The sequential description of various steps involved in the synthesis of low loss dielectric resonator materials and polymer composites are described in this chapter. A qualitative discussion on the structural as well as microwave characterization tools to determine the relative permittivity, quality factor (dielectric loss) and temperature coefficient of resonant frequency of ceramics is given. A brief description of the instrumentation techniques used for studying the structural, microstructural, dielectric and thermal characteristics of low loss materials and polymer composites studied in the purview of this thesis is also presented.
2.1 SYNTHESIS OF DIELECTRIC RESONATORS

2.1.1 Introduction

Innovation in technology has always resulted from improvement in materials. For ceramics to be the key to such innovation, new materials must be developed and processes established for their production. As new materials and even newer technologies are developed; methods of handling, forming and finishing are required to be devised to maintain pace with this rapid rate of development. One of the most prominent examples of this rapid and accelerating technological development is the electronics industry. The 20th century has produced the greatest advancement in ceramics and materials technology since humans have been capable of conceptive thought. As the limits of metal-based systems are surpassed, new materials capable of operating under higher temperatures, higher speeds, longer life factors and lower maintenance costs are required to maintain pace with technological advancements. Metals, by virtue of their unique properties: ductility, tensile strength, abundance, simple chemistry, relatively low cost of production, ease of forming, ease of joining, etc. have occupied the vanguard position in regard to materials development. By contrast ceramics: brittle by nature, having a more complex chemistry and requiring advanced processing technology and equipment to produce, perform best when combined with other materials, such as metals and polymers which can be used as support structures.

Ceramics for today’s engineering applications are synthesized using highly refined raw material, rigorously controlled composition, strictly regulated forming and sintering and are known as “Fine or Advanced Ceramics”. Advanced ceramics possess properties which allow their use in a variety of defense and commercial applications. In comparison with metals, these materials demonstrate superior wear resistance, high temperature strength, favorable electrical properties, chemical resistance, dimensional stability, and high strength-to-weight ratios. These properties place this new group of ceramics in a most attractive position, not only in the area of performance but also cost effectiveness. Ceramics are oxides or non-oxides of metallic and non-metallic elements which are
generally compounds of electropositive and electronegative elements of the periodic table. Ceramics are polycrystalline, and grain boundaries exist which have a large influence on the physical and chemical properties. The microstructure of the ceramics contains: fine crystalline grains, grain boundaries, impurities and crystal lattice defects in the grains and grain boundaries and pores in the grain as well as in grain boundaries.¹

Technical or Engineering ceramic production is a demanding and complex procedure. Most of the synthesis methods of organic and metallic counterparts are generally not suitable for ceramics, due to the brittleness and refractory nature of ceramic materials. Ceramic fabrication techniques generally include various powder processing methods with powder synthesis, forming and sintering. The powder synthesis processes of ceramics include several techniques² like (a) solid state reaction methods (b) mechanical methods and (c) chemical methods. High purity materials and precise methods of production must be employed to ensure that the desired properties of these advanced materials are achieved in the final product.

In the mechanical methods, small particles are produced from larger ones by mechanical forces, a process known as comminution. The process of comminution involves operations such as crushing, grinding and milling. Mechanical treatment of ceramic powders can reduce particle size and enables to obtain nano-structured powders. However, this method lacks the synthesis of phase pure ceramics, which is essential for the fabrication of dielectric ceramics with optimum dielectric properties.

2.1.2 Solid State Synthesis of Ceramics

Dielectric resonator applications require bulk artefacts of dielectric material. The most realistic method of preparing ceramic powders is by solid-state reaction methods, because it is the simplest, easier and cost effective method for producing bulk ceramics. Conventional solid state synthesis techniques involve heating mixtures of two or more solids to form a solid phase product. The conventional ceramic approach basically can be broken down into four stages³ (a) powder preparation (b) high temperature calcination (c) green body preparation and (d) sintering.
Both thermodynamic and kinetic factors are important in solid state reactions since solids react together only at higher temperatures for reaction to occur at an appreciable rate. Thermodynamic considerations show whether or not a particular reaction should occur by considering the changes in free energy that are involved; kinetic factors determine the rate at which reaction occurs. In heterogeneous reactions between two solids, the actual reaction to form the product occurs at an interface. In kinetic studies of reaction rates, there are three possibilities to know the slow, rate-controlling step in a reaction. They are (1) transport of matter to the reaction interface (b) reaction at the interface and (c) transfer of matter away from the reaction interface. Rates of reaction are controlled by three factors: i) The area of contact between reacting solids which in turn depends on the surface area ii) The rate of diffusion of ions through the various phases and especially through the product phase. Two ways to increase the rate of diffusion are: (a) increase temperature (b) introduce defects by starting with reagents that decompose prior to or during reaction, such as carbonates or nitrates iii) The rate of nucleation of the product phase which can be maximized by using reactants with crystal structures similar to that of the product. Extensive reaction will not occur until the temperature reaches at least 2/3 of the melting point of one or more of the reactants.

The solid-state reaction method, which is involved in the present work, involves the following steps. Since each of these steps affects the final ceramic properties they must all be understood, and a more holistic approach is required when processing ceramics compared to metals and polymers.

2.1.2.1 Powder Preparation

2.1.2.1.1 Select Appropriate Starting Materials

Fine grain powders to maximize surface area, reactive starting reagents and well defined compositions are the three criteria that must be taken into account while selecting appropriate starting materials. The oxides of the constituent cations are used in this method. In some instances, notably Ba, the oxide is not suitable because it is either unstable or highly hygroscopic. In such cases, the carbonate or nitrate is used, because
they will decompose to oxides on heating and are more reactive. The impurities are detrimental to dielectric properties and they affect reactivity of the fired ceramics too.\textsuperscript{3} Hence raw material purity of greater than 99.9\% is essential for obtaining phase pure compounds.

2.1.2.1.2 Weighing of Raw Materials

The most common route is the mixed oxide route, where oxides of the constituent cations which act as reactants are weighed in stoichiometric proportions. Electronic balance of accuracy up to four decimal places is used for weighing raw materials.

2.1.2.1.3 Stoichiometric Mixing

After the dry powders have been weighed out in their stoichiometric proportion, they must be intimately mixed to increase the point of contacts between reactant oxides, which act as “product layer formation centers”. The mixing and milling eliminates agglomeration and reduces particle size. If agglomerates are present they densify more rapidly resulting in pores. During the mixing process agglomerates are broken and defects are introduced into the grains that enhance diffusion mechanism. Therefore the mixture of powders is ground well and thoroughly mixed using distilled water or acetone. Generally ball mills and vibromills (or attrition mills) are the most widely used milling tools for advanced ceramics.

(a) Ball Milling

Ball Milling is a method of grinding and mixing material, with or without liquid, in a rotating cylinder or conical mill partially filled with grinding media such as balls. In ball mills, in which tumbling action is accompanied by size reduction of particles, shear is the predominant mechanism (see Fig. 2.1(a)).\textsuperscript{6} The mechanical stress leads to elastic and inelastic deformation. If the stresses exceed ultimate strength of the particle, it will not only fracture the particles but also produce other physical changes in the particle.\textsuperscript{7} Other factors that affect mixing of particles in a ball mill are the mill speed,\textsuperscript{8,9} grinding media to material density ratio,\textsuperscript{10} and charge fill level, a fraction of mill's total volume
occupied by the charge. Most mixing experiments have been carried out at low speeds with particles of either the same size or different size but same density. The rate of grinding (η) depends upon the radii of the mill bottle and density of the milling media and initial particle size of the powder.

$$\eta \approx \frac{AR^{1/2} \rho d}{r}$$  \hspace{1cm} (2.1)

where A is the numerical constant that is specific to the mill being used, R and r are the radius of the mill and balls respectively, ρ the density of the balls and d particle size of the powder.

