Chapter 2

Theory of dielectric materials and measurement techniques
2.1 Theory of dielectrics

2.1.1 Introduction

Dielectric materials are electrical insulators. They are used principally in capacitors and electrical insulators. They possess high dielectric strength, i.e. they withstand high voltages without undergoing degradation. They have low dielectric loss, i.e., in an alternating electric field, the loss of electrical energy appearing as heat is minimum. Application of potential difference across a dielectric leads to a polarization of charge within the material although long range motion of ions or electrons cannot occur. The polarization disappears when the voltage is removed. Dielectric properties may be defined by the behaviour of the material in a parallel plate capacitor. This is a pair of conducting plates, parallel to one another and separated by a distance, d, which is small compared with the linear dimensions of the plates. With a vacuum between the plates, the capacitance $C_0$ is defined as $C_0 = \varepsilon_o A/d$ where $\varepsilon_o$ is the permittivity of free space ($8.854 \times 10^{-12}$ Fm$^{-1}$) and A is the area of the plates. Since $\varepsilon_o$ is a constant, capacitance depends only on the dimensions of the capacitor. On application of a potential difference ($V$) between the plates, a quantity of charge ($Q_0$) is stored on them and $Q_0 = C_0 V$. If a dielectric substance is now placed between the plates and the same potential difference applied, the amount of charge stored increases to $Q_1$ and the capacitance therefore increases to $C_1$. The dielectric constant or relative permittivity ($\varepsilon'$) of the dielectric is related to this increase in capacitance by

$$\varepsilon' = C_1 / C_0$$

(2.1)
2.1.2 Dielectric Polarizability

The magnitude of \( \varepsilon' \) depends on the degree of polarization or charge displacement that can occur in the material. The polarizability \( (\alpha) \) of the dielectric is defined by

\[
P = \alpha \ E
\]

(2.2)

where \( P \) is the dipole moment induced by the local electric field, \( E \). The polarizability has four possible components and is given by the summation:

\[
\alpha = \alpha_e + \alpha_i + \alpha_d + \alpha_s
\]

(2.3)

These four components are as follows:

1. The **Electronic polarizability** \( (\alpha_e) \) is caused by a slight displacement of the negatively charged electron cloud in an atom relative to the positively charged nucleus.

2. The **Ionic polarizability** \( (\alpha_i) \) arises from a slight relative displacement of anions and cations in a solid. It is the principal source of polarization in ionic crystals.

3. The **Dipolar (Orientation) polarizability** \( (\alpha_d) \) arises in materials that contain permanent electric dipoles. These dipoles may change their orientation and they tend to align themselves with an applied electric field. The effect is usually temperature dependent since the dipoles may be ‘frozen in’ at low temperatures.

4. The **Space charge polarizability** \( (\alpha_s) \) occurs in materials that are not perfect dielectrics in which some long range charge migration may occur. In such materials, cations migrate preferentially towards the negative electrode by means of crystal defects such as cation vacancies. Consequently, an electrical double layer builds up at the grain boundaries as well as electrode-material interface. Apparent dielectric constants as high as \( 10^6 \) to \( 10^7 \) may be observed (corresponding to double-layer capacitances of \( \sim 10^{-6} \) F).
2.1.3 Frequency dependence of polarization processes

The frequency dependence of polarization processes is shown in figure 2.1. At low frequencies e.g. audio-frequencies (10^{-2} - 10^{3} Hz), all four components (α_s, α_d, α_i, and α_e) may contribute to α. At radio frequencies (~ 10^6 Hz), space charge effects may not have time to build up in most ionically conducting materials and are effectively ‘relaxed out’. At microwave frequencies (~10^9 Hz) dipoles do not usually have time to reorient themselves and are effectively relaxed out. The time scales of ionic polarizations is such that they do not occur at frequencies higher than infrared (~10^{12} Hz). This then leaves only the electronic polarization which is observable in to the UV region but is relaxed out at X-ray frequencies [1].

Fig. 2.1 Frequency dependence of the polarisation processes.
2.1.4 Complex dielectric constant and dielectric losses

When a dielectric is subjected to an alternating field, both \( P \) and \( D \) vary periodically with time. In general, however, \( P \) and \( D \) may lag behind in phase relative to \( E \). If

\[
E = E_0 \cos \omega t
\]

(2.4)

we have

\[
D = D_0 \cos (\omega t - \delta) = D_1 \cos \omega t + D_2 \sin \omega t
\]

(2.5)

where \( \delta \) is the phase angle and

\[
D_1 = D_0 \cos \delta \quad \text{and} \quad D_2 = D_0 \sin \delta
\]

(2.6)

For most dielectrics, \( D_0 \) is proportional to \( E_0 \), but the ratio \( D_0/E_0 \) is generally frequency dependent. To describe this situation, one may thus introduce two frequency dependent dielectric constants:

\[
\varepsilon'(\omega) = \frac{D_1}{E_0} = \frac{(D_0/E_0)}{\cos \delta}
\]

\[
\varepsilon''(\omega) = \frac{D_2}{E_0} = \frac{(D_0/E_0)}{\sin \delta}
\]

(2.7)

It is frequently convenient to lump these two constants into a single complex dielectric constant,

\[
\varepsilon^* = \varepsilon' - i \varepsilon''
\]

(2.8)

and

\[
D = \varepsilon^* E_{0} e^{i \omega t}
\]

(2.9)

The ratio of imaginary and real components of dielectric constant is given by

\[
\tan \delta = \frac{\varepsilon''(\omega)}{\varepsilon'(\omega)}
\]

(2.10)

and since both \( \varepsilon' \) and \( \varepsilon'' \) are frequency dependent, the phase angle \( \delta \) is frequency-dependent. The energy dissipated, in the dielectric in the form of heat, is shown to be proportional to \( \varepsilon'' \). The current density in the capacitor is equal to

\[
I = \frac{dq}{dt} = (1/4\pi). \frac{dD}{dt} = (\omega/4\pi). (-D_1 \sin \omega t + D_2 \cos \omega t)
\]

(2.11)
where \( q = \frac{D}{4\pi} \) in esu., \( q \) is the surface charge density on the capacitor plates. The energy dissipated per second in the dielectric per unit volume is

\[
W = \frac{\omega}{2\pi} \int I E \, dt
\]

By substituting of equations (2.11) and (2.4) into (2.12), one readily finds that the integral containing \( D_1 \) vanishes and one is left with

\[
W = \left( \frac{\omega}{8\pi} \right) E_0^2 \varepsilon''
\]

The energy losses are thus proportional to \( \sin \delta \). For this reason, \( \sin \delta \) is called the loss factor and \( \delta \) is the loss angle. One frequently calls \( \tan \delta \) as the loss factor or loss tangent. This is correct only for small values of \( \delta \), since \( \tan \delta \approx \sin \delta \approx \delta \) [2].

