CHAPTER-6

DIELECTRIC PROPERTIES OF SBN AND BNN CERAMICS

6.1 Introduction

This chapter focuses on the ferroelectric and dielectric properties of selected ferroelectric ceramics with tungsten bronze type structure. The dielectric properties and dissipation factor are discussed in terms of the effects of temperature and frequency. The important phenomena associated with ferroelectric materials such as dielectric constant, dissipation factor, polarization, phase transitions etc. are first introduced by giving basic definitions. A brief description of the experimental setup used is presented, along with the details of the dielectric cell, which was fabricated for temperature variation measurements.

6.2 Ferroelectric Ceramics

Ferroelectrics are polar materials that possess at least two equilibrium orientations of the spontaneous polarization vector in the absence of an external electric field, and in which the spontaneous polarization vector may be switched between those orientations by an electric field. Apart from the dependence of permittivity on electrical field intensity, the essential features of this class of dielectrics are the following:

(1) Hysteresis under the action of an alternating voltage: It is possible to obtain a loop of electric hysteresis for a ferroelectric.

(2) Very high value of permittivity $\varepsilon$. Thousands and even tens of thousands, in a number of cases have been reported.

(3) Pronounced dependence of dielectric parameters on temperature and the presence of ferroelectric properties only with in a definite range of temperatures.
(4) Presence of spontaneous polarization without an external electric field, usually acting on the ferroelectric.

A polycrystalline ceramic that has not been subjected to a static field behaves as a non-polar material, even though the crystals comprising it are polar. One of the most valuable features of ferroelectric behavior is that ferroelectric ceramics can be transformed into polar materials by applying a static field. This process is called 'poling'. The ceramic can be depoled by the application of appropriate electric fields or mechanical stresses.

The random directions of the crystallographic axes of the crystallites of a ceramic limit the extend to which spontaneous polarization can be developed. It has been calculated that the fractions of the single-crystal polarization value that can be attained in a ceramic in which the polar axes take all possible alignments are 0.83, 0.91 or 0.87 for pervokites with tetragonal, or orthorhombic or rhombohedral structures respectively. In ceramic tetragonal BaTiO₃ the saturation polarization is about half the single crystal value.

One very significant advantage of ceramic ferroelectrics is the ease with which their properties can be modified by adjusting the composition and the ceramic microstructure. Addition and substitution of alternative cations can have the following effects.
(1) Shift the Curie point and other transition temperatures.
(2) Restrict domain wall motion.
(3) Introduce second phases or compositional heterogeneity.
(4) Control crystal size.
(5) Control oxygen content.
Ferroelectric ceramics find applications in capacitors, infrared detection, sound detection in air and water, generation of ultrasonic energy, light switches, current controllers and small thermostatic devices. In all these cases some aspects of their ferroelectric activity have to be suppressed and others enhanced. A suitable compromise is achieved by a combination of composition and ceramic structure[1, 2].
6.3 Properties of Ferroelectrics

Most ferroelectric materials undergo a structural phase transition from a high temperature nonferroelectric (or paraelectric) phase to a low-temperature ferroelectric phase. The paraelectric phase may be piezoelectric or non-piezoelectric and is rarely polar. The symmetry of the ferroelectric phase is always lower than the symmetry of the paraelectric phase. The temperature of the phase transition is called the Curie point, $T_c$. Above the Curie point the dielectric permittivity falls off with temperature according to the Curie-Weiss law, given by:

$$\varepsilon = \varepsilon_0 + \frac{C}{T - T_0} \approx \frac{C}{T - T_0}$$  \hspace{1cm} (6.1)

where $C$ is the Curie constant and $T_0 (T_0 \leq T_c)$ is the Curie-Weiss temperature.

**Electrical Phenomena:** Here we define the dielectric properties that are of interest for ceramic applications. These include the dielectric constant, dielectric loss factor, dielectric resistivity and dielectric strength. Dielectric materials are extensively used as capacitors in electrical and electronic circuits. The principal characteristic of a capacitor is that an electrical charge $Q$ can be stored. The charge on a capacitor is

$$Q = CV$$  \hspace{1cm} (6.2)

where 'V' is the applied voltage and 'C' is the capacitance. The voltage is directly proportional to the charge stored, and the current passage through the capacitor is given by

$$V = \frac{Q}{C} = \int i dt \quad \text{Therefore} \quad i = C \frac{dV}{dt}$$  \hspace{1cm} (6.3)

With a sinusoidal voltage $V = V_0 \exp(i\omega t)$

(6.4)
as used in ac circuits, the charging current is given by

$$I_c = i\omega CV$$  \hspace{1cm} (6.5)

This is $90^\circ$ advanced in phase in relation to the applied voltage. Here $i = \sqrt{-1}$, and $\omega$ equals $2\pi f$, where $f$ is the frequency in cycles per second.

The capacitance 'C' contains both a geometrical and a material factor. For large plate capacitor of area 'A' and thickness 'd' the geometrical capacitance in vacuum is given by
\[ C_0 = \frac{A}{d} \varepsilon_0 \]  

(6.6)

where \( \varepsilon_0 \) is the permittivity of vacuum. If a ceramic material of permittivity \( \varepsilon' \) is inserted between the capacitor plates,

\[ C = C_0 \frac{\varepsilon'}{\varepsilon_0} = C_0 \varepsilon_r \]

where \( \varepsilon_r \) is the relative permittivity or relative dielectric constant. This is the material property which determines the capacitance of a circuit element and is of principal concern to a ceramist.

