Summary and Conclusions

Thermodynamic equilibrium calculations were carried out on the system B-O-C using FactSage 6.2 in order to identify the optimum reduction temperature and mole ratio of B\textsubscript{2}O\textsubscript{3} to C for the preparation of boron carbide by carbothermic reduction process. Novel and energy efficient methods were developed for the synthesis of nanocrystalline boron carbide, based on gel precursor route. A simple and fast method was developed for the digestion of boron carbide for the determination of boron, isotopic ratio of $^{10}$B/$^{11}$B and trace elements (Al, Cd, Co, Cr, Cu, Fe, Mg, Mn, Mo, Ni, Pb and Zn) present in it. Thermal expansion of boron carbide was measured by high temperature X-ray diffraction technique.

7.1 Thermodynamic analysis of carbothermic reduction of boric oxide

Thermodynamic equilibrium calculations were carried out on the system B-O-C using FactSage 6.2 in order to identify the optimum reduction temperature and mole ratio of B\textsubscript{2}O\textsubscript{3} to C for the preparation of boron carbide by carbothermic reduction process. The thermodynamic stability region of B\textsubscript{2}O\textsubscript{3}(l), B\textsubscript{4}C\textsubscript{(s)}, B\textsubscript{4}C\textsubscript{(l)}, B\textsubscript{(s)}, B\textsubscript{(l)} and C\textsubscript{(s)} for a mixture of B\textsubscript{2}O\textsubscript{3} and C with C to B\textsubscript{2}O\textsubscript{3} mole ratio of 0.5 to 1.75 in the temperature range 298-3573 K have been established. Based on these calculations, the optimum reduction temperature and stoichiometry of the reaction mixture were identified.

7.2 Synthesis of nanocrystalline boron carbide from gel precursors

In order to prepare nanocrystalline boron carbide, suitable gel precursors were developed in the present study. Systematic studies were carried out to optimize the process parameters such as stoichiometry of the reactants, pyrolysis temperature etc. The
precursors and boron carbide prepared from these precursors were characterized by chemical analysis and X-ray diffraction method. The physical properties such as specific surface area, bulk density and particle size distribution were also measured for the final product. The crystallite size of the powders was determined by the X-ray line broadening technique. The microstructure and surface morphology were studied 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 sources for the preparation of gel precursors 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. The yield of boron carbide could be improved by using a specially designed graphite cylinder with lids as the reaction vessel.

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. The yield is maximum (~60%) with minimum carbon content (~4%) when the boric oxide and sucrose were used as boron source and carbon source respectively.

### 7.3 Studies on the development of a method for the digestion of boron carbide for its chemical assay

A simple and fast digestion method was developed for the determination of boron, isotopic ratio of $^{10}\text{B}/^{11}\text{B}$ and trace elements (Al, Cd, Co, Cr, Cu, Fe, Mg, Mn, Mo,
Ni, Pb and Zn) in boron carbide. Boron carbide was digested using an acid mixture in a simple quartz apparatus. Boron was subsequently determined by the conventional method of titration of mannitol-boric acid complex using the standard potassium hydroxide solution. Trace elements and isotopic ratio of $^{10}\text{B}/^{11}\text{B}$ were determined by using inductively coupled plasma mass spectrometer. The digestion technique developed in this study was validated by comparing the analytical results with those obtained by conventional “sodium carbonate fusion” method. Comparison of the results of analyses of boron in boron carbide samples employing these two digestion techniques showed the accuracy of the present analytical method to be 99.8%. Good recoveries were obtained for Cr, Co, Cu, Cd, Ni, Fe, Mn, Pb, Zn and Mo. The new digestion technique facilitates relatively fast and accurate determination of total boron, its isotopic content and trace elements present in it. The use of expensive materials such as platinum crucibles is eliminated.

**7.4 Studies on thermal expansion of nanocrystalline boron carbide**

The thermal expansions of nanocrystalline (N-B$_4$C) and microcrystalline (M-B$_4$C) boron carbide were measured over the temperature range 298 to 1773 K by means of high temperature X-ray diffraction technique.

