CHAPTER 1

1.1 INTRODUCTION

In recent years, ceramic technology has developed intensively and is employed in many production and design applications. Ceramic products are required for day to day usage's and also in advanced applications like electronic, engineering and biomaterials etc. In common terminology, ceramic materials are considered to be substances, which are usually composed of compounds of "metallic" and "non-metallic elements". Unlike metals, most ceramic materials are not made by melting and cutting because the melting points are usually so high as to make such a route either impractical or economically non-viable.

Advanced ceramic materials are primarily produced in Japan, United States and Western Europe. The raw materials used in the industry are treated on an international basis, principally as powders, although there is also a significant amount of in-house processing. The estimated worldwide markets for advanced ceramics by end application for 1990, 1995 and 2000 are Electronic ceramics, Structural ceramics and Ceramic Coating. The extensive worldwide research and development are continually improving both powder and component properties, with new applications being generated.

The task of the ceramic process engineer is complicated by the fact that there is no single processing method for fabricating a ceramic component from a starting powder. This has resulted in the extensive development of powder based routes mostly for polycrystalline ceramic materials in which a green body is usually consolidated first, followed by high temperature densification process. The current focus is on the
improvement of reliability and fracture toughness of the ceramic materials. However, by the proper optimization of microstructure, the bending strength of ceramic materials can be improved equivalent to that of metals. Improvements on reliability and durability require continued effort in design, material property, component fabrication and quality control. Particularly, the development of an important mechanical property is the enhancement of fracture toughness of ceramic materials.

The superior electrical and mechanical properties of ceramics, in general, makes it suitable for the more demanding applications in hostile environment of high temperature, high frequency or severe corrosive atmospheres. However, ceramics are brittle in nature and may occasionally break down mechanically or electrically under high stress. Therefore, high quality materials and components are essential for a system for it to be used in more demanding environments. Alumina, glass-ceramics and related ceramic-based materials are used extensively in electrical, electronic and structural applications. The study of multi-compositional ceramics is of great technological importance for microelectronics packaging applications. Future devices technologies, especially high speed-high density GaAs integrated circuits, will lay great demands on substrate materials; for example, the high dielectric constant of conventionally used alumina introduced a substrate signal delay that exceeded the chip delay (Bortz and Ohuchi 1988). Perhaps more importantly, the high 1600°C sintering temperature of alumina allows only tungsten or molybdenum co-sintering metallization. This is incompatible with future multilayered substrate technologies that will incorporate interconnection and passive circuit elements into the substrate.

Due to its considerable importance to the ceramic industry, the multi-compositional oxide ceramic MgO.Al₂O₃.SiO₂ system has been widely investigated since the beginning of the century. Among different phases
existing in this system (Cordierite), which corresponds to the stoichiometric formula \( \text{Mg}_2\text{Al}_4\text{Si}_2\text{O}_{18} \), has received much attention owing to its unusual thermal and dielectric properties, making this material useful in a number of applications ranging from low-expansion refractories and electrical insulators to integrated electronic circuit substrates. Extensive studies have been devoted to the origin of the low thermal expansion coefficient in relation to the structure as well as to the enhancement of the mechanical properties by addition of second phases.

In view of its refractory character, cordierite is not easily obtained by solid-state reactions from oxides. Synthetic powders exhibit heterogeneous surface properties and even chemical inhomogeneity due to addition of sintering aids or impurities introduced through milling. Since the final (especially mechanical) characteristics of a ceramic body are strongly dependent on the nature of the starting powder, improvement in the reliability and reproducibility of cordierite properties is highly desirable. There are wide ranges of techniques available and each requires different characteristics in the starting powder. It is therefore essential that production processes are capable of being controlled to produce the desired properties and their characterization techniques exist to be able to monitor them. For these reasons, an alternative method for preparation of this material by chemical route, the so called, "Sol-Gel process" that would yield highly reactive and better controlled cordierite particles, have been developed by Roy and co-workers in early fifties (Gensse and Chowdhry 1986; Bernier et al 1986; Vestegham et al 1987).

