

4.0 Introduction

Commercially boron carbide is synthesized by carbothermic reduction of boric oxide/boric acid [156]. However, this method cannot be employed for the synthesis of boron carbide containing isotopically enriched boron since the loss of highly precious and expensive enriched boron in the form of its oxides during the reduction is high which renders this process uneconomical. As an alternative to this high-temperature reaction technique, there is a great interest in the development of gel precursors to produce sinteractive boron carbide powder at relatively lower temperatures [93]. Table 4.1 shows the studies reported in the literature on the synthesis of boron carbide using gel precursors.

In the present study, nonaqueous gel precursors have been developed for the first time for the synthesis of boron carbide.

4.1 Synthesis of boron carbide from boric acid-sucrose xerogel

4.1.1 Experimental

In a typical experiment, 9 g of sucrose was taken in a combustion bowl and melted using a silicone oil bath at 440 ± 5 K. To this melt, 11.3 g of boric acid was added slowly to obtain a homogeneous gel. Upon heating this gel at 440 ± 5 K, a black-coloured dry xerogel (XSG) was obtained. This product was placed in a high-density graphite boat and pyrolyzed using a kanthal wire-wound resistance furnace (horizontal) under flowing ultra high-pure (UHP) argon (purity 99.993%, oxygen <2 ppm, total impurities <30 ppm) at 1273 K for 2 h. The black mass thus obtained was designated as XSG1000 (Fig. 4.1).
Table 4.1 Summary of studies reported in the literature on the synthesis of boron carbide from gel precursors

<table>
<thead>
<tr>
<th>S.No</th>
<th>Gel Precursor</th>
<th>Processing Temperature, K</th>
<th>Holding time, h</th>
<th>Atmosphere</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Reaction product of $\text{H}_3\text{BO}_3$ and citric acid</td>
<td>1623</td>
<td>2</td>
<td>Vacuum</td>
<td>[98]</td>
</tr>
<tr>
<td>2</td>
<td>Reaction product of $\text{H}_3\text{BO}_3$ and citric acid</td>
<td>1773</td>
<td>2.5</td>
<td>Vacuum</td>
<td>[99]</td>
</tr>
<tr>
<td>3</td>
<td>Reaction product of $\text{H}_3\text{BO}_3$ and citric acid</td>
<td>1723</td>
<td>5</td>
<td>Argon</td>
<td>[101]</td>
</tr>
<tr>
<td>4</td>
<td>Solution of $\text{H}_3\text{BO}_3$, sugar and ethylene glycol</td>
<td>1973</td>
<td>5</td>
<td>$\text{H}_2$</td>
<td>[50]</td>
</tr>
<tr>
<td>5</td>
<td>Solution of $\text{H}_3\text{BO}_3$ and glycerin</td>
<td>1523</td>
<td>5</td>
<td>Argon</td>
<td>[95]</td>
</tr>
<tr>
<td>6</td>
<td>Reaction product of $\text{H}_3\text{BO}_3$ and mannitol</td>
<td>1573</td>
<td>0.5-20</td>
<td>Argon</td>
<td>[109]</td>
</tr>
</tbody>
</table>

**Fig. 4.1** Photograph of typical XSG1000
**Fig. 4.2** The scheme of preparation of boron carbide from boric acid-sucrose xerogel

This XSG1000 was crushed and compacted into pellets of 16 mm diameter by using a uniaxial hydraulic press. These pellets were placed in a high-density graphite boat (Fig. 2.1) and heated using a molybdenum wire-wound furnace at 1573, 1673 and 1773 K for 2 h (resultant products are designated as XSG13, XSG14 and XSG15 respectively) and at 1823 K for 2 and 3 h (resultant products are designated as XSG1552h and XSG1553h respectively) at a heating rate of 0.15 K s\(^{-1}\). In an another independent experiment, the pellets of XSG1000 were placed in a specially designed high-density graphite cylinder provided with lids on both sides (Fig. 2.2) and heated at 1823 K for 3 h at a heating rate of 0.15 K s\(^{-1}\). Lids having a central hole with different diameters viz., 8, 3, 1.5, 1, and 0.5
mm were used in different experiments and the resultant products were designated as XSGC8, XSGC3, XSGC1.5, XSGC1 and XSGC0.5 respectively. The scheme of the preparation is shown in Fig. 4.2.

The xerogels and the precursors were characterized by using Fourier transform infrared spectroscopy. The constituent phases were identified by using X-ray diffraction while their elemental composition was established with the help of chemical assay. The microstructure of boron carbide synthesized in this study was examined with the help of scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

4.1.2 Results and Discussion

4.1.2.1 IR analysis

![Fig. 4.3 IR Spectra of XSG and XSG1000](image)

The FTIR spectra of XSG and XSG1000 are shown in Fig. 4.3. Boric acid and sucrose form a complex during gelation as evidenced by the band at 1015 cm\(^{-1}\) in the IR spectrum of XSG. This feature could be assigned to the B–O–C stretch [104, 105]. The
absence of this feature in the IR spectrum pertaining to XSG1000 suggests its destruction during pyrolysis. In the IR spectra of both XSG and XSG1000, the broad band between 2900 and 3500 cm\(^{-1}\) could be assigned to the stretching of O–H pertaining to the moisture adsorbed on the surface of these samples. The band at 1450 cm\(^{-1}\) could be attributed to the B–O stretching and that at 1190 cm\(^{-1}\) to the B–O–H stretching. These results suggest that a complex is formed between boric acid and sucrose, which subsequently undergoes pyrolysis resulting in a precursor that yields boron carbide on further decomposition.