### 2.1.5 Dielectric Conductivity

Electrical conductivity measurements are useful for the study of electronic properties of materials. In dielectric materials, DC conductivity measurements are used to study the localization of electronic states, while AC conductivity measurements provide useful information concerning various relaxation phenomena related to the electrical polarization processes. In high frequency measurements, the characteristic hopping lengths and hopping rates of carriers between localized states can be determined. The low frequency data are however, more sensitive to slower relaxation process like the reorientation of dipoles. Most of the relaxation processes can be explained by the Debye theory of energy loss for dipole relaxations at higher frequencies [3]. It is well known fact that frequency dependent complex conductivity in case of disordered materials such as polycrystalline ceramics can arise from interfacial polarization at contacts, grain boundaries and other inhomogeneities present in the sample [4].
Hopping charge carriers are characterized by the fact that they spend most of the time in localized sites where they are subjected only to relatively very small thermal vibrations. They occasionally make a big jump or hopping transition to some neighboring localized sites which may be one or many atomic spacings away. In strongly disordered solids, the concept of band conduction by free charge carriers do not apply and instead the carriers become localized and can only move by hopping between localized sites. If these sites form a continuously connected network, the charges may be capable of traversing the entire physical dimensions of the sample, thus giving rise to direct current conduction that would be indistinguishable from free carrier conduction. Charge carriers hopping between localized states have much lower mobility, typically by many orders of magnitude, than the free charge carriers in the case of band conduction [5].

2.1.6 Dielectric relaxation

The dielectric relaxation phenomenon in dielectric materials reflects the delay (time dependence) in the frequency response of a group of dipoles when subjected to an external applied field. When an alternating voltage is applied to a sample, the dipoles responsible for the polarization are no longer able to follow the oscillations of the electric field at certain frequencies. The field reversal and the dipole reorientation become out-of-phase giving rise to a dissipation of energy. Over a wide range of frequency, different types of polarization cause several dispersion regions (Figure 2.1). The critical frequency characteristic of each contributing mechanism depends on the nature of the dipoles. The dissipation of energy which is directly related to the dielectric losses can be characterized by several factors: (i) the losses associated with resonant processes characteristics of the elastic displacing of ions.
and electrons and (ii) the dipolar losses due to the reorientation of the dipolar moment or the displacing of the ions between two equilibrium positions [6].

Fig. 2.2 General representation of relaxation and resonance types.

2.1.7 Interfacial phenomena and the Maxwell-Wagner effect

Strongly dispersive behaviour at low frequencies had been observed in many dielectric materials and it has attracted a considerable amount of attention. The simplest form of interfacial effect is represented by a capacitive layer arising near an electrode or grain boundary as a result of the formation of a Schottky barrier which is less conducting than the bulk material of the sample. This type of effect arises in the materials consisting of grains separated by more insulating inter-grain barriers. This can be represented by an equivalent circuit of a complete series-parallel array of capacitor and resistors. This kind of inhomogeneous medium effect is known under the general name Maxwell-Wagner effect [7].
2.1.8 Debye type relaxation

Whenever a dielectric material is kept in an alternating electric field, a certain length of time is required for the dipoles to become oriented in the direction of the applied field. This time is known as 'relaxation time'. In this time, a certain amount of energy is dissipated through the material which appears in the form of heat and is a measure of the dielectric loss.

The variation of real part ($\varepsilon'$-relative dielectric constant) and imaginary part ($\varepsilon''$-measure of dielectric loss) of the complex dielectric constant ($\varepsilon^*$) with frequency is shown in figure 2.2. It has a characteristic frequency dependence passing through a maximum value at the frequency where $\varepsilon'$ undergoes its maximum rate of change with frequency. The shape of the $\varepsilon''$ peak is called a Debye peak. This behavior is explained by two equations which are known as Debye equations.

\[
\varepsilon' (\omega) = \varepsilon_{\infty} + \frac{\varepsilon_s - \varepsilon_{\infty}}{1 + \omega^2 \tau^2} \tag{2.14}
\]

\[
\varepsilon'' (\omega) = \frac{(\varepsilon_s - \varepsilon_{\infty}) \omega \tau}{1 + \omega^2 \tau^2} \tag{2.15}
\]

where $\omega = 2\pi f$ and $\tau$ is the characteristic relaxation time or decay time of the ionic polarization, $\varepsilon_s$ is the static dielectric constant and $\varepsilon_{ea}$ is the electronic and ionic contribution to the dielectric constant. The maximum of the $\varepsilon''$ peak occurs when $\omega \tau = 1$. It is given by $\varepsilon'' (\omega) = (\varepsilon_s - \varepsilon_{ea}) / 2$. Thus the resonance peak is observed when the hopping frequency $(1/\tau)$ is equal to the applied frequency $\omega$ [8].
2.1.9 Non Debye relaxation

Dielectric constants may also be presented as complex plane diagrams, known as Cole-Cole plots, in which $\varepsilon''$ is plotted against $\varepsilon'$. The variations fall on a semicircle. In practice, the Cole-Cole plots are often not exactly semi circular but are distorted by varying degrees.

Similarly, the peaks in the dielectric loss, $\varepsilon''$, are not symmetric Debye peaks but are often broadened asymmetrically. The traditional approach in describing such distorted peaks is to regard them as the superposition of an appropriate number of individual Debye peaks, each occurring at different frequency. This then introduces the concept of a distribution of relaxation times. This behaviour of the material is regarded then as the Non-Debye relaxation [9].