Cordierite has poor mechanical properties compared to other ceramic materials, and in order to enhance its mechanical properties, zirconia has been added to the cordierite matrix as a second phase.
1.2 CRYSTALLINE STRUCTURE OF CORDIERITE

The crystal structure of cordierite is classified into two forms; an "Orthorhombic" low temperature form and a "Hexagonal" high temperature form known as "Indialite" (Miyashiro and Iiyama 1954; Gibbs 1966). This transformation has been examined by several workers (Cohen et al. 1977; Meagher and Gibbs 1977; Putnis 1980; Kitamura and Hiroi 1982) from the standpoint of the order-disorder distribution of Al and Si atoms. Cohen et al. (1977) found the order-disorder distribution to involve all tetrahedral atoms in the crystal structure and the atom to be completely ordered within the limits of error in low cordierite. Meagher and Gibbs (1977) found that Al and Si atoms were much less ordered in high cordierite. High cordierite has a limited field of stability at temperatures higher than the congruent melting point. The structure of cordierite is depicted in Figure (1). All the tetrahedral atoms (Al and Si) are linked to form four-and-six-membered tetrahedral rings. The six-membered rings are aligned perpendicular to c-axis to form channels. The tetrahedral cations forming these rings are designated as T2, while those cross-linking the rings are designated as T1. Likewise, the bridging oxygen (those linking to tetrahedral), which are on the inside of the six-membered rings are designated as O2; all others are O1 oxygen. The one crystallographically unique non-tetrahedral cation site in this structure is designated as M. It is octahedral coordinated and situated in the framework between six-membered rings. The channel sites are designated as C1 and C2.

The site occupancy for cordierite and indialite are designated in Table 1.1. In cordierite, 4Si and 2Al occupies the six-T2 tetrahedrals, which make up the ring, and the Si and Al are ordered about the ring shown in Figure 1.1.
Figure 1.1 Crystallographic Structure Arrangement in Two Cordierite Forms
### Table 1.1 Cation Site Occupancies and symmetry for Cordierite and Indialite

<table>
<thead>
<tr>
<th></th>
<th>Site Occupancy</th>
<th>Symmetry</th>
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<tr>
<td><strong>Cordierite</strong></td>
<td></td>
<td></td>
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<tr>
<td>T1</td>
<td>1Si, 1Al</td>
<td>4Si, 2Al</td>
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<td></td>
<td>(Ordered);</td>
<td>(Ordered);</td>
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<tr>
<td><strong>Indialite</strong></td>
<td>0.8Si, 2.2Al</td>
<td>4.2Si, 1.8Al</td>
</tr>
<tr>
<td></td>
<td>(disordered)</td>
<td>(Disordered)</td>
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The two distinct T1 sites contain 1Si and 1Al and these sites are also ordered. The resulting symmetry of the framework is orthorhombic. If Si and Al are disordered about the framework, then hexagonal symmetry results (Meagher and Gibbs 1977). The M site in cordierite contains Mg, such that the number of other cations is known to substitute in these sites.

### 1.3 PHASE DIAGRAM

#### 1.3.1 MgO-Al₂O₃-SiO₂ System

The ternary system MgO-Al₂O₃-SiO₂ is of great interest to the ceramists. The work of Rankin and Merwin (1918) first recognized cordierite in the ternary phase diagram (MgO-Al₂O₃-SiO₂) as shown in Figure 1.2. During the ensuing thirty years no revisions of the diagram have been found. The investigation of the system Al₂O₃-SiO₂ by Brown and Greig (1924); delineation of the diagram resulting two liquid area by Greig (1927) and the resulting Figure 1.2 is now generally accepted without question as the correct configuration for the system 2MgO·2Al₂O₃·5SiO₂. Bystron (1945) made an X-ray diffraction investigation of numerous sintered mixtures in the ternary system. He also found no evidence of a ternary compound other than cordierite and then it was investigated by partial substitution of iron for...
Figure 1.2 Phase Equilibrium Diagram of MgO-Al₂O₃-SiO₂ System
magnesium and by magnesium and silicon for aluminium, after which it was assigned such a simplified formula as $5\text{MgO} \cdot 6\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ or $2\text{MgO} \cdot 2\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$. Using one or other of these two formulas, the iron free sapphire falls either within cordierite-spinel-mullite triangle at point Z or on the cordierite-spinel joined at point X Figure 13. In either case, the temperature final consolidation of the molten material should on the basis of Figure 13 are $1460^\circ\text{C}$ the temperature of invariant point 3, at which the primary field of cordierite, spinel and mullite come together. From the phase diagram of MgO-Al$_2$O$_3$-SiO$_2$ system, cordierite melts above $1460^\circ\text{C}$ and dissociates into liquid and mullite phase. Kracek (1945) reported that sapphire dissociated to spinel and liquid phase at $1580^\circ\text{C}$. Dane (1944) stated that sapphire melted incongruently at $1500^\circ\text{C}$ yielded spinel, silluminite and silicious glasses. Later Foster (1950) observed from X-ray diffraction analysis the crystalline phases which exist with cordierite are spinel, mullite, frosterite, cristoballite, corundum, periclase and tridymite phases.

