Effect of processing parameters on synthesis of nanostructured boron carbide

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Abstract

Boron carbide is well known metallurgical product used in cutting/coating tool industry. Nanostructured boron carbide finds its application in medical, optical and defence industry due to its structural, mechanical and optical properties. In present paper, we report the effect of processing parameters (reaction time and temperature/pressure) on the synthesis of nanostructured boron carbide. Detailed X-ray diffraction (XRD), scanning and transmission electron microscopy (SEM and TEM) analysis was done along with theoretical studies of pressure. Results show that the best temperature for synthesis of nanoscale boron carbide is 800 °C. Copyright © 2017 VBRI Press.

Keywords: Boron carbide, processing parameters, solvothermal, TEM, nanoparticles.

Introduction

In the last few years, boron carbide (B_4C) have attracted attention of specialists such as chemists, materials scientists, physicists, owing to its low density, high hardness, high melting point, chemical inertness **[1]**, thermoelectric, semi-conducting, biological and elastic properties **[2]**. Combination of these properties makes B_4C a strong candidate for numerous applications. It is used in ballistic, armour radiation-resistant materials abrasive powder for polishing, lapping and wear resistant coatings of objects [**3-4]**. Also highly efficient catalytic activity with the abundant catalytic sites in B_4C makes this material to exhibit great catalytic activity as an efficient bi-functional catalyst for the oxygen reduction and evolution reactions in lithium oxygen batteries **[5]**. B_4C is also used as an absorbent for neutron radiation in nuclear power plants in the form of shielding, control rod, and shut down pellets **[6]**. B_4C nanoparticles have also shown promising results as a novel agent in T-cell directed boron neutron capture therapy (BNCT) for cancer treatment due to its biocompatibility **[7]**. Hardness and yield stress can be increased by decreasing grain size of particles. B_4C nanoparticles have been synthesized by numerous routes such as sol gel method **[8]**, solvothermal reduction method **[9]**, ball milling **[7]**, high temperature solid-state sintering **[10]**, gas-phase synthesis **[11]** thermal plasma **[12]** etc. Limitations like lack of a boron alkoxide source makes sol gel method as nonviable. In ball milling, time and energy consumption is more. Also uniformly sized nanoparticles and high-purity product were very difficult to obtain in ball milling process. In thermal plasma process high energy and high cost are involved but results remain unsatisfied for achieving B_4C nanoparticles. According to literature, B_4C nanoparticles were also synthesized by carbothermal and magnesiothermal reactions at very high temperature and are not cost effective **[13]**. The need of the hour is to synthesize B_4C nanoparticles at relatively low temperature with superior properties. For that reason, processing parameters like temperature and reaction time must be studied to get better results.

In this paper, we have studied the effect of temperature and duration of reaction on synthesis of B_4C nanoparticles. Due to cost effectiveness, high purity, and controlled processing parameters etc.; solvothermal route was employed to synthesize B_4C nanoparticles. The B_4C nanoparticles were successfully synthesized having uniformity and size less than 20 nm.

Experimental

Materials and methods

For present investigations, a specially designed stainless steel (304) autoclave of 50 ml capacity was used **[14]**. Boric Acid (H_3BO_3) (20 µm and 99.9 %), activated magnesium (98%) as reducing agent and acetone as a carbon source were used as initial ingredients. All the precursors were purchased from Sigma and used without further purification. In this paper, various processing parameters like temperature, reaction time and concentration of reducing agent has been varied and studied for their effect on the synthesis of boron carbide nanoparticles. The optimization of processing parameters has been done to find out the suitable temperature and time required to synthesis boron carbide nanoparticles. The temperature has been varied from 600 °C to 800 °C at an interval of 50 °C for 13 to 20 hrs respectively. The ingredients were put in autoclave of 50 ml capacity in an appropriate amount as given in **Table 1**. The charged autoclave was heated at different temperature and time which is also shown in **Table 1**. The Dark solid powders were taken out after the cooling of autoclave. Un-reacted Mg and other soluble phases were washed away with solution of hydrochloric acid and distilled water having 1:1 volume ratio. The acid treated samples were washed with ethanol for several times. The powders were dried at 70 °C for 4 hours in a vacuum heating oven. The obtained product was used for further characterization.

Characterization

After acid leaching, samples were characterized by X-ray diffraction (XRD) (X'pert pro PANanalytical) using monochromatic CuK_α radiations (λ = 1.5418 Å). The range of the 2θ angle for XRD patterns was $20° \leq 2\theta \leq 80°$. Fourier transform infrared spectroscopy (FTIR) was done using ATR Bruker spectrometer. The morphological and compositional study of crystalline phases of the synthesized sample was done using a high-energy beam of electrons with the help of scanning electron microscope (JSM-6510 LV (Jeol)). Transmission electron microscopy (TEM) was done using Hitachi H-7500 model.