2.1.10 Impedance Spectroscopy

Impedance Spectroscopy (IS) is a popular analytical tool in materials research and development because it involves a relatively simple electrical measurement that can readily be automated and whose results may often be correlated with many complex materials variables: from mass transport, rates of chemical reactions, corrosion and dielectric properties to defects, microstructure and compositional influences on the conductance of solids. The usefulness of IS lies in the ability to distinguish the individual contributions of the components of dielectric and electric properties under investigation.
The current \( I \) passing through a resistor \( R \), under an applied electric field \( E \), is given by Ohm’s law \( I = \frac{E}{R} \) and is independent of frequency. A pure capacitor does not allow the passage of a dc current but does allow a frequency dependent ac current given by \( I = j\omega CE \) where \( \omega \) is the angular frequency \( (\omega = 2\pi f) \) and \( j = \sqrt{-1} \). These equations for \( R \) and \( C \) may be written in the form

\[
I = \frac{E}{Z}
\]  

(2.16)

where \( Z \) is the impedance. The impedance of the capacitance is imaginary since it contains the term \( \sqrt{-1} \). This indicates that there is a phase difference of 90° between the sinusoidal current and voltage. In a circuit that contains a resistance and capacitance in series, the total impedance of the circuit is given by

\[
Z = R + \frac{1}{j\omega C} = R - \frac{j}{\omega C}
\]  

(2.17)

This impedance contains real and imaginary terms (i.e. \( R \) and \( 1/j\omega C \), respectively) and is therefore called the complex impedance \( Z' \), where

\[
Z' = Z^r - jZ^i
\]  

(2.18)

and

\[
Z^r = R \quad Z^i = \frac{1}{\omega C}
\]  

(2.19)

When the resistance and capacitance are connected in parallel, the reciprocal of the impedance (admittance) is given by the sum of the reciprocals of the resistance and the reactance of the capacitor and hence the reciprocal of the complex impedance. Therefore,

\[
A^r = \frac{1}{Z'^{-1}} = \frac{1}{R} + j\omega C
\]  

(2.20)
where $A^*$ is the complex admittance. It can be written in the form of real and imaginary components

$$A^* = A' + jA''$$  \hspace{1cm} (2.21)

where $A' = \frac{1}{R}$ and $A'' = \omega C$ \hspace{1cm} (2.22)

The complex impedance of the circuit in which the capacitor and resistor are connected in parallel may be evaluated by taking reciprocals,

$$Z^* = A^{*-1} = \left(\frac{\frac{1}{R} + j\omega C}{1 + j\omega RC}\right)^{-1}$$  \hspace{1cm} (2.23)

$$= \frac{R}{1 + j\omega RC}$$

$$= \frac{R (1 - j\omega RC)}{(1 + j\omega RC)(1 - j\omega RC)}$$

$$= \frac{R}{1 + (\omega RC)^2} - \frac{j\omega RC}{1 + (\omega RC)^2}$$

$$Z' = \frac{R}{1 + (\omega RC)^2}, \hspace{1cm} Z'' = R \frac{\omega RC}{1 + (\omega RC)^2}$$  \hspace{1cm} (2.24)

2.1.11 Analysis of impedance data

There are four basic formalisms that may be used to represent and analyse impedance data. They are as follows:

Complex impedance:

$$Z^* = R_s - \frac{j}{\omega C_s}$$  \hspace{1cm} (2.25)

where the suffix $s$ represents the components in series.
Complex admittance: \[ A^p = (\bar{\mathcal{Z}}^p)^{-1} \]
\[ = (R_p)^{-1} + j\omega C_p \]

where the suffix \( p \) represents the components in parallel.

Complex permittivity:
\[ \varepsilon^p = \frac{A^p}{j\omega C_0} \]
\[ = \varepsilon' - j\varepsilon'' \quad (2.26) \]

Complex electric modulus:
\[ M^p = (\varepsilon^p)^{-1} = \frac{1}{j\omega C_0} \mathcal{Z}^p \]
\[ = M' + jM'' \quad (2.27) \]

Analysis of impedance data is often carried out by complex plane methods which involve plotting the imaginary part of \( \mathcal{Z}^* \) i.e. \( Z'' \) against the real part, \( Z' \). When they are plotted on a linear scale, the data usually take the form of semicircles and of spikes. However, the equations (2.23) and (2.24) for the parallel circuit give rise to a semicircle in the \( Z^* \) plane. For more complex circuits, each parallel RC element gives rise to a semicircle in the complex \( Z^* \) plane. The observation of two semicircles would be attributed to the parallel combinations \( R_b, C_b \) and \( R_{gb}, C_{gb} \). The subscripts ‘b’ and ‘gb’ represent bulk and grain boundary contributions respectively. Thus in a polycrystalline material that has relatively large grain boundary resistances and small crystal resistances, these grain boundary resistances dominate the impedance response in the complex impedance plane and may even mask completely the effect of crystal resistances.

However, in the complex electric modulus formalism prominence is given to those elements that have the smallest capacitance. In this case, the response of the crystal dominates the results and the grain boundary effects may be effectively masked.
By a comparison of the results analyzed in these two different formalisms, it may therefore be possible to effectively separate grain boundary and bulk effects. For any RC circuit, the different formalisms correspond to different ways of writing the equations for the circuit and basically all contain the same information [10].

2.2 Combustion synthesis of perovskite oxide ceramics

The technique of making nanocrystalline perovskite oxide materials by ‘combustion process’ is an integrated approach, combining both breaking down and building up processes of producing nanomaterials. The solution combustion synthesis method being simple and fast is being practiced by many individuals and groups around the world. It has already made inroads into nanoscience and nanotechnology. Combustion synthesis is one of the novel methods in order to have a better control of stoichiometry, structure and phase purity of perovskites. This low temperature initiated self propagating method was first developed by Patil et. al.[11].

