

Low-temperature synthetic route for boron carbide

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Abstract

Boron carbide is one of the hardest materials with diamond-like mechanical properties, and is already used for a variety of applications including armor plating, blasting nozzles, and mechanical seal faces, as well as for grinding and cutting tools. It is produced on an industrial scale by classical carbothermal reduction of boric oxides at high temperatures, but the formation of pure boron carbide in processed forms, such as films and fibers, is difficult. As an alternative to high-temperature powder techniques, there is recently great interest in the development of polymer precursors to produce ceramic materials. The aim of the present work is to develop a cost effective and low-temperature manufacturing process to synthesize boron carbide from cheap and easily available raw materials. The initial objective of our research is the design and synthesis of a new type of boron–carbon polymer, which would serve as precursor for boron carbide. The polymeric precursor is synthesized by the reaction of boric acid and polyvinyl alcohol that after pyrolysis at 400 °C and 800 °C gives boron carbide. The polymeric precursor and its pyrolyzed products are characterized by Fourier transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD). X-ray diffraction shows that boron carbide (B_4C) obtained from this method has an orthorhombic crystal structure. It is a unique low-temperature (~ 400 °C) synthetic route for boron carbide.

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1. Introduction

Boron carbide is a highly refractory material that is of great interest for both structural and electronic applications. Of particular importance are its high-temperature stability, high hardness, high cross-section for neutron capture, and excellent high-temperature thermoelectric properties. This combination of properties gives rise to numerous applications, including uses as an abrasive wear-resistant material, ceramic armor, a neutron moderator in nuclear reactors, and, potentially, for power generation in deep-space flight applications. Boron carbide powders can easily be made by carbothermal reduction of boric oxides at high temperatures, but the formation of pure boron carbide in processed forms, such as films and fibers, is difficult. Recently, Zhang et al. discussed the importance of nanoscale boron carbide materials and demonstrated the use of plasma-enhanced chemical vapor deposition to generate boron carbide nanowires and nanonecklaces.¹ Han et al. recently reported on the formation of mixtures of crystalline boron carbide nanorods and boron-doped nanotubes upon the reac-

tion of boron oxide vapor with carbon nanotubes.² Pender et al. reported a simple, straightforward method for the generation of aligned, monodispersed boron carbide nanofibers based on the use of the porous alumina templating technique in combination with a new single-source molecular precursor.³

As an alternative to high-temperature powder techniques, there is recently great interest^{4,5} in the development of polymer precursors to produce ceramic materials. Such routes offer a number of potential advantages: (i) a suitable polymer could have a precisely controlled stoichiometry with a composition which could be systematically varied to optimize ceramic properties, (ii) the polymer could be formed into a desired shape or thin film and be converted to a ceramic with possible retention of form, and (iii) the polymer could undergo low-temperature decomposition, enabling ceramic formation under milder conditions than those used in conventional techniques.

Mirabelli et al. reported new selective routes to boron carbide and boron nitride based on the use of the new polymer systems, poly[2-(vinyl)pentaborane] and poly[B-vinylborazine], as precursors.⁶

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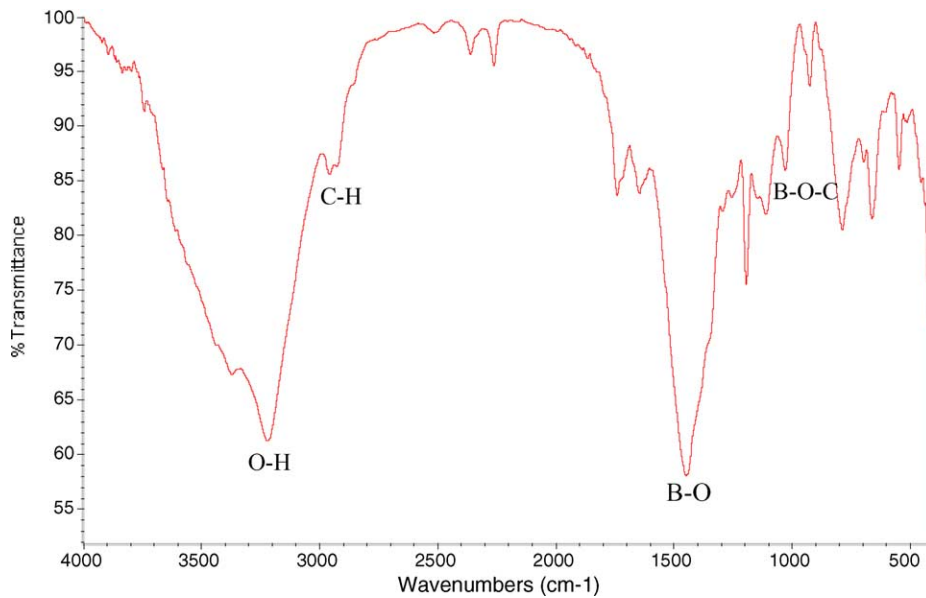


