kalyan Raidongia, Abhishek K. Mishra, Umesh V. Waghmare, A. Sundaresan, C.N.R. Rao *

Chemistry and Physics of Materials Unit, CSIR Centre of Excellence in Chemistry and International Centre for Materials Science, Theoretical Sciences Unit, Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur, Bangalore 560064, India

ARTICLE INFO

Article history:
Received 25 July 2011
Received in revised form
24 August 2011
Accepted 25 August 2011
Available online 10 September 2011

Keywords:
Borocarbonitrides
Vapor phase synthesis
Nanopans
First principles calculations

ABSTRACT

In order to synthesize borocarbonitrides of the general formula BC_xN where x varies between 1 and 2, we have carried out high-temperature gas phase reaction of BBr_3 with a mixture of ethylene and ammonia. The composition of the product was close to $BC_{1.6}N$ as shown by x-ray photon spectroscopy (XPS) and electron energy loss spectroscopy (EELS). The products were further characterized by infrared, Raman and other spectroscopic techniques. The borocarbonitrides obtained from the gas phase reaction have low surface areas, in contrast to those of similar compositions prepared by the urea method. First principles calculations show that the most stable structures of the compositions BCN and BC_2N contain BN-rich and carbon-rich domains where BN_3 and NB_3 units are present.

1. Introduction

Emergence of graphene as an exciting two-dimensional material has propelled research on analogous layered inorganic materials. Thus, recently graphene-like MoS_2 and BN have been synthesized and characterized [1,2]. Hexagonal borocarbonitrides of the general formula $B_xC_yN_z$ have attracted interest recently. $B_xC_yN_z$ is expected to possess properties intermediate between graphene and BN, which can be tuned by varying the carbon content as well as by changing the structural characteristics [3–6]. There are a few reports on the synthesis of $B_xC_yN_z$ type materials in the form of nanotubes by chemical vapor deposition (CVD), using transition metal nanoparticles as catalysts and also by methods such as arc-discharge and laser ablation [7–13]. Jansen and co-workers [14,15] have synthesized Si–B–N–C ceramics using molecular precursors. There is, however, limited information available on the borocarbonitrides, $B_xC_yN_z$, with well-defined compositions. Vinu et al. [16] reported mesoporous BCN obtained by the reaction of B_2O_3 and mesoporous carbon at very high temperatures under flowing nitrogen. Raidongia et al. [17] prepared a borocarbonitride of the composition $BC_{1.5}N_{1.1}$ by heating urea, boric acid and high-surface area activated charcoal in an inert atmosphere. Ci et al. [18] have synthesized layers of $B_xC_yN_z$ with separated graphene and BN domains by the reaction between NH_3–BH_3 complex and methane. In view of the marginal success in synthesizing $B_xC_yN_z$ materials and the potential uses of these materials, we have carried out vapor phase synthesis of $B_xC_yN_z$ by taking BBr_3, ethylene and ammonia as the sources of boron, carbon and nitrogen, respectively. Our interest has been to synthesize borocarbonitrides with compositions in the vicinity of BCN or BC_2N. A vapor phase synthesis of BCN was carried out by Kaner et al. [19] some years ago by the reaction of acetylene, BCl_3 and NH_3. These authors could not characterize the product adequately. We have prepared BC_xN ($x=1$–2) compositions by the gas phase reaction of ethylene, BBr_3 and NH_3 and compared their characteristics with those of similar compositions obtained by the reaction of activated carbon, boric acid and urea. We have also carried out first-principles calculations on the stable structures of BCN and BC_2N.

2. Experimental

2.1. Gas phase synthesis of BC_xN

Gas phase synthesis of composition BC_xN was carried out using liquid BBr_3, high purity ammonia gas and 20% ethylene gas mixed with nitrogen as the sources of boron, nitrogen and carbon, respectively. The experimental set up for the reaction is shown in Fig. 1. In this set-up, nitrogen gas, which acts as the carrier gas bubbles through liquid BBr_3 and carries its vapor into the hot zone of the tube furnace. In the hot zone, BBr_3 reacts with the mixture of ammonia and ethylene gas coming from the other two inlets. A quartz boat present in the hot zone was used to collect the deposited product. At the end of the boat, we keep a circular glass slide in order to keep the gaseous reactants in the hot zone. Before starting the reaction, the quartz tube was purged with ammonia for 30 min. The furnace temperature was set to 950 °C at the rate of

---

* Corresponding author. Fax: +91 80 22082760.
E-mail address: cnrrao@jncasr.ac.in (C.N.R. Rao).

0022-4596/$ - see front matter © 2011 Elsevier Inc. All rights reserved.
doi:10.1016/j.jssc.2011.08.034

7 °C/min. When the temperature reached to 850 °C, nitrogen gas was allowed to bubble through the liquid BBr_3 and the flow of ethylene also started at this temperature. The furnace was maintained at 950 °C for 1 h with the reactants. The supply of BBr_3 and ethylene was stopped, but the ammonia gas flow was continued till the furnace attained room temperature. The product deposited in the quartz boat was heated at 750 °C in an inert atmosphere for 5 h in order to remove traces of NH_4Br in the product.

2.2. Synthesis of BC_xN by the urea route

In the urea route, 0.1 g boric acid and 0.5 g high surface area activated charcoal (1250 m^2/g) were mixed with varied amount of urea in order to keep the molar ratio of boric acid to urea from 1:6 to 1:24. The mixture was heated at 900 °C for 12 h in an inert atmosphere. The product obtained was heated again at 930 °C in an ammonia atmosphere for 3 h.