Results and discussion

XRD analysis

In present study, the effect of temperature, pressure generated during growth and reaction time on conversion of boric acid to B_4C was studied in detail. XRD patterns of the synthesized samples are shown in **Fig. 1**. The reaction parameters are tabulated in **Table 1**.

Effect of temperature and pressure

The samples were heated at different temperatures with constant composition and constant time.

Table 1. Various processing parameters used in synthesis process.

Sr. No.	Composition: H_3BO_3, Mg, CH_3COCH_3	Time (hrs)	Temp. (°C)	Product	Calculated Crystallite Size (nm)
S1	4g, 2g, 20ml	20	600	Carbon	-
S2	4g, 2g, 20ml	20	650	Boron, Carbon	-
S3	4g, 2g, 20ml	20	700	Boron, Carbon	-
S4	4g, 2g, 20ml	20	750	Boron, Carbon	-
S5	4g, 2g, 20ml	13	800	Carbon	-
S6	4g, 2g, 20ml	15	800	Carbon	-
S7	4g, 2g, 20ml	17	800	Carbon	-
S8	4g, 2g,20ml	20	800	Boron carbide	8.7

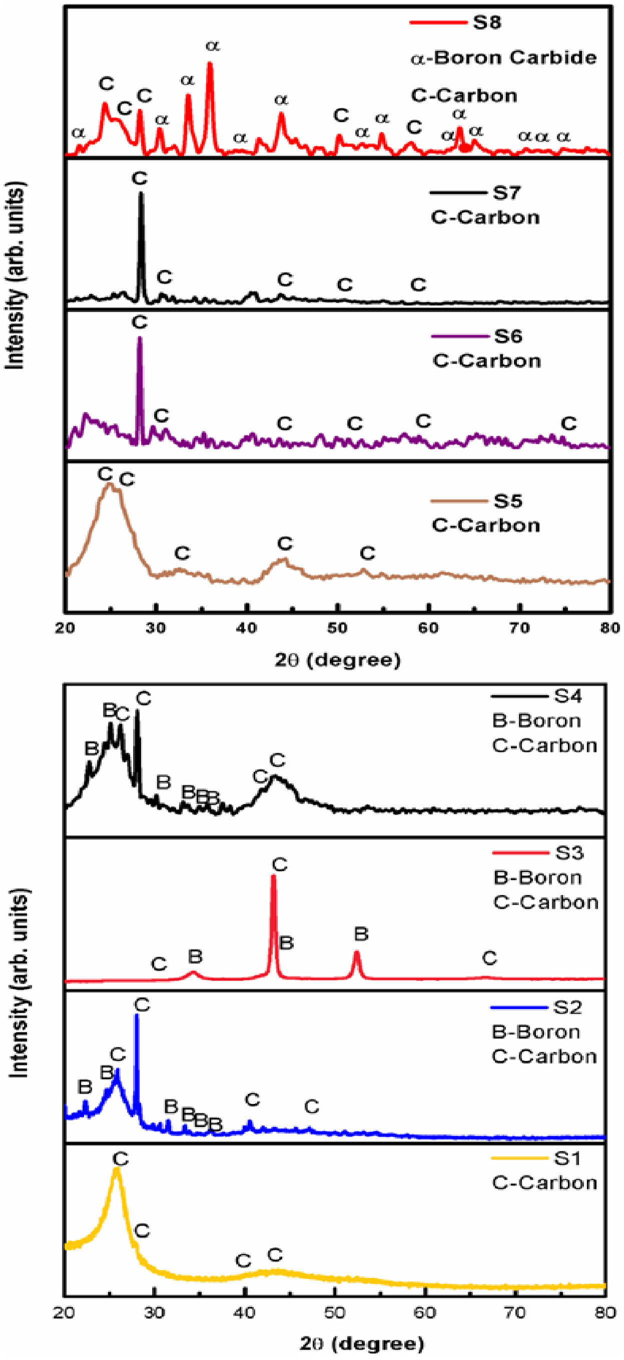


Fig. 1. XRD patterns of synthesized samples (S1, S2, S3 S4, S5, S6, S7, and S8).

The pressure generated during the reaction has been calculated from antoine equation **[15]** which is given as follow:

$$\frac{lnP}{kPa} = \frac{A - B}{t} + C \tag{1}$$

where, P is pressure; A, B and C are constants; t is temperature in degree Celsius.

