Combustion Synthesis of Boron Nitride by Glycine Route

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Abstract

Crystalline boron nitride (BN) powders were prepared by combustion method using glycine as a fuel. Experiments were carried out by heating dehydrated borax ($Na_2B_4O_7$) with $NaNO_2$, KNO_3, NH_4NO_3 in N_2 atmosphere at 350^0C and glycine was used as a fuel as well as a source for nitrogen. Borax was used as a boron source and nitrogen compounds ($NaNO_2$, KNO_3, NH_4NO_3) were used as the nitrogen source. The reactions were carried out in a tantalum autoclave having the provisions for the purging of N_2 and vent gases. The as prepared samples were systematically characterized by X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), Fourier Transform Infrared spectroscopy (FTIR), UV-Visible spectroscopy (UV) and Photoluminescence spectroscopy (PL). The reaction has resulted in the form of hexagonal boron nitride with high purity and good yield.

Keywords: Boron nitride, combustion synthesis, borax, glycine.

Introduction

Boron nitride (BN) forms both hard diamond like cubic phase and softer graphite like sp[2]-bonded phases analogous to carbon. Recently, it is found in many applications like cutting tools, grinding and abrasive machines, super hard protective coatings, high frequency and high temperature devices[1-4]. It possesses excellent properties such as extreme hardness, high thermal conductivity, chemical inertness, transparency and electrically insulating property[5,6]. Several investigations were made on the preparation of BN tubes and powders[7,8]. C-BN crystals were prepared by Hao *et al.*[9] by a low pressure benzene thermal synthesis using BCl_3 and Li_3N. BN nanotubes and nanowires have been synthesized by heating H_3BO_3 with MWCNT in NH_3 atmosphere[10]. Tang *et al.*[11] reported the synthesis of tubular form of BN by heating a mixture of B and Fe_2O_3 in flowing ammonia gas. Hao *et al.*[12] prepared BN nanocrystals using benzene thermal reactions at low temperature. Hollow sphere BN was synthesized by Chen *et al.* using BBr_3 and $NaNH_2$ as raw materials [13]. Crystalline BN nanoparticles were prepared by heating H_3BO_3 with urea in N_2 atmosphere[14]. Fu *et al.*[15] prepared BN nanotubes and nanocrystals by extended vapor-liquid-solid method. Nanocage like[16] nanocapsule like[17] boron nitride powders were synthesized using single source precursor method and arc melting process.

From the literature survey, it has been revealed that boron nitride has been prepared by vapor-liquid-solid method, crystal growth method, thin film techniques and conventional chemical method. In these studies, it has been often emphasized that the reaction time and temperature are the crucial factors controlling the properties of boron nitride. Further, from a commercial point of view, these methods are not economical since expensive reactants have been employed. Presently, there has been a concerted effort by many researchers on the preparation of boron nitride by low temperature synthesis routes. In this view, combustion method has been adapted for the synthesis of boron nitride. There have been many reports on the preparation of oxide nanomaterials[18,19], ferrites, orthoferrites, garnets[20] and advanced ceramics[21] by combustion synthesis. In the present work, we have reported the preparation of boron nitride by combustion method at relatively low temperature, short duration and low cost. Combustion synthesis is an efficient and economical method for the production of advanced materials in a short time with less operating cost[22].

Material and Methods

Analytical grade reagents were used in all the experiments for the synthesis of boron nitride. Borax was used as the boron source and the nitrogen compounds such as $NaNO_2$, KNO_3, and NH_4NO_3 were used as the nitrogen source. Glycine was used as a fuel as well as the nitrogen source. Borax which is one of the reactants contains water molecules, which should be removed to achieve an effective reaction in the system. If water is present in the reactant, it may lead to the formation of unwanted hydroxides and may need high temperature to form the desired compound. Hence, it was melted in a high purity graphite crucible under argon atmosphere and used in the form of fine powders. Prior to the experiment, the reactants were preheated in a vacuum oven to remove the moisture present in the reactants.

For the synthesis of boron nitride, stoichiometric quantities of reactants were taken in a high alumina crucible as shown in table-1. Then the reactants were thoroughly mixed and placed in

a tantalum autoclave. The autoclave was then placed in an electrically heated furnace. It had the provisions for purging of N_2 gas and ventilator for exhaust gases. Nitrogen gas was purged and the whole reaction was carried out in the controlled N_2 atmosphere. The reaction temperature was 350°C and the mixture was kept for 5 hours at this temperature. After the completion of the reaction, the resultant foamy product was removed from the alumina crucible and washed with double distilled water. A white crystalline solid was obtained, which was again thoroughly washed with acetone to remove surface impurities and then dried at 60°C in a vacuum oven.