The type of mixer used can affect particle mixing and each mixer is characterized by the predominant mixing mechanism. The mechanisms of particle mixing are diffusion, shear and convection. The grinding of solid matters occurs under exposure of mechanical forces that trench the structure by overcoming of the interior bonding forces. After grinding, the state of the solid is changed: the grain size, the grain size disposition and the grain shape. The ball mill must operate below the critical angular frequency ($F_C$), at which centrifuging of media takes place and all milling effectively stops. The suspension is very viscous slurry, which effectively decreases $F_C$ and ball milling normally operate at 0.7-0.8$F_C$.

For wet milling, the balls and slurry together should occupy 50% of the mill volume with the solid content of the slurry equal to 20-40%. For dry milling,
quantity of balls filling about 50 % of the mill volume, the permissible charge content is 25%. As the shape of the milling media (ball) determines the product size distribution, cylindrical balls with dome ends are used to ensure uniform size distribution with narrow distribution curves. Fig. 2.1(b) and (c) shows the optimum ball-to-powder ratio and optimum speed in ideal milling conditions. In the present investigation, the mixture of constituent powders taken in polythethylene bottles were ball milled for sufficient duration in distilled water medium using Yttria Stabilized Zirconia (YSZ) balls (10 mm diameter and 12 mm height cylindrical balls).

2.1.2.2 Calcination

Calcination is the intermediate heat treatment of a substance below the melting or fusing point to bring about thermal decomposition or a phase transition in its physical or chemical constitution. The modifications achieved by calcination are: coarsening, decomposition, reaction and dehydration. Coarsening involves crystallite growth or fusing or bonding small particles together to produce larger particles. Decomposition involves converting compositions such as carbonates and nitrates to a solid oxide and a gas.

The kinetics of solid state reactions occurring during calcination may be controlled by (i) the reaction at the interface between the reactant and the solid product, (ii) heat transfer to the reaction surface (iii) gas diffusion or permeation from the reaction surface through the porous product layer. The calcination conditions such as temperature, duration of heating and atmosphere are important factors controlling shrinkage during sintering. Though the final phases of interest may not be completely formed, the calcination yields a consistent product.

2.1.2.3 Green Body Preparation

2.1.2.3.1 Grinding

All dry powders have a tendency to agglomerate and there is a range of agglomerates in a ceramic mix. Grinding prepares the reacted material for ceramic forming. The calcined powder is ground to reduce the particle size, reduce agglomerates and mix the powder. The grinding also helps to homogenise the compositional variations
that still exist or may arise due to calcination. Generally after grinding, the powder size around 1-10 μm is advisable. If the grind is coarser, the ceramic may have large intergranular voids and low fired density. If grinding is too fine, the colloidal particles may interfere with subsequent forming operations. Generally, a ball mill or mortar with pestle is used. In large-scale operation, a grinding medium is chosen that suffers very little wear.

2.1.2.3.2 Addition of Polymeric Binder

Binders are particles, which form bridges between flocculated ceramic grains. The binder allows the powder particles to slide past each other to rearrange in the closest possible packing by forming temporary bonds. Binders have strong influence on the properties of granules, such as bulk density, flow rate and compaction behaviour. A good binder for ceramic applications should provide high green strength and appropriate elastic properties for handling and shaping during the post forming stage. Green strength is provided by polymer-polymer and polymer-ceramic powder interactions. The two most popular binders for dry pressed ceramics are polyvinyl alcohol (PVA) and polyethylene glycol (PEG). The research trends suggest that 3-4 wt % of PVA and PEG which are water thinnable polymeric dispersions are ideal binders for fabrication of microwave dielectric ceramics. PVA binders generally provide high green strength while PEG binders provide high green density. PVA at low level of usage of the binder will not affect the dielectric properties as it will burn out at low temperatures (~400°C).

2.1.2.3.3 Powder Compaction

Powder pressing, an important stage in the ceramic processing, either uniaxially or isostatically is the most common method used for high volume production of ceramic components. The aim of powder pressing is to form a net-shaped, homogeneously dense powder compact that is nominally free of defects. A typical pressing operation has three basic steps: (i) filling the mold or die with powder (ii) compacting the powder to a specific size and shape and (iii) ejecting the compact from the die.
filling/uniformity influences compaction density, which ultimately determines the size, shape, microstructure and properties of the final sintered product. To optimize die filling and packing uniformity, free-flowing granulated powders are generally used. During powder pressing, the compaction pressure promotes consolidation by granule rearrangement and granule deformation. Particle coordination number, green density and compact strength all increase with increasing pressure, while volume and size of the porosity in the compact decrease. Friction between the powder and die wall decreases the pressure available for compaction with increasing distance from the pressing punch which in turn increases the density gradient in the compact. Friction is influenced by the die material and its surface finish, as well as the powder and organic additives. Die-wall friction effects can be minimized with smooth surface dies and carbide tooling. Internal lubricants such as Stearic acid dissolved in Propan-2-ole, can aid processing. In the present study shaping is done using uniaxial press (Carver Inc., Wabash, U.S.)

Uniaxial pressing involves the compaction of powder into a rigid die by applying pressure in a single axial direction through a rigid punch or piston. The presses are usually mechanical or hydraulic. The pressure gradient in powder compact as a function of the distance from upper punch is given by the formula

\[ P_z = P_a \exp \left[ -4 \mu K \frac{L}{D} \right] \]  

where \( \mu \) is the coefficient of friction, \( P_a \) is the applied pressure, \( L \) is the length and \( D \) is the diameter of the powder compact. When the length to diameter ratio is smaller, the pressure distribution of a powder compact is more uniform. In the microwave dielectric measurements, \( D/L \) ratio \( \approx 2 \) and hence pressure distribution is more or less uniform. A pressure of 50-150 MPa is ideal in ceramic forming.

2.1.2.4 Sintering

Sintering is the process of heating a powder compact (40-60% of theoretical density) to a temperature between \( \frac{1}{2} \) to \( \frac{1}{4} \) of the absolute melting point by which particles are formed into a coherent body, to achieve higher strength and density. The criteria that
should be met before sintering can occur are (1) A mechanism for material transport must be present (2) A source of energy to activate and sustain this material transport must be present. The primary mechanism for transport is diffusion and viscous flow. Heat is the primary source of energy, in conjunction with energy gradients due to particle-particle contact and surface tension. The driving force for sintering is a decrease in the surface free energy of powdered compacts by the elimination of solid-vapor interfaces. Sintering is the bonding together of particles when heated to higher temperatures. On a microstructural scale, this bonding occurs as cohesive necks (weld bonds) grow at the points of contact between particles. During sintering, neck growth by the movement of mass to the neck is desirable because it reduces the surface energy by decreasing the total surface area. This can happen by (i) reduction of the total surface area by an increase in the average size of the particles, which leads to coarsening and (ii) the elimination of solid/vapor interfaces and the creation of grain boundary area, followed by grain growth, which leads to densification.

