CHAPTER 1
GENERAL INTRODUCTION

1.1 INTRODUCTION AND DEFINITIONS

The word “ceramics” comes from the Greek word keramiko, which means, “Burnt stuff” [1]. Ceramics can be defined as products made out of inorganic, non-metallic solid materials [1, 2] shaped first and then hardened by fire. These materials include clays, high temperature oxides, carbides, nitrides, borides, oxynitrides etc., [1, 3-5]. Generally, these materials are stable towards high temperature. Ceramic materials can be classified into categories such as refractory materials, cement, glass, structural ceramics, electronic ceramics, electrical and thermal insulators, semiconductors, superconductors etc., [1]. Ceramic materials are generally hard, brittle, and chemically inert and have high melting point.

The characteristic features of ceramics include (i) the presence of strong covalent chemical bond and (ii) microstructure. The strong covalent bond is responsible for the high melting point. The manifestation of slight variations in the chemical bonding results in a range of structural, electronic and magnetic properties of ceramics. Ceramics have microstructures comprising of crystalline inorganic compounds and or amorphous phase in varying proportions surrounding the grains and is termed as grain boundary.

1.2 CLASSIFICATION OF CERAMICS

Ceramics are subdivided into traditional ceramics and technical or advanced ceramics. Traditional ceramics include bricks, tiles, pottery etc., where clay, quartz and feldspar are the primary raw materials used for their production.
Technical ceramics require high purity synthetic raw materials [1] and hence possess better mechanical, electrical, optical and magnetic properties. They are employed in critical structural applications, which require high strength, hardness, chemical purity [6], refractoriness, thermal shock and wear resistance as well as in functional applications. Table 1.1 gives the distinction between traditional and advanced ceramics.

**Table 1.1: Distinction between Traditional and Advanced ceramics**

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Traditional Ceramics</th>
<th>Advanced Ceramics</th>
</tr>
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<tbody>
<tr>
<td>Raw materials</td>
<td>Natural minerals with little or no beneficiation e.g. clay, quartz, feldspar, magnetite, dolomite etc.</td>
<td>Synthetic materials e.g. Al₂O₃, ZrO₂, Si₃N₄, SiC,</td>
</tr>
<tr>
<td>Processing</td>
<td>Pressing, extrusion, Slip casting, drying, firing</td>
<td>Tape casting, hot isostatic pressing, injection moldings, CVD, in situ oxidation</td>
</tr>
<tr>
<td>Properties</td>
<td>Compressive strength, Refractoriness, thermal, electrical and chemical insulation</td>
<td>Fracture toughness, electrical conductivity, electro optics, dielectrics, piezo electrics, magnetic, superconductivity</td>
</tr>
<tr>
<td>Applications</td>
<td>Building materials, Refractories, sanitary ware, container glass, enamel, cement etc.</td>
<td>automobile engine, optical fiber, substrates parts, ferrites, capacitors, transducers</td>
</tr>
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The last few decades have seen the development of the enormous potential of functional ceramics based on unique dielectric, ferroelectric, piezoelectric, ferromagnetic, magnetoresistive, ionical, electronical, superconducting, electro optical, and gas-sensing properties. Such properties now constitute the basis of a broad field of applications as shown in Fig.1.1 Scientific advances concerning many ceramic materials have enabled technological breakthroughs of truly global proportions.

**Fig.1.1: Functional and structural applications of advanced ceramics**
Ceramic materials have now become the cornerstone of such advanced technologies as energy transformation, storage and supply, information technology, transportation systems, medical technology and manufacturing technology [7-9] and are shown in Fig.1.2.

![Fig.1.2: Technology areas, which benefit from advanced ceramics](image)

1.3 GENERAL METHODS OF SYNTHESIS OF CERAMIC POWDERS

Ceramic materials are generally prepared by solid phase reaction, liquid phase reaction and gas phase reaction. Some of the most common and general methods of synthesis of ceramic powders are described below.

a. **Solid phase reaction between powder oxides**: In this classic method, two or more solids are mixed together, homogenized and heated to a high temperature to form the required compound. The diffusion of the mixture of particles of different composition causes aggregation of the grains without the powder reaching perfect homogeneity. It is necessary to grind the calcined product before sintering but the crystals remain about a micron or more in size, which reduces the sintering rate. It has been found that considerable amount of impurities are picked up during the grinding process. The powder particles are
neither fully spherical nor angular. Ceramic particles are least plastic. The powder can be converted to granules of 0.5 to 1 mm, either by humidification and aggregation on a screen or by placing in suspension and spray drying at 150 °C. The mixing and grinding operations may produce contamination and significant change in properties of the products. Finally, mixing of particles with different dimensions and shapes raises reaction disorder during sintering [10].

b. **Double decomposition and reactive sintering:** To accelerate the formation reaction, one adds to the mixture a compound to provide a liquid phase which serves as a transfer medium. The process is improved by employing a double decomposition reaction between a salt and an oxide, with the cell in the molten or solid state. The homogeneity of the product is perfect but its suitability for sintering is not entirely satisfactory.

c. **Co-precipitation method:** In the co-precipitation method, the formation of the precipitate from a homogeneous liquid phase may occur as a result of physical transformations like change of temperature, solvent or solvent evaporation but most often is determined by chemical processes like addition of acids or bases and use of complex forming agents [11]. The precipitate is treated in subsequent preparation stages to form the active product. In a multi-component system, the composition of the precipitate depends on the difference in solubility between the components and the chemistry occurring during precipitation. One possibility is the sequential precipitation of separate chemical compounds. This occurs whenever there is a large difference in the solubility products of the compounds involved. The co-precipitates of hydroxides, hydroxocarbonates, oxalates and formates containing two or more different metals are generally non-homogeneous in composition and only very seldom generate a homogeneous mixed oxide [12].
d. **Powder synthesis with gas phase reactants:** Gas phase reactors are used to produce the purest ceramic powders because it is relatively easy to obtain purified reactant gases with impurities at the ppm to ppb level. Gas phase reactors produce very fine ceramic particles (<0.5 μm) at low volume fraction and narrow particle size distribution. However, the particles are difficult to separate from the large volume of gas and as a result, a significant fraction of the cost of producing gas phase ceramic powder is spent on particle–gas separation. For endothermic reactions, gas phase powder synthesis can be performed with an external energy source to provide the necessary heat of reaction. This external energy source can be provided by a furnace, laser or plasma [13].

e. **Cryochemical processing:** By this method, pure homogeneous powders of uniform particles and very small crystallite sizes can be prepared. Initially a mixture of soluble salts containing desired ratios of metal ions is dissolved in distilled water. The solution is made into droplets of usually 0.1 to 0.5 nm in diameter and is rapidly frozen so that no compositional segregation occurs and ice crystals that nucleate remain small. Water is removed from the system by sublimation under vacuum and the resulting powder is further calcined to get the desired oxide [14].

f. **Spray roasting:** In this method, fine atomized droplets of solution of a precursor in water or other solvent are sprayed into a heated chamber. The temperature of the chamber is selected such that evaporation and decomposition reaction occur so as to yield a high purity powder containing fine crystalline size [15].

g. **Flash combustion:** In this method, mixture of precursor salts in the form of nitrates is mixed with calculated amount of urea. The mixture is preheated to ~300 – 400 °C when a self propagated highly exothermic vigorous combustion
takes place whereby very fine powders with the final phase will be formed without any further requirement of calcinations. Calcium and copper oxide can be synthesized from calcium and copper nitrates by this method [16].