Table-1
**Reactants system for the synthesis of boron nitride**

No.	Experiments	Reactants
1	Route 1	Borax + Sodium nitrite + Glycine
2	Route 2	Borax + Glycine
3	Route 3	Borax + Potassium nitrate +Glycine
4	Route 4	Borax + Ammonium nitrate +Glycine

Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) of the precursor powders were carried out using a STA 1500 PL thermal sciences, version V4.30 analyzer. The DTA/TGA curves were recorded from room temperature to 1000 °C in air at a heating rate of 10 °C/ min. The dried product was examined for its crystallinity and phase purity by powder X-ray diffraction technique using Cu Kα (2.2 KW) radiation with 2θ value ranging from 10° to 70° in PANALYTICAL model X' PERPRO. The morphology of the crystalline BN powder was examined using a Scanning Electron Microscope (SEM) Hitachi model S-3000 instrument. FTIR spectra of the samples were recorded as the KBr disc in the range 600-4000 cm^{-1} by using thermo Nicolet model from NEXUS 670 spectrophotometer. UV-Vis spectra were recorded using VARIAN CARY 500 scan spectrophotometer. Photoluminescence measurements were carried out at room temperature using VARIAN CARY eclipse fluorescence spectrophotometer at the excitation wavelength of (λ_{max}=298 nm).

Results and Discussion

Thermogravimetric Analysis: Figure 1 shows the TGA/DTA curve for the precursor borax powder. It is noticed that a large amount of water has been removed from the compound from room temperature to 180°C. The maximum loss in weight occurred at 180°C is mainly due to removal of chemically bound water followed by the chemical decomposition of borax at 480°C. About 35% of the loss in weight is due to the dehydration of water and the chemical decomposition of borax. Beyond 500°C, there is not much loss in weight, which indicates that compound does not undergo any further change. On observing the DTA curve, three inverse peaks are noticed which are all responsible for the endothermic reactions. The first two

peaks at 85°C and 151°C are mainly responsible for the dehydration of water molecules. The third one at 720°C is responsible for the decomposition and the melting of the salt giving the compound boron tri oxide (B_2O_3). On further heating, the B_2O_3 decomposes giving boron for the reaction.
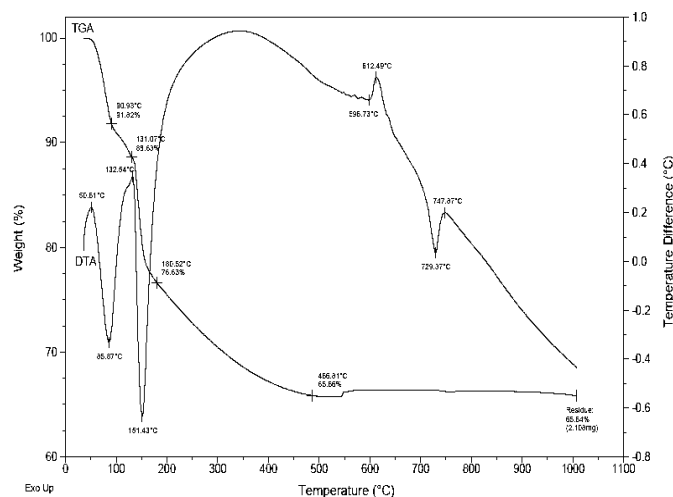
Figure-1
TGA/DTA curve for borax

Structural Characterization: Figure -2 shows the XRD spectra of BN sample prepared from the reactant systems described in table -2. The XRD spectrum of the BN samples prepared from route 1 to route 4 are coincided with the standard JCPDS data[23]. For BN sample obtained from route 1, the XRD data exhibits the peaks at 41°, 55° which can be indexed as the (1 0 0) and (0 0 4) diffractions of hexagonal phase BN (h-BN). For BN sample prepared from route 2, the XRD spectrum shows the peak positions at 41°, 77°, 83°, 88° corresponding to (1 0 0), (1 1 0), (1 1 2) and (0 0 6) planes of hexagonal phase BN. The XRD pattern for the BN sample prepared from route 3 shows the peaks at 41°, 44°, 58° which can be indexed as (1 0 0), (1 0 1) and (1 0 3) planes of hexagonal phase BN. For BN sample obtained from the route 4, XRD data exhibits the peaks at 41°, 59°, 75°, 81° corresponding to (1 0 0), (1 0 3), (1 1 0) and (1 1 2) planes of hexagonal phase BN. The calculated lattice constant value for the BN samples prepared from route 1 to route 4 are in good agreement with the standard JCPDS data of h-BN (a=b= 2.605 Å and c = 6.653 Å).