Combustion synthesis or fire synthesis is also known as self-propagating high temperature synthesis (SHS). An oxidizer, a fuel and the right temperature are required to generate fire. The process makes use of highly exothermic redox chemical reactions between an oxidizer and a fuel. All the self-propagating high temperature synthesis reactions are redox reactions. However, all redox reactions need not be SHS reactions. For the reaction to be self- propagating, the heat evolved should be more than the heat required for initiating the combustion. A redox reaction involves simultaneous oxidation and reduction processes. The classical definition of oxidation is addition of oxygen or any other electronegative element (nonmetal), while reduction is addition of hydrogen or any other electropositive element (metal). The term combustion involves flaming (gas-phase), smouldering (solid-
gas) as well as explosive reactions. It can be either linear combustion or volume combustion. In linear combustion, the burning surface recedes from top to bottom in layers, whereas in volume combustion, the entire reaction mixture ignites to burn with a flame.

Solution combustion synthesis (SCS) of oxide materials was unexpectedly discovered during the reaction between aluminium nitrate and urea. A mixture of Al(NO$_3$)$_3$.9H$_2$O and urea solution when rapidly heated around 500 °C in a muffle furnace, foamed and ignited to burn with an incandescent flame yielding voluminous white product which was identified as α-Al$_2$O$_3$ [12]. To understand the highly exothermic nature of this reaction, concepts used in propellant chemistry are employed [13]. A solid propellant contains an oxidizer like ammonium perchlorate and a fuel like carboxy terminated polybutadiene together with aluminium powder and some additives. The specific impulse ($I_{sp}$) of a propellant is given by the ratio of thrust produced per pound of the propellant. It is expressed as

$$I_{sp} = \frac{k\sqrt{T_c}}{\text{Molecular wt. of gaseous products}}$$

(2.28)

The highest heat $T_c$ (chamber temperature in the rocket motor) is produced when the equivalence ratio ($\phi_c = \text{oxidizer/fuel ratio}$) is unity. The equivalence ratio of an oxidizer and fuel mixture is expressed in terms of the elemental stoichiometric coefficient.

$$\phi_c = \frac{\sum (\text{coefficient of oxidizing elements in specific formula}) \times (\text{Valency})}{(-1) \sum (\text{Coefficient of reducing elements in specific formula}) \times (\text{Valency})}$$

(2.29)
A mixture is said to be stoichiometric when $\phi_c = 1$, fuel lean when $\phi_c > 1$, and fuel rich when $\phi_c < 1$. Stoichiometric mixtures produce maximum energy.

The oxidizer/fuel molar ratio (O/F) required for a stoichiometric mixture ($\phi_c = 1$) is determined by summing the total oxidizing and reducing valencies in the oxidizer compounds and dividing it by the sum of the total oxidizing and reducing valencies in the fuel compounds. In this type of calculation, oxygen is the only oxidizing element; carbon, hydrogen and metal cations are reducing elements and nitrogen is neutral. Oxidizing elements have positive valencies and reducing elements have negative valencies. In solution combustion calculations, the valency of oxidizing elements is considered as negative and that of the reducing elements as positive, similar to the oxidization number concept familiar to the chemists.

Accordingly, the elemental valency of C, Al and H is +4, +3 and +1, respectively and oxidizing valency of oxygen is -2. The valency of nitrogen is considered to be zero. Based on this concept, the oxidizing valency of aluminium nitrate and the reducing valency of urea are

$$\text{Al(NO}_3\text{)}_3 = -15; \quad [\text{Al} = +3, 3\text{N} = 0, 9\text{O} = (9\times -2) = -18]$$
$$\text{CH}_4\text{N}_2\text{O} = +6; \quad [\text{C} = +4, 4\text{H} = (4\times +1) = +4, 2\text{N} = 0, \text{O} = (1\times -2) = -2]$$

Accordingly, for the complete combustion of aluminium nitrate and urea mixture, the molar ratio becomes $15/6 = 2.5$. The stoichiometric equation for this reaction can be written as

$$2\text{Al(NO}_3\text{)}_3(\text{aq}) + 5\text{CH}_4\text{N}_2\text{O(\text{aq})} \rightarrow \alpha\text{-Al}_2\text{O}_3(\text{s}) + 5\text{CO}_2(\text{g}) + 8\text{N}_2\text{O(g)} + 10\text{H}_2\text{O(g)}$$

When the reaction of aluminium nitrate and urea is carried out in the molar ratio of $1 : 2.5$, the energy released is maximum and the combustion is complete with no carbon residue.

This type of stoichiometric balance of a redox mixture for a combustion reaction is
fundamental to the synthesis of an oxide material by the solution combustion method. This procedure is employed in the synthesis of CaSiO₃ nanopowders.

### 2.2.1 Combustion Synthesis of CaSiO₃

In the combustion synthesis of CaSiO₃, Ca(NO₃)₂.4H₂O and citric acid (C₆H₈O₇) are used as an oxidizer and fuel respectively. The stoichiometric calculation has been employed by considering the equation (2.29) as below:

\[
\begin{align*}
\text{Ca(NO}_3\text{)}_2 &= -10; \quad \text{[Ca = +2, 2N = 0, 6O = (6 x -2) = -12]} \\
\text{C}_6\text{H}_8\text{O}_7 &= +18; \quad \text{[6C = (6 x +4) = +24, 8H = (8 x +1) = +8 7O = (7 x -2) = -14]} \\
\end{align*}
\]

According to equation (2.29), we get

\[
\Phi_c = \frac{-10}{(-1)} (+18) = \frac{5}{9}
\]

Thus for complete combustion of calcium nitrate:citric acid mixture, the molar ratio becomes \( \frac{5}{9} = 0.544 \).

The stoichiometric chemical reaction can be written as

\[
9\text{Ca(NO}_3\text{)}_2(\text{aq.}) + 9\text{SiO}_2(\text{S}) + 5\text{C}_6\text{H}_8\text{O}_7(\text{aq.}) \rightarrow 9\text{CaSiO}_3(\text{S}) + 20\text{H}_2\text{O(g)} + 30\text{CO}_2(\text{g}) + 9\text{N}_2(\text{g}).
\]

When the reaction of calcium nitrate and citric acid is carried out in the molar ratio of 1 : 0.554, the energy released is maximum and the combustion is complete with no carbon residue.