h. **Hydrothermal processing**: This involves the synthesis of nanosize particulates where there is partial dehydroxylation cum crystallization in presence of hot pressurized conditions. Typical temperature of hydro processing ranges from 100-350 °C and pressure, limited to 15 MPa. Under these conditions wide variety of pure, fine particles having ceramic composition can be synthesized [17].

i. **Microwave processing**: Microwaves are electromagnetic waves in the range from 0.3-300 GHz with corresponding wavelength ranging from 1 mm to 1 m. Ceramic precursor such as metal nitrates and sulphates and any material containing OH or water of crystallization are reported to be active under this frequency range and readily absorb microwave energy. Absorption of microwave energy induces the polarization of the molecules and results in thermal heating. This phenomenon of absorption of microwave energy has been utilized for fine powder synthesis of ceramic oxides. Precursors are exposed under microwave and fine powders are obtained by decomposition of the precursors [18].

j. **Sol-Gel technique**: Sol-gel process is a very versatile technique, which is used in the synthesis of nanosized composites, monoliths, thin films, optical ceramics, electronic ceramics, catalysis etc [19-27]. This method provides heat resistant glass, antireflective coatings and ceramic fibers, which are very difficult to prepare by conventional methods [28-30]. Functionally gradient ceramic materials can be readily processed using sol-gel method [31]. Sol-gel method is generally understood to be based on a homogeneous or heterogeneous colloidal precursor.
1.4 SOL-GEL PROCESSING: AN OVERVIEW

Interest in sol-gel processing of ceramic materials began as early as in the mid 1800s with Ebelman and Graham's studies on silica gels. In the early investigation, the hydrolysis of tetraethyl ortho silicate, under acidic conditions yielded SiO₂ in the form of a glass like material. During late 1800s to the 1920s studies on gels became of considerable interest to chemists stimulated by the phenomenon of Liesegaging [32] rings that were observed in gels. Many noted chemists including Ostwald and Lord Raleigh investigated the problem of the periodic precipitation phenomena that led to the formation of Liesegaging rings and the from growth of crystals from gels. Roy et al., [33] recognized the potential for achieving very high level chemical homogeneity in colloidal gels and used the sol-gel method in the 1950s and 1960s to synthesize a large number of novel ceramic oxide compositions that could not be made using traditional ceramic powder urged methods. During the same period, Iler [34] was pioneer in doing research on silica powder. Stober et al., [35] extended Iler's findings to show that using ammonia as a catalyst for the TEOS hydrolysis reaction could control both the morphology and size of the powders.

Overbeek [36] and Sugimoto [37] showed that nucleation of particles in a very short time followed by growth without super saturation will yield monodispersed colloidal oxide particles. Matijevic et al., [38-41] employed these concepts to produce enormous range of colloidal powders in controlled size and morphologies, including oxides (TiO₂, Fe₃O₄, BaTiO₃, CeO₂), hydroxides (AlOOH, FeOOH) and various mixed phases or composites (Ni, Co, Sr ferrites) and coated particles (Fe₃O₄ with Al(OH)₃).

Sol-gel powder processes have also been applied to fissile elements [42] where spary formed sols of UO₂ and UO₂-PuO₂ were formed as rigid gel spheres during passage through a column of heated liquid. Both glass and polycrystalline ceramic fibers have been prepared by using the sol-gel method. Compositions
include TiO$_2$-SiO$_2$ and ZrO$_2$-SiO$_2$ glass fibers [42, 43]. A variety of coatings and films has also been developed using sol-gel method. Of particular importance are the antireflection coatings of indium tin oxide applied to glass windowpanes to improve insulation characteristics [44, 45].

1.4.1 Sol-gel process: Steps

Sols are dispersions of solid particles in a liquid with the particle size of 1-100 nm [46]. A gel is an interconnected, rigid network with pores of sub micrometer dimensions and polymeric chains whose average length is greater than a micrometer. The term gel embraces a diversity of combinations of substances that can be classified in four categories: (i) well-ordered lamellar structure, (ii) covalent polymeric networks completely disordered, (iii) polymer networks formed through physical aggregation, predominantly disordered and (iv) particular disordered structure.

Generally three approaches are used to make sol-gel monoliths: (I) gelation of a solution of colloidal particles, (II) hydrolysis and poly-condensation of alkoxide or nitrate precursors followed by hypercritical drying of gels and (III) hydrolysis and poly-condensation of alkoxide precursors followed by aging and drying under ambient atmosphere. The flow chart for the preparation of nanoparticles using sol gel process is shown in Fig.1.3.

In method I, a sol is formed by mechanical mixing of substances in water at suitable pH. In method II and III, a liquid metal alkoxide precursor is hydrolyzed by mixing with water [47]. The possible reactions for methods II & III may be written as,
\[
\text{M(OR)}_4 + 4\text{H}_2\text{O} \rightarrow \text{M(HO)}_4 + 4\text{ROH} \quad (1)
\]

\[
2\text{M(OH)}_4 \rightarrow \text{HO-M-O-M-OH} + \text{H}_2\text{O} \quad (2)
\]

\[\text{Starting materials} \]
\[
\text{A hydrolysis reaction is responsible for breaking down large molecules}
\]
\[
\text{A condensation reaction is responsible for building large molecules by polymerization}
\]
\[
\text{Milling}
\]
\[
\text{Nanoparticle}
\]

Fig.1.3: Flow chart for the preparation of nanoparticles using sol gel process

The hydrolysis and poly-condensation reactions eventually result in M-O-M network. The water/alcohol expelled from the reaction remains in the pores of the network. Srisuda Thitinun [48] observed that the reaction and the condensation reaction are not separated in time but takes place simultaneously. It has been established that the presence of H_2O^+ in the solution increases the rate of hydrolysis, whereas OH increases the condensation reaction. Catherine Henrist et al., [49] showed that the shape and size of Polymeric structural units are determined by the relative values of the rate constants for hydrolysis and poly-condensation.
reaction. Fast hydrolysis and slow poly-condensation favor formation of linear polymers. On the other hand, slow hydrolysis and fast condensation result in large, bulkier, and more ramified polymers [50].

1.4.2 Gelation

The sol particles link together with time to become a three dimensional network. As the sol particles grow and collide, condensation occurs and macro particles form. The sol becomes a gel when it can support a stress elastically [51]. This is typically defined as the gelation point or gelation time. One cannot precisely define the point when the sol changes from a viscous fluid to an elastic gel. The change is gradual as more and more particles become interconnected. The physical characteristics of the gel network depend greatly upon the size of the particles and extent of cross-linking prior to gelation. During gelation, the viscosity increases sharply. The structure of a gel is established at the time of gelation. The size and the degree of branching of the inorganic polymer and the extent of cross-linking have strong influence on porosity of gel, and later on the surface area, pore volume, pore size distribution, and thermal stability of the final oxide after calcinations [52].