### 6.3.1 Dielectric constant and dielectric loss

We know that the charge on a capacitor is given by

\[ Q = CV = \varepsilon_0 \varepsilon_r \frac{A}{d} V \]

(6.7)

where

\[ C = \varepsilon_0 \varepsilon_r \frac{A}{d} ; \]

\[ C_0 = \varepsilon_0 \frac{A}{d} \]

and

\[ \varepsilon_r = \frac{C}{C_0} = \frac{\varepsilon}{\varepsilon_0} \]  

(6.8)

In the expression above, 'A' represents area of the capacitor cell, 'd' its thickness, \( C_0 \) and \( C \) the respective air and material capacitance, \( V \) the voltage across the cell, and \( \varepsilon' \) the material permittivity. Thus \( \varepsilon_r \) represents the ratio of the permittivities or the charge stored in the capacitive cell relative to air or vacuum as dielectric. For the case of \( V \) being sinusoidal, equation (6.7) can be written as

\[ Q = C V_o \exp(\text{i} \omega t) \]

(6.9)

Therefore the current flow, on discharge of the capacitive cell in time 't' is,

\[ I = \frac{dQ}{dt} = i \omega CV \]

(6.10)

However, for a real dielectric the current 'I' has vector components \( I_c \) and \( I_r \), as shown in figure 6.1 for the condition of a lossy dielectric, represented by the circuit analog of a resistance in parallel a capacitor. The current \( I_c \) represents a (Wattless) capacitive current
proportional to the charge stored in the capacitor. It is frequency dependent and lead the voltage by \(90^0\). The current \(I_R\) is an ac conduction current in phase with the voltage \(V\), which represents the energy loss or power dissipated in the dielectric.

This condition can be represented by a complex permittivity or dielectric constant, in order to deal with the loss current, as follows.

\[
I = i\omega CV = i\omega C_0\varepsilon_0 \varepsilon_r V
= i\omega C_0\varepsilon_0 (\varepsilon' - i\varepsilon'') V
= i\omega C_0\varepsilon_0 \varepsilon' V + \omega C_0\varepsilon_0 \varepsilon'' V
= I_c + I_R
\]

From the magnitude of these currents, therefore, one can define a dissipation factor, \(\tan \delta\), as

\[
\tan \delta = \frac{|I_c|}{|I_c|} = \frac{\omega C_0\varepsilon_0 \varepsilon'' V}{i\omega C_0\varepsilon_0 \varepsilon' V} = \frac{\varepsilon''}{\varepsilon'}
\]

These vector relationships show the phase angle \(\phi\) as \((90 - \delta)^0\) and loss tangent, \(\delta\) representing the deviation from ideality of the lossiness in the dielectric.

Figure 6.1 Equivalent circuit diagram (a) Capacitive cell (b) Charging and loss current (c) Loss tangent for typical dielectric
The dielectric loss factor, $\varepsilon''$ is shown to be the product of the material parameters $\varepsilon'$ and $\tan\delta$. A quality factor $Q$, defined as,

$$Q = \frac{1}{\tan\delta} = \frac{Average\ energy\ stored\ per\ cycle}{Energy\ dissipated\ per\ cycle}$$  \hspace{1cm} (6.13)

is frequently used as a design parameter for dielectric usage [3].

6.4 The dielectric measurement setup

In this section we report the design and performance details of dielectric cum conductivity setup which has been installed in our lab for experimental measurements. In experimental solids state physics, we encounter systems where accurate determination of transition temperature is desirable. The dielectric constant and transition temperature of a sample is normally determined by measuring the capacitance of a capacitor with the sample as the dielectric.

A general Schematic diagram of a typical dielectric constant measurement system is shown in figure 6.2.

![Figure 6.2](image)

Figure 6.2 A general schematic diagram of the dielectric measurement set up.

6.4.1 Dielectric cell

The dielectric properties of ferroelectric ceramics have dependence on composition of the material, temperature, and frequency. In order to carry out these investigations, a versatile dielectric constant cum conductivity cell is designed and fabricated, the details of which are outlined below. A sketch of the cell is given in figure 6.3. Various parts of
the dielectric cell are listed in this figure. The dielectric cell mainly consists of an outer chamber and a sample holder.

In order to measure dielectric constant as a function of temperature, a high temperature and low temperature cell have been fabricated. Schematic diagrams of these cells are shown in Figure 6.3 (A and B). The high temperature dielectric cell consists of an outer chamber which is made of M. S. pipe of outer diameter 22 cm, thickness 10 mm and

![Diagram A](image)

(A)

![Diagram B](image)

(B)

**Figure 6.3** Schematic diagram of the dielectric cell (A) for high temperature measurements (B) Low temperature measurements

height 40 cm. M. S. flanges are welded at the top and bottom of this pipe. The flanges have 'O' ring grooves. The chamber is provided with a vacuum line which can be connected to a rotary pump so that the cell can be evacuated whenever necessary. External electrical connections to the cell are provided through a BNC connector and other connectors provided on the top of the plate of the chamber.
The sample holder, which is made of copper, is attached to an upper plate. Since copper is a good conductor with a high value for specific heat capacity, temperature gradients will be minimum across the sample holder. The heating coils are connected above the electrodes, with proper insulation with ceramic beads. The heating coil is then covered with ceramic wool in order to minimize the heat loss from the sample holder. The sample holder is thermally insulated from top plate by inserting thermal insulators between the connections.

The low temperature dielectric cell consists of additional windows on the outer chamber. A liquid nitrogen reservoir made of a stainless tube is welded at the center of the top line. The sample holder which is made of copper is attached to bottom of this reservoir. Since copper is a good thermal conductor with a high value for specific heat capacity, temperature gradients will be minimum across the sample holder. Both these cells have been calibrated by measuring dielectric constants of known samples like Fire 6.4

Figure 6.4 Shows the dielectric cell which was fabricated for dielectric measurements
perspex. Figure 6. 4 shows the dielectric measurement set up showing the dielectric cell, impedance analyzer and a diffusion pump for evacuating the cell.

6. 5 Experimental procedure

The solid solution ceramics of the strontium barium niobate (SBN), alkali, alkaline and rare earth modified SBN (SBN-La, SBN-KNa-La SBN-Li-Nd, SBN-LiEu) and barium sodium niobate (BNN) and BNN modified with neodymium ions were prepared by the method described in chapter-2. All the samples consist of tetragonal tungsten bronze type structure as identified by X-ray diffraction.

With regard to dielectric constant measurements, samples of disc-shape with thickness of about 1mm were used. Silver electrodes were deposited on the sample surfaces. The temperature dependence of both capacitance and dissipation factor were measured using a Hewlett-Packard 4129A impedance analyzer. The frequencies used in the measurement were between 100 Hz and 13 MHz. The level of signal was about 0.5 Vmm⁻¹ to ensure small-signal dielectric properties. Before the measurement, the samples were thermally heated at a temperature much higher than Tm to remove the effects of electrical history. The dielectric constant was calculated from the measured capacitance values. The temperature was measured using a digital temperature indicator with Chromel - Alumel thermocouple.