Sintering can occur in the presence or absence of a liquid phase. In solid state sintering, densification is achieved through changes in particle shape, without particle rearrangement or the presence of the liquid. In liquid phase sintering the compositions and firing temperatures are chosen such that some liquid is formed during processing which aids compaction.

2.1.2.4.1 Solid State Sintering

Solid state sintering is the process in which fine particles, which are in contact with each other, agglomerate when heated to a suitable temperature, which results in the decrease in porosity. The development of microstructure and densification during sintering is a direct consequence of mass transport through several possible paths and this bulk transport occurs by evaporation-condensation, surface diffusion, volume diffusion, grain boundary diffusion and viscous or creep flow.

The purpose of sintering is the reduction of compact porosity. Coble described sintering stage as an "interval of geometric change in which pore shape is totally defined..."
or an interval of time during which the pore remains constant in shape while decreasing in size.” Three stages of sintering are an initial, an intermediate and a final stage (shown in Fig. 2.2(a)-(d)). During the initial stage, the interparticle contact area increases by neck growth (see Fig. 2.2(e)) and relative density increases from about 60 to 65 percent. Fig. 2.2(f) shows the SEM micrograph of neck formation in sintered alumina. The intermediate stage is characterized by continuous pore channels that are coincident with three-grain edges. During this stage the relative density increases from 65 to 90 percent by having matter diffuse toward, and vacancies away from the long cylindrical channels. The final stage begins when the pore phase is eventually pinched off and is characterized by the absence of a continuous pore channel. Individual pores are either of lenticular shape, if they reside on the grain boundaries, or rounded, if they reside within a grain. An important characteristic of this stage is the increase in pores and grain boundary mobilities, which have to be controlled if the theoretical density is to be achieved.\textsuperscript{34} Solid state sintering involves movement of atoms that in turn is dependent on temperature and concentration of structural imperfections such as vacancies and interstitials. The process variables in sintering are (a) sintering temperature (b) sintering time (c) sintering atmosphere. The factors affecting solid state sintering are (a) particle size and particle size distribution (b) particle shape (c) uniformity of green microstructure (d) particle composition and (e) green density.\textsuperscript{34}

![Fig. 2.2 (a) & (b) Initial stage, (c) Intermediate stage and (d) Final stage of sintering (e) Neck formation during first stage and (f) SEM picture of neck formation in sintered alumina (After Ref. 37)](image_url)
2.1.2.4.2 Liquid Phase Sintering (LPS)

Liquid Phase Sintering is a subclass of the sintering process involving particulate solid along with a coexisting liquid during some part of the thermal cycle. Two major advantages of LPS over solid state sintering are it is more rapid and results in uniform densification. The disadvantages of LPS are that ceramics densified by LPS has a susceptibility to shape deformation and it may be difficult to control the sintering parameters due to additional complications from the liquid phase. The presence of a liquid phase greatly enhances grain boundary diffusion and grain boundary sliding. When solids and liquids are present together, capillary forces that result from the surface tension are generated. These forces can give rise to strong attractive forces between neighbouring particles, which when combined with the lubricating potential of the liquid, can lead to very rapid and significant particle rearrangement and densification. Upon melting, a wetting liquid will penetrate between grains and exert an attractive force, pulling them together. The combination of these forces and the lubricating effect of the liquid as it penetrate between grains leads to the following mechanisms that operate in succession: 36,37

a) Particle rearrangement

Initial densification results from particle rearrangement under the influence of capillary forces and the filling of pores by the liquid phase. The driving force for rearrangement arises because of an imbalance in capillary pressure as a result of particle size distribution, irregular particle shape, local density fluctuation in the powder compact and anisotropic material properties. Both solid and liquid are subject to rearrangement because of unbalanced capillary forces around solid particles as dictated by particle contact and liquid meniscus geometries that result in shearing and rotational movements of particles. As density increases, particles experience increasing resistance to further rearrangement due to crowding by neighbouring particles until the formation of a closed packing structure. Particle rearrangement is very rapid, and if during the early stages of
sintering, the liquid flows and completely fills the finer pores between the particles, 100 percent densification can result almost instantaneously.

b) Solution reprecipitation

In solution reprecipitation different solubilities of the solid in the liquid are responsible for the transport of the material from the points of solid-solid contacts to the free surfaces of the particles. When rearrangement becomes insignificant, additional densification can be achieved by dissolution of the solid at grain contacts thus resulting in the center-to-center approach of particles. The dissolved solute transfers to the uncompressed part of the grain structure by diffusion through a liquid phase followed by reprecipitation on uncompressed solid surface for a multicomponent system. There are two rate-limiting processes for solution-precipitation - diffusion controlled and interface reaction controlled material transport. The densification rate for diffusion controlled (equation (2.3)) and interface reaction controlled (equation (2.4)) material transport are

\[ \frac{d(\Delta \rho / \rho_s)}{dt} = B(g) \frac{\delta D_B C_1 \gamma_s \Omega}{kT} r^{-4} \]  
(2.3)

\[ \frac{d(\Delta \rho / \rho_s)}{dt} = C(g) \frac{K C_1 \gamma_s \Omega}{kT} r^{-4} \]  
(2.4)

where \( B(g) \) and \( C(g) \) are the geometrical constants, \( \delta \) is the thickness of the liquid boundary, \( \Omega \) is the molar volume of the solute, \( k \) is the Boltzmann constant, \( T \) is the absolute temperature, \( D \) is the grain boundary diffusion constant of the solute, \( K \) is the interface reaction constant and \( r \) is the initial particle size.

c) Solid state sintering

Once a rigid skeleton is formed, liquid phase sintering stops and solid state sintering takes over, and the overall shrinkage or densification rates are significantly reduced. Unless the liquid phase penetrates completely between solid particles, the presence of the liquid is not effective as an aid to sintering.

Based on the above discussion, for rapid densification to occur during LPS, the conditions that have to be met are (i) the composition is so chosen that the material which forms the solid phase during sintering is soluble in the liquid phase (ii) the sintering
temperature must be high enough so that an appreciable amount of liquid phase is present (iii) there must be good wetting of a liquid on solid. Clearly, LPS of ceramics is more forgiving in terms of powder packing, more rapid, and hence more economical than the solid-state version. The presence of a glassy film at the grain boundaries can have a very detrimental effect on properties. If the properties required are not adversely affected by the presence of a liquid, then LPS is the preferred route.

2.2 SYNTHESIS OF POLYMER-CERAMIC COMPOSITES

2.2.1 Powder Processing Method

In the present study, PTFE/ceramic composites were prepared by powder processing technology. In order to create an active surface for binding with polymer, the fine powder of ceramic was mixed with acrylic acid solution for 1 hour and then dried. The dried powder was again treated with 2 wt% tetra butyl titanate. The use of titanate based coupling agents provides excellent mechanical and electrical properties compared to other organic functional coupling agents like silane. The evaporation of the solvent gives ceramic powders cladded with coupling agents. Different volume fractions (0 to 0.6) of treated ceramics and PTFE powders were dispersed in ethyl alcohol using ultrasonic mixer for about 30 minutes. A dry powder mixture was obtained by removing the solvent at 70°C under stirring. This led to the formation of thoroughly mixed PTFE/ceramic powders. These homogeneously mixed composite powders were then compacted under uniaxial pressure of 50 MPa for 1 minute. The cylindrical and rectangular pellets thus obtained were kept at 310°C for 2hrs.