In general, if the gel contains polymeric chains with significant branching and cross-linking (Fig.1.4), it will have large void regions and the resulting oxide after calcination will mostly be macro-porous and mesoporous [53]. Conversely, if the gel contains polymeric chains with little branching and cross-linking, it will have smaller void regions and the resulting oxide will mostly be micro-porous with low surface area. The relative rates of hydrolysis and condensation determine the extent of branching of the inorganic polymer and colloidal aggregation in the gelation mixture as shown in Fig.1.4.
Fig. 1.4: Schematic diagram of sol-gel inorganic network formation

Fig. 1.5: Schematic diagram of gels (a) with significant branching and cross-linking (b) with little branching and cross-linking

In general, when the concentration of metal cation monomer is high and hydrolysis is slow relative to condensation, long, highly branched and cross-linked polymeric chains are formed as shown in Fig. 1.5. and the resulting oxide can be macro porous. If condensation and hydrolysis occur at comparable rates, short
polymeric chains with less branching and less cross-linking are formed, and the final oxide can be micro porous in nature. Since hydrolysis and condensation are chemical reactions, their relative rates are functions of many parameters such as pH, temperature, nature and concentration of the metal ion precursors and concentration of water.

1.4.3 Aging

When a gel is maintained in its pore liquid, its structure and properties continue to change long after the gel point. The process is called aging. Four stages can occur sequentially or simultaneously during aging poly-condensation, syneresis, [54] coarsening [34] and phase transformation. Poly-condensation reactions continue to occur within the gel network. Usually in alkoxide-based gels, chemical hydrolysis reactions are very rapid and are completed in the early stages of sol preparation, especially when the sol is acid catalyzed. Since the chemical reactions are faster at high temperature, aging can be accelerated by hydrothermal treatment, which increases the rate of condensation reaction.

The shrinkage of the gel and the resulting expulsion of liquid from the pores are called syneresis. Syneresis in alcoholic gel systems is greatly attributed to the formation of new bonds through condensation reactions, which increases the bridging bonds and causes the interaction of the gel network. In aqueous gel systems, the structure is controlled by the balance between electrostatic repulsions and attractive Van der wall’s forces. Coarsening or “Ostwald ripening [34] is the irreversible decrease in surface area through dissolution and re-precipitation processes. If a gel is immersed in a liquid in which it is soluble, the dissolved material will tend to precipitate on to regions of negative curvature. Necks between particles will grow and small pores will get filled in, resulting in an increase in the average pore size of the gel and decrease in the specific surface area. Washing the pore liquid out of a gel is also an aging step [55]. The pH of the water used for
washing is critical in the case of gels made from acid catalyzed precursors. The final properties of such gels depend on both the pH in which it is washed before drying.

During aging there are changes in physical properties of the gel. Since the condensation reaction creates additional bridging bonds, the stiffness of the gel network increases, as does the elastic modulus [56], the viscosity and the modulus of rupture. The strength of the gel also increases with aging. Del Gado et al., [57] showed that gel strength increased logarithmically with time ranging between 1 and 32 days. Therefore, large monolithic gels are subjected to aging process before drying to reduce the chance of cracking. The greater stiffness of the aged gel reduces the shrinkage during drying, especially if the aging treatment is performed under hydrothermal conditions.

Fig.1.6: Various stages of gel (a) Stabilized gel, (b) Wet-gel (c) Aero gel (d) Xerogel

1.4.4 Drying

During drying, the liquid is removed from the interconnected pore networks. When the pore liquid is removed, shrinkage occurs and the monolith is termed as xerogel [58] as shown in Fig1.6. If the pore liquid is primarily alcohol based, the monolith is often termed as an alcogel [59]. A gel is said to be dried when the physically adsorbed water is completely removed. This occurs when the gel is dried in the temperature between 100 and 180 °C. Large capillary stresses can develop during drying and this can cause the gels to crack unless the drying process
is controlled. It has been generally accepted that there are three stages of drying. During the first stage of drying, the decrease in volume of the gel is equal to the volume of liquid lost by evaporation. The complete gel network is deformed by the large capillary forces, which cause the shrinkage of the material. For large or small pore gels, the greatest change in volume, weight, density, and shrinkage occur during stage 1 drying. Stage 1 drying ends when shrinkage ceases. Stage 2 begins when the strength of the material has increased due to the greater packing density of the solid phase, sufficient to resist further shrinkage. As the network resistance increases, the radius of the meniscus is reduced. Eventually the contact angle approaches zero and the radius of the meniscus equals to the radius of pore. This condition creates the highest capillary pressure and unable to compress the gel any further, the pores begin to empty which is the start of stage 2. In stage 2 liquid is transported by flowing through the surface films that cover partially empty pores.

The liquid flows to the surface where evaporation takes place. The flow is driven by the gradient in capillary stress [60]. The third stage of drying is reached when the pores and diffusion of vapor occur in the surface. During this stage there are no further dimensional changes but just a slow progressive loss of weight until equilibrium is reached, and is determined by ambient temperature and partial vapour pressure of water [61]. A dried gel still contains a very large concentration of chemisorbed hydroxyls on the surface of the pores. Thermal treatment in the range of 500-800 °C desorbs the hydroxyls and thereby decreases the contact angle and the sensitivity of the gels to re-hydration stresses resulting in a stabilized gel [61].

1.4.5 Densification

Heating the porous gel at high temperature causes densification. Densification of a gel network occurs between 1000 °C and 1700 °C depending upon the radii of the pores, connectivity of the pores and surface area. Controlling the gel-glass transition is a difficult problem if it is necessary to retain the initial
shape of the starting material. It is essential to eliminate volatile species prior to pore closure and to eliminate density gradients due to non-uniform thermal or atmosphere gradients. The amount of water in the gel has a major role in the sintering behavior. The viscosity is strongly affected by the concentration of water, [62], which in turn determines the temperature of the beginning of densification. For example, a gel prepared in acidic conditions has a high surface area and water content than a gel prepared in basic conditions and starts to densify about 200 °C sooner than the base catalyzed gel [63]. During sintering, the driving force is a reduction in surface area [64]. Many authors report a diminution of the specific surface area when the densification temperature increases. However, it has been shown that certain samples display an increase of surface area in the temperature range between 300 °C and 400 °C and then a decrease with further increase of temperature [65]. Several studies show that despite the complex manner in which the gel evolves towards a glass, its structure and properties become indistinguishable from those of a melt-derived glass [66-69], once the gel has been densified and heated above the glass transition temperature. Generally the mechanisms responsible for the shrinkage and densification of gels are capillary contraction, condensation, structural relaxation and viscous sintering. It is possible that several mechanisms operate at the same time.

Using different models one can describe the sintering behavior of a gel. Frenkel’s theory [70], which is derived for spheres, is valid for the early stages of sintering, because of the geometrical assumptions. It is based on the fact that the energy dissipated during viscous flow is provided by the reduction in surface area. Scherer [71] developed a model for describing the early stages as well as the intermediate stage of sintering. It is assumed that the microstructure consists of cylinders interacting in a cubic array. To reduce their surface area, the cylinders become shorter and thicker. The above models predict reasonably well the behavior of gels upon heating.
1.5 ADVANTAGES OF SOL-GEL PROCESS

The motivation for sol-gel processing is primarily due to higher purity, homogeneity of the products and the lower processing temperature compared with traditional glass melting or ceramic powder methods [72]. During the past decade, there have been enormous growths of interest in sol-gel processing. This growth has been stimulated by several factors. On the basis of Kistler’s [73] early work, several teams produced very low-density silica monoliths called aerogels and large monolithic pieces of alumina by sol-gel methods. These demonstrations of potentially practical route for production of new materials with unique properties coincide with the growing recognition that powder processing of materials has inherent limitations in homogeneity due to difficulty in controlling agglomeration [74].