6. 6 Results and discussions

6. 6. 1 Dielectric studies on SBN ceramics

The measured temperature dependence of dielectric constant ε' for $\text{Sr}_{0.50}\text{Ba}_{0.50}\text{Nb}_2\text{O}_6$ (SBN-50), $\text{Sr}_{0.61}\text{Ba}_{0.39}\text{Nb}_2\text{O}_6$ (SBN-61), $\text{Sr}_{0.61}\text{Ba}_{0.39}\text{La}_{0.06}\text{Nb}_2\text{O}_6$ and $\text{Sr}_{0.61}\text{Ba}_{0.39}\text{La}_{0.1}\text{Nd}_2\text{O}_6$ samples at 1 MHz frequency are shown in figure 6. 5. Series 1 shows the variation of ε' with temperature for $\text{Sr}_{0.50}\text{Ba}_{0.50}\text{Nb}_2\text{O}_6$. Here the peak shows a diffuse nature. Series 2 shows the behavior of SBN-60, were the phase transition shifts to low temperature region and the dielectric peak broadens. Series 3 and series 4 show the behaviour of lanthanum modified samples. The introduction of lanthanum shifts the dielectric peak to low temperature region and a diffuse dielectric peak results.
Figure 6.5 Temperature dependence of dielectric constant for Sr_{0.5}Ba_{0.5}Nb_2O_6, Sr_{0.61}Ba_{0.39}Nb_2O_6, Sr_{0.61}Ba_{0.39}La_{0.06}Nb_2O_6 and Sr_{0.61}Ba_{0.39}La_{0.1}Nb_2O_6 shown in series 1, series 2, series 3 and series 4 respectively.

Figure 6.6 Temperature dependence of dissipation factor for Sr_{0.5}Ba_{0.5}Nb_2O_6, Sr_{0.61}Ba_{0.39}Nb_2O_6, Sr_{0.61}Ba_{0.39}La_{0.06}Nb_2O_6 and Sr_{0.61}Ba_{0.39}La_{0.1}Nb_2O_6 shown in series 1, series 2, series 3 and series 4 respectively.
The measured temperature dependence of the dissipation factor of the above samples at 1MHz frequency is shown in figure 6.6. The dissipation at room temperature is lowest for $\text{Sr}_{0.61}\text{Ba}_{0.39}\text{La}_{0.06}\text{Nb}_2\text{O}_6$, where as it is highest in SBN-60, which are plotted as series 2 and series 3 respectively. It is interesting to note that the dissipation shows peaks corresponding to the dielectric maximum temperature in all the samples.

The variation of dielectric constant $\varepsilon_r$ with frequency for the above samples in the measuring range 100 Hz-13 MHz is shown in figure 6.7. The dielectric constant decreases rapidly in low frequency region, then decreases very slowly up to 5 MHz. The variation of $\varepsilon_r$ in SBN-61 is rapid in comparison to other three compositions. This frequency dependent behavior confirms the presence of all types of polarization (electronic, ionic, dipolar and interfacial) at lower frequencies.

The measured frequency dependence of the dissipation factor in the high frequency region (>5MHz) is shown in figure 6.8. The dissipation factor remains below 0.15 for SBN-61, SBN-La$_{0.06}$, SBN-La$_{0.1}$ below 5MHz, where as at higher frequencies it increase rapidly. Series 1 shows the variation of dissipation factor of SBN-50 with frequency.

The steep increase of dielectric constants seen in the very high frequency region (above 5 MHz) are due to effects of an inductance (L) and a small resistance (R) which may derive from the measuring system and are unconnected with the specimen itself. So in the other samples we are limiting the measurement below 7MHz. When the specimen temperature is far below the phase transition region, the frequency dependence of the dielectric constants are explained by an equivalent R-C-Y* circuit with a single relaxation process as shown in figure 6.5 while another process appear when the temperature is raised near to phase transition region whose equivalent circuit is shown in figure 6.5 (B). [Here $Y^*$ is the frequency dependent admittance device $Y^* = A\omega^n + jB\omega^m$, where $B = A \tan(\pi/2)$]. The two C-R-Y* branches in the equivalent circuit indicate the presence of two relaxation processes in the specimen.
Figure 6.7 Frequency dependence of dielectric constant for Sr$_{0.5}$Ba$_{0.5}$Nb$_2$O$_6$, Sr$_{0.61}$Ba$_{0.39}$Nb$_2$O$_6$, Sr$_{0.61}$Ba$_{0.39}$La$_{0.06}$Nb$_2$O$_6$ and Sr$_{0.61}$Ba$_{0.39}$La$_{0.1}$Nb$_2$O$_6$ shown in series 1, series 2, series 3 and series 4 respectively.

Figure 6.8 Frequency dependence of dissipation factor for Sr$_{0.5}$Ba$_{0.5}$Nb$_2$O$_6$, Sr$_{0.60}$Ba$_{0.40}$Nb$_2$O$_6$, Sr$_{0.61}$Ba$_{0.39}$La$_{0.06}$Nb$_2$O$_6$ and Sr$_{0.61}$Ba$_{0.39}$La$_{0.1}$Nb$_2$O$_6$ shown in series 1, series 2, series 3 and series 4 respectively.
Figure 6. 9 shows the equivalent circuit for (A) below the phase transition (B) near the phase transition region.

The fitting between the experimental and calculated results are quite good, in the study of Tantalum bearing strontium barium niobate (Sr$_{0.5}$Ba$_{0.5}$Nb$_{2-x}$Ta$_x$O$_6$ with $x = 0.2$)[4]. There may be a possibility of finding another solution with different parameters, since the refinements of parameters are difficult because of the correlation between the parameters. But it is evident from the analysis that at least two relaxation processes, the first process below the phase transition region and the second in the transition region, occur in diffuse phase transition (DPT) of Sr$_{0.3}$Ba$_0.5$Nb$_{2-x}$Ta$_x$O$_6$. The peak frequency of first process is independent of temperature, while that of the second one increases with temperature.

