CHAPTER 1

INTRODUCTION

1.1 General Background:

Rapid technological advances along with faster and efficient communication medium have not only opened up plethora of opportunities for engineers and scientists but also thrown up immense challenges in various fields of science and engineering. Extensive research over the years in physics and chemistry of solids has paved way for greater understanding of properties of solids. A larger section of material scientists are involved in research and development of ceramics for device applications namely sensors, actuators, computer memory and display, microwave devices etc. In this regard mixed oxide ceramics have always been an attractive proposition. Ceramics, previously used only in applications such as insulators and filler materials are now extensively being used in device application owing to,

- cost effectiveness
- easy of fabrication
- scope to improve material properties with desired composition variation
- mechanical strength
- chemical and radiative resistance

Amongst the members of ceramic family of materials, most interesting group that has attracted scientists is the oxygen octahedral type dielectrics/ferroelectrics.

The basic difference between the dielectric and that of conductors in relation to electrical properties is dielectrics offer very high resistance to the passage of current through them compared to conductors. In order to get the clear idea of the dielectric materials, it is necessary to study all the physical phenomena, which occur in dielectrics placed in an electromagnetic field and the parameters of dielectrics, which quantitatively determine their electrical properties. However, to check suitability for the device applications of dielectric materials, it is required to know not only their electrical properties but also their physical and chemical properties, such as mechanical strength, elasticity, resistance to temperature, thermal conductivity, hygroscopicity, stability to chemical reagents and solvents, radiation stability, environmental friendly or not and many other parameters. Studies of the electrical and other properties of dielectrics in relation to their chemical composition and structure are significant in derivation of new materials.

All dielectrics, which are crystalline in nature, in which polarization or electric displacement can be induced by the application of suitable electric field are broadly divided into two types:

- polar
- non-polar dielectrics

In polar dielectrics, a finite and permanent polarization known as spontaneous polarization (P_s) exists even in absence of an applied electric field. Where as in case of non-polar dielectrics, no permanent or spontaneous polarization exists in the absence of an electric field.

Ferroelectric materials, which are of great importance from the application point of view, are the polar types. In bulk form these materials have high permittivity and large electromechanical coupling coefficients and show pyroelectric, piezoelectric and electro-optic properties. This class of materials has a wide variety of applications, such as multilayer capacitors, optical shutters and modulators, computer memory and display, piezoelectric detectors, ferroelectric random access memory (FRAM), etc. Significant advantages of thin film ferroelectric memories integrated on to semiconductors would be: (i) high bit density (ii) non-volatile low-voltage operation over a wide range of temperature (iii) random access read/write cycles (iv) low power requirements and (v) resistance to radiation effect than semiconductor or magnetic memories.

The spontaneous polarization of a polar material results from an inherent symmetry within the unit cell of the crystal. This symmetry gives rise to ionic and/or electronic forces, which produce elemental dipole moments. When interaction of any two dipoles differs markedly according to the state of orientation of the other dipoles, a state of co-operation exists. The surrounding dipoles can be represented by a single parameter, which deals the overall polarization. Because of the co-operative effects the addition of dipole moments gives a finite and permanent polarization. Any change in the temperature of the polar dielectric, affects the ionic or electronic forces within the basic crystal cell and the extent of thermal disorganization, which results in a change in the values of dipole moments of the polar material. In certain polar materials, the direction of the spontaneous polarization can be changed by the application of suitable electric field. In most of the polar materials, 180^{o} reversal of the direction of the polar axis takes place, but in some materials the polar axis reorient by less than 180^{o}. Valasek [1] in 1920 was the first to demonstrate the reversal of the direction of spontaneous polarization by the application of suitable electric field with the help of dielectric hysteresis loop in certain materials for a relatively short time. These materials have been termed as ferroelectric materials [2-4]. Phenomenologically, the ferroelectricity is much in semblance with ferromagnetism.

1.2 Ferroelectrics:

On the basis of crystal structure of ferroelectrics a necessary, but not a sufficient condition for a solid to be ferroeelctric is the absence of center of symmetry [5]. Ferroelectrics are mainly the sub-group of pyroelectrics in which the polarization can be reversed or re-oriented by applying an electric field for a short time in the appropriate direction. The spontaneous polarization of the ferroelectric materials disappears at a particular temperature, which is usually defined as transition or Curie temperature, T_c [6]. The material above this temperature is in the paraelectric state. The paraelectric state is the more ordered state than ferroelectric state. Ferroelectric materials also possess anomalous (non-linear) elastic, calorimetric and thermal properties, like hysteresis loop, dielectric constant (ε) and dielectric loss ($\tan\delta$), which too are distinguishing properties of ferroelectrics along with polarization. The dielectric constant of polar materials varies with applied field, frequency, stress, temperature and other parameters [7]. The ε value is maximum at T_c. Above T_c, thermal variation of ε obeys the Curie-Weiss law, $\varepsilon = \varepsilon_o + C/(T - T_c)$, where ε_o is a constant (electronic contribution independent of temperature) and C is the Curie constant.

It is found that at T_c, ferroelectrics undergo a structural change, which can be expressed in terms of structural symmetry. The properties of ferroelectric materials are very sensitive to composition, dopants and defects, grain size, porosity and as well as poling [8]. In general, dielectric and mechanical properties of ferroelectric crystals below their T_c are functions of the state of polarization and stress. Because of the numerous and very significant properties exhibited by ferroelectric materials in the form of a single crystal, thin film and/or bulk ceramics they find major applications in modern technology.

1.3 Phase Transition:

The change in structure of many dielectric/ferroelectric crystals with temperature without affecting its chemical composition is known as phase transition. Phase transition in crystals is due to changes in the forces of interaction between the atoms. As a result, the crystals can produce various new properties. If the spontaneous polarization of the crystal changes, then such a phase transition is termed as ferroelectric phase transition. The difference in crystal structure on either side of T_c may be large or small.

There are two types of phase transitions i.e. first and second order. In first order phase transition the change in structural parameters like atomic positions, thermal