The goal of sol-gel processing is to control the surface and interfaces of materials during the early stages of production. Long-term reliability of materials is usually limited by localized variations in the physical chemistry of the surface and interfaces within the material. Each step of the process can be controlled and modified in order to obtain a specific material, with better characteristics than those obtained by traditional methods of preparation. The important advantages of sol-gel processing are compositional homogeneity and the ability to prepare shaped materials such as spherical particles, fibers and thin film. The sol-gel process presents inherent advantage for the preparation of porous ceramic oxides, because the nano structure of the derived materials can be controlled together with their porous structure. At present sol-gel, processing is employed for the preparation of new generation of advanced materials for structural, electrical, optical, electronic and catalytic applications.

The sol-gel process is of particular interest for designing catalytically active materials with specific properties and/or with improved performances compared to those of classical catalysts. It allows preparation of catalytically active
materials, which can be directly cast on the support at the sol stage itself. This is a
great advantage for catalytic membrane development [75]. The classical synthesis
methods for conventional catalysts often start from salts or oxide precursors and
involve precipitation, impregnation, or even solid/solid reactions. These methods
are not adapted to a homogeneous casting of the catalyst on a support and lead to
limited specific surface areas and to a heterogeneous distribution of active species.
The sol-gel process starting from a homogeneous distribution of the precursors at
the molecular level can in many cases improve these specific criteria. Indeed a large
range of methods and precursors can be investigated to obtain the required powders
or films either as pure catalyst or homogeneously doped or dispersed in a matrix.
Furthermore, the specificity of the process can lead to original materials which can
help in a better understanding of the catalytically active sites in a specific catalyst.

1.6 DIELECTRIC MATERIALS

Dielectric materials are also called insulators. In dielectric materials, all
the electrons are tightly bound in their valance band and there is no free electron in
the conduction band. The band gap between the valence band and the conduction
band in a dielectric material is more than 3 eV. Therefore, it is not possible for the
electrons to jump from the valence band to the conduction band, under normal
voltage or thermal energy. Because of this, no electrical conduction takes place.
Generally, dielectrics are non-metallic materials of high specific resistance and
negative temperature coefficient of resistance.

1.6.1 Active and Passive Dielectrics

The dielectric materials can be classified into active and passive
dielectric materials. When a dielectric material is kept in an external electric field
and it actively accepts electricity, then it is known as active dielectric material.
Thus, active dielectrics are the dielectrics, which can easily adapt themselves to
store the electrical energy in it.
Examples: Piezo-electrics, Ferro-electrics etc.
Passive dielectrics are the dielectrics, which restrict the flow of electrical energy in them so, these dielectrics act as insulators.

Examples: All insulating materials such as glass, mica, rubber etc.,

The dielectric constant or relative permittivity ($\varepsilon_r$) of a material determines its dielectric characteristics. It is the ratio of the permittivity of the material ($\varepsilon$) and the permittivity of free space ($\varepsilon_0$) and is given by

$$\varepsilon_r = \frac{\varepsilon}{\varepsilon_0}$$

It is a measure of polarization in the dielectric material.

1.6.2 Polarization mechanisms in Dielectrics

Dielectric polarization is the displacement of charged particles under the action of the external electric field. Several microscopic mechanisms are responsible for electric polarization. Specially, in the case of d.c. electric field, the macroscopic polarization arises due to the following four types of microscopic polarization mechanisms.

i. Electronic polarization

ii. Ionic polarization

iii. Orientation polarization and

iv. Space-charge polarization
i. **Electronic polarization:**

![Diagram of electronic polarization]

**(a)** Position of +ve and -ve charges in an atom without field  
**(b)** Position of +ve and -ve charges in an atom with field

Electronic polarization occurs due to the displacement of positively charged nucleus and negatively charged electrons in opposite directions, when an external electric field is applied, and thereby a dipole moment is created in the dielectric as shown in Fig.1.7:

\[ \therefore \text{The induced dipole moment} \quad \mu = \alpha_e E \]

Where \( \alpha_e \) = electronic polarizability.

Monoatomic gases exhibit this kind of polarization; Electronic polarizability is proportional to the volume of the atoms and is independent of temperature.

The electronic polarizability = \( \alpha_e = 4\pi\varepsilon_0 R^3 \) (Farad.m\(^3\)) where \( R \) is the radius of the atom.

ii. **Ionic polarization**

Ionic polarization arises due to the displacement of -ve ions and +ve ions in opposite directions and it occurs in ionic solids, in the presence of electric field as shown in Fig.1.8 (a) and (b). The displacement is independent of temperature.  
Example: NaCl crystal
The ionic polarizability $\alpha_i = \frac{\mu^2}{3K_BT}$

Where $e$ is the charge of the electron $\omega_0$ is the angular frequency, $m$, mass of the positive ion and $M$, mass of the negative ion. Therefore, the ionic polarizability $(\alpha_i)$ is inversely proportional to the square of the natural frequency of the ionic molecule and directly proportional to its reduced mass, which is given by $\left(\frac{1}{m} + \frac{1}{M}\right)$.

iii. Orientation Polarization

Polar Molecules are the molecules, which have permanent dipole moments even in the absence of an electric field as shown in Fig.1.9.(a). The orientation polarization arises due to the presence of polar molecule in the dielectric medium. When polar molecules, are subjected to an electric field, the molecules align themselves along the field direction. So there is a resultant dipole moment along the field direction, as shown in Fig. 1.9 (b).
In the case of CH$_2$Cl molecules, the positive and negative charges do not coincide. The Cl has more electonegativity than hydrogen. Therefore, the chlorine atoms pull the bonded electrons towards them more strongly than hydrogen atoms. Therefore, even in the absence of field, there exists a net dipole moment.

Now, when the field is applied, positive portion aligns along the direction of field and negative portion aligns in the opposite direction of the field. This kind of polarization is called orientation polarization. This depends on temperature; when temperature is increased, the thermal energy tends to randomize the alignment. From Langevin’s theory of Para magnetism, net intensity of magnetization $= \frac{N \mu^2 B}{3K_B T}$ since, the same principle can be applied to the application of electric field, we can write,

Orientation polarization $P_o = \frac{N \mu^2 E}{3K_B T} = N\alpha_o F$ Where $\alpha_o = \frac{\mu^2}{3K_B T}$

Therefore, orientation polarizability is inversely proportional to the temperature of the material.
iv. Space-Charge Polarization

The Space-Charge Polarization occurs due to the diffusion of ions, along the field direction, thereby giving rise to redistribution of charges in the dielectrics, as shown in the Fig1.10. (a) and (b).

![Image of space-charge polarization](image)

(a) Without field (b) With field

Without the application of external field, the ions are orderly arranged as shown in the Fig1.10. (a). Now, when the field is applied, the ions diffuse with respect to the direction of applied field. Thus the polarization occurs, known as space charge polarization. The space charge polarization occurs due to the accumulation of charges at the grain boundaries (interfaces) and at the electrodes. The contribution of space charge polarization in a dielectric material is very small compared to other polarisabilities normally; this type of polarization occurs in ferrites and semiconductors, which is very small.