### 1.3.2 MgO-Al$_2$O$_3$-SiO$_2$-ZrO$_2$ System

Using techniques developed by Goldschmidt et al (1926) and later utilized by Foster (1951), solid state phase equilibrium were studied in the system MgO-Al$_2$O$_3$-SiO$_2$-ZrO$_2$. The ternary systems MgO-Al$_2$O$_3$-SiO$_2$ and MgO-SiO$_2$-ZrO$_2$ are the only phases of this four-phase system that have been studied extensively. Composition in each of the four phases was heated to temperature below their fusion point and, after they have been cooled, they were examined by x-rays to identify the phases present. Herold et al have studied the phase relationship of cordierite-zirconia system (Figure.14-a) and reported that there was no evidence of quartary compound formed in this system (MgO-Al$_2$O$_3$-SiO$_2$-ZrO$_2$). An exploded view aids which in the visualization of this system is shown in Figure. 14-b.
Figure 1.3  High-Alumina Portion of the MgO-Al₂O₃-SiO₂, Showing the Compositions Studied
Figure 1.4 Phase Equilibrium Diagram of MgO-Al₂O₃-SiO₂-ZrO₂ System (a) Phase relationship & (b) Exploded View
1.4 PREVIOUS WORK ON THE PREPARATION OF CORDIERITE AND CORDIERITE-BASED SYSTEM

Cordierite ceramics apart from having attracted renewed interest in recent years, also has gained considerable importance in electronics. It is a prime candidate for as the substrate material (Tummala. Rao 1991) for large scale IC devices because of their superior properties such as low dielectric constant, low thermal expansion, good conductivity with high chemical stability, hence, their high resistance to thermal shock.

With the increasing development of ceramic materials, there has been enormous interest in their preparation. The preparative technique depends on, the applications of a particular material, such as the mixed oxide method (conventional) and chemical route for structural applications. Some investigations have already been done on this system (2MgO.2Al₂O₃.5SiO₂) using the conventional process to explore the potentiality of these materials (Gebbler and Wisely 1949; Hummal and Reed 1951; Grosjean 1993).

1.4.1 Conventional Method

Since Rankin and Merwin 1918 first recognized cordierite in the ternary system MgO-Al₂O₃-SiO₂ and discovered its unusually low thermal expansion, considerable research has been devoted to characterizing the phase relationships and the polymorphism of the mineral. The first qualitative structural analysis of cordierite was carried out independently by Takane and Takenche (1936) and by Bystrom (1941). They assigned a random distribution of one Al and five Si atoms to the six membered rings and determined the space group symmetry “Cccm”. Later, in an investigation of the system MgO-Al₂O₃-SiO₂ -H₂O, Yolder (1952) discovered that the cordierite synthesized below 830°C. This evidence led by Karkhanavala and...
Hummel (1953) to propose, that the two forms synthesized by Yolder were polymorphs related by a high and low form of cordierite. A year later, Miyashiro et al (1955) published results of an extensive powder x-ray diffraction for cordierite. The nature of this transformation has been examined by several workers (Miyashiro, 1957, Iiyama, 1960; Schreyer and Schairer 1962; Schreyer et al 1964) whose researches indicate that the mineral can exist in all structurally intermediate states ranging from high cordierite (hexagonal) to low cordierite (orthorhombic). Later Gregory et al (1971/ 1972 and 1973) studied the crystallization behavior of cordierite-type glasses and the effect of oxide addition on the devitrification characteristic. Zdaniewski (1973) investigated structure and volume changes during crystallization of cordierite - titanium glass by heat-treatment at temperatures in the range 740° to 1300°C and also studied the surface topography of the cordierite-TiO₂ glass ceramic. Barry et al (1978) has studied the series of glasses of stoichiometric and MgO-enriched cordierite with TiO₂ and TiO₂/ZrO₂ addition. Their main interest was the crystallization sequence upon heating and the nucleation effects of both TiO₂ and TiO₂/ZrO₂ mixtures. The cordierite glass-ceramics was developed by Holand et al (1982) who studied the nucleation and crystallization of these glasses by the addition of TiO₂ and LiO₂ and also compared that with conventional molten glasses.