2.2.2 Sigma Blend Method

The starting materials, polyethylene and ceramic were mixed thoroughly in a kneading machine. The kneading machine consists of variable speed mixer having two counter rotating sigma blades with a gear ratio of 1:1.2 and heating facility up to 350°C (Fig. 2.3). The counter rotating sigma blades ensure fine mixing by applying high shear force on the dough-like mixture. Different volume fractions ceramics were added to the
melted polyethylene and blended at suitable temperature for 30 minutes. Thus obtained composites were thermo laminated under a pressure of 200 MPa and optimized temperature for 15 min. After thermolamination, the composites with desired shapes were polished for dielectric measurements. In the present investigation, HDPE/CeO₂ composites were prepared by sigma blend method.

2.3 STRUCTURAL AND MICROSTRUCTURAL CHARACTERIZATION OF DIELECTRIC RESONATORS

2.3.1 X-Ray Diffraction

The X-Ray diffraction method is most useful for qualitative, rather than quantitative, analysis (although it can be used for both). Qualitative analysis usually involves the identification of a phase or phases in a specimen by comparison with "standard" patterns (i.e., data collected or calculated by someone else), and relative estimation of proportions of different phases in multiphase specimens by comparing peak intensities attributed to the identified phases. Quantitative analysis of diffraction data usually refers to the determination of amounts of different phases in multi-phase samples and also the precise determination of crystal structure or crystallite size and shape.

An X-Ray diffractometer utilizes a powdered sample, an X-ray generator, a goniometer and a fixed-position detector to measure the diffraction patterns of unknowns. When Monochromatic x-rays strikes a powder sample mounted on a slide, diffraction occurs in every possible orientation of 2θ. Mount is then rotated to ensure all diffractions are obtained. The diffracted beam may be detected by electronic x-ray counters (detectors) that can measure intensities much more accurately. Computers are used to process data and make necessary complex calculations. The resulting analysis is described graphically as a set of peaks with percentage intensity on the Y-axis and goniometer angle on the X-axis. The exact angle and intensity of a set of peaks is unique to the crystal structure being examined. A monochromator is used to ensure that a specific wavelength reaches the detector, eliminating fluorescent radiation. The resulting trace consists of a recording of the intensity against counter angle (2θ). The trace can
then be used to identify the phases present in the sample. Then use the Bragg equation to solve for the interplanar spacings (d) for all the major peaks and look up a match with JCPDS cards. (JCPDS = Joint Committee on Powder Diffraction Standards) Routinely, a 2θ range of 5 to 70 degrees is sufficient to cover the most useful part of the powder pattern. Comparing the observed data with that in the PDF allows the phases in the sample to be identified.\textsuperscript{40,41} In this investigation XRD spectra were recorded using CuKα radiations employing Philips X-ray Diffractometer (Model- Expert Pro), Netherlands.

### 2.3.2 Scanning Electron Microscopy

The Scanning Electron Microscope (SEM) is critical in all fields that require characterization of solid materials. In the present investigation SEM is used to analyze
the microstructure of sintered and thermally etched surface of ceramic samples. SEM generates high-resolution images of shapes of objects (SEI) and Energy Dispersive X-ray Analysis (EDXA) is used to show spatial variations in chemical compositions. A schematic diagram of SEM is shown in Fig. 2.4. In this method, an electron beam is produced at the top of the microscope by an electron gun. The electron beam, which typically has an energy ranging from a few hundred eV to 100 keV, is focused by one or two condenser lenses into a beam with a very fine focal spot sized 0.4 nm to 5 nm. The beam passes through pairs of scanning coils or pairs of deflector plates in the electron optical column, typically in the objective lens, which deflect the beam horizontally and vertically so that it scans in a raster fashion over the sample surface. When the primary electron beam interacts with the sample, the type of signals gathered include secondary electrons, characteristic x-rays, and back scattered electrons. In SEM these signals come not only from the primary beam impinging upon the sample, but from other interactions within the sample near the surface. The SEM is capable of producing high-resolution images of a sample surface in its primary use mode, secondary electron imaging. Due to the manner in which this image is created, SEM images have great depth of field yielding a characteristic three-dimensional appearance useful for understanding the surface structure of a sample. The resolution of SEM can fall somewhere between less than 1 nm and 20 nm. An electrically conductive (usually gold) coating must be applied to electrically insulating samples. In this study we have used a Scanning Electron Microscope of Jeol JSM-5600LV, Japan for the microstructural evolution of ceramic samples prepared.

2.3.2.1 Energy Dispersive X-ray Analyzer (EDXA)

An Energy Dispersive X-ray Analyzer (EDXA) is a common accessory which gives the SEM a very valuable capability for elemental analysis. The electron beam in an SEM has energy typically between 5,000 and 20,000 electron volts (eV). The energy holding electrons in atoms (the binding energy) ranges from a few eV up to many kilovolts. Many of these atomic electrons are dislodged as the incident electrons pass
through the specimen, thus ionizing atoms of the specimen. Ejection of an atomic electron by an electron in the beam ionizes the atom, which is then quickly neutralized by other electrons. In the neutralization process an x-ray with an energy characteristic of the parent atom is emitted. By collecting and analyzing the energy of these x-rays, the constituent elements of the specimen can be determined. Its characterization capabilities are due in large part to the fundamental principle that each element of the periodic table has a unique atomic structure allowing the x-rays that are characteristic of an element's atomic structure to be uniquely distinguished from each other. There are four primary components of the EDXA setup: the beam source; the X-ray detector; the pulse processor; and the analyzer. Electron microscopes are equipped with a cathode and magnetic lenses to create and focus a beam of electrons. A detector is used to convert X-ray energy into voltage signals; this information is sent to a pulse processor, which measures the signals and passes them onto an analyzer for data display and analysis.

2.4 MICROWAVE CHARACTERIZATION OF DIELECTRIC MATERIALS

2.4.1 Introduction

Microwave materials have been widely used in a variety of applications ranging from communication devices to military satellite services, and the study of material properties at microwave frequencies and the development of functional microwave materials have always been among the most active areas in solid-state physics, materials science, and electrical and electronic engineering. In recent years, the increasing requirements for the development of high-speed, high frequency circuits and systems require complete understanding of the properties of materials functioning at microwave frequencies. All these aspects make the characterization of material properties an important field in microwave electronics. This section deals with the microwave methods applied to materials property characterization.

The dielectric properties at microwave frequency range can be measured by resonant and non-resonant methods. Non-resonant methods are often used to get
general knowledge of electromagnetic properties over a frequency range, while resonant methods are used to get accurate knowledge of dielectric properties at a single frequency or at several discrete frequencies. Precisely measuring the dielectric properties of a material are important to predict the system performance. The generally adopted methods for characterization of dielectric properties of materials at microwave frequencies fall into (i) reflection methods (ii) transmission line methods (iii) optical methods (iv) perturbation methods (v) exact resonance methods. The choice of method will depend on the value of $\varepsilon_r$ and loss factor, the amount of material available and the accuracy required. Once the resonant frequencies, $Q$-factors of the resonant structures and dimensions of the test samples are measured, computations have to be performed to obtain $\varepsilon_r$ and loss factor.

