Preface

There has been growing interest in advanced ceramics such as silicon nitride silicOns silicon carbide etc because of the special advantages they offer for technological applications. Newer methods of synthesis are therefore constantly developed. Applications of these materials require them to be formed into dense objects. There is therefore continuous effort in discovering newer methods of sintering ceramics. This thesis comprises investigations related to both synthesis and consolidation of advanced ceramic materials. The thesis is presented in six chapters and following is a brief outline of the contents.

The first introductory chapter deals with some basic details of the structure, thermodynamics, and methods of preparation of Si₃N₄ and SIALONs. Isothermal phase diagram of Si₃N₄, Al₂O₃, AlN, SiO₂ system and the occurrence of various SIALON phases in the pseudo quartenary phase diagram. A brief review of the important contributions in the area of silicon nitride ceramics has been presented. The chapter also overviews application of microwaves in the processing of ceramic materials. Basic fundamentals of microwave material coupling and thermal runaway phenomenon are presented. Powder preparation using microwaves have been discussed in some detail. Earlier work on sintering studies of different ceramic materials have also been reviewed.

Chapter 2 discusses carbothermal reduction and nitridation of an industrial byproduct namely SiO. The chemical composition of amorphous SiO has been analysed by oxidation studies and was found to be SiO₁.₇. SiO₁.₇ appears to be a monophasic amorphous material on the basis of ²⁹Si nuclear magnetic resonance, high resolution electron microscopy, and comparative behaviour of a physical mixture of Si and SiO₂. Carbothermal reduction and nitridation reactions have been carried out on amorphous SiO₁.₇ and amorphous SiO₂. The SiO₂ is found to result from the oxidation of SiO₁.₇. At 1623 K reactions of SiO₁.₇ lead exclusively to the formation of Si₃N₂O while those of SiO₂ lead exclusively to the formation of Si₃N₄. Formation of copious fibres of α Si₃N₄ was observed in the latter reaction. It
has been suggested that the partial pressure of SiO in equilibrium with reduced SiO$_1$$_7$ and SiO$_2$ during the reaction is the crucial factor which determines the chemistry of the products. The differences in the structures of SiO$_2$ and SiO$_1$$_7$ have been considered to be the origin of the differences in the SiO partial pressures of the reduction products formed prior to nitridation. The effect of the ratios C SiO$_1$$_7$ and C SiO$_2$ in the reaction mixture as well as the effect of the temperature on the course of the reactions have been investigated.

Chapter 3 describes preparation of single phase $\beta$ SiAlON. A simple method for the preparation of monophasic $\beta$ SiAlON has been achieved using direct nitridation of Si admixed with AlN. The N$_2$ gas employed for the purpose had a partial pressure of $10^{-4}$ atm. Monophasic $\beta$ SiAlON powder was obtained when AlN/Si ratio was 0.66 or more. The sialon powder had the composition $\beta$ Si$_4$$_7$Al$_3$O$_1$$_3$N$_6$$_7$ as derived from energy dispersive analysis (EDX), X ray diffraction (XRD) and Fourier Transform infra red spectroscopy (FTIR) results. These samples have also been characterized by transmission electron microscopy (TEM), electron diffraction (ED) and nuclear magnetic resonance (MASNMR) techniques. The shift in FTIR frequencies of $\beta$ SiAlON from that of $\beta$ Si$_3$N$_4$ shows partial substitution of Al and O have occurred in place of Si and N. The presence of low oxygen partial pressure ($\sim 10^{-4}$ atm) and excess AlN seem to be the important conditions to form a single phase $\beta$-SiAlON. The effect of AlN/Si ratio on the product formation has been discussed. The likely mechanism of $\beta$ SiAlON formation has also been outlined.

Amorphous aluminosilicate gel powders have been subjected to carbothermal reduction and nitridation reaction at high temperature (1673 K). Preparation of pure reactive aluminosilicates with different SiO$_2$ : Al$_2$O$_3$ compositions were achieved by sol gel route. These aluminosilicate powders were mixed thoroughly with carbon powder and were subjected to nitridation. The influence of Al$_2$O$_3$ content in the gel powder on the nature and structure of the product phases has been examined. Pure $\beta$ SiAlON results above 5% alumina. Between 5% and 9% Al$_2$O$_3$ in the gel $\beta$ SiAlON is formed almost exclusively. When 12% Al$_2$O$_3$ is present in the gel, AlN appears as minor constituent in the product and in the
case of aluminosilicate containing 20% $\text{Al}_2\text{O}_3$ the amount of AlN in the product becomes very high (nearly >30%). The powders were further characterised by FTIR spectroscopy. Based on the aluminosilicate structure a structural model has been proposed for selective formation of $\beta\text{ SiAlON}$.