In 1984, Hirose et al; have studied the thermal expansion behavior, density and 3-point bending strength of the cordierite prepared by melting the powder of MgO, Al₂O₃ and SiO₂ and these glass powders were then pressed by hot-pressing. Mussler and Shafer (1984) reported the mullite-cordierite composite with various mullite contents and their physical and mechanical properties and the dependence of the densification and microstructure evolution for the composites prepared by melt process. The
crystallization mechanism of high-cordierite glass (Wantanabe et al 1985) containing B$_2$O$_3$ and P$_2$O$_5$ as nucleating agents was studied, which shows the growth rate increases with temperature and the maximum rate occurs at about 1250°C. The mechanical and thermal properties of cordierite-based glass ceramics containing ZrO$_2$ was reported by Musseler et al (1985). McCoy et al (1986, 1988) studied the well-defined orientation of t-ZrO$_2$ rods by the addition of ZrO$_2$ in the α-cordierite matrix and observed the transformation of the dendrites to monoclinic symmetry under some condition and also reported the beneficial effects of ZrO$_2$ on the fracture toughness and microstructure characterization of cordierite-based glass ceramics. Wadsworth et al (1990) reported the improvement of mechanical properties of cordierite by the addition of ZrO$_2$-2mol% Y$_2$O$_3$ in the cordierite matrix. Such improvements are due to stress-induced transformation toughening and to the generation of residual stresses.

Stabilized (t-ZrO$_2$) and un-stabilized (m-ZrO$_2$) has been added to cordierite, which exhibits a fracture toughness of approximately 4.1 MPa m$^{1/2}$, while m-ZrO$_2$ particles show the highest fracture toughness approximately 4.7 MPa m$^{1/2}$ (Travitzky et al 1992). These composites are obtained when cordierite was sintered at 1400°C for 1 hour. According to Akazava et al (1993), cordierite ceramics was prepared by solid state reaction with Mn$^{2+}$ ions-substitution of which lowers the sintering temperature for densification (99% relative density obtained) and also a low thermal expansion is observed by increasing the Mn$^{2+}$ ion content. To examine the formation of pores in the cordierite body consisting of kaolin, talc and alumina, the melting behavior of talc particles in the body during firing and its relation to the pore formation was studied (Nakahara et al 1994, 1995) by XRD, SEM and EPMA and it was observed that the melting point of talc particles decreased with increase in alumina content in the matrix phase and also the distribution of Mg and Al showed (EPMA) that the eutectic melt
of talc and alumina penetrated into the surrounding matrix phase and left the pores behind them. Sampath kumar et al 1995 studied the effect of using fly ash as one of the starting raw material for high temperature hexagonal form of cordierite, which shows the presence of only cordierite phase and also it indicates the needless formation in the matrix within the fine grained microstructure. Best mechanical, thermal and physical properties of cordierite were observed by the addition of mullite in the matrix as 70:30 percent of cordierite and mullite (Ibrahim et al 1995). Montorsi et al (1994) describes the effect of CeO₂ on cordierite used as a catalyst. CeO₂ does not react with cordierite up to 1200°C and no remarkable modification of the microstructure and thermo-mechanical properties have been found. By melt process, the addition of CeO₂ enhances the crystallization properties and sinterability increased with increasing the CeO₂ content below 1000°C (Kim and Lee 1994). The kinetic studies of Rutile formation in the cordierite glass-ceramics; containing 9.6 wt% of TiO₂ as a nucleator and behavior on heating at high temperatures was investigated by Tosic et al (1996). Dense cordierite ceramics from ultra fine particles of Magnesium hydroxide and kaoline was investigated by Sumi et al (1998).