### Preparation of CaSiO₃

The stoichiometric quantity of Analar grade calcium nitrate \((\text{Ca(NO}_3\text{)}_2 \cdot 4\text{H}_2\text{O})\) is added to stoichiometric quantity of citric acid \((\text{C}_6\text{H}_8\text{O}_7)\) which acts as a fuel for redox reaction) in a
borosil petry dish to get a redox mixture. To this mixture a stoichiometric quantity of fumed silica (SiO$_2$ of 99.9% purity and surface area of 200 m$^2$/gm), is mixed in order to get a heterogeneous mixture. A sufficient quantity of double distilled water is slowly poured into it and the solution is thoroughly stirred by keeping the solution on a magnetic stirrer for about 20 minutes. Thus we get a homogeneous solution which is then kept in a muffle furnace at 500 °C. Soon after 5-7 minutes, the solution starts boiling and the gases (CO$_2$, N$_2$ and H$_2$O) start evolving and combustion takes place making the reaction totally exothermic. The heat evolved is used up to form a voluminous and porous product CaSiO$_3$. This entire process takes place within 10-12 minutes.

2.2.2 Precaution and safety requirements

The combustion of redox mixtures if not controlled can lead to explosions. Hence, all reactions are to be carried out in open containers with minimum quantity of redox mixture in fume cupboard with effective exhaust. One should wear safety glasses and carry out the reactions under the protection of safety shield.

2.2.3 Method to get nanomaterials

It is possible to control the particle size of solid combustion product (ash) in the nano-range by using suitable fuels that control the nature of combustion. This results in

(i) Slow burning rate.

(ii) Reduction in exothermicity

(iii) Increase in number of gaseous products (water, nitrogen, carbon dioxide, etc.), which dissipate the heat.

(iv) Linear combustion which helps to yield nanooxides unlike volume combustion.
Hydrazide compounds like CH, ODH, glycine, ammonium acetate, citric acid or metal acetate appear to serve this purpose. In this way a large number of nano crystalline oxide materials have been prepared and characterized by the choice of appropriate precursors in the redox mixture. Formation of nano crystalline oxide materials is confirmed by X-ray line broadening and surface area measurement.

2.3 Physics of Luminescence

2.3.1 Introduction

The spontaneous emission of light upon electronic excitation (e.g. excitation by ultraviolet radiation) is called luminescence. It is the emission of optical radiation (infrared, visible, or ultraviolet light) by matter. This phenomenon is to be distinguished from incandescence, which is the emission of radiation by a substance by virtue of it being at a high temperature (blackbody radiation). Luminescence can occur in a wide variety of matter and under many different circumstances. Thus, atoms, polymers, inorganic, organic or organo metallic molecules, organic or inorganic crystals, and amorphous substances all become luminescent under appropriate conditions.

2.3.2 Photoluminescence and Stoke’s law

The process of photoluminescence, in which some of light radiation of a shorter wavelength of greater energy incident on a material is absorbed and re-emitted as a light of a longer wavelength of smaller energy is known as Stoke’s law. In the process of luminescence wavelength of light emitted is characteristic of a luminescent substance and not of the incident radiation. The light emitted could be visible light, ultra-violet, or infrared light.
This cold emission (luminescence) that does not include the emission of blackbody radiation thus involve two steps.

(i) The excitation of electronic system of a solid material to higher energy state and

(ii) Subsequent emission of photons or simply light.

The emission of light takes place at characteristics time \( \tau_c \) after absorption of the radiation. This parameter allows us to sub classify the process of luminescence into fluorescence and phosphorescence. Thus, if the characteristic time \( \tau_c \) is less than \( 10^{-8} \) s, then it is known as fluorescence and if the characteristic time \( \tau_c \) is greater than that of \( 10^{-8} \) s, then it is known as phosphorescence. A large number of substances both organic and inorganic show the property of luminescence. Luminescent solids are usually referred to as Phosphors [14].

### 2.3.3 Brief theory of Photoluminescence

The ability of a material to exhibit luminescence is associated with the presence of impurities, known as activators. These activators or impurity ions occurring in relatively small concentrations in the host material play an important role in producing luminescence. The incorporation of an activator atom in a crystalline solid will in general give rise to localized energy levels in the normally forbidden energy gaps. These localized levels may be classified into two categories [15]:

(i) Levels which belong to the activator atoms themselves and

(ii) Levels belonging to host atoms which are under the perturbing influence of the activators

Luminescent materials, also called phosphors, are mostly solid inorganic materials consisting of a host lattice, usually intentionally doped with impurities. The impurity
concentrations generally are low in view of the fact that at higher concentrations the efficiency of the luminescence process usually decreases (concentration quenching).

**Excitation and Emission**

The energy of the emitted light is generally less than that of the exciting radiation and is, therefore, of longer wavelength. This effective increase in wavelength is known as the Stoke’s shift. In phosphors, the exciting radiation is UV light which is converted in to light in visible region after emission. The absorption of energy (UV light) which is used to excite the electrons, takes place by either the host lattice or by intentionally doped impurities. In most cases, the emission takes place by the impurity ions, which are called activator ions. When the activator ions show too weak absorption, a second kind of impurities (called sensitizers) can be added which absorb the energy and subsequently transfer the energy to the activators. This process involves transport of energy through the luminescent materials. The emission colour can be adjusted by choosing the proper impurity ion, without changing the host lattice in which the impurity ions are incorporated. On the other hand, quite a few activator ions show emission spectra with emission at characteristic spectral positions [16].

**2.3.4 Thermoluminescence**

Thermoluminescence (TL) or more specifically called Thermally Stimulated Luminescence (TSL) is the phenomenon of emission of light from a solid which has been previously exposed to ionizing radiation under conditions of increasing temperature. Excitation is achieved by any conventional sources of ionizing radiation viz., α-rays, β-rays, γ-rays, UV rays and X-rays. Unlike other luminescence process such as Electroluminescence and Chemiluminescence, heat is not an exciting agent in this case but it acts only as a stimulant. Hence it is better known as thermally stimulated luminescence (TSL). TSL is exhibited by
a host of materials, glasses, ceramics, plastics and some organic solids. Insulating solids doped with suitable chemical impurities, termed as activator, are the most sensitive TL materials. The band theory of solids is normally used to explain this phenomenon.