Figure 6. 10 shows the measured temperature dependence of dielectric constant at 1 MHz. Series 1, which correspond to Sr$_{0.61}$Ba$_{0.39}$Na$_{0.12}$K$_{0.14}$La$_{0.06}$Nb$_2$O$_6$, does not show any phase transition in the measured range (30-400 °C). The dielectric constant decreases slowly up to 325 °C and then it starts increasing rapidly. Series 2 corresponding to Sr$_{0.61}$Ba$_{0.39}$Na$_{0.12}$K$_{0.14}$La$_{0.08}$Nb$_2$O$_6$ shows a peak at 225 °C, then decreases rapidly and shows a minimum at 330 °C; then it rapidly increases over the higher temperature region. Series 3 shows the variation of $\varepsilon_r$ for Sr$_{0.61}$Ba$_{0.39}$Na$_{0.14}$K$_{0.12}$La$_{0.01}$Nb$_2$O$_6$. It shows a broad peak around 120 °C then decreases slowly, shows a minimum value at 310 °C then gradually increases. The increase of lanthanum content shifts the phase transition to lower
Figure 6.10: Temperature dependence of dielectric constant for $\text{Sr}_{0.61}\text{Ba}_{0.39}\text{Na}_{0.12}\text{K}_{0.14}\text{La}_{0.06}\text{Nb}_2\text{O}_6$, $\text{Sr}_{0.61}\text{Ba}_{0.39}\text{Na}_{0.12}\text{K}_{0.14}\text{La}_{0.08}\text{Nb}_2\text{O}_6$ and $\text{Sr}_{0.61}\text{Ba}_{0.39}\text{Na}_{0.12}\text{K}_{0.14}\text{La}_{0.06}\text{Nb}_2\text{O}_6$ corresponding to series 1, series 2 and series 3 respectively.

Figure 6.11: Temperature dependence of dissipation factor of $\text{Sr}_{0.61}\text{Ba}_{0.39}\text{Na}_{0.12}\text{K}_{0.14}\text{La}_{0.06}\text{Nb}_2\text{O}_6$, $\text{Sr}_{0.61}\text{Ba}_{0.39}\text{Na}_{0.12}\text{K}_{0.14}\text{La}_{0.08}\text{Nb}_2\text{O}_6$ and $\text{Sr}_{0.61}\text{Ba}_{0.39}\text{Na}_{0.12}\text{K}_{0.14}\text{La}_{0.06}\text{Nb}_2\text{O}_6$ corresponding to series 1, series 2 and series 3 respectively.
temperature side. Another significant result is the peak broadening with increase in lanthanum concentration.

Figure 6. 11 shows the variation of dissipation factor with temperature at 1MHz frequency for the above lanthanum modified samples. The dissipation factor is small below 300 °C and over higher temperature it increases rapidly. The temperature dependent behavior is similar for all samples.

Figure 6. 12 shows the measured frequency dependence of dielectric constant for the above three samples. The dielectric constant slowly decreases as frequency is increased. Above 5 MHz it shows complex behaviour. Similarly figure 6. 13 shows the frequency dependence of dissipation factor for (SBN)Nak-La0.06, SBN-NaK-La0.08, SBN-NaK-La0.1 samples. For medium frequencies till 500 KHz it remain below 0.2, but at higher frequency range the behavior is complex.

Figure 6. 14 shows the temperature dependence of dielectric constant for [Sr0.61Ba0.39]4-2x
Li2+x Nd3xNb10O30 system at 1 MHz. Series 1 corresponds to x = 0.1. The curve shows a peak around 205 °C. The phase transition region covers a wide temperature region. Series 2 corresponds to the composition with x = 0.2. Here the peak value increases, but with a shift in the whole pattern towards low temperature side. The room temperature dielectric constant increases. The dielectric maximum is more diffuse in nature. As the concentration of Neodymium increases (ie. x = 0.3, 0.4 and 0.5) the transition temperature decreases. The dielectric maximum peak becomes more diffuse and it becomes nearly flat for x = 0.4 and 0.5 as shown for series 4 and series 5. Another significance is the decrease in room temperature dielectric constant.

In the well known compositional inhomogeneities/fluctuations model of Smolensky [5], Smolensky and Isopov [6] and Kirillov and Isupov, [7], different micro regions on a scale of a few hundred to a few thousand angstroms in the sample are believed to possess different Tc's because of compositional variations from one micro region to another. A broad envelop of these local transitions, which are assumed to be sharp, may lead to diffuse phase transitions in this system. Diffusion of ferroelectric phase transition exists in such ferroelectrics where the equivalent site in the crystal lattice are occupied by different types of ions. In the above composition fluctuation model it has
Figure 6.12 Frequency dependence of dielectric constant for $\text{Sr}_{6.61}\text{Ba}_{0.39}\text{Na}_{0.12}\text{K}_{0.14}\text{La}_{0.06}\text{Nb}_2\text{O}_6$, $\text{Sr}_{6.61}\text{Ba}_{0.39}\text{Na}_{0.12}\text{K}_{0.14}\text{La}_{0.06}\text{Nb}_2\text{O}_6$, and $\text{Sr}_{6.61}\text{Ba}_{0.39}\text{Na}_{0.12}\text{K}_{0.14}\text{La}_{0.06}\text{Nb}_2\text{O}_6$ corresponding to series 1, series 2 and series 3 respectively.

Figure 6.13 Frequency dependence of dissipation factor for $\text{Sr}_{6.61}\text{Ba}_{0.39}\text{Na}_{0.12}\text{K}_{0.14}\text{La}_{0.06}\text{Nb}_2\text{O}_6$, $\text{Sr}_{6.61}\text{Ba}_{0.39}\text{Na}_{0.12}\text{K}_{0.14}\text{La}_{0.06}\text{Nb}_2\text{O}_6$, and $\text{Sr}_{6.61}\text{Ba}_{0.39}\text{Na}_{0.12}\text{K}_{0.14}\text{La}_{0.06}\text{Nb}_2\text{O}_6$ corresponding to series 1, series 2 and series 3 respectively.
Figure 6.14 Temperature dependence of dielectric constant for $[\text{Sr}_{0.6}\text{Ba}_{0.39}]_2 \text{Li}_{2+x}\text{Nd}_x\text{Nb}_{10}\text{O}_{30}$ with $x = 0.1, 0.2, 0.3, 0.4, 0.5$ corresponding to series 1, series 2, series 3, series 4 and series 5 respectively.