**Optical methods:** Optical methods are applicable for below wavelength of one centimetre. Since this method requires large amount of material, it is not suitable for DRs.\textsuperscript{42}

**Transmission line technique:** This method has a serious disadvantage of the very small waveguide size used below 4 mm, which gives rise to practical difficulties. Moreover, imperfections in the sample dimensions produce errors in the measurement. It was reported that the accuracy of transmission mode measurements of the dielectric properties is more in weak coupling conditions.\textsuperscript{43}

**Reflection method:** In this method, waves reflected from the dielectric are studied. When the dielectric constant becomes large, there occurs considerable error in the measurement of complex voltage reflection coefficient.\textsuperscript{44}

**Perturbation Technique:** The perturbation methods are highly suitable for materials of small size since the material should not alter the field configuration considerably. These techniques are suitable for relative permittivities less than 10, although this range can be extended by an exact solution of the resonator containing the specimen.\textsuperscript{45} Hence this technique is not commonly used for DR characterization. In the present study this
technique is used to measure the dielectric properties of polymer ceramic composites which are having low relative permittivity less than 10.

**Resonance method:** This is the most accurate method as compared to the above-mentioned methods for the measurement of DRs. In this method, the exact resonant frequency of the resonator is measured using different techniques. From the resonant characteristics, parameters like $\varepsilon_r$, $Q$ etc are determined.

The ideal technique for the determination of the microwave dielectric properties of low loss materials is exact resonance methods, which will be discussed in detail in this chapter. Apart from this technique, alternate methods to characterize DRs such as Whispering Gallery Mode Technique and Split-Post Dielectric Resonator Method will be discussed in the following section.

### 2.4.1.1 Whispering Gallery Mode Resonators

Whispering Gallery Mode (WGM) Dielectric Resonators are often used in characterizing extremely low loss dielectrics, high relative permittivity materials, anisotropic dielectrics and ferrites. WGM DRs are very interesting due to (i) their relatively large dimensions even in millimeter wavelength band (ii) the quality factors are very high since they depends only on the loss tangent of the material used as the DR (iii) the radiation losses are negligible (iv) WGM resonators have good suppression of spurious modes because the propagation constant along the Z-axis is very small and the unwanted modes leak out axially and can be absorbed without perturbation (v) they offer high level of integration to planar circuits. The resonant frequencies were calculated from the dimensions and relative permittivity, determined by the end-shorted method assuming $\varepsilon_{_{11}} = \varepsilon_{_{||}}$ where $\varepsilon_{_{11}}$ is the relative permittivity parallel to the anisotropic axis and $\varepsilon_{_{\perp}}$, the one perpendicular to it. The modes which have high electric energy filling factor (WGM modes) will have the highest quality factor. The dielectric loss tangent for the isotropic dielectric can be determined using the equations
\[ Q_{(E)}^{-1} = \tan \delta (P_{e} + P_{s_n}) + R_s/G_{(E)} \]  
\[ Q_{(H)}^{-1} = \tan \delta (P_{e} + P_{s_n}) + R_s/G_{(H)} \]  

where \( R_s \) is the surface resistance of the cavity enclosing the DR.

### 2.4.1.2 Split-Post Dielectric Resonator Method

Split-post resonator methods are suitable for the characterization of dielectric sheet samples, including dielectric substrates for planar circuits.\(^{50}\) In a split-post dielectric resonator (SPDR) method,\(^{51}\) the measurement fixture usually has a cylindrical structure working at a TE mode, and the resonator is split into two parts at the electric current node along a plane perpendicular to the cylinder axis. The sample under test is placed in the gap between the two parts of the resonator, and usually the sample is at the place of maximum electric field. The loading of a dielectric sheet sample changes the resonant properties of a split resonator, and the dielectric properties of the sample can be derived from the resonant properties of the resonator loaded with sample and the dimensions of the resonator and the sample.

![Fig 2.5 Geometry of a split-post dielectric resonator fixture for the measurement of the complex permittivity of dielectric sheet sample](image)

The proposed geometry of a split-dielectric resonator fixture for the measurement of the complex permittivity of dielectric sheet samples is shown in Fig. 2.5. Split-post dielectric resonator usually operates with the TE\(_{01\alpha} \) mode, which has only azimuthal electric field component, so the electric field remains continuous on the dielectric
interfaces. The field distributions are affected by the introduction of the sample, which in turn changes the resonant frequency, and the unloaded $Q$-factor of the sample. For low-loss materials, the influence of losses on the resonant frequencies is negligible, so the real part of permittivity of the sample under test is related to the resonant frequencies and physical dimensions of the cavity and sample only. The calibration technique is used and we compare the difference of resonant frequency of the split dielectric resonator before and after the sample is inserted. The relative permittivity of the sample is an iterative solution to the following equation\(^{52}\)

$$

\varepsilon_r = 1 + \frac{f_o - f_s}{h f_o K_\varepsilon(\varepsilon_r, h)}
$$

(1.47)

where $h$ is the thickness of the sample under test, $f_o$ is the resonant frequency of empty resonant fixture, $f_s$ is the resonant frequency of the resonant fixture with dielectric sample, $K_\varepsilon$ is a function of $\varepsilon_r$ and $h$. The dielectric loss tangent of the sample can be determined by

$$

\tan \delta = \frac{1}{P_{es}} \left( \frac{1}{Q_c} - \frac{1}{Q_{DR}} - \frac{1}{Q_{c0}} \right)
$$

(1.48)

with

$$

P_{es} = h \varepsilon_r K_1(\varepsilon_r, h)
$$

(1.49)

$$

Q_c = Q_{c0} K_2(\varepsilon_r, h)
$$

(1.50)

$$

Q_{DR} = Q_{DR0} \frac{f_o}{f_s} \frac{P_{eDR0}}{P_{eDR}}
$$

(1.51)

where $P_{es}$ and $P_{eDR}$ are the electric-energy filling factors for the sample and for the split resonator respectively; $P_{eDR0}$ is the electric-energy filling factor of the dielectric split resonator for empty resonant fixture; $Q_{c0}$ is the quality factor depending on metal enclosure losses for empty resonant fixture; $Q_{DR0}$ is the quality factor depending on dielectric losses in dielectric resonators for empty resonant fixture; and $Q$ is the unloaded quality factor of the resonant fixture containing the dielectric sample. The values of $P_{eDR}$, $P_{es}$ and $Q_c$ for a given resonant structure can be calculated using numerical
techniques. In terms of sample geometry, the only requirements are that the sample must extend beyond the diameter of the two cavity sections and the sample must be flat. This provides the accuracy of a resonator technique without having to machine the sample. Typical uncertainty of the permittivity measurements of a sample of thickness $h$ can be estimated as $\Delta \varepsilon = \pm (0.0015 + \Delta h/h)$ and uncertainty in loss tangent measurements $\Delta \tan \delta = 2 \times 10^{-5}$.