### 4.1.2.2 Chemical analysis

Boric acid and sucrose were taken in the molar ratio of 1:0.145 since this mixture could yield \(\text{B}_2\text{O}_3\) and carbon required for the formation of \(\text{B}_4\text{C}\) in the subsequent step shown in Eq. 1.2 (Chapter 1). The overall reaction between boric acid and sucrose could be represented by Eq. 4.1.

\[
4\text{H}_3\text{BO}_3 + 7\text{C}_{12}\text{H}_{22}\text{O}_{11} \rightarrow 12\text{B}_4\text{C} + 72\text{CO} + 149\text{H}_2\text{O}
\]

Table 4.2 shows typical chemical composition of XSG, XSG1000, XSG1552h and XSG1553h. According to Eq. 1.2 (Chapter 1), the number of moles of boron and carbon in the final reaction mixture should bear the stoichiometric weight ratio 1:1.9 to facilitate the complete conversion of \(\text{B}_2\text{O}_3\) and C into \(\text{B}_4\text{C}\). However, the chemical analysis indicates that the gel XSG is carbon deficient (B:C is 1:1.36). However, in the pyrolyzed product XSG1000, the boron to carbon weight ratio was found to be 1:1.7 which is close to the desired value mentioned above. It is interesting to note that Yanse et al. [105] have reported significant loss of boron due to volatilization at temperatures above 1273 K and recommended the use of a carbon-deficient starting mixture (C/B weight ratio 1.8) than demanded by Eq. 1.2 (Chapter 1) for the synthesis of boron carbide.
Table 4.2 Chemical analyses of XSG, XSG1000, XSG1552h and XSG1553h

<table>
<thead>
<tr>
<th>Sample</th>
<th>Boron (wt %)</th>
<th>Carbon (wt %)</th>
<th>Phases present</th>
</tr>
</thead>
<tbody>
<tr>
<td>XSG</td>
<td>13.3</td>
<td>18.2</td>
<td>-</td>
</tr>
<tr>
<td>XSG1000</td>
<td>18.5</td>
<td>30.7</td>
<td>B$_2$O$_3$</td>
</tr>
<tr>
<td>XSG1552h</td>
<td>49.2</td>
<td>35.3</td>
<td>B$_4$C, B$_2$O$_3$, carbon</td>
</tr>
<tr>
<td>XSG1553h</td>
<td>59.1</td>
<td>40.5</td>
<td>B$_4$C, carbon</td>
</tr>
</tbody>
</table>

In the gel-based processes, the yield cannot be improved unless the loss of boron is avoided during the crucial carbothermic reduction step. In order to achieve the above objective a special sample container was designed out of high-density graphite. By suitably tailoring the design of this sample cell, CO was effectively removed from the reaction site while the oxides of boron (mostly B$_2$O$_3$) were retained within the reaction zone. The molecular masses of the various gaseous species vary in the following order B$_2$O$_3$ > B$_2$O$_2$ > BO$_2$ > B$_2$O > CO. Thus their root mean square velocities and rates of effusion from the reaction site through an orifice would follow the reverse order. Thus CO would effuse out faster compared to the oxides of boron through the orifice in the sample container. However, arriving at an optimum value for the diameter of the orifice in this sample container had to be achieved through careful experimentation. The results obtained after heat treating the precursor XSG1000 at 1823 K for 3 h under flowing argon in the graphite cylinder with lids having different orifices are depicted in Table 4.3 and Fig. 4.4. The results show that the diameter of the orifice had a bearing on the composition of the final product. The amount of B and C in the product has a dependence on the diameter of the orifice. The rate of effusion through an orifice has an inverse dependence on the area.
of the orifice (or the square of its radius). Thus it is reasonable to conclude that the loss of
vapour species during the reduction is controlled probably by an effusion mechanism. An
orifice with a diameter of 0.5 mm proved to be the most suitable for it yielded a product
with boron to carbon ratio closest to the desirable value.

The use of graphite as the container material helped to promote the reaction of the
boron containing moieties emanating from the precursor with the walls of the graphite
cylinder with lids. Progressive deterioration of the container and the loss of its weight
upon repeated usage testified this premise. The design of a closed container and its orifice
thus turn out to be critical in controlling both the yield and composition of the final
product. This is a novel feature reported for the first time.