Table-2
XRD data of BN samples prepared from route 1 to route 4

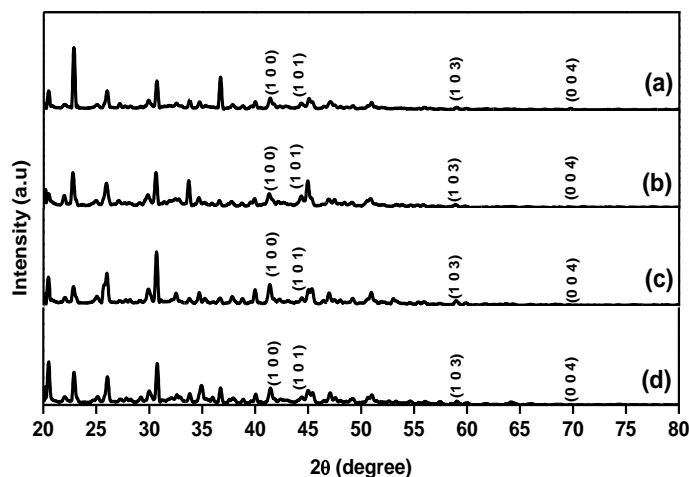| Reactant System	Crystal structure	Estimated lattice constant (Å)
Route 1	Hexagonal	a, b = 2.520 ; c = 6.597
Route 2	Hexagonal	a, b = 2.526 ; c = 6.857
Route 3	Hexagonal	a, b = 2.502 ; c = 6.894
Route 4	Hexagonal	a, b = 2.514 ; c = 6.857

Figure-2
XRD pattern of boron nitride samples synthesized by combustion method (a) Route 1 (b) Route 2 (c) Route 3 and (d) Route 4

Morphological Characterization: Figure -3 shows the SEM micrographs of BN samples prepared from Route 1 to Route 4. It depicts the uneven distribution of particles spread over a wide area. It consists of large faceted particles with small incrustations on the surface. The presence of large faceted particles is due to the absorption of moisture on the surface of the samples.
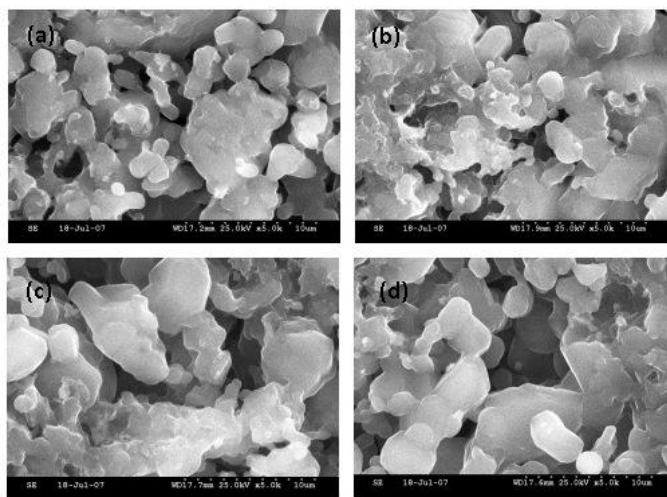

Figure-3
SEM image of boron nitride samples prepared from (a) Route 1 (b) Route 2 (c) Route 3 and (d) Route 4

Spectral Characterization: Figure -4 shows the FTIR spectrum of BN samples prepared from route 1 to route 4. For BN sample prepared from route 1, the peaks appeared at 708 cm^{-1} and 1345 cm^{-1} which are assigned to be B-N-B bending and B-N stretching modes of h-BN phase. These values are in good agreement with the literature [24, 25]. Similarly, in other three experiments, these values are coinciding with the literature values.
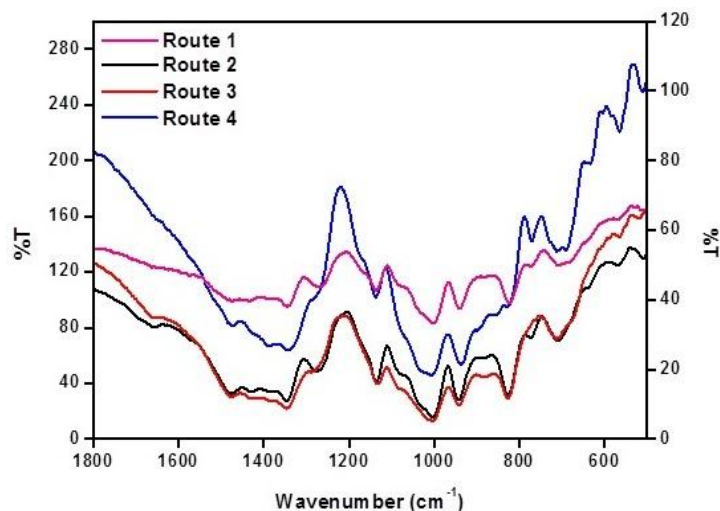