### 2.4.2 Network Analyzer

Network Analyzer is the major instrument used in this investigation for the characterization DRs. A measurement of the reflection from and/or transmission through a material along with knowledge of its physical dimensions provides the information to characterize the permittivity and permeability of the material. Network Analyzer is a swept frequency measurement equipment to completely characterize the complex network parameters in comparatively less time, without any degradation in accuracy and precision. Two types of network analyzers are available, scalar and vector network analyzers. Scalar network analyzer measures only the magnitude of reflection and transmission coefficients while the vector network analyzer measures both the magnitude and phase. Both the magnitude and phase behavior of a component can be critical to the performance of a communications system. A vector network analyzer can provide information on a wide range of these devices, from active devices such as amplifiers and transistors, to passive devices such as capacitors and filters.

A basic network analyzer is designed to show graphically, a plot of the voltage gain or loss of a network versus frequency. The network analyzer measures the magnitude, phase and group delay of two-port networks to characterize their linear behaviour. A vector network analyzer consists of a signal source, a receiver and a display. The source launches a signal at a single frequency to the material under test. The receiver is tuned to that frequency to detect the reflected and transmitted signals from the material. The measured response produces the magnitude and phase data at that frequency. The source is then stepped to the next frequency and the measurement is
repeated to display the reflection and transmission measurement response as a function of frequency (Bode response plot). The analyzer can operate in ramp or in step mode. In the ramp mode the analyzer directs the source to sweep in a linear ramp over the frequency and in the step mode, it provides maximum precision.

2.4.3 Measurement of Relative Permittivity ($\varepsilon_r$)

![Diagram of Hakki Coleman setup](image)

Fig. 2.6 (a) Hakki Coleman set up used for DR measurements and (b) dielectric rod kept end shorted between two mathematically infinite conducting plates

The complex permittivity of dielectric resonator is often measured by the method developed by Hakki and Coleman$^{53}$ and modified by Courtney.$^{54}$ This set up is shown in Fig. 2.6 (a). A cylindrical disc of material having relative permittivity $\varepsilon_r$, length $L$ and diameter $D$ is sandwiched between two mathematically infinite conducting plates (well polished copper plates coated with silver or gold), is shown in Fig. 2.6 (b). The $TE_{0m1}$ mode is widely used in this method. If the dielectric material is isotropic then the characteristic equation for this resonant structure operating in the $TE_{0m1}$ mode is written as

$$\alpha \frac{J_0(\alpha)}{J_1(\alpha)} = -\beta \frac{K_0(\beta)}{K_1(\beta)}$$

(2.5)
where $J_0(\alpha)$ and $J_1(\alpha)$ are Bessel functions of the first kind of orders zero and one respectively. The $K_0(\beta)$ and $K_1(\beta)$ are the modified Bessel functions of the second kind of order zero and one respectively. The parameters $\alpha$ and $\beta$ depend on the geometry, the resonant wavelength inside and outside the DR respectively and dielectric properties. Thus

$$\alpha = \frac{\pi D}{\lambda_n} \left[ \varepsilon_r - \left( \frac{l \lambda_n}{2L} \right)^2 \right]^{1/2} \quad (2.6)$$

$$\beta = \frac{\pi D}{\lambda_n} \left[ \left( \frac{l \lambda_n}{2L} \right)^2 - 1 \right]^{1/2} \quad (2.7)$$

where $l$ = the longitudinal variations of the field along the axis, $L$ = Length of the DR, $D$ = Diameter of the DR, $\lambda_n$ = free space resonant wave length. The characteristic equation is a transcendental equation and hence a graphical solution is necessary. Corresponding to each value of $\beta$ there are infinite number of $(\alpha_n)$ that solves the characteristic equation. Hakki and Coleman obtained a mode chart showing the variation of $\alpha$ values as a function of $\beta$ and are shown in Fig. 2.7.

Fig. 2.7 Mode charts of Hakki-Coleman giving $\alpha_1$ as functions of $\beta$.  

Fig. 2.8 The cavity set up for the measurement of Q-factor.
The relative permittivity of the resonator can be calculated using the mode chart parameters ($\alpha_i$ and $\beta_i$), the resonant frequency ($f_r$) and the dimensions of the dielectric puck using the equation

$$\varepsilon_r = 1 + \left[ \frac{c}{\pi D f_r} \right]^2 \left( \alpha_i^2 + \beta_i^2 \right)$$

(2.8)

Courtney proposed two horizontally oriented E-field probes for coupling microwave to the dielectric resonator, which enabled to span a wide range of frequencies, since there is no cut-off frequency for coaxial lines. The $TE_{011}$ mode is used for the measurements since this mode propagates inside the sample but is evanescent outside the geometry of DR. Therefore a large amount of electrical energy can be stored in the high $Q$ dielectric resonators. In the end shorted condition the $E$-field becomes zero close to the metal wall and electric energy vanishes in the air gap. The $TE_{011}$ mode is chosen for measurement because for this mode only azimuthal component of electric field exists and the error due to the air gap is practically eliminated.

A Vector Network Analyzer (Model 8753 ET, Agilent Technologies, Hewlett-Packard, Palo Alto, CA) is used for taking measurements at microwave frequencies. The HP 9000, 300 series instrumentation computer, interfaced with network analyzer makes the measurement quicker and accurate. The specimen is placed approximately symmetrical with the two $E$-probes. The resonant modes (represented by spikes in the resonance spectrum) are visualized by giving a wide frequency range by adjusting the Network Analyzer. To select the $TE_{011}$ resonance from the several modes having non zero $E_z$ components, the upper metal plate is slightly tilted to introduce an air gap. As the plate is tilted the entire $TM$ modes move rapidly to the higher frequencies while the $TE_{011}$ mode remains almost stationary. It is well known that in exact resonance technique, $TE_{011}$ is least perturbed by the surroundings. After identifying the $TE_{011}$ resonant frequency or central frequency ($f_r$), the span around $f_r$ is reduced as much as possible to get maximum resolution. The 3 dB bandwidth of the curve decreases and a stage of saturation is reached when the width will remain the least possible. The coupling loops are fixed at
this position and the centre frequency can be noted corresponding to the maxima as $f_r$. By knowing the diameter ‘$D$’ and length ‘$L$’ of the sample $\beta$ is calculated using equation (2.7). From the mode chart, the value of $\alpha_i$ corresponding to $\beta_i$ value is noted. The relative permittivity $\varepsilon_r$ is calculated using equation (2.8). The advantages of this method are very simple measurement configuration and easy access for introducing and removing the test samples. This is one of the fairly accurate and the most frequently used techniques for measurement of permittivity and this method is proposed as one of the international standards IEC techniques for measurements of the complex permittivity of low loss solids.