The yield of boron carbide was found to be 48% when the precursor XSG1000
was heated at 1823 K for 3 h in a graphite cylinder with lids having an orifice diameter of
0.5 mm and the free carbon in the final product (XSGC0.5) was reduced to about 6 wt%.

**Table 4.3** Chemical analyses of the boron carbide obtained after heat treating XSG1000 at
1823 K for 3 h in a graphite cylinder with lids

<table>
<thead>
<tr>
<th>Sample</th>
<th>Boron (wt %)</th>
<th>Carbon (wt %)</th>
<th>Phases present</th>
<th>SSA (m² g⁻¹)</th>
<th>B.D (g cm⁻³)</th>
<th>XCS (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>XSGC8</td>
<td>59.5</td>
<td>39</td>
<td>B₄C, carbon</td>
<td>15.72</td>
<td>0.29</td>
<td>66</td>
</tr>
<tr>
<td>XSGC3</td>
<td>65.1</td>
<td>34.5</td>
<td>B₄C, carbon</td>
<td>15.94</td>
<td>0.48</td>
<td>74</td>
</tr>
<tr>
<td>XSGC1.5</td>
<td>72.9</td>
<td>26.8</td>
<td>B₄C, carbon</td>
<td>17.21</td>
<td>0.61</td>
<td>58</td>
</tr>
<tr>
<td>XSGC1</td>
<td>75.5</td>
<td>24.3</td>
<td>B₄C, carbon</td>
<td>29.5</td>
<td>0.71</td>
<td>52</td>
</tr>
<tr>
<td>XSGC0.5</td>
<td>75.8</td>
<td>23.9</td>
<td>B₄C, carbon</td>
<td>30.5</td>
<td>0.74</td>
<td>52</td>
</tr>
</tbody>
</table>

SSA: specific surface area, XCS: X-ray crystallite size, B.D: bulk density
Fig. 4.4 Variation of amount of boron and carbon in the reaction product with the
diameter of the cylinder orifice when precursor XSG1000 was heat treated at 1823 K for
3 h

4.1.2.3 XRD analysis

The XRD patterns of XSG1000 and the products obtained after subjecting it to
heat treatment at different temperatures and durations are shown in Fig. 4.5. The XRD
patterns pertaining to the pyrolysed gels XSG1000, XSG13, XSG14 (Fig. 4.5a, 4.5b and
4.5c respectively) revealed the presence of only B$_2$O$_3$ phase and the absence of B$_4$C. The
carbon present in those samples pyrolyzed at temperatures below 1773 K was X-ray
amorphous. Hence the formation of boron carbide is not feasible at temperatures below
1773 K. The XRD patterns (Fig. 4.5d and 4.5e) of XSG15 and XSG1552h indicate the
presence of B$_2$O$_3$ and graphite in addition to boron carbide. The presence of B$_2$O$_3$ and
carbon along with B$_4$C in XSG1552h (Fig. 4.5e) indicate that the reaction did not proceed
to completion.
However, the product XSGC0.5 shows the presence of $B_4C$ along with free carbon as the second phase (Fig. 4.6). The absence of any peak pertaining to $B_2O_3$ in this product indicates the completion of the reaction or due to the evaporation of $B_2O_3$ from the reaction mixture or both.

The average size of boron carbide crystallites in the sample XSGC0.5 calculated by using the Scherrer formula was found to be 55 nm. A plot for $Bcos\theta$ versus $4sin\theta$ corresponding to the diffraction pattern of XSGC0.5 is shown in Fig.4.7. The lattice strain computed from the slope of this plot was found to be rather insignificant (0.012 %) and the crystallite size obtained from the intercept was found to be 52 nm. This value is in good agreement with the X-ray crystallite size calculated from the Scherrer formula.
4.1.2.4 Microstructure and particle size analysis

Fig. 4.8 reveals the microstructure of XSGC0.5. From this microstructure it is clear that the crystallites of boron carbide formed during the heat treatment agglomerate into irregular fine particles. Selective growth of crystallites of $B_4C$ is also observed.
A typical TEM image of XSGC0.5 is shown in Fig. 4.9 and the SAD (Selected area diffraction) pattern pertaining to an area where boron carbide crystallite was present is shown as the inset in Fig. 4.9. Spotty ring pattern confirms the nanocrystallinity of the randomly oriented boron carbide crystallites while diffraction pattern corresponds to the hexagonal B₄C phase.