1.4.2 Non-Conventional Process

Although various non-conventional routes are available for the preparation of fine ceramic materials, the sol-gel method is a promising process technique because of its inherent advantages, which is based on low-temperature chemistry. This method offers control over homogeneity, stoichiometry as well as physical characteristics such as particle size, size distribution and morphology. In the previous process (conventional method), it is difficult to sinter pure, homogeneous and dense cordierite ceramics (without sintering aid) because of the narrow sintering range near cordierite's incongruent melting point (Lamar and Warner 1954) and
because of water molecules in the cavities of the cordierite structure which vaporize near the melting point, having cracks and pores within the sintered body and these have prevented its widespread applications. In order to overcome the above difficulties, the cordierite ceramics was prepared by sol-gel process (Suzuki et al 1987, part I and II). Later Kazakos and co-workers (1990) optimized the sintering temperature and the effect of seeding in the cordierite matrix, which enhanced the densification behavior of powder compacts sintered at 1300°C for 2 hours resulted in 100% of theoretical density for tri-phasic gel (three sols) and 80% of theoretical density prepared by mono-phasic gel (single sol). Following this process Awano et al (1992), optimized the grinding effect of cordierite, prepared by colloidal processing which promoted the homogeneous distribution of element in the gel, resulting in improved reactivity for the formation of cordierite. Werckmann et al (1993) and Mazza et al (1993) describe the various analytical techniques for green and sintered sol-gel cordierite on a microscopic scale and identified α-cordierite containing mullite and spinel phase.

1.5 POWDER PREPARATION METHODS

A variety of methods exist for the preparation of ceramic powders. In practice, the choice of a powder preparation method will depend on the method for achieving a certain set of desired powder categories: Conventional and Non-conventional methods. In conventional method, the required composition of individual powders are mixed together in any one of the milling techniques, followed by heat treatment to get the desired compound. In this method, the produced powders normally are chemically inhomogeneous and can have complex microstructures. In the second method (non-conventional), stoichiometric amounts of inorganic salts are mixed in a medium, the prepared powders have sub-micron size and uniformity in properties. Among the non-conventional methods; hydrothermal, co-
precipitation, spray drying, freeze-drying and sol-gel processing are the most popular techniques for the preparation of powders with desired properties. The detailed discussion of these various powder preparation methods are presented in chapter-2.

1.6 THERMAL EVALUATION METHODS

Methods of thermal analysis are related groups of techniques whereas the dependence of the parameters of any physical property of a substance on temperature is measured. The majority of them follow changes in some property of the system as a dynamic function of temperature. The basic parameter important for the methods of thermal evaluation is the change in heat content (ΔH). Every substance can be characterized by its free energy (G), given by the expression

\[ G = H - TS \]

where H is enthalpy, T is absolute temperature and S is entropy.

At a given temperature, every system has tendency to attain a state in which the free energy is at a minimum, viz., the transition from one crystalline form of a substance to another which, at a given temperature, has a lower free energy and is therefore more stable. The formation of a more stable crystalline structure, or of another state with a lower free energy, may take place on gradually heating the sample or by intermediate steps. The transformation is characterized by the temperature at which it occurs and by a change in heat content, manifested by an increase or decrease in the temperature, depending on whether the reaction is exothermic or endothermic. This is the basis of differential thermal analysis (DTA).

The change in heat content can be also be accompanied by a change in weight, e.g, during a chemical degradation, dehydration, sublimation or
oxidation. Observation of such a change is the basis of the thermogravimetric method (TG). When a substance is heated or cooled, reversible or irreversible change in its dimension take place, depending on the initial dimensions and on the temperature. Thermal expansion coefficient (TEC) is a result of increase in dimension due to the vibration of atoms around equilibrium position in the crystal structure. The observation of the change in dimension during heating is the basis of dilatometry and has great importance in metallurgy, physics and ceramic technology. The coefficient of expansion of crystalline substance and the resulting change in dimension may also be observed by X-ray diffraction technique (XRD) which determine the exact phase formation, lattice parameters and crystalline size of the materials.

1.7 SINTERING PROCESS

Sintering can be defined as removal of the pores between starting particles accompanied by shrinkage of the component combined with growth together and formation of strong bonds between adjacent particles. The processes which take place on heating ceramic compacts are controlled by the atmosphere, pressure and temperature (including heating and cooling rates) used for sintering behavior include both the composition of the component powders and the green density. High green density is desired for a good end mechanical strength. Pal. et al (1996) has reported that if the densification of pure and homogenous cordierite - powder compact occurs below the crystallization temperature, it would be possible to obtain pure and dense cordierite ceramics with relatively high mechanical properties. Other important green body characteristics are the pore content (size, distribution and shape), the particle size distribution, shape and alignment and the extent of mixing of each component powder. A detailed description regarding the various types of sintering process will be given in Chapter-3.
1.8 MECHANICAL BEHAVIOR OF CERAMICS

