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Non-stoichiometric boron carbide synthesized in moderate temperature conditions

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Non-stoichiometric boron carbide was successfully synthesized through a chemical synthetic route by using tribromide and carbon tetrachloride as reactants and metal sodium as co-reductant at 700 °C. The synthesized sample was characterized by X-ray powder diffraction, transmission selected area electron diffraction, electronic energy loss spectra (EELS) and scanning electron microscopy. The results of the analysis revealed that the synthesized boron carbide crystals have rhombohedral structure and equiaxial morphology. Results of the EELS analysis indicate that the compositions of the synthesized boron carbide are not uniform, the carbon content can range from 9 at. % to 11 at. %.

Key words: *non-stoichiometric boron carbide; chemical synthesis; X-ray diffraction; electron energy loss spectroscopy*

1. Introduction

Boron carbide is an important non-metallic material possessing many excellent properties such as high melting point, high elastic modulus, high hardness, high corrosion and oxidation resistance. These properties make boron carbide suitable for high performance applications such as armour plating, nozzles, bearings and cutting tools [1–4]. Boron carbide can be also used as a neutron absorber and shielding material in nuclear plants due to a high neutron reactivity and high neutron absorption cross section of ^{10}B [5].

Boron carbide has a rhombohedral structure in which B_{12} icosahedra are linked by direct covalent bonds and 3-atom intericosahedral chains along the main diagonal of

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the rhombohedron. Boron carbide is not a stoichiometric compound, the carbon content can range from ca. 8 at. % (the boron-rich limit) to about 20 at. % (the carbon-rich limit) [6]. This large range of the B/C ratio implies that the carbon atoms substitute, to various extents, boron atoms within intericosahedral chains and the icosahedra, and the structure of boron carbide still keeps a single phase throughout the entire range [7].

Traditionally, boron carbide can be synthesized by chemical reactions including carbothermal reduction of boron oxide (B_2O_3), boric acid (H_3BO_3), borax ($Na_2B_4O_7$) etc., as well as by the direct combination of boron and carbon [3]. Other routes for the synthesis of boron carbide powder are the magnesiothermal reduction of B_2O_3 in the presence of carbon at 1000–1200 °C [3, 8] the reduction of BCl_3 by CH_4 at 1500 °C with laser [9] and the carbothermal reduction of boric acid–citric acid gel precursor [10]. The industrial method for the production of boron carbide is carbothermal reduction of boric acid at above 2000 °C [11]. To our knowledge, these methods are carried out at high temperature (higher than 1000 °C). Recently, some high melting point materials have been successfully synthesized under low temperature synthesis conditions, such as diamond [12], c-BN [13] and boron carbide [14]. The stoichiometric rod-like B_4C crystals were obtained at low temperature (450 °C) through a co-reduction route by using boron tribromide (BBr_3) and carbon tetrachloride (CCl_4) [15]. Because boron carbide is a non-stoichiometric compound, in principle, it is easier to obtain the crystals whose compositions deviate from B_4C. In this paper, we report a moderate temperature synthesis route for non-stoichiometric boron carbide by using BBr_3 and CCl_4 as reactants in the presence of metal sodium as co-reductant.

2. Experimental

The synthesis was were carried out in a glove box, which was filled with Ar gas. 10 cm^3 of CCl_4 and 5 cm^3 BBr_3 were put into a 50 cm^3 stainless steel autoclave. 13 g of sodium was also used as a co-reductant. No catalyst was needed in this procedure. The autoclave was sealed and heated to 700 °C at the heating rate of 70 °C/h and kept for 20 h before being cooled to room temperature naturally. The dark precipitate was collected and washed with distilled water three times. Dilute hydrochloride acid was used, in order to remove some metal impurity. Then, the precipitate was boiled with mixed acid (H_2SO_4: HNO_3 = 3:1) to remove the created carbon and washed 3 times with distilled water. After being dried under vacuum at 100 °C for about 4 h, a black powder was obtained. The whole reaction process for the synthesis of boron carbide can be formulated as follows

$$4BBr_3 + CCl_4 + 16Na \xrightarrow{700\,^{\circ}C} B_4C_{1-x} + 4NaCl + 12NaBr + xC$$