The particle size distribution of XSGC0.5 is shown in Fig. 4.10. It is seen that the size distribution of the boron carbide particles is unimodal and falls in the range of 10–100 µm while the product obtained in an earlier study [100] from a citrate gel precursor had a bi-modal distribution.
Fig. 4.9 Transmission electron micrograph of XSGC0.5. The inset shows the SAD pattern of nanocrystalline boron carbide

Fig. 4.10 Particle size distribution of XSGC0.5
4.2 Synthesis of boron carbide from boric acid-citric acid xerogel

4.2.1 Experimental

In a typical experiment, 22.5 g of citric acid was taken in a combustion bowl and melted using a silicone oil bath at 423 ± 10 K. To this melt, 11.3 g of boric acid was added slowly in order to obtain a homogeneous gel. Upon heating this gel at 423 ± 10 K, a yellow coloured dry xerogel (XCG) was obtained. This product was placed in a high-density graphite crucible and pyrolyzed using a kanthal wire-wound resistance furnace (vertical) under a flowing stream of UHP argon at 773, 873, 973 and 1073 K for 2 h and the products thus obtained were designated as XCG500, XCG600, XCG700 and XCG800 respectively. Based on the C/B weight ratio, XCG600 was selected for the high temperature pyrolysis. This precursor was compacted into pellets of 16 mm diameter by using a uniaxial hydraulic press. These pellets were placed in a high-density graphite cylinder with lids on both sides (lids having an orifice diameter of 0.5 mm) and heated at 1573, 1673, 1773 and 1823 K for 3h under UHP argon. The resultant products are designated as XCG61300, XCG61400, XCG61500 and XCG61550 respectively. The scheme of preparation is shown in Fig. 4.11.

The xerogel and the precursor (XCG600) were characterized by using Fourier transform infrared spectroscopy. The constituent phases were identified by using X-ray diffraction while their elemental composition was established with the help of chemical assay. The microstructure of boron carbide synthesized in this study was examined with the help of SEM.
Fig. 4.11 The scheme of preparation of boron carbide from boric acid-citric acid xerogel precursor

4.2.2 Results and discussion

4.2.2.1 IR analysis

Fig. 4.12 shows the FTIR spectra of XCG and XCG600. A complex is formed between $\text{H}_3\text{BO}_3$ and citric acid during the gelation as indicated by the band at 1015 cm$^{-1}$ that could be assigned to the B-O-C stretching frequency in the IR spectrum of XCG. The absence of this feature in the IR spectrum of XCG600 suggests the destruction of the
complex formed between boric acid and citric acid during pyrolysis. A broad band between 2900 and 3500 cm\(^{-1}\) could be assigned to the stretching frequency of O-H pertaining to the moisture absorbed on to the surface of the samples XCG and XCG600. The broad band at 1450 cm\(^{-1}\) could be attributed to the B-O stretching frequency and that at 1190 cm\(^{-1}\) to the B-O-H stretching. These results show that a complex is formed between boric acid and citric acid during gel formation and is decomposed during the pyrolysis.

![The IR spectra of XCG and XCG600](image)

**Fig. 4.12** The IR spectra of XCG and XCG600

### 4.2.2.2 Chemical analysis

The overall reaction between boric acid and citric acid could be presented by Eq. 4.2.

\[
12 \text{H}_3\text{BO}_3 + 7 \text{C}_6\text{H}_8\text{O}_7\cdot\text{H}_2\text{O} \rightarrow 3 \text{B}_4\text{C} + 39 \text{CO} + 46 \text{H}_2\text{O} \quad (4.2)
\]

Table 4.4 shows the chemical composition of XCG, XCG500, XCG600, XCG700 and XCG800. The C/B weight ratio in the products (XCG, XCG500 and XCG600) are
less than that demanded by stoichiometric Eq. 1.2 (Chapter 1) whereas the the products (XCG700 and XCG800) contain C/B weight ratio more than the stoichiometric value. However, the C/B weight ratio in the product XCG600 is very close to the optimum value found in the earlier study on the synthesis of boron carbide from boric acid-sucrose gel precursor (Section 4.1.2.2). This suggests that the optimum temperature of pyrolysis of boric acid-citric acid xerogel is 873 K. The chemical analysis of the product (XCG61550) obtained after heat treatment of XCG600 at 1823 K for 3 h is also shown in Table 4.4. The final product contain about 10.3 wt% free carbon which is slightly lower than that in studies using citric acid as a gel forming agent [99].

Table 4.4 Chemical analysis of XCG, XCG500, XCG600, XCG700, XCG800 and XCG61550

<table>
<thead>
<tr>
<th>Sample</th>
<th>B (wt%)</th>
<th>C (wt%)</th>
<th>C/B weight ratio</th>
<th>B.D (g/cc)</th>
<th>SSA (m² g⁻¹)</th>
<th>XCS (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>XCG</td>
<td>12.2</td>
<td>16.4</td>
<td>1.34</td>
<td>0.22</td>
<td>2.5</td>
<td></td>
</tr>
<tr>
<td>XCG500</td>
<td>15.7</td>
<td>23.3</td>
<td>1.48</td>
<td>0.43</td>
<td>13.5</td>
<td></td>
</tr>
<tr>
<td>XCG600</td>
<td>15.1</td>
<td>26.1</td>
<td>1.72</td>
<td>0.44</td>
<td>21.3</td>
<td></td>
</tr>
<tr>
<td>XCG700</td>
<td>14.5</td>
<td>27.8</td>
<td>1.92</td>
<td>0.35</td>
<td>22.3</td>
<td></td>
</tr>
<tr>
<td>XCG800</td>
<td>14.8</td>
<td>29.7</td>
<td>2.01</td>
<td>0.27</td>
<td>24.1</td>
<td></td>
</tr>
<tr>
<td>XCG61550</td>
<td>71.3</td>
<td>28.2</td>
<td>0.69</td>
<td>33.5</td>
<td>181</td>
<td></td>
</tr>
</tbody>
</table>

SSA: specific surface area, XCS: X-ray crystallite size, B.D: bulk density
However, the yield of boron carbide was found to be only 36% when the precursor XCG600 was heated at 1823 K for 3 h. The yield is much less than that obtained from boric acid-sucrose gel precursor.