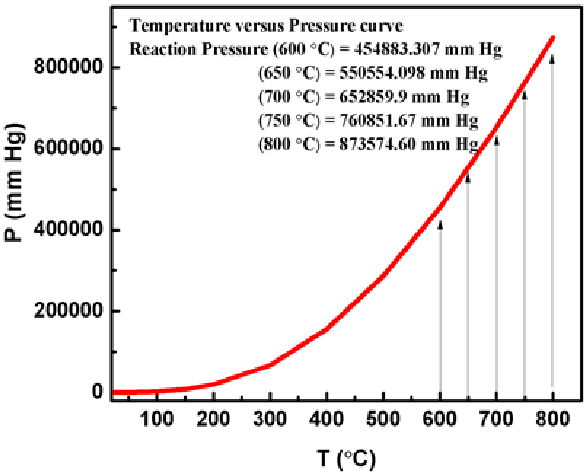


Fig. 2. Plot of pressure vs. temperature.

From the curve (**Fig. 2**), it can be concluded that 600 °C pressure 454883.307 mm Hg is not as sufficient for completing the reaction as the formed resultant product is amorphous carbon (**Fig. 1**) indexed with ICDD card no. 75-1621. At 650 °C, 700 °C and 750 °C (S2, S3 and S4) carbon and hexagonal boron (ICDD card no 01-080-0322) is formed. From 650 ºC to 750 ºC with pressure range up to 760851.67 mm Hg is not as much sufficient for decomposition of boric acid into boron carbide. In sample (S8) boron carbide nanoparticles have been formed at 800 °C with pressure 873574.60 mm Hg for 20 hrs. XRD peaks are indexed with boron carbide (ICDD card no. 06-0555). Thus it is the requisite temperature and pressure for synthesis of boron carbide nanoparticles. The presence of peaks of B_4C in XRD pattern of this sample indicates the conversion of H_3BO_3 to B_4C. The proposed reaction which may have occurred is:

$$4H_3BO_3 + CH_3COCH_3 + Mg \rightarrow B_4C + 2CO_2 + H_2 + MgO + 8H_2O \tag{2}$$

In this case, hydrogen generated is helping in reduction of Boric acid. Magnesium might have provided the active sites for nucleation of B_4C. The oxygen molecules which are released during the reaction, they consumed by access carbon. The crystallite size of the prepared sample (S8) is 8.7 nm which was calculated using Hall Williamson formula **[16]** given as follows:

$$\frac{\beta cos\theta}{\lambda} = \frac{1}{L} + \frac{\varepsilon sin\theta}{\lambda} \tag{3}$$

Critical analysis of XRD shows that the synthesized powder is highly crystalline in nature and highly textured along (012) plane with texture coefficient 2.0912. Texture coefficient is calculated using the relation given below **[17]**:

$$P(h_ik_il_i) = \frac{\mathrm{I}(h_ik_il_i)}{I_0(h_ik_il_i)}\left[\frac{1}{n}\sum_{i=1}^{n}\frac{\mathrm{I}(h_ik_il_i)}{I_0(h_ik_il_i)}\right]^{-1} \tag{4}$$

where, P (hkl) is texture coefficient of the plane specified by miller indices, I (hkl) and I_0 (hkl) are the specimen and standard intensities respectively for a given peak and n is the number of different peaks. From texture analysis; it can be concluded that material was grown along least dense plane.

Effect of time

In order to see the effect of duration of reaction time on the synthesis of Boron Carbide nanoparticles, the reaction time has been varied from 13 hrs to 20 hrs (S5, S6, S7 & S8) which has been shown in **Table 1**. The sample synthesized at 800 °C for different time intervals (13 hrs, 15 hrs and 17 hrs) shows amorphous carbon (**Fig. 1**) indexed with ICDD card no.75-1621; as the resultant product. This reaction time was not sufficient for conversion of boron carbide. When the material was heated for 20 hrs; boric acid complex converted to B_4C labeled as S8 in **Table 1**. Finally, boron carbide nanoparticles have been synthesized with 873574.60 mm Hg pressure for 20 hrs at 800 °C. This range can be further useful for synthesis of uniformly boron carbide nanoparticles.

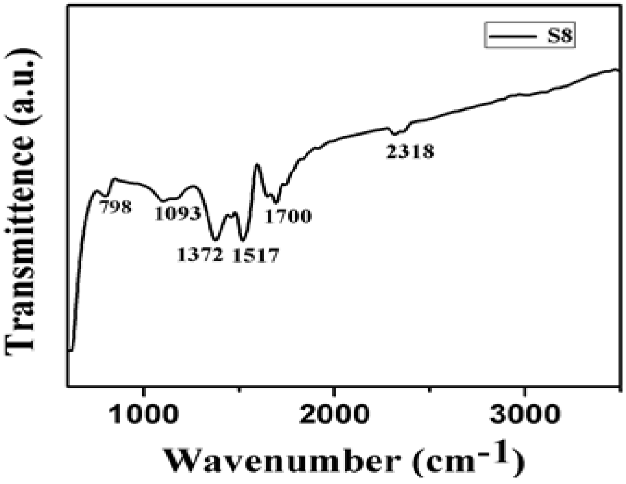


Fig. 3. FTIR spectrum of sample S8.