2.3. Characterization

X-ray diffraction of the samples were carried out by Bruker-D8 X-ray diffractometer using Cu $K\alpha$ radiation. FESEM images were obtained using FEI Nova-Nano SEM-600, The Netherlands. TEM and HRTEM analyses were carried out by FEI TITAN3 80–300 kV aberration corrected transmission electron microscope. Quantification of the electron energy loss spectra (EELS) was possible with a Gun monochromator (resolution better than 0.3 eV), camera length 73 mm and GIF aperture 1 mm, which gives collection angle ~3.336 mrad. AFM measurements were performed using NanoMan instrument in the tapping mode. XPS was performed in ESCALAB MKIV spectrometer employing Al $K\alpha$ (1486.6 eV) as photon source. IR spectra were recorded by a Bruker IFS 66 v/S spectrometer. Raman spectroscopy was carried out in a LabRAM HR with a 633 nm line from a HeNe laser. TGA was performed in Mettler Toledo Star system. Nitrogen adsorption–desorption measurements were carried out in a QUANTACHROME AUTOSORB-1C instrument.

2.4. First-principles calculations

We have used plane-wave self consistent field (PWSCF) [20] implementation of density functional theory (DFT) with a generalized gradient approximation (GGA) [21] to exchange correlation energy of electrons and first-principles ultra-soft pseudopotentials [22] to represent interaction between ionic cores and valence electrons. Kohn–Sham wave functions were represented with a plane wave basis with an energy cut off of 35 Ry and charge density cut off of 210 Ry. Integrations over Brillouin zone were sampled with $16\times4\times1$, $8\times8\times1$ and $4\times8\times1$ meshes of k points in different unit cells chosen depending on their size, shape and occupation numbers were smeared using Methfessel–Paxton scheme [23] with broadening of 0.006 Ry. To simulate various configurations of chemical ordering of B and N, we consider supercells consisting of 8 and 16 atoms with 10 symmetry inequivalent configurations of BC_2N, and use six different configurations with 18 atoms supercell of BCN [17] for comparison (see Fig. 2(a) and (b), respectively). We determined the structure for each configuration through optimizing the energy with respect to atomic positions as well as the size and shape of the supercell.

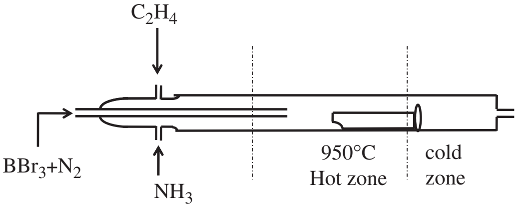

Fig. 1. Schematic of the experimental set-up for gas phase synthesis of BCN.

3. Results and discussion

For the gas phase synthesis of BC_xN, we have employed the reaction of BBr_3 with a mixture of CH_4 and NH_3 at high temperatures. The product of the reaction was analyzed by x-ray photoelectron spectroscopy (XPS) to determine the elemental composition. We show typical core-level spectra of one of the samples in Fig. 3(a), with B (1*s*), C (1*s*) and N (1*s*) with peaks centered at 191.5, 284 and 399 eV respectively. The B (1*s*) signal can be deconvoluted into two peaks at 190.5 and 192 eV corresponding to boron atoms bonded to carbon and nitrogen, respectively. The C (1*s*) signal can be deconvoluted to three peaks centered at ~284, 286 and 290 eV corresponding to carbon atoms bonded to boron, carbon and nitrogen, respectively. The N 1*s* signal can be deconvoluted into two peaks at 397.5 and 400 eV corresponding to nitrogen atoms bonded to boron and carbon, respectively. From the areas under the 1*s* features, we obtained the elemental composition B:C:N to be 1:1.6:1 after taking the relevant capture cross sections into account. We also obtained a composition BC_xN with $x=1.8$ by the vapor phase method at 950 °C under a flow of 200 sccm (standard cubic centimeter) of ammonia, 40 sccm of 20% C_2H_4 in N_2 and 40 sccm of N_2 through BBr_3. Core level XP spectra of B, C and N of this composition are shown in Fig. 3(b). Our XPS data are well supported by the first-principles calculations.

In order to ensure the compositions of the $B_xC_yN_z$ products obtained by the gas phase reaction, electron energy loss spectroscopy (EELS) was carried out in several regions of the sample. In Fig. 4, we show the spectrum of one of the samples showing K shell ionization edges. The EELS peaks are split into two peaks corresponding to the π^* and σ^* bands showing thereby that boron, carbon and nitrogen atoms are all in the sp^2 hybridized

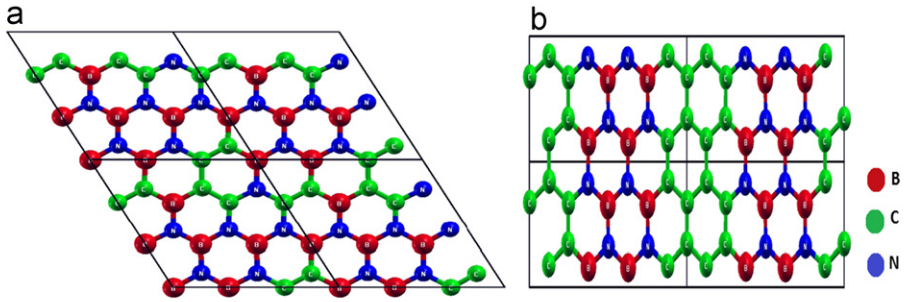

Fig. 2. Most stable structures of BCN (a) and BC_2N (b).