### 4.2.2.3 Phase identification and microstructure analyses

Fig. 4.13 shows the X-Ray diffraction (XRD) patterns of XCG500, XCG600, XCG700 and XCG800. All these patterns show the presence of only cubic boric oxide in the precursors. However, due to amorphous nature of carbon present in these precursors, peaks pertaining to carbon were not seen in the XRD patterns of the precursors. XRD patterns pertaining to XCG61300, XCG61400 and XCG61500 (products obtained when XCG600 heated at 1573, 1673 K and 1773 K for 3 h respectively) are also shown in Fig. 4.13.

![Fig. 4.13 X-ray diffraction pattern of the precursor (XCG500, XCG600, XCG700 and XCG800) and heat-treated products](image-url)
The absence of peaks pertaining to boron carbide indicates that the formation of boron carbide is not feasible at temperatures at least up to 1773 K. The XRD pattern of the product XCG61550 is shown in Fig. 4.14. This product shows peaks pertaining to boron carbide (JCPDS file No. 35-0798) and carbon (JCPDS file No. 89-7213). The absence of characteristic peaks corresponding to boric oxide indicates the completion of the reaction or the evaporation of boron in the form of its oxides or both. The presence of carbon in these samples indicates the loss of boron in the form of its gaseous oxide species. The average crystallite size calculated from Scherrer formula was found to be 181 nm.

![Fig. 4.14 X-ray diffraction pattern of XCG61550](image)

Microstructure of XCG61550 is shown in the Fig. 4.15. The figure shows the agglomeration of nanocrystalline boron carbide particles of different sizes and different shapes.
4.3 Synthesis of boron carbide from boric oxide-citric acid gel precursor

4.3.1 Experimental

In a typical experiment, 12.6 g of boric oxide and 43.8 g of citric acid were taken in a stainless steel (SS) vessel (Fig. 2.4). This vessel containing the reactants was then placed inside an SS reactor as shown in Fig. 2.4. The residual moisture present in the reaction mixture was removed by vacuum degassing at 393 K for 2 h. Subsequently the reaction mixture was heated in a kanthal wire-wound resistance furnace (vertical) in a stream of UHP argon at 773, 873, 973 and 1073 K for 2 h and the products thus obtained were labelled as BOC500, BOC600, BOC700 and BOC800 respectively. Based on C/B weight ratio, BOC700 was chosen for high temperature pyrolysis. This powder was compacted into pellets of 16 mm diameter and 10 mm height. These pellets were placed in a graphite cylinder with lids (lids having an orifice diameter of 0.5 mm) and heated in a molybdenum wire-wound resistance furnace at 1573, 1673, 1773 and 1823 K for 3 h.
under a flowing stream of UHP argon. The resultant products are designated as BOC71300, BOC71400, BOC71500 and BOC71550 respectively. The scheme of preparation is shown in the Fig. 4.16.

The constituent phases were identified by using X-ray diffraction while their elemental composition was established with the help of chemical assay. The microstructure of boron carbide synthesized in this study was examined with the help of scanning electron microscopy.

![Fig. 4.16 The scheme of preparation of boron carbide from boric oxide-citric acid gel precursor](image-url)
4.3.2 Results and Discussion

4.3.2.1 Chemical analysis

The overall chemical reaction between boric oxide and citric acid could be represented as:

\[ 6 \text{B}_2\text{O}_3 + 7 \text{C}_6\text{H}_8\text{O}_7 \rightarrow 3 \text{B}_4\text{C} + 39 \text{CO} + 28 \text{H}_2\text{O} \]  

(4.3)

Table 4.5 shows the chemical composition of BOC500, BOC600, BOC700 and BOC800. The C/B weight ratios of the products BOC500, BOC600 and BOC700 are less than the one demanded by stoichiometric Eq. 1.2 (Chapter 1) whereas the the products BOC800 contain higher than the stoichiometric value. However, the C/B weight ratio in the product BOC700 is very close to the optimum value found in the earlier study on the synthesis of boron carbide from boric acid-sucrose gel precursor (Section 4.1.2). Hence BOC700 is the most suitable precursor for the preparation of boron carbide as it contains the optimum C/B weight ratio. The results of the chemical analysis of the product (BOC71550) obtained after heat treatment of BOC700 at 1823 K for 3 h is also shown in Table 4.5. This product contains about 8.6 wt% free carbon. However, the yield of boron carbide was found to be about 41 %.