The final product was characterized using X-ray powder diffraction (XRD) and transmission electron microscopy (TEM, JEM-2010) to confirm the formation of the boron carbide phase. XRD spectra were obtained on a Rigaku Dmax-2000PC X-ray

diffractometer with Ni filtered Cu K_α radiation at the scanning rate of 5 deg/min. An electron energy loss spectrometer (EELS, Gatan-ENFINA-776) was employed to determine the chemical composition of the individual crystal in the synthesized powder in the TEM. The crystal size and morphology of the synthesized powders was investigated using scanning electron microscopy (SEM, KYKY-2800).

3. Results and discussion

XRD was used to check the structure of the synthesized sample. In its XRD spectrum (Fig. 1), all the reflection peaks correspond to rhombohedral boron carbide. The lattice parameters determined from XRD are a = 5.621 Å and c = 12.11 Å (due to the symmetrical relationship between the rhombohedral structure and the hexagonal structure, the lattice parameters of the rhombohedral lattice can also be given for the hexagonal lattice), both of which being slightly higher than the reported values of the standard B_4C (PCPDF 35-0789: a = 5.600 Å, c = 12.08 Å) and the synthesized B_4C in ref. [15] (a = 5.604 Å, c = 12.09 Å), and slightly smaller than the reported values of the standard $B_{13}C_2$ (PCPDF 26-0233: a = 5.617 Å, c = 12.09 Å).

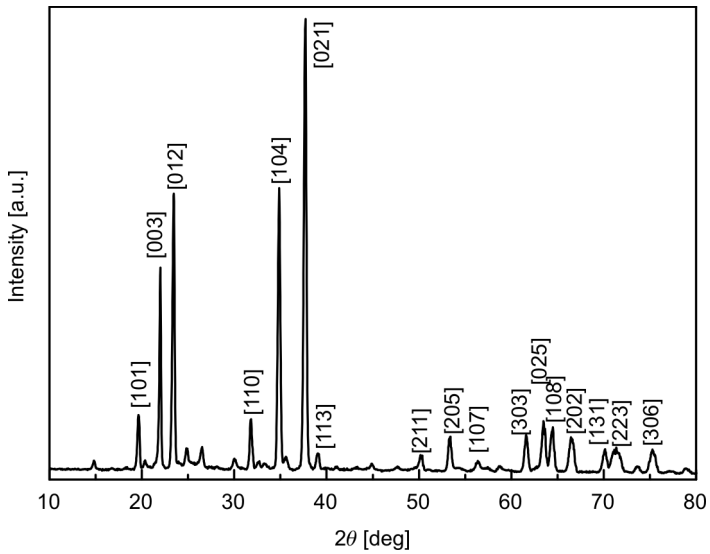

Fig. 1. XRD spectrum of the synthesized sample

In order to further determine the crystal structure and chemical composition of the obtained sample, SAED and parallel EELS measurements were performed on the synthesized crystals. Figure 2 shows typical SAED patterns of a synthesized rhombohedral boron carbide crystal along the <111> and <4 $\bar{3}$ 1> axes. From the clear spots appearing in Fig. 2, it can be seen that the synthesized boron carbide has high crystallinity. Figure 3 shows the corresponding EELS spectrum of the boron carbide crystal

shown in Fig. 2. In Figure 3, the characteristic K-shell ionization edges of elemental boron (188.4 eV) and carbon (284.8 eV) are observed, and no traces of other elements such as chlorine, bromine or sodium, are detected, suggesting that the synthesized boron carbide crystals contain no major impurities.