**Total Polarization:** Since space charge polarization is very small when compared to other kinds of polarization it can be neglected. Therefore, the total polarizability is given by

\[ \frac{k''}{k'} = \tan \delta = \frac{\varepsilon''}{\varepsilon_r} \quad P = NE\alpha \]
\[ \therefore P = NE \left[ 4\pi \varepsilon_0 R^2 + \frac{e^2}{\omega_0^2} \left( \frac{1}{m} + \frac{1}{M} \right) + \frac{\mu^2}{3K_B T} \right] \]

This equation is called as Langevin-Debye equation.

1.6.3 Frequency and Temperature Dependence of Polarization Mechanisms

When a.c field is applied, the polarization occurs as a function of time. The polarization \( P(t) \) as a function of time \( t \) is given by

\[ P(t) = P \left[ 1 - e^{-t/T} \right] \]

Where \( P \) is the maximum polarization, which occurs at a static field, applied for a long time and \( T \) is the relaxation time, i.e., the time taken for polarization. It is a measure of the time scale of a polarization process. Relaxation time is the time taken for the polarization process to reach 0.63 of the maximum value of polarization. The relaxation times are different for different kinds of polarization mechanisms.

(a) Frequency dependence

Electronic Polarization is very rapid and will complete at the instant the voltage is applied; the reason is that the electrons are very light elementary particles than ions, even for very high frequency of the applied voltage i.e. in the optical range \((-10^{15} \text{Hz})\) as shown in Fig.1.11. This kind of polarization occurs during every cycle of the applied voltage.

Ionic Polarization is slightly slower than the electronic polarization. Since ions are heavier than the electrons. In addition, the frequency of the applied electric field with which the ions will be displaced is equal to the frequency of the lattice vibrations \((-10^{13} \text{Hz})\). At optical frequencies, there is no ionic polarization. If the frequency of the applied voltage is less than \(10^{13}\text{Hz}, \) i.e. infrared range as shown
in Fig.1.11, the ions have enough time to respond during each cycle of the applied field.

Orientation Polarization is even slower than ionic polarization. The relaxation time for this case varies with respect to the dielectric materials (i.e. solids or liquids) used. The relaxation time for orientation polarization is much higher \((10^{-6}-10^{-10} \text{ sec})\) since the inertia is associated with the dipoles. Here the polar molecules in a liquid easily reorient themselves than that of solids. This type of polarization occurs at audio and radio frequency ranges \((=10^6\text{Hz})\) as shown in Fig.1.11

![Diagram of polarization mechanisms](image)

**Fig.1.11:** Frequency dependence of various polarization mechanisms

![Diagram showing frequency versus power loss](image)

**Fig.1.12:** Frequency versus Power loss of various polarization mechanisms
Space charge Polarization is the slowest process, because in this case the ions have to diffuse (jump) over several interatomic distances. In addition, this process occurs at a very low frequency in the order of $10^2$ Hz as shown in Fig.1.11. Therefore, from the Fig.1.11, we can observe that, at lower frequencies all the four types of polarizations occur and the total polarization is maximum. In addition, the total polarization value decreases with the increase in frequency and becomes minimum at optical frequency range. The power loss during various polarization processes as a function of frequency is also given in Fig.1.12 When a dielectric material is subjected to an alternating electric field, there will be an energy loss during each cycle and heat is produced. The energy loss is proportional to the product of voltage and current. In an ideal dielectric energy loss should be equal to zero. However, in real dielectric, the energy loss is appreciable depending on the frequency of the applied field as shown in Fig.1.13.

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**Fig.1.13:** Variation of $\varepsilon_r^1$ and $\varepsilon_r^{11}$ with frequency of the applied field
Temperature dependence
The electronic and ionic polarizations are independent of temperature, whereas the orientation and space charge polarizations are temperature dependent. The orientation polarization decreases with the increase in temperature because the randomizing action of thermal energy decreases the tendency of the permanent dipoles to align along the field direction. Hence, in this case the $\varepsilon_r$ decreases. However, in space charge polarization, when the temperature is increased, the ions can easily overcome the activation barrier and hence they diffuse through the interatomic distances. Thus, it gives rise to polarization. So in this case the $\varepsilon_r$ will increase with the increase in temperature.

1.7 Dielectric constant of ceramics and glasses

The electronic and ionic polarisabilities are operative at very high frequencies ranging from $10^{12}$ to $10^{15}$ Hz. However, the maximum useful frequency for many applications is limited to $10^{10}$ Hz. Hence, the orientation and space charge polarisabilities are active in the low frequency range. The orientation polarization depends on dipole moment and higher inertial is associated with this polarization. Similarly, the space charge polarization is associated with the diffusion of ions with the grains and the electrode interfaces. Therefore, these two polarizability are strongly responsive to temperature at lower frequencies. Also at high temperature, the d.c conductivity increases. So the combined effect results in sharp increase in dielectric constant with temperature at low frequency range. However, the variation in dielectric constant with the increase in temperature at high frequencies is minimal. The dependence of dielectric constant on temperature at different frequencies are shown for alumina ceramics in Fig1.14(a) and for soda-lime silica glass in Fig. 1.14(b).
Fig. 1.14: Temperature dependence of dielectric constant for (a) alumina ceramics and (b) soda-lime-silica glass

Dielectric loss: If a dielectric is subjected to an electric field, the electrical energy is absorbed by the dielectric and certain quantity of electrical energy is dissipated in the form of heat energy. This is known as dielectric loss. The dielectric loss can occur both in direct and alternating voltages. The dielectric loss is less in direct voltage than that of alternating voltages.

Loss in Purified Gas: If an alternating voltage is applied across the capacitor having vacuum (or) purified gas, the resulting current leads the applied voltage by 90°, as shown in Fig. 1.15 (a). If ‘I’ leads ‘V’ exactly by 90°, there is no electrical energy is lost.

Power loss \( P_L = VI\cos\theta \); Then \( \theta = 90^\circ \); \( P_L = 0 \)
Fig.1.15: (a) charging an ideal dielectric with no energy loss  
(b) Charging an real dielectric with energy loss

**Loss in commercial dielectric:** Now, when a practical dielectric is present the current leads by (90-δ); then it shows that there is some loss in electric energy and δ is called loss angle, as shown in Fig.1.15 (b).

In this case, the power loss \( L = VI \cos \theta \)

Since \( \theta = (90-\delta) \) we have \( P_L = VI \cos (90-\delta) \)

\[ P_L = VI \sin \delta, \quad \text{But} \quad V = IR \quad \text{(or)} \quad I = \frac{V}{R} \]

If the capacitive reactance is \( X_C \), then \( I = \frac{V}{X_C} \)

Naturally, the power loss varies with frequency.

In the radio frequency region, the power loss is high, due to the diffusion of ions from one equilibrium position to another. In the optical region the power loss is less because here the dielectric loss is associated with the electrons. The current-voltage relation for the charging and discharging a dielectric can be explained using a 'phasor' diagram. In an ideal dielectric, the current leads the voltage by 90° as shown in Fig1.15(a). The phasor digram is an instantaneous
snapshot of the voltage and current vectors as they rotate in an anticlockwise sense with angular frequency $\omega$ of the applied, electric field maintaining a constant phase difference of 90°. However in real dielectrics, there will be a power loss due to the relaxation time associated with the different polarizations. Hence the current leads the voltage by $(90-\delta)$ where $\delta$ is known as ‘loss angle’ and $\tan \delta$ is taken as the measure of the electrical energy loss due to resonance effect and is known as ‘loss tangent’ or loss factor and is represented in Fig. 1.15(b). The dielectric field and flux density in complex notation can be represented as

$$E = E_0 \exp(i\omega t)$$

\[
\frac{k''}{k'} = \tan \delta = \frac{e''}{e'}
\]

Where $k'$ and $k''$ are the real and imaginary parts of dielectric constant and $e'$ and $e''$ are the real and imaginary parts of the relative permittivity.