Fig. 1. FTIR spectrum of the polymer precursor.

Limitations in traditional ceramic processing have encouraged interest in the development and utilization of polymer pyrolysis as low-temperature synthetic routes to nonoxide ceramic materials. Boron carbide is an example of a material where preparation from a polymer precursor might offer advantages over conventional synthetic techniques. Mirabelli et al. reported that 2-(H₂C=CH)B₅H₈ will undergo thermal polymerization to vinylpentaborane oligomers and that these species can be converted to pure boron carbide (B₄C) with high ceramic yields under mild conditions.⁷ Isao et al.⁸ re-

ported that boric acid and 2-hydroxybenzyl alcohol (HBA) were used as the B and C source of B₄C. H₃BO₃ and HBA in DMF solution gave a phenolic resin-B₂O₃ hybrid. The hybrids swelled upon heating, and the swelled hybrids could be easily ground into fine powders. Heat treatment of the powdered hybrids at 1500 °C in Ar for 4 h led to the formation of B₄C powders. Boron carbide has also been prepared by carbothermal process using boric acid and citric acid as raw materials.⁹ Aqueous solution of boric acid in presence of citric acid forms a stable gel under controlled pH conditions.

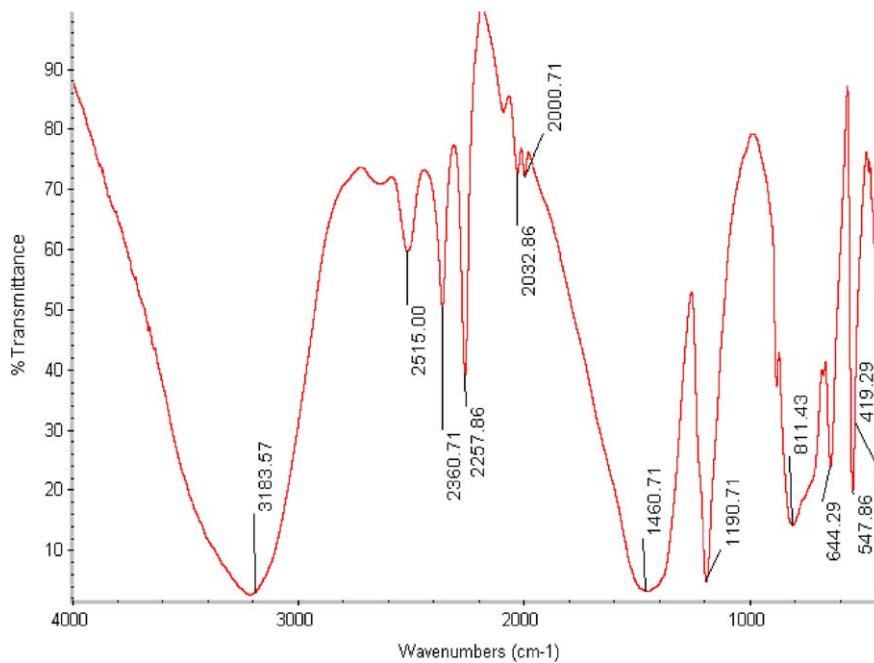


Fig. 2. FTIR spectrum of boric acid.