When a solid is irradiated, electrons and holes are produced. The defects in the solid results in the presence of localized energy levels within the forbidden gap. On irradiation, electron and holes can be trapped at these defect sites. When the solid is heated, these trapped electrons/holes get enough thermal energy to escape from the trap to the conduction band (or valence band). From here they may get re-trapped again or may recombine with trapped holes/electrons. The site of recombination is called recombination center. If this recombination is radiative, then center is called luminescence center. Alternatively a trapped hole can be released by heating which can recombine with a trapped electron resulting in luminescence.

The plot of intensity of emitted light versus the temperature is known as a TL glow curve. A glow curve may exhibit one or many peaks depending upon the number of electron/hole traps with different trap depths, present in the lattice. These peaks may or not be well separated. The position, shape and intensity of the glow peaks therefore are characteristic of the specific material and the impurities and defects present. Therefore each TSL peak corresponds to the release for an electron (or hole) from a particular trap level within the band gap of the material. The nature of the TL glow peaks gives information about the luminescent centers present in the material. It is important that TSL is highly sensitive to structural imperfections in crystals.
TL glow curve can be obtained if TL emission is detected and plotted as a function of time during readout using a linear time-temperature heating profile. The glow peak is analyzed by an empirical method in which a parameter called the order of kinetics is introduced. When the trapped electrons jump up to the conduction band by the thermal energy, they have two kinds of chances to jump down. One is the retrapping process returning to the same kind of traps and another is the recombination with the hole accompanied by the emission of TL light. When the probability of being retrapped is negligible, the glow curve has a narrow peak shape by a rapid recombination process explained by Randall and Wilkins [17]. Instead, if retrapping dominates, the recombination with the holes is suppressed and the curve has a wide peak as explained by Garlick and Gibson [18]. These two descriptions are called the first order kinetics and the second order kinetics respectively. Thermoluminescence phosphors generally exhibit glow curves with one or more peaks when the charge carriers are released. The glow curve is characteristic of the different trap levels that lie in the band gap of the material. The shouldered at lower temperature, represents a shallower trap where as the peak at higher temperature represents a deeper trap within the energy band gap. The traps are characterized by certain physical parameters that include trap depth (E) and frequency factor (s). For many TL applications, a clear knowledge of these physical parameters is essential.

**Analysis of trap parameters**

The study of thermoluminescence phenomena and their applications to thermoluminescence dosimetry includes computerized curve fitting methods which is known as deconvolutions of the multi peak structure of TL glow curves. These which are purely mathematical and analytical approaches and imply the necessity of both estimating
the number of peaks within the relevant regions of the glow curve and restricting the values of trapping parameters, namely, trap depth or activation energy (E) and frequency factor (s) [19]. The glow peak parameters required for the determination of trap parameters are

\[
\begin{align*}
\delta &= T_2 - T_m \\
\tau &= T_m - T_1 \\
\omega &= T_x - T_x \\
\mu_g &= \frac{\delta}{\omega}
\end{align*}
\]

(2.30)

where \(T_1\) and \(T_2\) are low and high half intensity temperatures of the glow peak, \(T_m\) is the maximum temperature of the peak, \(\delta\) is the high temperature half width, \(\tau\) is the low temperature half width, \(\omega\) is the full width at half maximum and \(\mu_g\) is the geometry or form factor.

Several attempts have been made by various researchers such as C.B. Lushchik, A. Halperin and A.A. Braner to derive equations for both first order and second order kinetics. R. Chen has established expressions for general order kinetics dependent on the geometry factor of the glow peaks. When the geometry factor (\(\mu_g\)) is nearly equal to 0.42, the glow peak would represent first-order, whereas when \(\mu_g\) is nearly equal to 0.52, the peak would represent second-order kinetics.

Chen’s equation for general order kinetics is given by

\[
E = C_q \frac{\kappa T_m^2}{\eta} - b_\eta (2kT_m)
\]

where \(\eta\) stands for \(\delta, \tau\) and \(\omega\). The values of \(C_\eta\) and \(b_\eta\) for the three methods are given by

\[
\begin{align*}
C_\xi &= 1.51 + 2(\mu_g - 0.42) \\
C_g &= 0.976 + 7.3(\mu_g - 0.42)
\end{align*}
\]
\[ C_{\alpha} = 2.52 + 10.2(\mu_0 - 0.42) \]
\[ b_{\gamma} = 1.58 + 4.2(\mu_0 - 0.42) \]
\[ b_D = 0 \quad b_{\alpha} = 1 \]

After the determination of the activation energy (E) and the order of kinetics (b), an estimate of the frequency factor (s) can be made using the following expressions

\[ \frac{\beta E}{kT_m^2} = s \exp \left[ \frac{-E}{kT_m^2} \right] \] 
First-order kinetics

\[ \frac{\beta E}{kT_m^2} = s \exp \left[ \frac{-E}{kT_m^2} \right] \left[ 1 + \frac{2kT_m}{E} \right] \] 
Second-order kinetics

Here \( \beta \) is the heating rate (a constant) and \( k \) is the Boltzmann’s constant.

2.4 Effect of ionizing radiations on the properties of the ceramic materials

2.4.1 Interaction of radiation with matter

There are two basic types of radiation which can affect the structure and physical properties of the ceramic materials: (i) Electromagnetic radiation (X-rays, \( \gamma \)-rays) and (ii) Particle radiation (\( \beta \)-particle or electron, proton, neutron, heavy ions). The various types of interactions that occur between the high energy radiation and target atoms are dependent on the nature of the radiation (like energy, dose and dose rate) and the properties of the target material.