4.3.2.2 Phase identification, microstructure and particle size distribution

Fig. 4.17 shows the XRD patterns of BOC500, BOC600, BOC700 and BOC800. All these patterns show the presence of only cubic boric oxide. The XRD patterns of BOC71300, BOC71400 and BOC71500 are also shown in Fig. 4.17. The presence of only cubic boric oxide indicates that boron carbide does not form under these conditions of temperature and time duration. This precursor needed to be heated above 1773 K. The XRD patterns of the product BOC71550 is shown in Fig. 4.18. This shows peaks
Table 4.5 The results of chemical analysis of the BOC500, BOC600, BOC700, BOC800 and BOC71550

<table>
<thead>
<tr>
<th>Sample</th>
<th>B</th>
<th>C</th>
<th>C/B weight ratio</th>
<th>B.D (g/cc)</th>
<th>SSA (m² g⁻¹)</th>
<th>XCS (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BOC500</td>
<td>14.1</td>
<td>22.4</td>
<td>1.58</td>
<td>0.34</td>
<td>11.3</td>
<td></td>
</tr>
<tr>
<td>BOC600</td>
<td>14.3</td>
<td>23.8</td>
<td>1.66</td>
<td>0.25</td>
<td>23.6</td>
<td></td>
</tr>
<tr>
<td>BOC700</td>
<td>15.8</td>
<td>27.3</td>
<td>1.73</td>
<td>0.38</td>
<td>21.1</td>
<td></td>
</tr>
<tr>
<td>BOC800</td>
<td>14.5</td>
<td>27.8</td>
<td>1.92</td>
<td>0.46</td>
<td>19.7</td>
<td></td>
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<tr>
<td>BOC71550</td>
<td>72.9</td>
<td>26.8</td>
<td></td>
<td>0.61</td>
<td>48.2 261</td>
<td></td>
</tr>
</tbody>
</table>

SSA: specific surface area, XCS: X-ray crystallite size, B.D: bulk density

Fig. 4.17 X-ray diffraction pattern of the precursor and heat-treated products
Fig. 4.18 X-ray diffraction pattern of BOC71550

Fig. 4.19 Scanning electron micrograph of BOC71550
pertaining to boron carbide (JCPDS file No. 35-0798) and carbon (JCPDS file No. 89-7213). The absence of characteristic peaks corresponding to boric oxide indicates the completion of the reaction. The average crystallite size calculated from Scherrer formula was found to be 260 nm.

Microstructure of BOC71550 is shown in the Fig. 4.19. It can be seen from the figure that the particles are irregular in size and shapes.

The particle size distribution of BOC71550 is shown in Fig. 4.20. It is seen that the size distribution of the particles (100–500 µm) exhibit a unimodal distribution.

![Fig. 4.20 The particle size distribution of BOC71550](image)

4.4 Synthesis of boron carbide from boric oxide-sucrose gel precursor

4.4.1 Experimental

In a typical experiment, a homogeneous mixture of 12.6 g of boric oxide and 18.2 g sucrose was taken in a stainless steel (SS) vessel (Fig. 2.4). This vessel along with the reactants was then placed in an SS reactor (Fig. 2.4). The residual moisture present in the
reaction mixture was removed by vacuum degassing at 443 K for 2 h. Subsequently this reaction mixture was heated at 973 K for 2 h using a kanthal wire-wound resistance furnace (vertical) in a stream of UHP argon. A black spongy precursor was formed. This precursor (resultant product is designated as BOS700) was subsequently crushed, ground into fine powder and compacted into pellets of 16 mm diameter and 10 mm height. These pellets were placed in a graphite cylinder with lid (lids having an orifice diameter of 0.5 mm) and heated in a molybdenum wire-wound resistance furnace at 1573, 1673 for 3 h and at 1773 K for 2 and 3 h under flowing UHP argon. The resultant products are designated as BOS713, BOS714, BOS7152h and BOS715 respectively.

In another set of independent experiments the precursors were also prepared by heating a stoichiometric mixture of boric oxide and sucrose at 773, 873 and 1073 K for 2 h (resultant products are designated as BOS500, BOS600, and BOS800 respectively) in order to optimize the temperature of synthesis of the precursor. These precursors (BOS500, BOS600 and BOS800) were also compacted into pellets and heated at 1773 K for 3 h as described above. The resultant products obtained after heat treatment at 1773 K for 3 h are designated as BOS515, BOS615 and BOS815 respectively. The scheme of the synthesis is depicted in Fig. 4.21 as a flow chart.