The basic distinction between a semiconductor and a dielectric (or insulator) lies in the difference in the energy band gap. At the normal range of temperatures and pressures, the dominant charge carriers in a semiconductor are generated mainly by thermal excitation in the bulk because the semiconductor has a small energy band gap; hence, a small amount of energy is sufficient to excite electrons from fully occupied valence band to an upper empty conduction band. In a dielectric, charge carriers are mainly injected from the electrical contacts or other external sources simply because a dielectric's energy band gap is relatively large, so a higher amount of energy is required for such band-to band transitions. A material consists mainly of atoms or molecules, which comprise electrons and nuclei. The electrons in the outermost shell of atoms, bound to the atoms or molecules coupled with the free charges interact with external forces, such as electric fields, magnetic fields, electromagnetic waves, mechanical stress, or temperature, resulting in the occurrence of all dielectric phenomena. For nonmagnetic dielectric materials, the dielectric phenomena include mainly electric polarization; resonance; relaxation; energy storage; energy dissipation; thermal, mechanical, and optical effects and their interrelations; and electrical aging and destructive breakdown [76,77].
Dielectric Ceramics

A material with high electrical resistivity is categorized as an insulator material. When we pay attention to their dielectric polarization and apply the materials to the electronic circuits, we usually call them "dielectrics". Dielectric ceramics are essential electrical materials for today's advanced electronic devices. Production quantity of the dielectric ceramic is the largest among the other electronic ceramics such as magnetic, semiconductors, insulators, resistors and piezoelectric and electro-optic materials. Main applications are for ceramic capacitors and microwave resonators. The dielectric ceramics is classified into two groups based on their dielectric properties.

CLASSIFICATION OF THE DIELECTRIC CERAMICS

High- Q materials

The dielectrics of this group are called "temperature compensating dielectrics", because they can compensate the temperature dependence of other components. Dielectric constant changes linearly with temperature. Ceramic capacitors with these materials stabilize the resonant circuits in which a high quality factor (Q value) and a resonant frequency are extremely important. In some cases, the ceramics are also called "linear dielectrics", because the polarization changes linearly with an applied electric field. Dielectric constant of this group ranges from about 4 to 400. The temperature coefficient ranges from 4120 to 4700 ppm / °C. Q value (defined as a reciprocal number of a dissipation factor tan δ) is in the range from $10^3$ to $10^5$. These characteristic values are intrinsically given by the compositions, and are modified with kinds and contents of the composed elements. Titanate-based materials are dominant compositions, which sinter at normally higher than 1100 °C. Some of the high Q materials for microwave application need very high soaking temperature (>1400 °C). Today, on the other hand, glass ceramics are widely used for ceramic multilayer substrate with Ag and Cu as an inner conductor. About 40-50% of glass elements such as $\text{Al}_2\text{O}_3$, $\text{SiO}$, $\text{MgO}$ and
alkali-earth elements compose the dielectrics, which can sinter at relatively lower temperature (<900 °C).

**High- $\varepsilon_r$ Materials**

Barium titanate (BaTiO$_3$) is the main dielectric material in this category, which provides the dielectric constant $\varepsilon_r$ higher than 1000. Many BaTiO$_3$-based dielectrics are developed to have the composition with the other titanate such as SrTiO$_3$, CaTiO$_3$, BaTiO$_3$ and zirconate such as BaZrO$_3$, CaZrO$_3$. Wide variety of the dielectric properties has been developed to perform the high volumetric efficiency. With increasing the dielectric constant at room temperature, the capacitance change increases at rated temperature range. Stabilizing the high dielectric constant at wider temperature range has been the principal work for the capacitor engineers. Lead-based relaxor dielectrics have been also developed, which have much higher $\varepsilon_r$ of 30000 at room temperature, and provide better temperature and bias voltage performances than BaTiO$_3$-based dielectrics. The representative composition is Pb (Mg$_{1/3}$Nb$_{2/3}$) O$_3$ - PbTiO$_3$, which is used for ceramic capacitors providing high volumetric efficiency. With the advent of advanced electronic devices such as handy phone and personal computer, the demand for surface mountable chip components continues to increase. Under this circumstance, the principal developments in ceramic capacitor industry are miniaturization, improvement of volumetric efficiency, cost reduction, improvement in reliability and the design of new products with high performance.

The present use of electro ceramic components requires increasing control of the materials to get a better mastery of the final properties, which are becoming more and more critical for practical applications. In the last few decades, a big effort has been made to "tailor" the microstructures of different components to answer the needs of different applications, improving the performance and the reliability of the final products. From this perspective, therefore, the main endeavor has been directed toward the control of both the chemical parameters (composition,
stoichiometry, homogeneity, purity, etc.) and the physical properties (particle size
distribution, morphology, formation of aggregates, etc.) of the powders on which
the final performance depends. Moreover, a wide field of research is represented by
the study of the addition of different chemical species to traditional compounds with
the aim of modifying the conventional properties according to the new requirements
of the market. In any case, the results of the current research point out the
importance of precursor preparation: to have a reliable product, it is necessary to
have high quality ceramic powders available.

The conventional synthesis for multicomponent ceramics is the solid
state reaction between oxide and/or carbonate powder precursors. High
temperatures are required because the reaction rate is often controlled by the slow
solid-state diffusion. For barium titanate (BaTiO₃), mixtures of TiO₂ and BaCO₃
have to be fired at temperatures between 950 and 1250 °C. Disadvantages of the
solid-state route are the large particle size, which is due to the high firing
temperature, and the poor chemical homogeneity. Often, small quantities of
undesirable secondary phases can form; for example, Ba₂TiO₄ forms during
synthesis of BaTiO₃. To overcome these limitations, repeated cycles of calcination
and milling are carried out. However, prolonged milling introduces substantial
amounts of impurities. Poor chemical homogeneity and impurities affect
microstructure evolution during the sintering stage (variable grain size and porosity,
exaggerated grain growth, presence of secondary or glassy phases at grain
boundaries and triple points) that, in turn, determine the final properties of the
ceramic. Thus, chemical routes are attracting much attention because they have the
potential to achieve improved chemical homogeneity on the molecular scale. This
is, in particular, important for electro ceramic materials, whose properties are often
determined by small addition of dopants. Furthermore, many chemical routes are
attractive because they allow the production of sub micrometer or nanometer
powders that can be sintered at lower temperatures in comparison to traditional
preparations, resulting in dense fine-grained ceramics. A present challenge for
chemical routes is the production of fully dense BaTiO$_3$ with a homogeneous grain size of $\approx 0.5$ $\mu$m for application in multilayer capacitors. Dielectrics are used not only in monolithic form, but also as coatings and thin films. Conventional synthesis of ceramics yields powders, and these are not particularly suitable for realization of coatings and films. Chemical routes have been developed for direct formation of dielectric thin films and coatings.