The mechanical properties of a material determine its limitation for structural applications where the material is required to sustain a load. Mechanical behavior of ceramics is also of interest in many cases when the primary purpose of the ceramic is to perform some other function, such as failure may occur unexpectedly. The characteristics of crack propagation in most ceramics are such that a failure is likely to be instantaneous and total. Understanding the nature of the device using the ceramics can do much to afford relief from this problem. The concept and basic mathematical treatment of continuum mechanics are necessary foundation for the development of a fundamental science of mechanical properties and the use of this theory to understand the effect of microstructure on these properties. Much of the progress in ceramics in recent years comes from the development of microstructures that enhance their properties. However, we describe here the mechanical properties of polycrystalline ceramics. Polycrystalline ceramics comprise an extensive variety of materials with wide range of mechanical properties. Ceramics are conveniently considered as traditional and advanced ceramics (Phelps and Watchman 1986). Traditional ceramics are usually made in bulk form using relatively inexpensive (usually natural raw material) starting materials and tend to have low modest strength values and creep resistance. Advanced ceramics are usually prepared from more highly homogeneous, high purity synthetic starting materials and often have microstructures designed to optimize mechanical or other functional properties.

In recent years, research intention is to improve the mechanical properties by carefully controlled compositions and microstructures of the material through advanced ceramics rather than on traditional ceramics.
1.8.1 MgO-Al2O3-SiO2 SYSTEM

The mechanical properties of cordierite (2MgO-2Al2O3-5SiO2) are influenced by chemical processing technique (Suzuki, et al 1988); this method offers control over homogenity, stoichiometry as well as physical characteristics such as particle size, size distribution and morphology. Because of the fine particle size, the desiccated gel has higher free surface energy and as a result, a significant reduction in sintering and densification temperature occurs without any sintering aid (Kazakos et al 1990), exhibits higher fracture toughness and hardness to attribute to their fine microstructure (Figure  ) of the ceramics. The high-temperature flexural strength of α-cordierite ceramics is reduced below 1000°C because of high-purity of the ceramics. However, their use remains limited by relatively poor mechanical properties. A relatively new method of glass-ceramic preparation, the mechanical properties of glass-ceramics showed intrinsic high strength and modulus values (Yun-Mo sung 1997), whereas the β-spodumene glass-ceramics showed rather low values.

1.8.2 MgO-Al2O3-SiO2-ZrO2 SYSTEM

Improvement in mechanical properties of ceramics by transformation toughening have been demonstrated in a wide variety of routes such as precipitation, dispersion-toughened ceramics, and by sol-gel process containing tetragonal (t) ZrO2 particles (Heuer and Hobbs 1984). Mechanical properties of glasses and ceramics can be enhanced by the addition of second phase (Hasselman and Fulrath 1968; Swearengen et al 1978; Claussen 1976; Claussen 1978; Evans and Heuer 1980). Dispersion toughening of oxide ceramics by a zirconia as a second phase is a well established process and has been successfully employed to improve the
mechanical properties of alumina, mullite, and spinel. Such toughened ceramics are developed by utilizing toughening mechanism such as stress-induced transformation toughening, micro-cracking and crack deflection. The cordierite system is particularly attractive for enhancement of properties by zirconia additions, because it has many potential applications, arising from its excellent properties, but its mechanical properties are poor compared to many engineering ceramics. Investigations have been carried out to determine the effect of systematic zirconia addition on the mechanical properties of cordierite and various techniques involved in preparation of cordierite-zirconia composites has been discussed in Chapter-4

1.9 ELECTRICAL BEHAVIOUR

Ceramic materials have a wide range of electrical properties. The insulation and dielectric properties of ceramic-based materials (including glass ceramics) are of considerable importance in the fields of electrical engineering and solid-state electronics. During the last decade, technological developments have placed increasing demands upon the electrical and structural properties of insulators and have revealed the inadequacy of some existing materials. Some do not allow passage of an electric current even in a very strong electric field and thus are excellent insulators. Others allow an electric current to pass only under certain conditions or when an energy threshold has been reached and thus are useful semiconductors. Still others do allow passage of an electric current and have application as electrical conductors. Some ceramics do not conduct electricity but undergo internal polarization that allows the material to be used for storage of an electrical charge in capacitor. These electrical properties are determined primarily by the nature of the atomic bonding and crystal structure.
1.9.1 DIELECTRICS

Dielectrics and insulators can be defined as materials with high electrical resistivities. Dielectrics fulfill circuit functions for which their permittivities and dissipation factors are also of primary importance. Insulators are used principally to hold conductivity elements in position and to prevent them from coming in contact with one another. A good dielectric is, of course necessarily a good insulator, but the converse is by no means true.