2.4.4 Measurement of Unloaded Quality Factor ($Q_u$)

![Experimental setup](image)

Fig.2.9 Experimental set up used in our lab to measure the microwave dielectric properties

The $Q$-factor of microwave resonators is measured using various methods.\textsuperscript{58,59,60,61} However, all these methods failed to account for the practical effects such as noise, cross talk, coupling losses, transmission line delay, and impedance mismatch introduced by a
real measurement system. Inadequate accounting of these effects may lead to significant uncertainty in the measured quality factor of the DRs. Moreover the microwave loss factors of DRs are affected by many other intrinsic and extrinsic factors (See section 1.6 of Chapter 1). When Q of a DR sample is measured by the end shorted method of Courtney, the measured Q factor is affected by the conductor and radiation losses. Hence to reduce these effects, in our present study, we use a transmission mode cavity proposed by Krupka et al. (Fig. 2.8). Fig. 2.9 shows the experimental set up used in our laboratory to measure the dielectric properties. The specimen was placed on a low loss quartz spacer of height 8 mm inside a copper cavity of inner diameter 40 mm and height 22 mm whose inner side was finely polished and silver plated to reduce radiation loss. The use of low loss single crystal quartz spacer reduces the effect of losses due to the surface resistivity of the cavity. Samples with diameter/length (D/L) ratio of 1.8 - 2.2 is preferable to get maximum mode separation and to avoid interference from other modes. Microwaves are fed into the sample using two loop coaxial antennas, which provides a magnetic coupling to excite the transmission mode resonance spectrum of dielectric cylinder. The coupling is adjusted to be optimum (weak coupling for high $Q_u$ and strong coupling for lossy samples). Observe $S_{21}$ versus frequency spectrum. In principle the cavity has infinite number of modes, when excited with microwave spectrum of frequencies. $TE_{01\delta}$ mode is identified as the fundamental mode with least perturbation when the tunable top lid is adjusted properly. After identifying the desired mode, the lid is fine tuned to get maximum separation between $TE_{01\delta}$ and any nearby cavity modes, to attain maximum possible accuracy in the $Q_u$ measurement. Measure $TE_{01\delta}$ mode frequency and the unloaded and the 3 dB bandwidth from the resonance spectrum (Fig. 2.10) to calculate the $Q$ factor as

$$Q = \frac{f_u}{\Delta f} \quad (2.9)$$

Fig. 2.11 shows the microwave resonance spectrum of CeO$_2$ ($\varepsilon_r=23$) in transmission configuration. The electromagnetic field could penetrate into the
conducting walls of the cavity which lowers the measured $Q$ value of the DR. Usually the dimensions of the cavity are such that the $TE_{018}$ mode of the DR is the lowest resonance. The quality factor decreases when the cavity diameter/puck diameter ratio is smaller than three. Hence the cavity normally used is 3-5 times the size of the sample. The surface resistance of copper can be calculated from the quality factor of the $TE_{011}$ resonance of the empty cavity to apply correction to the measured $Q$ of the sample for the loss due to cavity walls.\textsuperscript{63}

\begin{figure}
\centering
\includegraphics[width=0.4\textwidth]{figure10.png}
\caption{The method of calculating $Q$-factor from resonant mode using equation (2.9)}
\end{figure}

\begin{figure}
\centering
\includegraphics[width=0.4\textwidth]{figure11.png}
\caption{The microwave resonance spectrum of CeO$_2$ ($c_r=23$) in transmission configuration}
\end{figure}

### 2.4.5 Measurement of Temperature Coefficient of Resonant Frequency ($\tau_f$)

The temperature coefficient of resonant frequency ($\tau_f$) is the parameter which indicates the stability of the resonator. The electronic devices with microwave resonators should have $\tau_f$ values as close to zero as possible. The $\tau_f$ can be measured by the cavity method used for measuring the quality factor. The use of invar cavity can minimize the inaccuracy caused due to the thermal expansion of the cavity while heating. The cavity is then kept on a hot plate and the entire system is insulated in an isothermal enclosure. The setup is then slowly heated ($\sim 1^\circ$C/minute) in the range 25 to 80°C. The probe of the
thermocouple is kept just inside the isothermal enclosure so that it does not disturb the resonant frequency. Shift in the resonant frequency of $TE_{010}$ mode is noted at every $2^\circ C$ increment in temperature. The variation of resonant frequency is plotted as function of temperature and the $\tau_f$ is calculated from the slope of the curve using the equation (2.10)

$$
\tau_f = \frac{1}{f} \frac{\Delta f}{\Delta T}
$$

(2.10)

The temperature coefficient of relative permittivity $\tau_e$ is of considerable interest to users of dielectric substrates. This can be obtained by the parallel plate capacitor method using an LCR meter at low frequency (e.g., 1 MHz) and heating the sample. From the $\varepsilon_r$ noted at different temperatures the $\tau_e$ can be obtained.

### 2.4.6 Cavity Perturbation Method

The most used technique to determine the measurement of dielectric parameters of materials depends on the measurement of either reflection coefficients or resonant frequencies. In a resonant perturbation method, the sample under test is introduced to a resonant cavity, and the electromagnetic properties of the sample are deduced from the change of resonant frequency and quality factor of the resonating cavity. Resonant perturbation method using hollow metallic cavity is called cavity perturbation method. Bethe and Schwinger first proposed the perturbation theory of resonant cavities. In the past cavity perturbation technique was the only method available to obtain approximate solutions but its applications were limited not only to low permittivity samples but also to a specific modes and specific samples.

Cavity perturbation methods are widely used in the study of the electromagnetic properties of dielectrics, semiconductors, magnetic materials and composite materials. It works well for the determination of the dielectric characteristics of thin sheet samples of low and medium dielectric loss. In the cavity perturbation technique, a small piece of the material usually in the form of a disk or sheet is placed in a metallic resonant cavity operating in a known mode. The material characteristics are estimated from the shift in the resonant frequency and change in the $Q$ of the system. This technique was
pioneered by Slater\textsuperscript{70} and is a suitable method for measuring the dielectric properties of materials with permittivity less than 10. The cavity perturbation method is not a swept frequency measurement since the measurement frequencies are determined by the cavity as well as the DR dimensions. Hence it can be used only for discrete frequency measurements. In this method a rectangular wave guide with a small slot at the broader wall at the middle is used and the cavity is excited with optimum iris coupling, typically the diameter of the iris is equal to the shorter dimension of the Wave Guide (WG)/2.2 can be used for the measurement of dielectric properties of the samples. The resonant frequency and quality factor of the empty cavity is determined for different cavity modes. Then the thin sheet sample is inserted and positioned at the E-field antinode. If the sample is purely dielectric the maximum electric field can be easily determined by simply moving the sample across the slit. The mode will shift to low frequency side and retraces from there. The sample is kept at the retracing position, this is the electric field maximum position. If it is slightly magnetic the permittivity can be measured only for the odd modes by keeping it at the middle of the cavity. The new resonant frequency and $Q$ of the sample is again measured. The complex relative permittivity ($\varepsilon_r = \varepsilon'_r + \varepsilon''_r$) of the sample is calculated using the following Equations (2.32-2.34).\textsuperscript{57,59,71}

\begin{align*}
\varepsilon'_r &= 1 + \left[ \frac{V_c (f_0 - f_s)}{4 f_s V_s} \right] \\
\varepsilon''_r &= \frac{(\varepsilon' - 1) f_s}{2 \varepsilon' (f_0 - f_s)} \left[ \frac{1}{Q_v} - \frac{1}{Q_s} \right] \\
\tan \delta &= \frac{\varepsilon''_r}{\varepsilon'_r} 
\end{align*}

(2.32) \hspace{1cm} (2.33) \hspace{1cm} (2.34)

where $f_0 =$ resonant frequency of the empty cavity, $f_s =$ resonant frequency of the cavity with sample, $V_c =$ Volume of the cavity and $V_s =$ Volume of the sample, $Q_v$ is the quality factor of the empty cavity and $Q_s$ is the quality factor of the cavity with sample. The experimental error was found to be less than 2\% in case of permittivity and 1.3\% in the
case of dielectric loss. Here also the measured $Q_s$ and $Q_0$ can be corrected by measuring $S_{11}$ and $S_{22}$ as mentioned earlier by proper calibration of the Network analyzer. It is better to use Wave guide TRL calibration for better accuracy at the ends of the waveguide to coaxial adaptor. Calibrate the Network Analyzer for full 2 port using TRL calibration. Now $S_{11}$ and $S_{22}$ are measured at the resonant frequency. As mentioned earlier calculate the coupling coefficients for the two ports and find the unloaded quality factors $Q_u$ and $Q_s$. The main advantage of this method is the easiness of determining the permittivity and loss using simple device with moderate accuracy.