Figure 6.15 Temperature dependence of dissipation factor for $[\text{Sr}_{0.6}\text{Ba}_{0.39}]_2 \text{Li}_{2+x}\text{Nd}_x\text{Nb}_{10}\text{O}_{30}$ with $x = 0.1, 0.2, 0.3, 0.4, 0.5$ corresponding to series 1, series 2, series 3, series 4 and series 5 respectively.
been proposed that the diffusion is due to a compositional inhomogeneity in the crystal where domains with different compositions have different Curie temperatures. The peculiarity of these ferroelectrics is the relaxation of dielectric polarization. The relaxation polarization of lead magnesium niobate (PMN) has been interpreted by the compositional fluctuation model as a relaxation of isolated polar regions surrounded by nonolar regions, and assume a distribution of relaxation times to explain the complex dielectric constant in the phase transition region. Another peculiarity of ferroelectrics with DPT is that the Curie-Weiss law is not valid in these ferroelectrics above the temperature of maximum $\varepsilon'$ but $\varepsilon'(T)$ fits the equation $1/\varepsilon' - 1/\varepsilon'_{\text{max}} = A(T-T_0)^\gamma$, with $1 < \gamma < 2$ [8]. The deviation from the Curie-Weiss law was also apparently explained by assuming that the local Curie temperature of the domains possess a Guassian distribution. Another model presented by Burn et at. [9, 10] in which local variations from one unit cell to next are important rather than the macroscopic compositional fluctuations.

Figure 6.15 shows the temperature dependence of dissipation factor for $[\text{Sr}_{0.61}\text{Ba}_{0.39}]_{4-2x}\text{Li}_{2+x}\text{Nd}_x\text{Nb}_{10-0.30}$. The dissipation factor remains low (less than 0.2) in the measured temperature region for all samples. The first two samples of the system show a decreasing trend above 150 °C, which is plotted as series 1 and series 2. For other samples with high neodymium content it remains steady up to 200 °C and then increases in the higher temperature region.

Figure 6.16 and 6.17 show the frequency dependence of the dielectric constant and dissipation factor for the above system respectively. The dielectric constant decrease steeply in the 100 Hz - 500 KHz frequency region and then increases slowly above 2 MHz to the higher frequency region.

Figure 6.18 shows the temperature dependence of dielectric constant for $[\text{Sr}_{0.61}\text{Ba}_{0.39}]_{4-2x}\text{Li}_{2+x}\text{Eu}_x\text{Nb}_{10-0.30}$ system at 1 MHz. Series 1 corresponds to $[\text{Sr}_{0.61}\text{Ba}_{0.39}]_{3.8}\text{Li}_{2.1}\text{Eu}_{0.1}\text{Nb}_{10-0.30}$ composition. The curve shows a peak around 180 °C. The phase transition covers a broad temperature region and is diffuse. Series 2 represents the curve for $[\text{Sr}_{0.61}\text{Ba}_{0.39}]_{3.6}\text{Li}_{2.2}\text{Eu}_{0.2}\text{Nb}_{10-0.30}$. Here the peak value decreases with a shift in the whole transition region towards low temperature side. The room temperature dielectric constant is highest for this composition in this system. With increased Europium Concentration
Figure 6. 16 Frequency dependence of dielectric constant of \([\text{Sr}_{0.61}\text{Ba}_{0.39}]_4\text{Li}_{2-x}\text{Nd}_x\text{Nb}_{10}\text{O}_{30}\) with \(x = 0.1, 0.2, 0.3, 0.4, 0.5\).

Figure 6. 17 Frequency dependence of dissipation factor for \([\text{Sr}_{0.61}\text{Ba}_{0.39}]_4\text{Li}_{2-x}\text{Nd}_x\text{Nb}_{10}\text{O}_{30}\) with \(x = 0.1, 0.2, 0.3, 0.4, 0.5\) corresponding to series 1, series 2, series 3, series 4 and series 5 respectively.
the transition region become more diffuse and broader and covers a wide range of
temperature as plotted for series 3 and series 4. Another significance is the decrease in
room temperature dielectric constant.

Figure 6.19 shows the temperature dependence of dissipation factor for \([\text{Sr}_{0.61}
\text{Ba}_{0.39}]_4 - 2x \text{Li}_{2+x} \text{Eu}_x \text{Nb}_{100-x}\). The dissipation factor does not show much variation and
remain low (less than 0.15) in the measured region.

Figure 6.20 shows the frequency dependence of the dielectric constant for the
above system. The dielectric constant decrease steeply in the 100 Hz - 500 KHz range,
then decreases very slowly over the higher frequency range as plotted for series 1,
series 2, series 3 and series 4.

Similarly Figure 6.21 shows the frequency dependence of the dissipation factor
for \((\text{Sr}_{0.66}\text{Ba}_{0.39})_4 - 2x \text{Li}_{2+x} \text{Eu}_x \text{Nb}_{100-x}\) system. The dissipation decreases very steeply in the
0-100 Hz range, then decrease very slowly over high frequency region. An exception is
the this is series 4, composition with \(x = 0.5\), where it increase slowly over high
frequency region.

6. 6. 2 Dielectric studies of barium sodium niobate ceramics

Though some studies have been reported on \(
\text{Ba}_2\text{Na}_3\text{RNb}_{10}\text{O}_{30} (R=\text{La}, \text{Y}, \text{Gd}, \text{Eu}, \text{Dy}) [11] \)
and \(
\text{Ba}_2\text{Na}_2\text{Nb}_{10}\text{O}_{30} [12] \) earlier, no work has so far been reported on \(
\text{BaNaRNb}_{10}\text{O}_{30} \)
(R=Nd) compositions. Further, it has been observed that the size of the substituted ion
has significant effect on the disorderness of the structure [13] and diffuseness of the
phase transition in this composition. In view of the importance of the materials and non-
availability of ferroelectric data, we have carried out studies on structure and dielectric
properties of \(
\text{Ba}_{3-2x}\text{Na}_{4+x}\text{Nd}_x\text{Nb}_{10}\text{O}_{30} \)
ceramics.