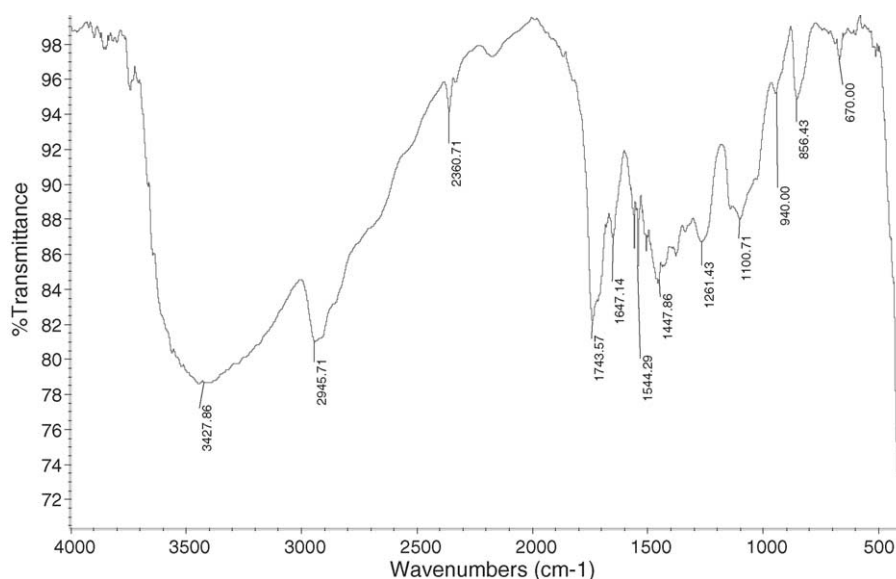


Fig. 3. FTIR spectrum of polyvinyl alcohol.

Subsequent pyrolysis under vacuum yields a precursor powder consisting of boron oxide and carbon. The precursor is heated under vacuum at 50 °C/h up to 1450 °C and the product obtained has been characterized by X-ray diffraction, chemical analysis and SEM. XRD pattern shows that the product consists of B₄C and carbon.

As evident from the foregoing discussions, pentaboranes, borazines, and their derivatives are used as polymeric precursors for synthesis of boron carbide. Problems associated with borazines and boranes are that they are highly toxic and expensive materials. So, in search for low cost precursors, an attempt has been made to synthesize a variety of boron-containing polymeric precursors from inexpensive, non-toxic and readily available starting materials. Accordingly, a straightforward synthesis adaptable to laboratory or large-scale production of B₄C is of interest. Hence the objective of the present work is the designing of an inexpensive and non-hazardous polymer in which boron is incorporated

into the polymer backbone, which on pyrolysis gives boron carbide. Besides, pyrolysis temperature is a main drawback of the previous systems. In most of the previous works a very high temperature was used during pyrolysis. Hence, to synthesize boron carbide in a low-temperature polymer pyrolysis route is an additional economic incentive. In the present work a boron-containing polymeric precursor is synthesized by the reaction between boric acid and polyvinyl alcohol.

2. Experimental

Boric acid was obtained from SRL Ltd., India and was purified by crystallizing from warm water. Polyvinyl alcohol was obtained from SD fine chemicals Ltd., India and used as received.

26.4 g (0.6 mol) of polyvinylalcohol (PVA) was made soluble in distilled water taken in a 500 ml beaker and heated on a water-bath. 12.366 g (0.2 mol) of boric acid {B(OH)₃} was made soluble in distilled water taken in a 250 ml beaker and heated in the water bath. Then the boric acid solution was added to the PVA solution in hot condition with constant stirring with a glass rod. A white fluffy and rubbery material was obtained which was collected on a Petridish and dried in oven at about 100 °C. Then the dry material was ground to white powder.

The polymer was placed in a porcelain crucible and heated in a furnace. A heating rate of 120 °C per hour was maintained till the desired temperature was reached. Pyrolysis of the precursor compound in air for three hours yields a black powder at both temperatures (400 °C and 800 °C).

Fourier transform infrared spectra of the polymer and the pyrolyzed material in KBr pellets were carried out using a Thermo-Nicolet Nexus-870 FT-IR spectrometer.

