

# Ethylene glycol assisted low-temperature synthesis of boron carbide powder from borate citrate precursors



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## ABSTRACT

B<sub>4</sub>C powders were synthesized by carbothermal reduction of ethylene glycol (EG) added borate citrate precursors, and effects of EG additions (0–50 mol% based on citric acid) on the morphologies and yields of synthesized B<sub>4</sub>C powders were investigated. The conditions most suitable for the preparation of precursor were optimized and optimum temperature for precursor formation was 650 °C. EG additions facilitated low-temperature synthesis of B<sub>4</sub>C at 1350 °C, which was around 100–300 °C lower temperature compared to that without EG additions. The lowering of synthesis temperature was ascribed to the enlargement of interfacial area caused by superior homogeneity and dispersibility of precursors enabling the diffusion of reacting species facile. The 20% EG addition was optimal with free residual carbon lowered to 4%. For smaller EG additions, the polyhedral and rod-like particles of synthesized product co-existed. With higher EG additions, the morphology of synthesized product was transformed into needle and blade-like structure.

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## 1. Introduction

Boron carbide (B<sub>4</sub>C) has a leading role in numerous high performance applications owing to its extreme hardness, low density, high melting point, high Young's modulus, great resistance to chemical agents, excellent thermoelastic and thermoelectric properties and high corrosion and oxidation resistance. The combination of these properties renders B<sub>4</sub>C a promising material for numerous applications including body and vehicle armor, abrasive powder, nuclear applications and aerospace applications [1–4].

B<sub>4</sub>C is generally produced by carbothermal reduction of boron oxide at high temperatures according to reaction (1) and magnesiothermic reaction of boron oxide [5–10].



However, this process has many associated problems, including, considerable amount of free carbon residue in the final product due to substantial loss of boron by volatilization of its oxides; difficulty and associated greater cost to grind the product into fine particle size for densification; requiring a high temperature furnace operation; contamination in the final product; and time consumption.

An alternative to above processes is the utilization of polymer precursors, e.g. sucrose and glucose, glycerin, polyols, and phenolic resin, as low-temperature synthetic route to B<sub>4</sub>C facilitated by improving the homogeneity and dispersibility of B<sub>2</sub>O<sub>3</sub> and carbon [11–22]. Nevertheless, the disadvantage of using organic precursors is the presence of residual carbon in the products synthesized at lower temperatures. Citric acid (CA) has been employed to produce B<sub>4</sub>C with significant residual carbon at 1500–1900 °C [15–18]. Recently, it is indicated that the addition of tartaric acid to boric acid (BA)–glycerin ameliorates the dispersion of B<sub>2</sub>O<sub>3</sub>/C [21]. It is concluded that the hydroxyl group can be easily condensed with BA, enhancing the esterification (B–O–C) and yielding the precursors with fine homogeneous dispersion.

Ethylene glycol (containing hydroxyl groups) is extensively utilized to synthesize a variety of compounds by esterification with metal citrate [23,24]. It is expected that EG addition to condensed

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borate citrate will modify the thermodynamics of carbothermal reaction by promoting the esterification reaction. In this work, the effects of EG additions on the synthesis of  $B_4C$  from condensed BA-CA are investigated. The optimum starting compositions and optimum conditions for pyrolysis of precursor and preparation of products have been determined. FTIR, XRD, and SEM analyses are utilized to investigate the yield and morphology changes of precursors and synthesized  $B_4C$ .

## 2. Experimental

Materials used were boric acid [(BA), Wako, 99.5%], ethylene glycol [(EG), Merck, 99.5%], and citric acid [(CA), Riedel-de Haen, 99.5%]. BA/CA of 2:1 was used and EG additions were 0–50 mol% ( $P_0$ – $P_{50}$ ) based on CA. The BA solution (2.5 M) in distilled water was prepared at 80 °C. CA was added slowly to the solution and held for 20 min until a yellowish solution was obtained. Subsequently, EG was added to the stirred solution. The solution was then slowly heated to 130 °C and maintained at this temperature to facilitate the polyesterification reaction. The condensed products changed from golden yellow to transparent light yellow with EG additions. The condensed products were pyrolyzed over the temperature range of 550–800 °C in air for 2 h. The obtained dark gray precursors were compacted and heated at 1050–1400 °C for 0–4 h in an Ar flow.

The  $B_2O_3$  contents were determined by titration of mannitol–boric acid complex with standard NaOH solution (0.1 M). The residual carbon in the final products was determined by the method used in [9,22]. Fourier transform infrared (FTIR) spectra of starting materials and condensed products were recorded on Shimadzu Prestige 21 spectrometer. X-ray diffraction (XRD) patterns of pyrolyzed powder and products were obtained using powder X-ray diffractometer (Rigaku). The  $B_4C$  peak intensity ratio ( $I_{B_4C}/I_{B_4C} + I_C + I_{B_2O_3}$ ) of the products was estimated from the main peak intensities of each of the  $B_4C$ , carbon, and  $B_2O_3$ . The morphology of pyrolyzed powder and products was examined using a scanning electron microscope (LEO 440). A Cilas 1064 laser particle size analyzer was utilized for determining the average particle size and particle size distribution. The BET specific surface area, pore size distribution by pore diameter, and pore volume were determined by Quanta chrome Autosorb 1C BET Surface Area & Pore Volume Analyzer. The surface areas and pore volumes (or pore size distribution) were determined from nitrogen adsorption–desorption isotherms by using the Brunauer–Emmett–Teller (BET) equation and Barret–Joyner–Halenda (BJH) methods.