2.4.7 Radio Frequency Dielectric Measurements

LCR meters are generally used for measurement of the capacitance and dissipation factor of capacitors in the radio frequency region by the well-known parallel plate capacitor method. One can also measure the $\varepsilon_r$ and tan $\delta$ at radio frequencies by the parallel plate capacitor method using an LCR meter for new materials. This will give an approximate idea of $\varepsilon_r$ and tan $\delta$ which in turn helps to calculate the approximate resonant frequency of the DR using the equation (1.19) of section 1.5.1, Chapter 1. The knowledge of the value of the resonant frequency further helps to know the size of the DR at a given frequency or the size of the cavity required to measure the Q-factor. In the present study, the dielectric properties at radio frequency are measured using LCR meter (HIOKI 3532-50 LCR Hi TESTER, Japan).

2.4.8 Error Calculations in Dielectric Property Measurements

The measurement of microwave dielectric properties is done with two decimal point accuracy. Usually three samples were prepared in a batch corresponding to a particular composition and the measurements were made at least twice per each specimen. The sample should be well polished to avoid the error due to surface roughness. The error in $\varepsilon_r$ is calculated using the root sum of squares (RSS) method. The accuracy of $\varepsilon_r$ measurement is restricted to the accuracy in measurement of resonant frequency and dimensions of the sample. The possible error in the measurement of
permittivity is of the order of 0.3%. Such an error is possible when dimensional uncertainties of the samples are in the order of 0.15%. Hence the possible errors in the measured value of relative permittivity of a sample of height \(L\), radius \(r\) and resonant frequency \(f_r\) given by

\[
\Delta \varepsilon_r = \left[ \left( \frac{\partial \varepsilon_r}{\partial L} \Delta L \right)^2 + \left( \frac{\partial \varepsilon_r}{\partial r} \Delta r \right)^2 + \left( \frac{\partial \varepsilon_r}{\partial f_r} \Delta f_r \right)^2 \right]^{1/2}
\]

(2.19)

If the independent sources of error correspond to one standard deviation, then the error in \(\varepsilon_r\) will also correspond to one standard deviation. The uncertainty in quality factor using \(\text{TE}_{016}\) mode cavity method with optimized enclosure is of the order of ±2x10^-4. The errors in unloaded quality factor \(Q_u\) and temperature coefficient of resonant frequency \((\tau_f)\) were calculated using Root Sum Square (RSS) method by taking partial derivative of these parameters with respect to independent variables. A measurement calibration is used to eliminate the systematic (stable and repeatable) measurement errors caused by the imperfections of the system. Random errors due to noise, drift, or the environment (temperature, humidity, pressure) cannot be removed with a measurement calibration. This makes a microwave measurement susceptible to errors from small changes in the measurement system. These errors are minimized by adopting good measurement practices, such as visually inspecting all connectors for dirt or damage and by minimizing any physical movement of the test port cables after a calibration.

2.5 THERMAL CHARACTERIZATION

Thermal analysis is “A group of techniques in which a physical property of a substance and/or its reaction products is measured as a function of temperature whilst the substance is subjected to a controlled temperature program.” Three methods which provide primarily chemical rather than physical information about samples of matter are Thermogravimetry, Differential Thermal Analysis and Differential Scanning Calorimetry.
2.5.1 Thermo Gravimetric Analysis (TGA) and Differential Thermal Analysis (DTA)

In a thermo gravimetric analysis the mass of a sample in a controlled atmosphere is recorded continuously as a function of temperature or time as the temperature of the sample is increased. Thermo gravimetric methods are largely limited to decomposition and oxidation reactions and to physical processes such as vaporization, sublimation and desorption. DTA is a technique in which the difference in temperature between a substance and a reference material is measured as a function of temperature while the substance and reference material are subjected to a controlled temperature program. Information on the inorganic compounds such as dehydration, oxidation, reduction and solid-state reactions is provided by DTA.

2.5.2 Differential Scanning Calorimetry (DSC)

DSC is a thermal technique in which differences in heat flow into a substance and a reference are measured as a function of sample temperature while the two are subjected to a controlled temperature program. Both the sample and reference are maintained at nearly the same temperature throughout the experiment. The basic principle underlying this technique is that, when the sample undergoes a physical transformation such as phase transitions, more (or less) heat will need to flow to it than the reference to maintain both at the same temperature. Whether more or less heat must flow to the sample depends on whether the process is exothermic or endothermic. Differential scanning calorimetry can be used to measure a number of characteristic properties of a sample like fusion, crystallization events and glass transition temperatures ($T_g$), oxidation and other chemical reactions. In the present investigation DSC is used to determine the melting and crystallization temperature of the polymer-ceramic composite.

2.5.3 Thermo Mechanical Analysis (TMA)

In this technique (TMA), dimensional changes in a sample are primarily measured, with negligible force acting on it, while the sample is heated, cooled,
studied at a fixed temperature. It is particularly suited to polymer materials but a wide range of materials can be examined. In the present study, TMA (TMA-60H, Shimadzu, Kyoto, Japan) is used to determine the thermal expansion coefficient and softening temperature (by application of load and hemisphere-plugs) of composites. TMA is also used to confirm the softening and melting temperature of glass-ceramic composites used for low temperature cofired ceramic applications.

2.5.4 Photopyroelectric Technique

An improved photopyroelectric technique\textsuperscript{78,79} is used to determine the thermal conductivity of the polymer composites. A 70 mW He-Cd laser of wavelength 442 nm, intensity modulated by a mechanical chopper (model SR540) is used as the optical heating source. A PVDF film of thickness 28 µm, with Ni-Cr Coating on both sides, is used as pyroelectric detector. The output signal is measured using a lock in amplifier (model SR 830). Modulation frequency is kept above 60 Hz to ensure that the detector, the sample and backing medium are thermally thick during measurements. The thermal thickness of the composites is verified by plotting photopyroelectric (PPE) amplitude and phase with frequency at room temperature. Thermal diffusivity ($\gamma$) and thermal effusivity ($e$) are also measured from PPE signal phase and amplitude\textsuperscript{80}. From the values of $\gamma$ and $e$ the thermal conductivity and specific heat capacity of the samples are obtained. In the present investigation thermal conductivity is measured for polymer-ceramic composites used for microwave substrates and electronic packaging applications.
2.6 REFERENCES


CHAPTER 2


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