Table 1
List of interplanar spacing values (*d*) for the polymeric precursor

2θ	d (Å)
13.45	6.57
14.70	6.02
19.55	4.53
20.85	4.25
28.00	3.18
34.00	2.63
37.35	2.40
40.10	2.24
45.00	2.01
49.75	1.83
61.73	1.50
65.25	1.43
76.25	1.25
77.10	1.23
82.90	1.16

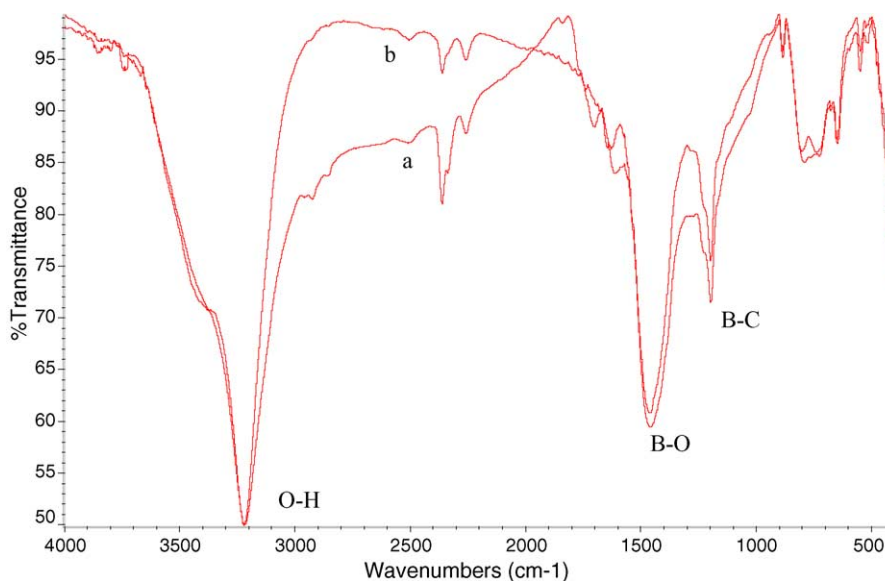


Fig. 4. FTIR spectra of the pyrolyzed material at 400 °C (a) and 800 °C (b).

X-ray diffraction measurements of the polymer and its pyrolyzed products were obtained with a Philips PW-1729 X-ray diffractometer using a Cu K α source with a scan speed of 0.05 degree per second.

3. Results and discussion

The possible reaction pathway between boric acid and polyvinyl alcohol is represented as follows.

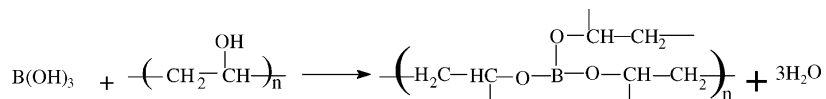


Fig. 1 shows the infrared spectrum of the precursor material. The absorption band at around 3200 cm⁻¹ is due to O–H stretching vibrations. The spectrum also shows aliphatic C–H stretching vibration at 2952 cm⁻¹. The bonding of B–O–C

is supported by the absorption peak at 1030 cm⁻¹.³ The absorption band at around 1450 cm⁻¹ is ascribed to the B–O stretching vibration. To compare the precursor material with the raw materials (boric acid and PVA), FTIR spectra of both B(OH)₃ and PVA are taken (Figs. 2 and 3). The spectrum of the precursor material does not match with that of the boric acid and polyvinyl alcohol. From the FTIR spectrum it is observed that B–O–C bonds are formed indicating that the reaction occurs between boric acid and PVA. Fig. 4 shows the

Table 2

List of interplanar spacing values (*d*) for the material pyrolyzed at 400 °C and 800 °C

2 θ	<i>d</i> (Å)	<i>hkl</i>
16.2	5.46	
22.50	3.94	8 2 0
27.7	3.22	
30.69	2.91	12 0 0
34.14	2.62	8 4 1
40.2	2.24	2 7 1
43.61	2.07	7 7 1
46.59	1.95	0 9 0
54.85	1.67	0 1 0 1
73.9	1.28	
82.2	1.17	
90.05	1.09	

infrared spectra of the material pyrolyzed at 400 °C (a) and 800 °C (b), respectively. O–H stretching vibrations appear at around 3200 cm⁻¹. The absorption at around 1450 cm⁻¹ is attributed to B–O stretching vibration and B–C absorption band appears at around 1190 cm⁻¹.¹⁰ From the FTIR spectra it is also observed that B–C bond formation occurs suggesting that boron carbide is obtained during pyrolysis. Fig. 5 shows the X-ray diffraction pattern of the polymeric precursor. The interplanar spacing values (*d*) calculated from the corresponding 2 θ values are tabulated in Table 1. But there is no scope to verify the results obtained as the precursor is new type of crystalline material and no published result on the crystal structure has been found.