Figure 6.22. show the variation of dielectric constant with temperature at 1MHz
for (1) \(
\text{Ba}_2\text{Na}_4\text{Nb}_{10}\text{O}_{30} \), (2) \(
\text{Ba}_3\text{Na}_4\text{Nb}_{10}\text{O}_{30} \), (3) \(
\text{Ba}_{2.6}\text{Na}_{4.2}\text{Nd}_{0.2}\text{Nb}_{10}\text{O}_{30} \), (4)
\(
\text{Ba}_{2.2}\text{Na}_{4.4}\text{Nd}_{0.4}\text{Nb}_{10}\text{O}_{30} \), (5) \(
\text{Ba}_2\text{Na}_{4.5}\text{Nd}_{0.5}\text{Nb}_{10}\text{O}_{30} \), (6) \(
\text{Ba}_{1.8}\text{Na}_{4.6}\text{Nd}_{0.6}\text{Nb}_{10}\text{O}_{30} \), and (7)
\(
\text{Ba}_{1.4}\text{Na}_{4.8}\text{Nd}_{0.8}\text{Nb}_{10}\text{O}_{30} \). For the pure BNN samples BNN-1 and BNN-2, the
compositional variation does not alter the dielectric constant significantly. The presence
of neodymium in \(
\text{Ba}_{2.6}\text{Na}_{4.2}\text{Nd}_{0.2}\text{Nb}_{10}\text{O}_{30} \) increases the room temperature dielectric
Figure 6. 18 Temperature dependence of dielectric constant for [Sr_{0.61}Ba_{0.39}]_{4-2x}Li_{2+2x}Eu_{x}Nb_{10}O_{30} with x = 0.1, 0.3, 0.4, 0.5 corresponding to series 1, series 2, series 3 and series 4 respectively.

Figure 6. 19 Temperature dependence of dissipation factor for [Sr_{0.61}Ba_{0.39}]_{4-2x}Li_{2+2x}Eu_{x}Nb_{10}O_{30} with x = 0.1, 0.3, 0.4, 0.5 corresponding to series 1, series 2, series 3 and series 4 respectively.
Figure 6. 20 Frequency dependence of dielectric constant for \([\text{Sr}_{0.61}\text{Ba}_{0.39}]_4\cdot 2x\text{Li}_{2x}\text{Eu}_x\text{Nb}_{10}\text{O}_{30}\) with \(x = 0.1, 0.3, 0.4, 0.5\) corresponding to series 1, series 2, series 3 and series 4 respectively.

Figure 6. 21 Frequency dependence of dissipation factor for \([\text{Sr}_{0.61}\text{Ba}_{0.39}]_4\cdot 2x\text{Li}_{2x}\text{Eu}_x\text{Nb}_{10}\text{O}_{30}\) with \(x = 0.1, 0.3, 0.4, 0.5\) corresponding to series 1, series 2, series 3 and series 4 respectively.
Figure 6. 22 Temperature dependent variation of dielectric constant for \( \text{Ba}_4\text{Na}_2\text{Nb}_{10}\text{O}_{30} \), \( \text{Ba}_3\text{Na}_4\text{Nb}_{10}\text{O}_{30} \) and \( \text{Ba}_{3-2x}\text{Na}_{4+x}\text{Nd}_x\text{Nb}_{10}\text{O}_{30} \) where \( x = 0.2, 0.4, 0.5, 0.6, 0.8 \) for series 1, series 2, series 3, series 4, series 5, series 6, series 7 respectively.

Figure 6. 23 Temperature dependent variation of dissipation factor for \( \text{Ba}_4\text{Na}_2\text{Nb}_{10}\text{O}_{30} \), \( \text{Ba}_3\text{Na}_4\text{Nb}_{10}\text{O}_{30} \) and \( \text{Ba}_{3-2x}\text{Na}_{4+x}\text{Nd}_x\text{Nb}_{10}\text{O}_{30} \) where \( x = 0.2, 0.4, 0.5, 0.6, 0.8 \) for series 1, series 2, series 3, series 4, series 5, series 6, series 7 respectively.
constant. As the concentration of Neodymium increases, the room temperature dielectric constant increases, where as the $T_c$ shifts to the low temperature side. Here the maximum covers a wide range of temperature resulting in a diffuse phase transition. The broadening of the dielectric constant is believed to result from the compositional fluctuations caused by the addition of neodymium and is analogous to SBN system. The doping of neodymium ions in BNN plays an important role in modifying the dielectric and ferroelectric properties.

Figure 6. 23 shows the temperature dependence of dissipation factor for the above compositions of BNN system at 1 MHz. The dissipation factor at room temperature is lowest for $\text{Ba}_{2.6}\text{Na}_{4.2}\text{Nd}_{0.2}\text{Nb}_{16}\text{O}_{30}$ as plotted for series 3. Generally the dissipation factor decreases as the temperature increases, remains steady in the 150 °C-300 °C and above 300 °C it increases.

Figures 6. 24 and 6. 25 show the frequency dependence of dielectric constant and dissipation factor. In the 50 Hz to 5000 Hz region, both dielectric constant and dissipation factor decrease very rapidly, then over the high frequency region it increase very slowly.

6. 7 Ferroelectric phase transitions

The order of the transition from the paraelectric to the polar state is important. First order phase transitions are, by definition, abrupt and are accompanied by temperature hysteresis. Second order transitions are less abrupt and without hysteresis. There are also materials having diffuse phase transitions which are spread over an appreciable temperature interval and are accompanied by frequency sensitive dielectric behaviour, these are now usually termed relaxors.

Modern theory of ferroelectricity is based on lattice dynamics and the concept of so called soft modes [13, 14, 15]. Ferroelectric phase transitions are a special case of structural phase transition and can thus be interpreted in terms of stability of the crystal-lattice dynamics. In a structural phase transition, the order parameter (polarization in the case of ferroelectric phase transition) may be associated with a lattice vibrational mode which exhibits an instability at the transition temperature. For a second order transition,
Figure 6.24 Frequency dependent variation of dielectric constant for Ba$_4$Na$_2$Nb$_{10}$O$_{30}$, Ba$_3$Na$_2$Nb$_{10}$O$_{30}$ and Ba$_{3.2}$Na$^{0.8}$Nd$_{0.2}$Nb$_{10}$O$_{30}$ where $x = 0.2, 0.4, 0.5, 0.6, 0.8$ for series 1, series 2, series 3, series 4, series 5, series 6, series 7 respectively.