The constituent phases were identified by using X-ray diffraction while their elemental composition was established with the help of chemical assay. The microstruture of boron carbide synthesized in this study was examined with the help of scanning electron microscopy.
4.4.2 Results and Discussion

4.4.2.1 Chemical analysis

The overall reaction of boric oxide with sucrose is represented as:

$$24 \text{B}_2\text{O}_3 + 7 \text{C}_{12}\text{H}_{22}\text{O}_{11} \rightarrow 12 \text{B}_4\text{C} + 72 \text{CO} + 77 \text{H}_2\text{O}$$  \hspace{1cm} (4.4)

Table 4.6 shows typical chemical composition of various boric oxide-sucrose precursors prepared in this study. Except BOS500, which was brown in colour, all the other precursors were black in colour. It is surmised that this brown colour might be due to incomplete decomposition of sucrose. All the precursors have a value of C/B weight ratio (1.58 for BOS500, 1.68 for BOS600, 1.77 for BOS700 and 1.73 for BOS800) lower than that demanded by Eq. 1.2 (1.9) for the quantitative formation of boron carbide. This
lower C/B weight ratio may be due to the loss of boron in the form of its oxides as the vapour pressures of the latter increases with temperature. As discussed in section 4.1.2.2, Yanase et al. [105] suggested the use of reaction mixtures with lower C/B value than the stoichiometric value demanded by Eq. 1.2 (Chapter 1) to synthesize single phase boron carbide. The results of the chemical analyses of BOS515, BOS615, BOS715 and BOS815 are shown in Table 4.7. These results show that the product BOS615 contains minimum free carbon compared to BOS515, BOS715 and BOS815. Hence the optimum temperature for preparation of boric oxide-sucrose precursor in order to obtain boron carbide with minimum free carbon is 873 K. The yield of boron carbide obtained in this study is 61% and the free carbon in the final product BOS615 is found to be about 4 wt%. From this study it is inferred that boron carbide with maximum yield and minimum free carbon content can be prepared from the boric oxide (boron source)-sucrose (carbon source) gel precursor. The bulk density and specific surface area of the precursor powders and boron carbide powders synthesized in this study are also shown in Table 4.6 and 4.7.

4.4.2.2 Phase identification, microstructure and particle size distribution

Fig. 4.22 shows the XRD patterns of BOS500, BOS600, BOS700 and BOS800. All these patterns show the presence of only cubic boric oxide in the precursors. Peaks pertaining to carbon were not seen in the XRD patterns of the precursors because the carbon present in these precursors is amorphous. The presence of carbon, however, was established by the chemical analysis of these samples. XRD patterns BOS713, BOS714 and BOS7152h are shown in Fig. 4.23. The XRD patterns of BOS713 and BOS714 show the presence of only cubic boric oxide. However, the XRD pattern of BOS7152h shows the presence of a mixture of boron carbide, boric oxide and carbon.
Table 4.6 Results of the chemical analysis of the precursors BOS500, BOS600, BOS700 and BOS800

<table>
<thead>
<tr>
<th>Sample</th>
<th>Boron (wt %)</th>
<th>Carbon (wt %)</th>
<th>Phases present</th>
<th>Bulk density (g/cc)</th>
<th>Specific surface area (m² g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BOS500</td>
<td>14.9</td>
<td>23.6</td>
<td>B₂O₃ and C</td>
<td>0.22</td>
<td>13.1</td>
</tr>
<tr>
<td>BOS600</td>
<td>16.1</td>
<td>27.2</td>
<td>B₂O₃ and C</td>
<td>0.35</td>
<td>26.5</td>
</tr>
<tr>
<td>BOS700</td>
<td>16.1</td>
<td>28.5</td>
<td>B₂O₃ and C</td>
<td>0.29</td>
<td>21.3</td>
</tr>
<tr>
<td>BOS800</td>
<td>16.2</td>
<td>28.1</td>
<td>B₂O₃ and C</td>
<td>0.32</td>
<td>22.3</td>
</tr>
</tbody>
</table>

Table 4.7 Results of the chemical analysis of BOS515, BOS615, BOS715 and BOS815

<table>
<thead>
<tr>
<th>Sample/Element</th>
<th>Boron (wt%)</th>
<th>Carbon (wt%)</th>
<th>Phases present</th>
<th>X-ray crystallite size (nm)</th>
<th>Bulk density (g/cc)</th>
<th>Specific surface area (m² g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BOS515</td>
<td>68.4</td>
<td>30.9</td>
<td>B₄C and C</td>
<td>56</td>
<td>0.42</td>
<td>32.2</td>
</tr>
<tr>
<td>BOS615</td>
<td>76.2</td>
<td>23.1</td>
<td>B₄C and C</td>
<td>48</td>
<td>0.53</td>
<td>40.1</td>
</tr>
<tr>
<td>BOS715</td>
<td>70.5</td>
<td>28.8</td>
<td>B₄C and C</td>
<td>52</td>
<td>0.77</td>
<td>34.3</td>
</tr>
<tr>
<td>BOS815</td>
<td>69.1</td>
<td>29.8</td>
<td>B₄C and C</td>
<td>63</td>
<td>0.81</td>
<td>30.9</td>
</tr>
</tbody>
</table>
The presence of boric oxide in this product mixture suggests incompletion of the reaction.