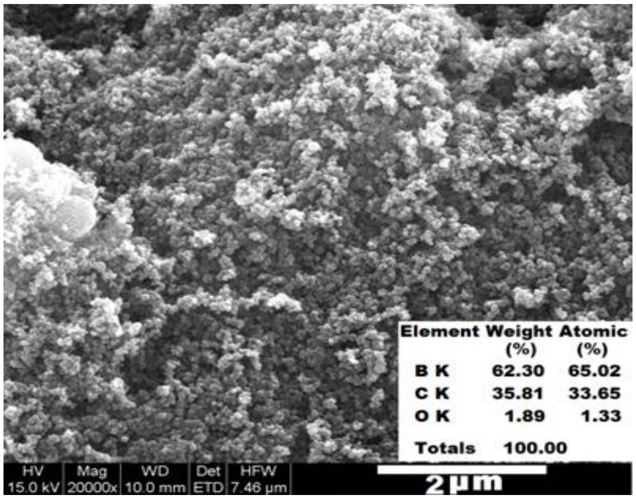
FTIR analysis

Fig. 3 shows the FTIR spectrum of Boron Carbide (B_4C) nanoparticles. It shows peak at 798 cm^{-1} which is due to vibration of different hydrocarbon species. The peak at 1093cm^{-1} is associated to C-B bond shows the formation of Boron Carbide **[18]**. The peak demonstrated at

1372cm^{-1} is due to presence of C-O-C group **[18]**. The peak at 1517 cm^{-1} is contributed due to anti-symmetric stretching of chain in the crystalline B_4C Boron Carbide. The peak at 1700 cm^{-1} is due to vibration of C=C bonds **[19]**. The transmittance band at 2318 cm^{-1} is attributed due to C-O stretching of the CO_2 molecule **[20]**.

SEM and EDX analysis

Detailed field emission scanning electron micrograph as well as EDX analysis of the sample S8 was shown in **Fig. 4**. The SEM micrographs showed that the particles are nearly spherical but agglomerated. EDX analysis gives the percentage of various elements present in the synthesized sample; is shown in **Fig. 4** (inset).



Element	Weight (%)	Atomic (%)
B K	62.30	65.02
C K	35.81	33.65
O K	1.89	1.33
Totals	100.00	

Fig. 4. FESEM image of sample S8.

TEM analysis

Fig. 5 shows TEM image of the sample S8. It has been observed from micrograph, that the particle size is less than 10 nm. The observed particle size is in close proximity with the size estimated using Hall Williamson equation.

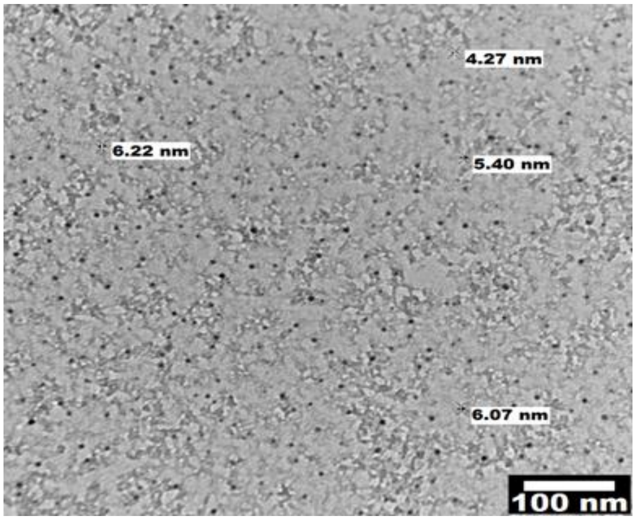


Fig. 5. TEM image of sample S8.

Conclusion

Nanostructured boron carbide has been synthesized by heating boric acid and acetone at 800°C for 20 hrs. It is concluded that the processing parameters (temperature, pressure and time) plays a vital role in the synthesis of nanostructured boron carbide.

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Author's contributions

Conceived the plan: Akshay Kumar, Ramovatar Meena; Performed the expeirments: Paviter Singh, Bikramjeet Singh, Mandeep Singh; Data analysis: Kulwinder Singh, Manjeet Kumar, Rajni Bala; Wrote the paper: Gurpreet Kaur, Manpreet Kaur, Harpreet Kaur. Authors have no competing financial interests.

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