Figure 6.25 Frequency dependent variation of dissipation factor for Ba$_4$Na$_2$Nb$_{10}$O$_{30}$, Ba$_3$Na$_2$Nb$_{10}$O$_{30}$ and Ba$_{3.2}$Na$^{0.8}$Nd$_{0.2}$Nb$_{10}$O$_{30}$ where $x = 0.2, 0.4, 0.5, 0.6, 0.8$ for series 1, series 2, series 3, series 4, series 5, series 6, series 7 respectively.
the frequency spectrum of the lattice vibration related to the order parameter is proportional to \((T-T_c)\) so that this mode 'softens' (its frequency goes to zero) as the material is cooled towards \(T_c\). Freezing of the vibrations at \(T_c\) gives rise to a non zero order parameter and the corresponding reduction in symmetry.

The crystal symmetry of the prototypic form of a ferroelectric is of primary importance, since it controls the alternative directions in which the polar axis may lie. There are other technologically important considerations, such as single crystal and ceramic forms. The extremum which occur in the dielectric, pyroelectric, piezoelectric and opto-electric properties of ferroelectrics at temperatures close to the phase transitions take the properties into exceedingly interesting and practically important ranges. It is thus important to implore the mechanism which can modify and control the transition behavior.

For tungsten bronze ceramic system, five types of mechanisms control the transition behaviour. These are the following.

1. For solid solutions, the phase transition temperature often change continuously with composition so that in homogenous compositions the transitions may be placed at optimum temperature. Further, by controlling heterogeneity deliberately, the transitions can be engendered spreading and smoothing the sharp extremum.

2. In some solid solutions, ferroelectric: Ferroelectric phase transitions occur at fixed compositions and are nearly independent of temperature. These so called morphotropic phase boundaries are extremely important in piezoelectric ceramics.

3. Elastic stress can have a marked effect on the transition behavior and the property extremum near the transition so that self generated stresses in ceramics may be engineered to improve the properties.

4. For ceramic compositions the grain boundary heterogeneity can be invoked to modify the extremum and control the field distribution in the ceramic.

5. Since ferroelectricity is a co-operative phenomenon the scale of the ferroelectric region is of critical importance. Nano-scale heterogeneity can engender completely new properties and give rise to spin glass behavior which can be exploited in both capacitors and transducers [16].
6. 7. 1 Diffuse phase transitions

In recent years, the phenomenon of diffuse phase transition (DPT) in ferroelectrics with perovskite and tungsten bronze structures have received considerable attention. The prominent materials exhibiting DPT can be broadly classified into the following

Solid-solution compositions such as Sr$_{1-x}$Ba$_x$Nb$_2$O$_6$ [4] and K$_{2-x}$Sr$_{4+x}$Nb$_{10}$O$_{30}$ [17] possessing tungsten bronze structure. Extensive investigations of DPT behaviour have been performed in the above mentioned compounds and solid solutions. The important characteristics of DPT behaviour in solid solutions and complex compounds are the following [18, 19, 20].

(i) The dielectric constant ($\varepsilon'$) does not change abruptly at some fixed temperature; instead it shows a diffuse, smeared out maximum. The spontaneous polarization also decreases gradually with rising temperature. The temperature at which $\varepsilon'$ show its maxima ($T_m'$) usually does not coincide with the temperature at which spontaneous polarization disappears ($T_p$). In general $T_p > T_m'$.

(ii) The real and imaginary parts of the dielectric permittivity maxima i.e. $\varepsilon_m'$ and $\varepsilon_m''$ in the $\varepsilon'$, $\varepsilon''$ versus temperature plots, generally do not coincide. The temperature $T_m''$ corresponding $\varepsilon_m''$ is found to be lower than $T_m'$ corresponding to $\varepsilon_m'$.

(iii) The Curie-Weiss law is not obeyed over a wide temperature range above the so-called average transition temperature $T_m$.

(iv) Temperature-dependent relational dielectric dissipation is observed at radio frequencies. The relaxation time is found to decrease with increasing temperature.

Relaxor materials have the following typical dielectric characteristics.

(a) Broadened phase transition- Ferroelectric-paraelectric phase transition is not sharp as in the case of normal ferroelectric, but is gradual and spans over a wide temperature range. The dielectric peak will not be sharp and the dielectric constant
change slowly in the whole Curie range. Spontaneous polarization develops slowly and complete polarization occurs only at temperatures well below the transition range. Spontaneous polarization and non-linearity of the dielectric permittivity with electric field can be seen above the temperature of the maximum dielectric constant. The same broadened character has been observed in other properties. The increase in the differences of the transition may be attributed to the (1) increase in the Curie constant values (2) higher temperature of transition (3) lower spontaneous polarization at the transition, and (4) smaller fluctuating volume. Also, the main assumption is that the local Curie point of different micro regions are statistically distributed around the mean Curie temperature. Sometimes close to the Curie point a ferroelectric crystal consists of micro regions, in which spontaneous polarization appears and disappear under the influence of thermal fluctuation.

Two theories have been proposed to explain the ferroelectric relaxor behaviour. One of them relates the behavior to composition fluctuation in the material and the other attribute it to sensitivity of heterophase fluctuation. The two theories are not completely unrelated. Both the theories may be applied and the relaxor behavior is a result of a combination of both the effects. If the material is ferroelectric and the paraelectric-ferroelectric transition is sensitive to the composition, then each microvolume will have a slightly different Curie temperature and the macroscopic behavior will be a broad envelop of the behavior of the separate microregions. The width of the Curie range will depend upon the range of the composition fluctuations and the sensitivity of the Curie temperature to compositional changes.

The broad nature of the peaks indicates the diffuse nature of the phase transition in them. A particular point cannot be regarded as the Curie point, rather a region called Curie region is to be considered. Any temperature within the region can be regarded as the Curie temperature of a small fraction of the total volume while some micro regions may have higher Curie temperature and lower one for others. The macroscopic dielectric permittivity and ferroelectric behavior will be a broad envelop of individual regions. The broadening of the dielectric peaks has been attributed to the disorders in the arrangements of rare earth ions, leading to a microscopic heterogeneity in the composition and thus a distribution of different local Curie points.
6.8 Dielectric loss factor for ferroelectric ceramics

The power dissipation in an insulator or capacitor is directly proportional to the dielectric loss factor, $\varepsilon'\tan\delta$. Consequently this factor is of great concern for many applications of ceramic materials. Indeed one of the main advantages of ceramics as dielectrics is that the loss factor is small compared to that of other available materials such as plastics. Energy loss in dielectrics result from following three primary processes.