The XRD patterns of the BOS515, BOS615, BOS715 and BOS815 are shown in Fig. 4.24. These products show the presence of boron carbide (JCPDS file No. 35-0798) and carbon (JCPDS file No. 89-7213). The absence of boric oxide in these products indicates the completion of the reaction. The presence of carbon residue in these samples indicates the loss of boron in the form of its gaseous oxide species swept in the carrier gas stream. From Fig. 4.24, it is also observed that the intensity of peak corresponding to carbon in the XRD pattern of BOS615 is lower than those of other products (BOS515, BOS715 and BOS815). This indicates that the product BOS615 contains relatively lower free carbon compared to other products. This observation is in agreement with the results obtained by the chemical analysis.

![X-ray diffraction pattern of the precursors](image)

**Fig.4.22** X-ray diffraction pattern of the precursors
Fig. 4.23 X-ray diffraction patterns of the heat-treated products

Fig. 4.24 X-ray diffraction patterns of BOS515, BOS615, BOS715 and BOS815
The average size of boron carbide crystallites in the sample BOS615 calculated from the Scherrer formula was found to be 60 nm. Fig. 4.25 shows the Hall Williamson plot pertaining to BOS615. Lattice strain calculated from the slope of this plot is 0.015%. The crystallite size calculated from the intercept of the Hall Williamson’s plot is 62 nm. The crystallite size calculated from the Scherrer formula and from the Hall Williamson plot are in good agreement with each other.

Fig. 4.25 Williamson–Hall plot pertaining to BOS615

Fig. 4.26 shows the microstructure of BOS615. From the microstructure it is evident that the particles of the product BOS615 are irregular in shape and size. In addition, these particles are nanocrystalline agglomerates of boron carbide.
Fig. 4.26 Scanning electron micrograph of BOS615

![Fig. 4.26 Scanning electron micrograph of BOS615](image)

Particle size distribution of BOS615 is shown in Fig. 4.27. As seen in the plot, the particles exhibit bimodal size distribution with 90% of the particles (D90) in the size
range of 0.02 – 0.2 µm. About 10% of the powder has particles with size range of 300 to 500 µm. These particles are much smaller than those synthesized from boric acid-sucrose gel precursor and boric acid-citric acid gel precursors described in earlier sections.

4.5 Summary of studies carried out on the synthesis of nanocrystalline boron carbide

Table 4.8 Summary of studies carried out on the synthesis of nanocrystalline boron carbide

<table>
<thead>
<tr>
<th>Gel Precursor</th>
<th>% B (wt%)</th>
<th>% C (wt%)</th>
<th>Free carbon (wt%)</th>
<th>Yield (%)</th>
<th>X-ray crystallite size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boric acid-Citric acid</td>
<td>71.3</td>
<td>28.2</td>
<td>10.5</td>
<td>36</td>
<td>181</td>
</tr>
<tr>
<td>Boric oxide-Citric acid</td>
<td>72.9</td>
<td>26.8</td>
<td>8.5</td>
<td>41</td>
<td>260</td>
</tr>
<tr>
<td>Boric acid-Sucrose</td>
<td>75.8</td>
<td>23.9</td>
<td>5.5</td>
<td>48</td>
<td>52</td>
</tr>
<tr>
<td>Boric oxide-Sucrose</td>
<td>76.2</td>
<td>23.1</td>
<td>4.1</td>
<td>61</td>
<td>60</td>
</tr>
</tbody>
</table>

Table 4.8 compares the results of the chemical analyses of boron carbide prepared using various gel precursors. This study clearly brings out the fact that the use of sucrose as a gel forming agent has definite advantages over the use of citric acid. Similarly boric oxide was found to be a better boron source compared to boric acid for the synthesis of boron carbide through gel precursor method.

4.6 Conclusions

Alternate energy efficient low temperature methods based on the pyrolysis of suitable gel precursors for the synthesis of boron carbide were developed. Systematic studies were carried out to optimize the process parameters such as composition of the initial reactant
mixture and temperature and time for the pyrolysis of the precursors. The precursors and boron carbide prepared from these precursors were characterized by both chemical methods and XRD. The physical properties such as specific surface area, bulk density, and particle size distribution of the precursors as well as the final products measured. The crystallite size of various powders was determined by the X-ray line broadening technique. The microstructure and surface morphology were studied by using scanning electron microscopy and transmission electron microscopy. The performance of boric acid and boric oxide as boron sources and sucrose and citric acid as the carbon source was compared. The studies led to the following conclusions.

1. The products obtained through the gel precursor route were found to be nanocrystalline, free flowing and porous.

2. Yield of boron carbide could be improved by using a specially designed graphite cylinder with lids by minimizing the loss of boron.

3. This study clearly brings out the fact that the use of sucrose as a gel forming agent has definite advantages over the use of citric acid.

4. This study also brings out the fact that the use of boric oxide as a boron source has definite advantages (in improving the yield and lowering the free carbon residue in boron carbide) over the use of boric acid.

5. A novel method for the synthesis of nanocrystalline boron carbide with high yield (~60%) and low free carbon (~4 %) was demonstrated.