The generalized equations for the lattice parameters (both $a$ and $c$) of both nanocrystalline and microcrystalline boron carbides (in nm) as a function of temperature are given below:

For M-B$_4$C:

\[
\begin{align*}
a(\text{nm}) &= 8.0908 \times 10^{-10} (T-298)^2 + 5.2418 \times 10^{-7} (T-298) + 0.5599 \\
c(\text{nm}) &= 2.7382 \times 10^{-9} (T-298)^2 + 1.2719 \times 10^{-6} (T-298) + 1.2085
\end{align*}
\]
For N-B₄C:

\[ a \text{ (nm)} = 8.5188 \times 10^{-10} (T-298)^2 + 6.2606 \times 10^{-7} (T-298) + 0.5600 \]  \hspace{1cm} (7.3)

\[ c\text{ (nm)} = 2.9407 \times 10^{-9} (T-298)^2 + 1.9671 \times 10^{-6} (T-298) + 1.2083 \]  \hspace{1cm} (7.4)

The percentage linear thermal expansions were evaluated from the temperature variation of lattice parameter in the temperature range 298 to 1773 K.

The generalized equations for the percentage linear thermal expansions of M-B₄C and N-B₄C are given below:

For M-B₄C:

\[ \% \text{ Expansion (a axis)} = 1.442094 \times 10^{-7} T^2 + 9.406820 \times 10^{-5} T - 0.04094628 \]  \hspace{1cm} (7.5)

\[ \% \text{ Expansion (c axis)} = 2.263169 \times 10^{-7} T^2 + 1.054712 \times 10^{-4} T - 0.05164089 \]  \hspace{1cm} (7.6)

For N-B₄C:

\[ \% \text{ Expansion (a axis)} = 1.517726 \times 10^{-7} T^2 + 1.123957 \times 10^{-4} T - 0.04712794 \]  \hspace{1cm} (7.7)

\[ \% \text{ Expansion (c axis)} = 2.433414 \times 10^{-7} T^2 + 1.626109 \times 10^{-5} T - 0.07019606 \]  \hspace{1cm} (7.8)

The generalized equations for the temperature dependence of the coefficient of thermal expansion of both M-B₄C and N-B₄C are given below:

\[ \alpha_{\text{ave}} = 5.30656 \times 10^{-15} T^2 + 3.63777 \times 10^{-9} T + 1.29243 \times 10^{-6} \]  \hspace{1cm} (for M-B₄C)  \hspace{1cm} (7.9)

\[ \alpha_{\text{ave}} = 6.02386 \times 10^{-15} T^2 + 3.42333 \times 10^{-9} T + 9.79992 \times 10^{-7} \]  \hspace{1cm} (for N-B₄C)  \hspace{1cm} (7.10)

The average thermal expansion coefficients in this temperature range for the nanocrystalline and the microcrystalline boron carbides were found to be \(7.76 \times 10^{-6}\) and \(7.06 \times 10^{-6} \text{ K}^{-1}\) respectively. The difference observed in the thermal expansion behaviour is probably due to increase in the surface energy of the lattice in the nanocrystalline material.
Chapter 7

Scope of future studies

This study has established the feasibility of synthesis of nanocrystalline boron carbide using citric acid and sucrose as the carbon source and boric acid and boric oxide as the boron source. Systematic studies on sintering of boron carbide powders synthesized in this study using various methods viz., conventional sintering, microwave assisted sintering and spark plasma sintering can be studied to understand the sinterability of these powders.

This study clearly brings out the fact that the use of sucrose (containing 12 carbons) as a gel forming agent has definite advantages over the use of citric acid (containing 6 carbons). It will be of interest to study the feasibility of synthesis of boron carbide using gel forming agents which contain more than 12 carbons such as stearic acid. Studies to explore the feasibility of synthesis of boron carbide using other boron sources such as borax is another interesting area as its melting point is higher than that of boric oxide and boric acid. This study would give a better understanding of the effect of boron source on the nature and quality of the powders prepared through gel precursors. Systematic studies can be carried out to explore the feasibility of microwave assisted synthesis of boron carbide from the gel precursors. This study may help to improve the yield of boron carbide as it is a bulk and uniform heating method.

It would be interesting to study the synthesis of boron carbide from boric acid/boric oxide and citric acid/sucrose gel precursors in presence of oxidants such as ammonium nitrate.

In the present study, thermal expansions of boron carbides with of two different average crystallite sizes (52 and 300 nm) have been measured. However, systematic
studies on the effect of crystallite size on coefficient of thermal expansion could be studied in detail.

In the present study thermodynamic calculations were carried out to understand the carbothermic reduction of boric oxide. It would be of interest to carry out detailed thermodynamic modelling of carbothermic reduction of other boron sources viz., boric acid, borax.