Fig. 6 shows the X-ray diffraction patterns of the pyrolyzed products of the precursor at 400 °C (i) and 800 °C (ii). The diffraction peaks appear almost at the same positions at both temperatures. The interplanar spacing values (*d*) are calculated from the corresponding 2 θ values and are tabulated in Table 2.

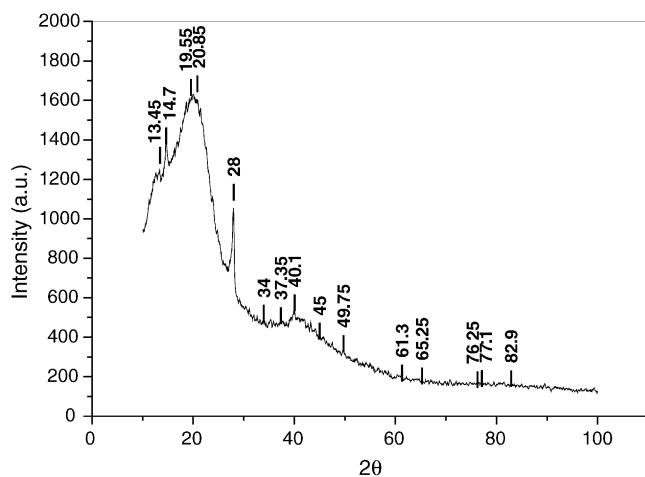


Fig. 5. X-ray diffraction pattern of the polymeric precursor.

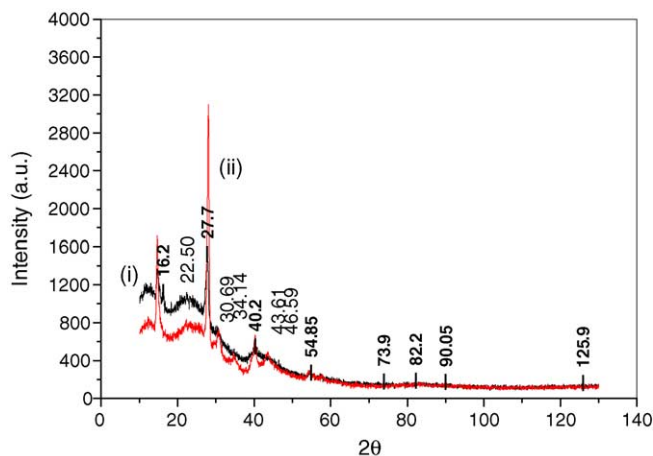


Fig. 6. X-ray diffraction patterns of the pyrolyzed material at 400 °C (i) and 800 °C (ii).

The d -values obtained from XRD are compared with the values of boron carbide reported in the JCPDS file number 26-232. The d -values obtained from the XRD match with the maximum number of the Bragg peaks of orthorhombic boron carbide. From the d - and hkl values the lattice parameters

are calculated. The values are $a = 35.25 \text{ \AA}$, $b = 17.55 \text{ \AA}$ and $c = 4.86 \text{ \AA}$ which closely match with the reported values ($a = 35.90 \text{ \AA}$, $b = 17.65 \text{ \AA}$ and $c = 5.09 \text{ \AA}$). The space group of boron carbide is not mentioned in the JCPDS file number 26-232. Hence it is not mentioned in the present paper. The presence of considerable amount of oxygen in the material indicates that boric oxides may be present as impurity.

4. Conclusions

Here, we reported that a boron-containing polymeric precursor could be obtained by the reaction between boric acid and polyvinyl alcohol. Pyrolysis of the precursor material at 400 °C and 800 °C in air atmosphere yields boron carbide. XRD results showed that the polymeric precursor is crystalline in nature. During pyrolysis the precursor material changes to crystalline boron carbide. Since the experimental and theoretical values of the lattice parameters are in good agreement, it is concluded that the present boron carbide has orthorhombic crystal structure. It is a unique low temperature and inexpensive synthetic route for boron carbide.

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