Figure-4
FTIR spectrum of boron nitride samples prepared *via* (a) Route 1 (b) Route 2 (c) Route 3 and (d) Route 4
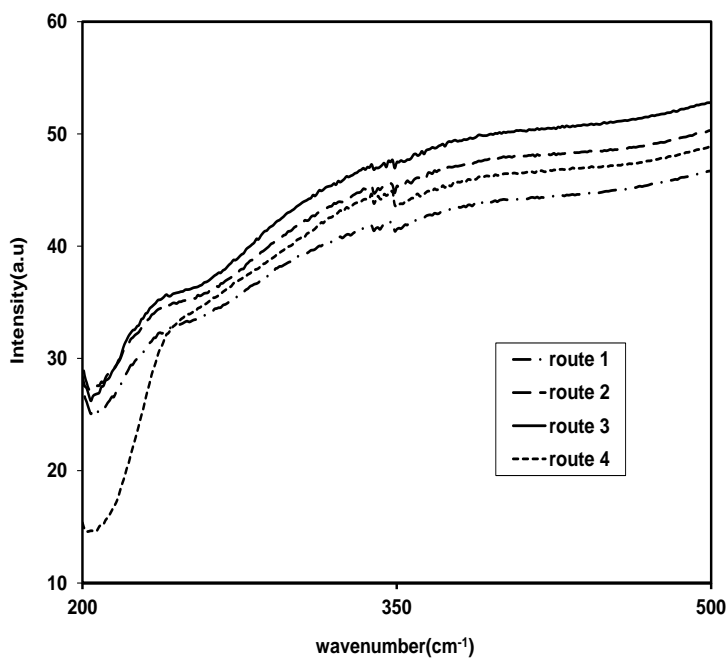
Figure -5 shows the UV reflectance spectra for the BN samples prepared from four different reactant systems. From the reflectance spectra, we have calculated the energy band gap as described by Joshi *et al.*[26] (i.e.) by plotting the graph between E (eV) and $\{Ln[h\nu(R_{max}-R_{min})/(R-R_{min})]\}^2$. Here R_{max} and R_{min} are the maximum and minimum reflectance value in the reflectance spectra and R the reflectance at a given photon energy, *hv*. The extrapolation of straight line to $\{Ln[h\nu(R_{max}-R_{min})/(R-R_{min})]\}^2 = 0$ gives the value of direct band gap for all the BN samples prepared from route 1 to route 4 are shown in Fig. 6. The band gap value of the BN samples prepared from route 1 to route 4 was estimated to be 5.4 eV, which reveals that homogenous compound formation takes place in all the experiments.

Figure -7 shows the photoluminescence spectra for BN samples prepared from four different reactant systems. From the PL spectrum, we have determined the band gap values for the BN samples using the Planck's equation,

$$E_g = 1.24/\lambda_{max} \tag{1}$$

where λ_{max} is the maximum emission wavelength. By using the equation -1, the band gap energy value is determined and it is found to be 5.7 eV, which is in good agreement with the literature [27].

The characterization data for all the BN samples showed that there is no any significant change in the phase composition of the product for all the reactant system. From the above results, we have concluded that glycine played a vital role in the formation of boron nitride. When borax was heated at high temperature in the presence of glycine, combustion reaction takes place and due to that exothermic reaction, borax decomposed into B_2O_3[28]. Subsequently it reacts with nitrogen to form BN.