An overview of the scientific literature of the last 20 years clearly indicates that the synthesis of dielectric ceramic powders is recognized as the critical step in the preparation of those materials that have to fulfill the technological requirements of a developing market. As a consequence, the interest in powder and film preparation has been continuously increasing. The many different methods designed for powder and film preparation are rather difficult to classify. However, Riman [78] proposed a possible classification on the basis of the mutual interactions of the different reacting phases from which four different categories of reactions can be distinguished:

- Reactions among different liquid phases. This method can be defined as "homogeneous co precipitation." The morphology of the powders depends on nucleation, growth, and aging processes that occur in the solutions.
- Reactions among heterophases, where at least one solid phase is present. This class comprises hydrothermal, pyrolytic, self-propagating high-temperature synthesis (SHS), and traditional solid-state processes.
- "Droplet reactions, for which the volume of the reactants corresponds to one drop of the liquid solvent inside a liquid (emulsion) or vapor phase (aerosol).
- Reactions taking place in a vapor phase. In this case, the powder characteristics are determined by precipitation in the vapor phase.

Among the different types of electro ceramics, a particular interest is toward the so called dielectric materials, which can be defined as those systems with high electrical resistivity. Two main factors, permittivity ($\varepsilon$) and dissipation (tan $\delta$), have
to be considered to state the performance during practical applications. Based on
different domains of application, other parameters related to these factors are
currently used: loss factor ($\varepsilon'' = \varepsilon \tan \delta$) and quality factor ($Q = 1 / \tan \delta$).

**Classification of dielectrics based on permittivity**

The relative permittivity (dielectric constant) of dielectric materials
varies over a wide range from 6 to 20,000. The dielectrics are classified into three
categories depending on their relative permittivity as (i) low permittivity dielectrics,
(ii) medium permittivity dielectrics and (iii) high permittivity dielectrics.

- Low permittivity ($\varepsilon$ up to 15)
- Medium permittivity ($\varepsilon$ between 15 and 500)
- High permittivity ($\varepsilon$ between 500 and 20,000)

Low- and medium-permittivity dielectrics are called Class I dielectrics, whereas
high permittivity materials are called Class II dielectrics. A third class (Class III)
comprises a conductive phase that can be very useful, because it reduces the
thickness of the dielectric in capacitors. Syntheses have been developed especially
for the high-permittivity materials for which a variety of innovative methods have
been proposed.

**1.7.1 Low-permittivity ceramic dielectrics**

Low dielectric constant material can store less amount of charge. The
low permittivity dielectrics have permittivity less than 15 with dissipation factor
less than 0.003. These dielectrics are used for electrical insulation in power
transmission and hence dielectric breakdown voltage is another important electrical
parameters. The mechanical properties are more important than dielectric
properties. Since the Table requirement of such insulators are in tonnage quantities,
they are made from low cost naturally occurring materials. These insulators are
manufactured from clay and alumina based raw materials. The typical properties of
some low permittivity dielectrics are given in Table 1.2.
### Table 1.2: Electrical properties of low permittivity dielectrics

<table>
<thead>
<tr>
<th>Material</th>
<th>Dielectric constant</th>
<th>$\tan \delta$ (x $10^{-3}$)</th>
<th>Dielectric Strength (kV.mm$^{-1}$)</th>
<th>Resistivity At 25 °C Ω.cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Porcelain ($\text{R}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$)</td>
<td>$5.0 - 6.5$</td>
<td>$0.8 - 2.0$</td>
<td>$6.1 - 13$</td>
<td>$10^{14}$</td>
</tr>
<tr>
<td>Steatite</td>
<td>$6.1$</td>
<td>$0.8 - 3.5$</td>
<td>$7.8 - 13.8$</td>
<td>$10^{17}$</td>
</tr>
<tr>
<td>Cordierite</td>
<td>$4.1 - 5.3$</td>
<td>$0.3 - 0.5$</td>
<td>$5.5 - 9.1$</td>
<td>$10^{16}$</td>
</tr>
<tr>
<td>Forsterite</td>
<td>$5.8 - 6.7$</td>
<td>$0.5 - 1.0$</td>
<td>$7.9 - 11.9$</td>
<td>$10^{17}$</td>
</tr>
<tr>
<td>Zircon</td>
<td>$8.0 - 9.6$</td>
<td>$1.0$</td>
<td>$6.3 - 11.5$</td>
<td>$&gt;10^{14}$</td>
</tr>
<tr>
<td>Alumina</td>
<td>$8.8 - 10.1$</td>
<td>$0.3 - 2.0$</td>
<td>$9.9 - 15.8$</td>
<td>$10^{16}$</td>
</tr>
<tr>
<td>MgO</td>
<td>$9.7$</td>
<td>$1.0$</td>
<td>$8.5 - 11.0$</td>
<td>$&gt;10^{14}$</td>
</tr>
<tr>
<td>BeO</td>
<td>$6.0$</td>
<td>$0.1 - 1.0$</td>
<td>$9.5 - 13.8$</td>
<td>$&gt;10^{16}$</td>
</tr>
<tr>
<td>ZrO$_2$</td>
<td>$12.0$</td>
<td>$1.0$</td>
<td>$15.8 - 19.8$</td>
<td>$10^{9}$</td>
</tr>
<tr>
<td>Mullite</td>
<td>$6.2 - 6.8$</td>
<td>$0.5$</td>
<td>$7.8$</td>
<td>$10^{14}$</td>
</tr>
<tr>
<td>Spinel</td>
<td>$7.5$</td>
<td>$0.4$</td>
<td>$11.9$</td>
<td>$10^{14}$</td>
</tr>
<tr>
<td>AlN</td>
<td>$8.8 - 8.9$</td>
<td>$1.0$</td>
<td>$15.0$</td>
<td>$10^{13}$</td>
</tr>
<tr>
<td>Si$_3$N$_4$</td>
<td>$6.1$</td>
<td>$0.1$</td>
<td>$15.8 - 19.8$</td>
<td>$&gt;10^{13}$</td>
</tr>
<tr>
<td>Fused silica glass</td>
<td>$3.8 - 5.8$</td>
<td>$0.3$</td>
<td>$15.0 - 30.0$</td>
<td>$&gt;10^{14}$</td>
</tr>
<tr>
<td>Vycor glass</td>
<td>$5.5 - 6.3$</td>
<td>$0.1 - 1.3$</td>
<td>$9.9 - 11.9$</td>
<td>$10^{12}$</td>
</tr>
<tr>
<td>Soda-lime-silica glass</td>
<td>$4.0 - 8.0$</td>
<td>$0.5 - 10.0$</td>
<td>$7.8 - 13.2$</td>
<td>$10^{12}$</td>
</tr>
</tbody>
</table>
The effect of temperature and frequency on the permittivity and dissipation factor of high purity alumina ceramics is the increase of temperature, the permittivity and the loss factor increase strongly at low frequency range of the applied field when compared to high frequency range. As the temperature is increased, the defects and charge carriers become more responsive to the applied field leading to an increase in permittivity and loss factor. However, the inertia prevents from responding effectively at higher frequency range and temperature. The intergranular phase present in alumina ceramics has significant effect on both permittivity and loss factor.

Needs of low dielectric constant materials

- Lower propagation delay
- Lower power dissipation
- Lower crosstalk

Uses of low dielectric constant materials

Low-permittivity dielectrics can be used in advanced semiconductor factories for multi-level interconnects, for interlayer Dielectrics (ILDs) for passivation layer.