Interactions of \( \gamma \)-rays with matter

\( \gamma \)-rays consists of photons. These photons have zero rest mass and are electrically neutral. They interact with target atoms through the photoelectric effect, Compton scattering and pair production. In all the three cases, the interaction produces energetic free electrons. The
energy range in which photoelectric collisions dominate depends on the atomic number $Z$ of the material. The probability of a photoelectric interaction decreases with increasing photon energy and increases with $Z$. If the incident photon is energetic enough to emit an electron from the K-shell, then most (~80%) of the collisions are with K-shell electrons. In the photoelectric process, the incident photon energy is completely absorbed by the emitted electron (photoelectron). If a K-shell electron is ejected, then an L-shell electron will occupy into the available lower energy state. Depending on the value of $Z$, either a characteristic X-ray or a low-energy Auger electron is emitted from the L-shell.

In contrast to the photoelectric effect, Compton scattering does not involve complete absorption of the incident photon. In Compton scattering, the photon energy is much greater than the binding energy of atomic electrons (such as those in the K-shell). The incident photons give up a portion of its energy to scatter an atomic electron thereby creating an energetic Compton electron and the lower energy photon continues to travel in the target material. As the photon energy increases, Compton scattering dominates over photoelectric effect. The third type of photon interaction namely, pair production has threshold energy of 1.02 MeV. At this energy, a photon striking a high $Z$ target will be completely absorbed and results in a positron-electron pair production.

**Transient radiation effects**

Transient radiation effects are the manifestations of the interactions of radiation with matter associated with the excitation (including ionization) and de-excitation of electrons. These are temporary effects in ceramic materials and they usually produce significant changes only in the electrical properties of the materials. The ionization effects are caused by electrons created via photon or other charged particle interaction. The effects are
proportional to dose rate or dose of the radiation pulse [20]. Transient effects are significant when materials receive high dose rate.

**Displacement effects**

The displacement effects usually involve the following occurrences.

(a) A fast nuclear particle entering a material makes a close collision with the nucleus of an atom, imparting to it sufficient energy to displace the atom from its lattice site.

(b) The displaced atom moves through the solid losing energy in collisions with other atoms and displaced atoms eventually occupies interstitial sites and comes to rest.

(c) The lattice defects so formed may be thermally unstable even at room temperature. Some of them may anneal either annihilating the defect entirely or forming a secondary defect.

(d) The defects influence various macroscopic physical properties, which lead to change in the electrical properties of the material.

If the primary radiation is charged (for example high-energy \( \beta \)-particles or electrons, protons and deuterons), the interaction between the particle and the atom produces a displacement of the atom usually via the coulomb electrostatic force between the nuclear charge of the atom and the moving particle [21].

Gamma rays interact with atoms by first generating electrons through the photoelectric, Compton or pair-production processes. These secondary electrons produce the atomic displacements. High energy (10 MeV) \( \gamma \)-rays can also produce some displaced atoms as recoils from photo nuclear reactions. These may cause permanent damage to crystal structure in ceramic materials.
**Total dose effects**

High energy particles like gamma photon and charged light particles like β-particle or electron impinging on a material generate electron-hole pairs in the material along their tracks. A fraction of these pairs will recombine, but a fraction will be separated by the electric field. Percentage of non-recombined charges depends on the kind of radiation and material. Following the creation, electrons and holes transport under the applied electric field. These charges will cause total ionizing dose damage. The total dose $D$ is defined as the mean energy absorbed $\Delta E_d$ per unit mass $\Delta m$ of irradiated material [22].

**2.4.2 Radiation induced thermoluminescence**

From the point of view of TL dating, exposure to ionizing radiation has two important consequences:

(i) Generation of radiation induced defects (both electron and hole traps) and

(ii) Generation of free electrons and holes created in the conduction band and the valence band respectively.

As long as the concentration of radiation induced defects is small, the number of defects usually increases with increasing radiation dose. Ultimately, for very high doses, one might expect that the concentration of the radiation induced defects saturates. i.e., with increasing dose the concentration of radiation induced defects reaches a maximum value. The continuous production of free electrons and holes as a result of the exposure to ionizing radiation is essential for the production of sufficiently stable defects leading to TL. Due to the high mobility, free electrons and holes can migrate in the crystal until they are trapped by impurities, luminescent centers and other imperfections in the crystal. During irradiation the electrons and holes are redistributed continuously over the available electron...
and hole traps. A necessary condition for a material to be a suitable as a luminescent material for TL dating is that the relevant traps should be deep, i.e., not easily emptied. This implies that the energy of the trapped electron should be located sufficiently far from the bottom of the conduction band. Similarly, the energy of the trapped hole should be located sufficiently far from the top of the valence band [23].

2.5 Measurement techniques

This section describes the instruments and experimental techniques employed for the measurement of dielectric, electrical and luminescent properties of the CaSiO$_3$ ceramic samples. The instruments and experimental techniques used for the characterization of the CaSiO$_3$ samples viz., powder X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), Fourier Transform Infrared Spectroscopy (FTIR) are also briefly describes in the following sections.

2.5.1 Measurement of dielectric parameters

Dielectric measurements are made in the frequency range 50 Hz to 5 MHz at room temperature using a Hioki impedance analyzer 3532-50 (JAPAN), available in the Department of Physics, Gulbarga University. For measurements of dielectric parameters, the samples are pressed into pellets of diameter 5 mm and thickness 2 mm. A specially made stainless steel die and a hydraulic press are used for pellet making. The samples are coated with silver paste for better electrical contact and placed between the electrodes of the impedance analyzer. The samples holder in dynamic vacuum during the course of the measurements eliminates the moisture contamination. The impedance analyzer used is a completely automated system and records the values of impedance ($Z$), phase angle ($\Phi$),
parallel capacitance ($C_p$) and Dissipation factor ($D$) as a function of frequency in the desired range. The values of Dielectric constant ($\varepsilon'$), dielectric loss ($\varepsilon''$), loss tangent ($\tan\delta$), Dielectric ac conductivity ($\sigma_{ac}$), real and imaginary parts of Impedance ($Z'$ and $Z''$) and Electric modulus ($M'$ and $M''$) of the samples are evaluated (as described in Chapter 1) using the following equations. The parallel resistance ($R_p$) and the required dielectric parameters $\varepsilon'$, $\varepsilon''$, $\tan\delta$, $\sigma_{ac}$, $Z'$, $Z''$, $M'$ and $M''$ are calculated using following formulae.

\[
R_p = \frac{Z}{\left(1 + \left(\frac{\varphi \times \frac{3142}{180}}{\varepsilon''}\right)^2 \right)^\frac{1}{2}}
\]

\[
\rho = R_p \times \frac{A}{t}
\]

where $R_p$, $\rho$, $t$ and $A$ are the parallel resistance, resistivity, thickness and area of cross section of the sample respectively.