Chapter 4 discusses attempts made to prepare sialon starting from kaolinite. It is found that carbon/kaolinite ratio, temperature of the reaction and duration of nitridation make profound differences in the product chemistry. Lower reaction temperatures and substoichiometric amounts of carbon lead to a diversity of products. O SiAlON 15R and J phases $\text{SiO}_2$ (crystobalite) $\text{Al}_2\text{O}_3$ mullite and SiC are among the phases identified at various stages in the reaction. The possible implications of the observed chemistry on the mechanism of CTR/N reaction of kaolinite are discussed. It is found that complete conversion to sialon (based on total silicon in the kaolinite) is not possible at the reaction conditions generally employed.

Chapter 5 describes the role of microwaves on the synthesis of $\beta\text{ SiC}$ and AlN which are technologically very important materials. Syntheses of $\beta\text{ SiC}$ and AlN powders using microwave heating in a fraction of the time usually required in the conventional methods have been achieved. A commercial microwave oven operating at 2.45 GHz with variable power levels up to a maximum of 980 W have been used for the purpose. For SiC preparation the charge consisted of a mixture of metallic silicon powder and activated charcoal. Reactions were carried out in silica and porcelain crucibles using two ambients, air and iodine vapors. The duration of reaction ranged from 4-10 minutes. Virtual disappearance of XRD peaks corresponding to reactants suggested the completion of the reaction. Occurrence of this reaction at low temperature (1250 K) suggests that microwaves possibly excite the graphitic bonds (interplanar) during initiation of the silicon carbon reaction. For AlN powder preparation a mixture of fine aluminium and charcoal powders were taken in a specially designed quartz tube which was irradiated with microwaves. Microwaves assist in nitriding aluminium powder to aluminium nitride at surprisingly low
temperatures (1200 K). Our observations revealed that intermediate grinding is necessary for completion of the reaction. Nearly full conversion had been achieved with intermediate grinding in 105 minutes. This could possibly be due to the formation of AlN on the surface of Al and in its wurtzite structure, does not allow easy diffusion of molecular nitrogen. The grinding increases the reaction rate by breaking up the AlN layers and exposing new Al surface for nitridation. These reactions are also found to be oxygen sensitive. The samples were further characterized by XRD, IR, particle size analysis, and ED. The mode of microwave coupling could possibly be due to eddy currents generated in Al particles and due to microwave susceptibility of carbon.

Chapter 6 is devoted to the description of microwave sintering of ZrO$_2$-CeO$_2$ ceramics. Sintering of ZrO$_2$-CeO$_2$ pellets of compositions varying from pure ZrO$_2$ to pure CeO$_2$ have been achieved within 35 minutes using a cooking microwave oven of 980 W power and operating at 2.45 GHz. Densification of 95% and above was achieved in most cases. The laboratory temperature phase boundaries have been established which indicates a slight departure of the compositional limits of phase stability compared to those obtained from conventional sintering. The observations also confirm that the formation of composition dependent phases were a function of sintering time. Formation of metastable phase Ce$_2$Zr$_9$O$_{10}$ ($\phi$ phase) has been ruled out. Also, cubic phases were generally oxygen deficient and hence no t → $\gamma$ ($\text{Ce Zr})$O$_2$ resulting from diffusionless $\gamma$ → $\delta$ transformation at high ceria compositions was found to form. The Vickers hardness value was maximum for mixed t ($\text{Ce Zr})$O$_2$ + c ($\text{Ce Zr})$O$_2$ system and minimum for cubic solid solution. The apparent toughness value was maximum for t ($\text{Ce Zr})$O$_2$ phase and the value was minimum for pure cubic system. The microwave sintering seems to be superior compared to conventional sintering process.

Chapters 2, 3, 4, 5, and 6 are provided with independent conclusions.
The following publications have resulted from this thesis


[9] Microwave sintering studies in ZrO$_2$ CeO$_2$ system P D Ramesh Panka Sarin Siddharth Jeevan and K J Rao *Ceramics Int* (communicated)