## 3. Results and discussion

In order to comprehend the formation of borate ester, FTIR spectra of the starting materials and the condensed products, with and without addition of EG, are depicted in Fig. 1. Fig. 1(ii a and b) indicates the FTIR spectra of condensed products with and without the addition of EG. The peak observed at 2964  $cm^{-1}$  is attributed to the asymmetric stretching of  $-CH_2$ ,  $-CH_3$  groups present in organic derivatives [24,25]. The appearance of the band at 1730  $cm^{-1}$  for  $-COOH$  groups, the bands at 1585 and 1380  $cm^{-1}$ , respectively, for the asymmetric and symmetric stretching of  $C=O$ , and the bands at 1020  $cm^{-1}$ , 1080  $cm^{-1}$ , 1130  $cm^{-1}$ , and 1287  $cm^{-1}$  for  $C-O$  and  $B-O-C$  [13,14,21,24,25] strongly suggest that some  $-COOH$  groups in CA have reacted with ethylene glycol and boric acid, while some have not. This phenomenon is further strengthened by the fact that band at 1730  $cm^{-1}$ , for carbonyl groups ( $COO-$ ), becomes weaker, and  $O-H$  stretching band becomes stronger with the addition of EG (Fig. 1(ii a)). The broad peak observed at 3230  $cm^{-1}$  (Fig. 1(ii a)) is due to the presence of  $-OH$  groups in CA and ethylene glycol

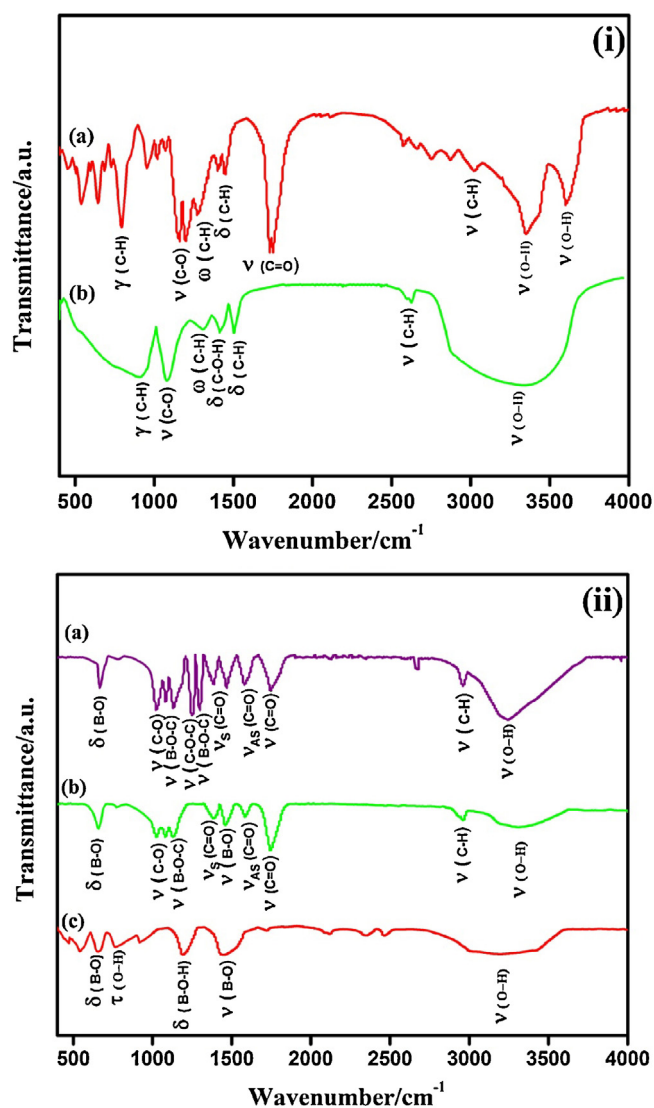


Fig. 1. FT-IR spectra of (i) (a) CA and (b) EG, and (ii) (a)  $P_{20}$  condensed product, (b)  $P_0$  condensed product, and (c) BA.

derivatives [13–17,21,23–25], which is much weaker than that of starting citric acid and ethylene glycol. This result suggests the consumption of OH group by esterification and also the existence of unreacted OH groups. With the introduction of EG, a band at 1250  $cm^{-1}$  also appears which is attributed to the  $C-O-C$  structure from ethylene glycol [25]. Addition of EG also induces an additional  $B-O-C$  stretching vibration at 1287  $cm^{-1}$  [14,21]. These results indicate the reaction of borate citrate with EG. Furthermore, the  $B-O-H$  bending band at 1190  $cm^{-1}$  and  $O-H$  torsion band at 752  $cm^{-1}$  [14,21] derived from BA disappear (Fig. 1(ii a and b)) in the condensed products. These results indicate that firstly, the borate citrate ( $B-O-C$ ) is formed in the prepared condensed product by dehydration condensation of BA and citric acid (Fig. 1(ii b)). The borate citrate undergoes further esterification with ethylene glycol to grow into a polymer network. The polymeric structure is broken down and releases carbon and  $B_2O_3$  in the firing process.

The  $C/B_2O_3$  contents of the pyrolyzed samples, with and without the additions of ethylene glycol, at 550–750 °C for 2 h are depicted in Fig. 2. According to the stoichiometric carbothermal reaction between  $B_2O_3$  and C to afford boron carbide, the  $C/B_2O_3$  ratio in the pyrolyzed sample should be about 3.5. Moreover, the carbothermal reaction is also accompanied by a slight boric species loss

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