**Conductivity:**

\[
\sigma = \frac{1}{\rho}
\]

**Permittivity:**

Real

\[
\varepsilon' = \frac{C_p \times t}{\varepsilon_0 \times A}
\]

Imaginary

\[
\varepsilon'' = D \times \varepsilon'
\]

**Impedance:**

Real

\[
Z' = \text{Mod} \ Z (\cos\phi)
\]

Imaginary

\[
Z'' = \text{Mod} \ Z (\sin\phi)
\]

**Electric modulus:**

\[
M' = \frac{\varepsilon'}{\varepsilon''^2 + \varepsilon'^2}
\]

\[
M'' = \frac{\varepsilon''}{\varepsilon'^2 + \varepsilon''^2}
\]
where $M'$ and $M''$ are the real and imaginary parts of Electric modulus respectively.

The real part of dielectric constant and $\tan \delta$ are plotted as a function of frequency. The ac conductivity values are obtained from the resistivity values and plotted as a function of frequency. Similarly, the real part of the impedance is plotted as function a function of imaginary part to get Cole-Cole plot. Real and imaginary parts of electric modulus are plotted to obtain information about contribution of grains and grain boundaries to dielectric conductivity.

### 2.5.2 Measurement of photoluminescence and Thermoluminescence

The basic instrumental requirements for measuring fluorescence are (i) light source, (ii) light dispersing element, (iii) light detector, (iv) excitation monochromator, (v) emission monochromator and (vi) photomultiplier tube. Photoluminescence (PL) measurements are made using a Spectroflourimeter (Flourolog-3, Model FL3-11). Thermoluminescence measurements are made using a TSL analyser (TL 1007). Powder samples of CaSiO$_3$ are used for both photoluminescence and thermoluminescence studies.

Optically stimulated Luminescence (OSL) is measured by OSL reader, which is similar to TSL reader. OSL is an advanced technique of measuring the radiation dose through luminescence dosimetry. This is similar to TSL except that in OSL, heat is used to detrapping the charge carriers. On the other hand, in OSL light (from LED) is used to detrapping the charge carriers. Compared to TSL, the efficiency of OSL is high since the application of heat generally reduces the luminescence intensity. For the purpose detrapping, either a blue LED or red LED can be used depending upon the stimulabilty of the trap. In our case, a blue LED is used for optical stimulation to detrapping the charge carriers.
2.5.3 Gamma ray irradiation facility

For γ-ray induced studies, Co$^{60}$ γ-ray irradiation facility (Blood Irradiator-2000) available at ISRO Satellite Centre (ISAC), Bangalore has been utilized. The Blood Irradiator-2000 is a compact, portable, self-shielded type Cobalt-60 γ-ray irradiator. The unit is designed to house Cobalt-60 source of 675 Ci and provides irradiation volume of about 2000 cc approximately. The doubly encapsulated sealed radioactive source is used in cylindrical form which are completely contained in a dry container called flask unit. The sealed sources are shielded at all times, making it human inaccessible. The irradiation chamber is located in a vertical shaft (Drawer). The shaft moves up and down with the help of a drive system, which enables exact positioning of the irradiation chamber in the center of the radiation field. Access holes of 8 mm diameter are provided in the vertical shaft for introduction of connecting wires for electrical parameter measurements and thermocouple sensors etc. for temperature measurement inside irradiation zone.

Specifications of the γ-irradiator (Blood irradiator 2000) are

(i) Cobalt-60 source capacity: 675 Ci
(ii) Dose rate at maximum capacity at the time of installation: 9.23 Gy/min
(iii) Irradiation volume: 2000 cc approximately
(iv) Energy of $^{60}$Co γ-photon: 1.17 MeV & 1.30 MeV

For irradiation of the ceramic samples by β-particles, $^{90}$Sr β-source of capacity 50 milli Ci. is used for irradiation.
2.5.4 Characterization techniques

Powder X-ray diffraction

In general, X-ray diffraction technique is used to determine the atomic arrangement (i.e., crystal structure) of solids since the inter-planar spacing (d-spacing) of the diffracting planes is of the order of X-ray wavelength. For a crystal of given d-spacing and wavelength \( \lambda \), the various orders of reflection occurs only at the precise values of angle \( \theta \) which satisfies the Bragg condition, \( 2d \sin \theta = n\lambda \). The determination of inter-planar spacing, lattice parameters and \( hkl \) values etc. provide a basis for the understanding of the structure of the solids. In the present work, powder X-ray diffractometer (Phillips X’pert) using CuK\( \alpha \) radiation (\( \lambda = 0.15405 \) nm) with a Ni-filter was used to record the powder diffractograms to characterize the ceramic powders. The diffraction peaks were recorded over a wide range of angles (\( 10^\circ \leq 2\theta \leq 70^\circ \)) at a scan rate of \( 2^\circ /\text{m} \).

SEM and TEM

The surface morphology and size distribution of the grains were examined by Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM). A Philips (XL30-ESEM) instrument was used to record SEM photographs. A JEM 2000 Ex instrument was used for Transmission Electron Microscopy.

FT IR

Infrared spectroscopy is usually used for the identification of the functional groups in materials. The various functional groups or constituent units in the compound give rise to characteristic vibrational bands in the IR spectrum in the specific wavelength region. In the
present study an Alpha Bruker FTIR spectrometer has been used to record the IR spectra of the investigated ceramic powders.

**Thermal Analysis**

The thermal analysis of CaSiO$_3$ powder was carried out using TGA/SDTA 851° analyzer in Indian Institute of Science. The experiment yielded the loss in mass as a function of temperature from which crystallization data of the sample was obtained.
2.6 References

[16] Cees Ronda, Luminescence From Theory to Applications

[22] Short Course Report 3rd European Symposium, Radiations and their effects on Components and Systems, Aracachon, France, 1995