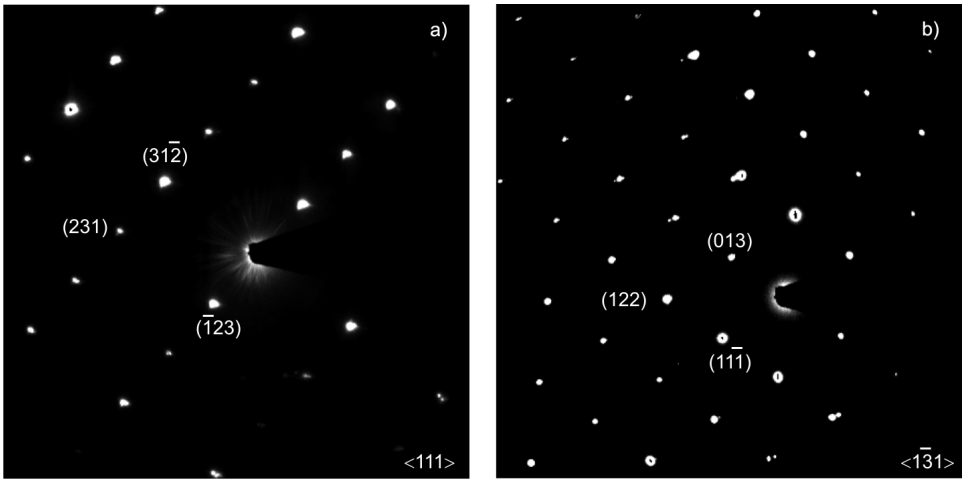

Fig. 2. SAED patterns of a rhombohedral boron carbide crystal in: a) <111> axis and in b) < 4$\bar{3}$1 > axis

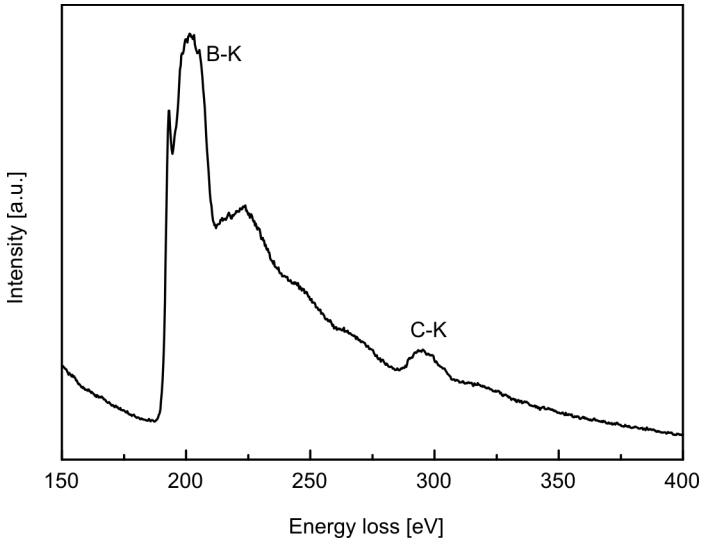

Fig. 3. The EELS spectrum taken from the crystal corresponding to Fig. 2, exhibiting characteristic K-shell ionization edges of boron at 188 eV and carbon at 284 eV with the carbon contents 10.7 at. %

From the background-subtracted EELS spectra of Fig. 3, the atomic percents of the boron carbide crystal have been quantified by using the usual hydrogenic cross-

sections. The quantified result reveals that the contents of B and C in the synthesized boron carbide crystal are 89.3 at. % and 10.7 at. %, respectively. Further EELS measurements were performed on more than 30 various crystals selected randomly in the sample to determine their compositions. It was found that the carbon contents of the synthesized boron carbide crystals are not uniform, and range between 9 at. % to 11 at. %. Thus, it can be expressed as B_4C_{1-x} ($0.5 < x < 0.6$). Such carbon contents are obviously different from those in crystals synthesized at 450 °C [14].