Figure-5
UV-reflectance spectra of boron nitride samples synthesized by combustion method
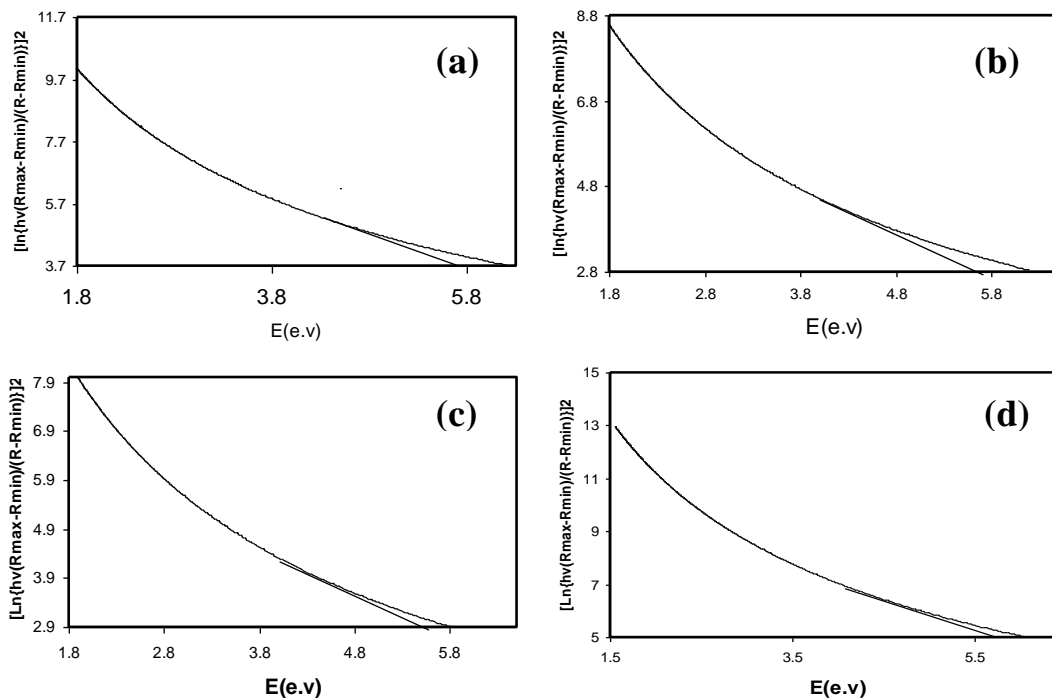
Figure-6
Plot between E (eV) and $\{Ln[h\nu(R_{max}-R_{min})/(R-R_{min})]\}^2$ for the determination of band gap value (a) Route 1 (b) Route 2 (c) Route 3 and (d) Route 4
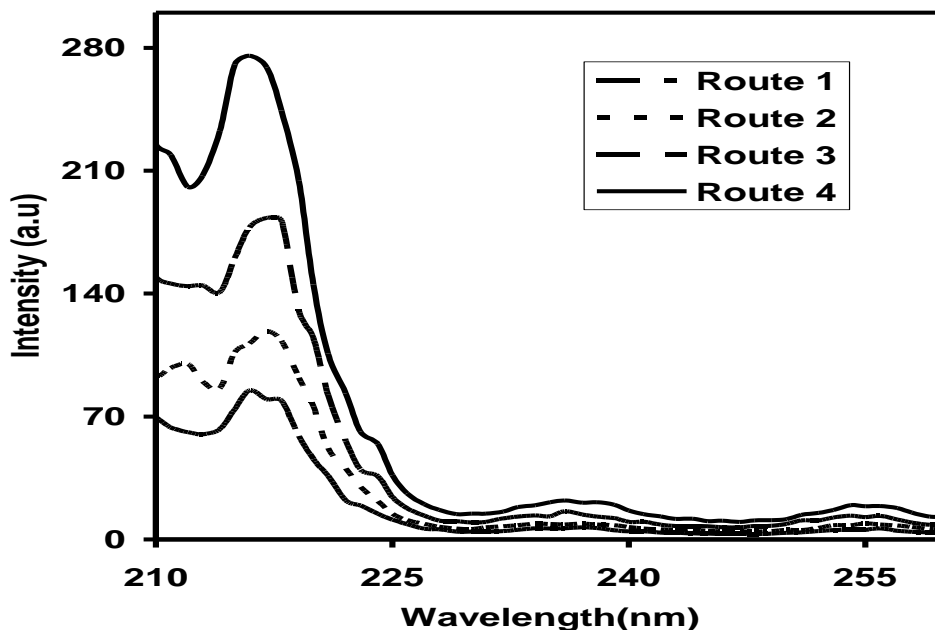
Figure-7
Photoluminescence spectrum of boron nitride samples synthesized by combustion method

Conclusion

Glycine based combustion synthesis is found to be a convenient method to prepare boron nitride. XRD spectra for the samples prepared from four reactant systems confirm the presence of hexagonal boron nitride with high degree of crystallinity. UV reflectance spectra for all the BN samples indicate that the estimated band gap value having same magnitude reveals that homogenous compound formation takes place in all the experiments. The synthesized boron nitride is found to be pure and it is expected to be a suitable material for high temperature applications.

Acknowledgement

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