Advantages of low dielectric material:

Low dielectric constant materials have the advantage of facilitating manufacture of higher performance integrated-circuit (IC) devices with minimal increase in chip size. The reduced capacitance of these materials permits shrinkage of spacing between metal lines to below 0.25 μm and the ability to decrease the number of levels of metal in a device.

Low dielectric constant materials;

- Nano porous silica
- Hydrogensilsesquioxanes (HSQ)
Teflon-AF (Polytetrafluoroethylene or PTFE)
Silicon oxy fluoride (FSG)

Natural mineral compounds, in particular some kinds of silicates and alumina, are used for low-permittivity ceramic dielectrics. Therefore, a true chemical synthesis is not strictly needed but only a more or less high degree of purification is required. However, in the case of alumina, different synthesis routes have been designed to obtain powders with tailored particle size and controlled chemical purity.

The need to decrease the delay time (dependent upon the resistance–capacitance product, RC) along interconnections has led not only to the use of lower resistivity interconnection material (copper) but also to a search for low dielectric constant materials suitable for interlevel and interline dielectric insulation in multilevel integration. The latter direction is necessary because the line-to-line capacitance increases with the decrease in the feature size. The standard material that has been used until recently is SiO₂ with a dielectric constant in the range between 3.8 and 4.2. Polymeric thin films have lower dielectric constants ranging from 1.8 to 3.0. Still lower dielectric constants may be obtained with porous materials. These data provide the hint of one possible effect of structure on the dielectric constant. Covalently bonded material is composed of polarizable species and space not containing electrons. Porous material obviously contains electron-free space, which has unity dielectric constant. Further, as the number of atoms in unit volume of a homogeneous covalently bonded material increases the dielectric constant will also increase as one may deduce from the Lorenz–Lorentz equation.

1.7.2 Medium-permittivity ceramic dielectrics

Medium permittivity dielectrics cover the dielectric constant from 15 to 500. The rutile phase of TiO₂ exhibits anisotropic behaviour in permittivity at room temperature. The permittivity of single crystal TiO₂ is approximately 170 along the
c-axis and about 90 along the axis. The polycrystalline ceramics have the permittivity around 80-90. The permittivity and loss tangent as a function of temperature for different frequencies are shown in Fig. 5.32. The non-stoichiometric character in composition of titania TiO$_{2-δ}$ is exploited for gas sensing applications.

Table 1.3. gives some of the medium permittivity dielectrics with their dielectric properties and applications. Major applications of medium-permittivity ceramic materials are represented by low loss stable capacitors and microwave resonators. Titanium dioxide is probably the most common compound for this class, and particularly is used for capacitors. For other purposes, complex oxides most currently within the families of titanates or zirconates, are used with compositions corresponding to Ba$_2$Ti$_9$O$_{20}$, BaTi$_4$O$_9$, Zr$_5$Ti$_3$Sn$_2$O$_{14}$ (ZTS) and (Ba,Pb)Nd$_2$Ti$_5$O$_{14}$. It is also possible to recall a partially Zn substituted barium tantalate (Ba (Zn$_{2/3}$Ta$_{2/3}$) O$_3$), which seems to be an appealing material.

1.7.3 High-permittivity ceramic dielectrics

The dielectrics having permittivity (dielectric constant) above 1000 are based on ferroelectric materials. The permittivity of such material is very sensitive to temperature, frequency and field strength. These dielectrics are primarily used as high permittivity capacitors, pyroelectric sensors. Piezoelectric/electrostrictive transducers, electro-optic devices and PTC thermistors.

Lead Niobates and Other Compounds

Based on perovskite-like oxides, peculiar dielectric properties can be obtained with various ceramic materials with complex formulas. The most important class is represented by dielectric relaxors, which exhibit extremely high dielectric constants (~$10^5$) associated with a broad ferroelectric transition, called a diffuse phase transition (DPT). Lead niobates, substituted with Ba, Mg, Zn, Ni, Sc, and other cations, are the reference compounds, but relaxors based on lead
tantalates, with moderate permittivity, are widely prepared for dielectric applications in the microwave region. Solid-state powder mixing routes have been successfully applied for the preparation of a great many relaxors like (Ba_{0.5}Sr_{0.5}) (Nb_{2-x}Ta_x)O_6 [79], Pb (Zn_{0.65}Mg_{0.35})_{1/3}Nb_{2/3}O_3 [80], solid solutions in the system Pb(Zn_{x/3}Mg_{(1-x)/3})_{1/3}Nb_{2/3}O_3-PbTiO_3-(Ba,Sr)TiO_3 [81, 82], Ba(Mg_{1/3}Ta_{2/3})O_3 [83, 84], Ba(Zn_{1/3}Ta_{2/3})O_3 [85], Ba(Sn_{x}Zn_{(1-x)/3}Nb_{1-x/3}O_3 [86], PbSe_{0.5}Ta_{0.5}O_3 based compositions [87], and Ba_{4}Bi_{2}Ti_{4}Nb_{6}O_{30} [88]. Alternative chemical methods also have been used to obtain niobates and complex lead magnesium niobate, tungstate, and titanate. In particular, Kim and Matijevic [89] exploited the reaction between a peroxoniobium complex, chelated by ethylene diamine tetra acetic acid (EDTA) or nitrilotriacetic acid (NTA), with lead nitrate in acid or alkaline solutions to obtain uniform sub micrometer particles that convert to Pb_{2}Nb_{4}O_{3} or Pb_{3}Nb_{2}O_{8} after thermal treatment at moderate temperature. Aruga et al.,[90] reported preparation of 0.4Pb(Mg_{1/3}Nb_{2/3})O_3-0.3Pb(Mg_{1/2}W_{1/2})O_3-3PbTiO_3 by calcination of gels obtained from the hydrolysis of methoxy ethanolic solutions of metal alkoxides.

1.8 APPLICATIONS OF HIGH DIELECTRIC MATERIALS

- Capacitors
- Piezoelectric sensors
- Piezoelectric/ electrostrictive transducers
- Electro-optic devices and
- PTC thermistors
- Miniaturizing the electronic devices
### Table 1.3: Dielectric properties and applications of some ceramics

<table>
<thead>
<tr>
<th>Material</th>
<th>Dielectric constant</th>
<th>$\tan \delta$ (x $10^{-4}$)</th>
<th>Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$</td>
<td>80-90</td>
<td>2 - 4</td>
<td>Sensor element, microwave filter, transformer capacitors</td>
</tr>
<tr>
<td>MgTiO$_3$</td>
<td>12 - 16</td>
<td>1 - 3</td>
<td>Transformer capacitors</td>
</tr>
<tr>
<td>CaTiO$_3$</td>
<td>140</td>
<td>2.0</td>
<td>High power capacitors</td>
</tr>
<tr>
<td>PbZrO$_3$</td>
<td>110</td>
<td>28</td>
<td>High power capacitors</td>
</tr>
<tr>
<td>BaTi$_4$O$_9$</td>
<td>35 -40</td>
<td>1 – 3</td>
<td>Microwave filters, transformer capacitor</td>
</tr>
<tr>
<td>Zr$_3$Ti$_7$Sn$<em>2$O$</em>{14}$</td>
<td>35 – 40</td>
<td>1 – 3</td>
<td>Dielectric resonator</td>
</tr>
<tr>
<td>CaSiTiO$_5$</td>
<td>45</td>
<td>5.0</td>
<td>High power capacitors</td>
</tr>
</tbody>
</table>