Ceramics as insulating materials have definite advantages over plastics, which are major competitors. Lack of flexibility is a problem in most instances where this feature of insulation is required. However, ceramics posses superior electrical properties, and are absent from creep or deformation under stress at room temperatures and resist environmental changes particularly at high temperatures where as plastics oxidize, glassify or decompose. Ceramics can form glass-tight seals with metals and other ceramics components, and thereby become an integral part of an electronics device.

Dielectric properties are of special importance when ceramics are used either as a capacitave element in electronic applications or as insulation. The dielectric constant, dielectric loss factor and dielectric strength usually determines the suitability of a particular material for such applications. Variation of dielectric properties with frequency, field strength and other circuit variables influence performance.

Ceramics, glass-ceramics and related ceramic-based materials are extensively used in electrical, electronic and structural applications. The mechanical properties of most suitable ceramic materials have been investigated in some detail, but as yet we have only a limited understanding
of electrical processes occurring in these solid insulators. In particular, the literature suggests that the electrical properties of sol-gel ceramics have received comparatively little attention.

The dielectric constant and loss factor measurements were performed and discussed in detail in Chapter-5.

1.10 APPLICATION OF CORDIERITE CERAMICS

The study of multicompositional ceramic is of great interest for microelectronics packaging application especially for high-frequency circuits. The material which is almost exclusively used now a days for these purposes is alumina, because of its high electrical resistance, good thermal conductivity and high mechanical strength. The dielectric constant of alumina is quite high causing significant signal propagation delay in the devices. Secondly, the thermal expansion coefficient of alumina is high which introduces stresses at the chip package interface. Finally, the sintering temperature of alumina is very high, which restricts the choice of the metal for interconnections. A promising material, alternative to alumina, is Cordierite-based multicompositional ceramic system (2MgO.2Al₂O₃.5SiO₂) for future substrate applications.

Cordierite ceramics have attracted renewed interest in recent years. Also, it has gained considerable importance in electronics. It is a prime candidate for as substrate material (Tummala R.Rao 1991) for large-scale IC devices.

Cordierite honeycomb structures have been widely employed in the automotive industry in the last 15 years (Howitt and Sekella 1974 and Howitt 1980). They have performed as catalytic converter for hydrocarbons,
carbon monoxide and nitrous oxide emissions of gasoline-powered cars and also as traps and incinerators for particulate material from the exhaust gases of diesel-powered cars (Howitt 1981 and Lachman et al 1981). Since, the cordierite materials are having low thermal expansion, high thermal shock resistance and good thermal stability, which make the cordierite materials most successful in the automobile industries.

In ceramic industries, when fine ceramics bodies like tableware and artware are being fired, it is necessary to support these bodies in the kiln with the help of kiln furniture. The materials, which are used for fabricating, kiln furniture such as slabs, stilts, setters, etc. must be of high quality (free from iron and other fluxing agent) because the products must have a very long life. The kiln products must also be mechanically strong and good spalling resistant. Cordierite kiln furniture is widely used in ceramic industries due its low thermal expansion and therefore a better resistance to thermal shock than any other ceramic kilns furniture.

1.11 OBJECTIVES OF THE PRESENT WORK

The scope and the objectives of the present work include,

- to synthesize cordierite (MgO-Al₂O₃-SiO₂), Ti-doped cordierite and Cordierite-ZrO₂ (MgO-Al₂O₃-SiO₂-ZrO₂) composites by sol-gel process.
- to discuss various physico-chemical characterization of synthesized powders.
- to study the sintering behavior and microstructure of sintered samples.
- to study the mechanical properties such as hardness, fracture toughness and strength.
- to study the dielectric constant and loss factors of cordierite and cordierite-based ceramics (in the system MgO-Al₂O₃-SiO₂-TiO₂).