The different experimental results may imply that through such a reaction procedure, a higher reaction temperature (700 °C) favours the formation of the non-stoichiometric B_4C_{1-x} ($0.5 < x < 0.6$), but not the stoichiometric B_4C. It is well known that boron carbide it is a non-stoichiometric compound, whose carbon content can range from 8at. %-20at. %. Generally, since the atomic radius of carbon (0.91 Å) is smaller than that of boron (1.17 Å), different carbon contents in rhombohedral boron carbide will result in slight changes of the lattice parameters. In other words, with the increased of carbon content in the rhombohedral boron carbide crystals, the dimensions of the unit cell will be slightly shrunk (see the comparison of the lattice parameters between B_4C, $B_{13}C_2$ and the synthesized boron carbide sample shown in Table 1). That is why the lattice parameters of the synthesized rhombohedral boron carbide are slightly larger than that of the standard B_4C and the as-prepared B_4C in ref. [15].

Table 1. Lattice parameters of B_4C, $B_{13}C_2$ and boron carbide synthesized in the present paper

Boron carbide	Carbon content [at. %]	Lattice parameters [Å]	
		a	*c*
B_4C_{1-x} ($0.5< x <0.6$) synthesized in this work	9–11	5.621	12.11
$B_{13}C_2$, PCPDF 26-0233	13.3	5.617	12.09
B_4C, PCPDF 35-0789	20	5.600	12.08
B_4C, synthesized in ref. [15]		5.604	12.09

It should be noted that besides the reaction temperature, the reaction pressure may also play an important role in the formation of boron carbide with various carbon content. At the beginning of the reaction, the pressure should be relatively high, due to the evaporation of BBr_3 and CCl_4. Based on the ideal gas law, we estimate that the initial pressure in the autoclave is about 24 MPa. As the reaction proceeds, CCl_4 and BBr_3 are consumed gradually by sodium, thus the pressure should gradually become lower. At the end of the reaction, the pressure should reach a minimum. The changes in pressure may be a reason for the different carbon contents in the formed boron carbide crystals.

In order to determine the size and the morphology of the synthesized boron carbide crystals, SEM measurements were performed. Figure 4 shows the SEM image of the synthesized boron carbide crystals. The crystal size of the synthesized boron carbide is between 5 and 30 μm and its morphology is nearly equiaxial. In our samples,

we did not find any rod-like crystals as described in the Ref. [15]. This implies that the reaction temperature may play an important role in the morphology of boron carbide. In other words, the lower reaction temperature (450 °C) is favourable to the formation of rod-like boron carbide, whereas the higher reaction temperature (700 °C) is favourable to the formation of equiaxial boron carbide.

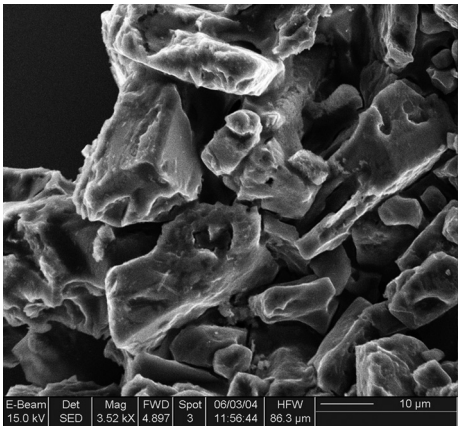

Fig. 4. SEM image of the synthesized boron carbide crystals

4. Conclusions

Highly crystalline non-stoichiometric boron carbide crystals were successfully synthesized through a facile co-reduction synthetic route by using CCl_4 and BBr_3 as reactants and metal Na as co-reductant at 700 °C. The carbon content of the synthesized boron carbide crystals ranges from 9 at. % to 11at. %. The size of the synthesized boron carbide crystals is between 5 and 30 μm and their morphology is nearly equiaxial. Due to a simple process and cheap carbon resource (CCl_4) such a co-reduction method may also be used to synthesize other carbides, for example the attractive carbon nitride and boron carbon nitride compounds.

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