1. Ion migration losses.
   - (a) DC conductivity loses.
   - (b) Ion jump and dipole relaxation losses.
2. Ion vibration and deformation losses.
3. Electron polarization losses.

Of these, the electron polarization losses give rise to absorption and color in the visible spectrum. The ion vibration and deformation losses become important in the infrared but are not a major concern for frequencies below about $10^{10}$ Hz. By far the major factor affecting the use of ceramic materials is the ion migration loss, which tend to increase at low frequencies and with rise in temperature.

The loss factor can be written in terms of electrical conductivity as

$$\omega\varepsilon'' = \sigma = \omega\varepsilon'' \tan\delta$$  \hspace{1cm} (6.14)

or

$$\tan\delta = \frac{\sigma}{2\pi f\varepsilon_0} = \frac{\sigma}{(8.85 \times 10^{-12})(2\pi f)k_1}$$  \hspace{1cm} (6.15)

The conduction migration losses are normally small. As in equation (6.15), the power factor increases at low frequencies and is inversely proportional to the frequency. In general, ion jump relaxation between two equivalent ion positions is responsible for the largest part of the dielectric loss factor for crystals and ceramics at moderate frequencies. If the relaxation time for an atom jump is $\tau$, the maximum energy loss occurs for a frequency equal to the jump frequency, $\frac{1}{\tau}$. When the applied alternating field frequency is much smaller than the jump frequency, atoms follow the field and the energy loss is
small. Similarly, if the applied frequency is much larger than the jump frequency, the atoms do not have an opportunity to jump at all, and losses are small.

For an ion jump the jump frequency depends on the energy barrier separating the two ion positions. If we assume for simplicity that there is only one relaxation time, it is given by

$$\tau = \tau_0 \exp \left( \frac{u}{KT} \right)$$  \quad (6.17)

Where $\tau_0$ is the period of atomic vibrations, of the order of $10^{-13}$ sec. Ion vibration and deformation losses become important at room temperature only at frequencies in the infrared corresponding to $10^{12}$ to $10^{14}$ Hz. This is beyond the range of frequencies that are of concern for electronic applications. These processes begin to become apparent in the higher frequency measurements, of the order of $10^{10}$ Hz. The total value for $\tan \delta$ is the sum of individual contribution already discussed. At room temperature the resulting curve for a glass or a crystal having considerable impurities or defects is as shown in figure 6.22.

![Diagram](image)

**Figure 6.26** Frequency response of dielectric loss for materials

At lower frequencies conduction losses become important. At moderate frequencies ion jump and dipole losses are most important, at intermediate frequencies dielectric losses are small, and at sufficiently high frequencies ion polarization effects
give rise to energy absorption. For reasonably good insulators, the conductivity increases exponentially with temperature. Consequently, for this process $\tan \delta$ increases exponentially with temperature.

6.9 Dielectric conductivity

The dielectric loss phenomena can also be expressed in terms of ac conductivity of solids. This is in accordance with the equation, which defines the dielectric conductivity, given by

$$\sigma = \omega \varepsilon^*$$  \hspace{1cm} (6.18)

Conductivity increases as frequency increases, as shown in figure 6.23.

**Figure 6.27** Variation of conductivity with inverse of relaxation time (frequency) for a typical dielectric.

In fact, a whole alternative mathematical expression of material behavior can be formulated on the basis of a real (giving power losses) and an imaginary (charge current) conductivity.

This charging current is particularly important in determining the conductivity of glasses at low temperatures. Near room temperature the anomalous charging current resulting from an ion jump or several ion jumps which do not contribute to the dc conductivity leads to relaxation times measured as several seconds or several minutes. As a result, measured conductivity depends on frequency used, ac measurements giving higher values than dc measurements.
At higher temperatures the fraction of ions contributing to the dc conductivity becomes nearly equal to the fraction contributing to the ac conductivity, provided, no blocking layers exist at the electrodes. As a result of this, at temperatures above about 250 K the ac measurements and dc measurements are generally comparable.

6.10 Dielectric relaxation in solids

Dielectric relaxation in solids represent one of the most intensely studied topics in physics. For reasons which are difficult to pinpoint exactly, relaxation is singularly sensitive to the stochastic nature of the process involved and the necessary mathematical tools are not sufficiently well understood by the scientific community at large while the experimental investigations are, for the most part, directed towards narrow specific classes of materials with relatively few ‘integrating’ approach aimed at encompassing the entire subject.

Relaxation consist in the recovery of strain on removal of stress and it implies therefore a time dependence, typically, under sudden removal or sudden application of a steady stress. This is the basis of time-domain (TD) measurement [21]. An equivalent and often preferable method is to subject the material to a harmonically varying stress of an analysis frequency \( \omega \) and this forms the basis of frequency domain (FD) measurements [22, 23]. In materials responding linearly with respect to the amplitude of the applied signal, TD and FD responses are Fourier transforms of one another, as given by.

\[
\chi'(\omega) = \int_0^\omega f(t)\cos(\omega t)\,dt
\]

\[
\chi''(\omega) = \int_0^\omega f(t)\sin(\omega t)\,dt \tag{6.19}
\]

and

\[
f(t) = \left(\frac{2}{\pi}\right)\int_0^\omega \chi'(\omega)\cos(\omega t)\,d\omega
\]

\[
= \left(\frac{2}{\pi}\right)\int_0^\omega \chi'(\omega)\sin(\omega t)\,d\omega. \tag{6.20}
\]
While the TD response corresponds to the variation of a current in time and is therefore a
real function \( f(t) \) of the real time variable, FD response defines two components, of
amplitude variation in phase and in quadrature with respect to the driving harmonic
signal and has to be defined as real and imaging functions \( \chi'(\omega) \) and \( -i\chi''(\omega) \) of the
real frequency variable, where \( \omega = 2\pi\gamma \) is the angular frequency, \( \gamma \) being the circular
frequency in Hertz. These two functions are related to one another by the Kramers-
Kronig transformation which corresponds mathematically to the Hilbert integral
transformation [24].

The subject of relaxation covers all types of stress relief in solids—dielectric, 
mechanical, photoconductive, chemical and so on, and several of these may have points
in common. It is not expected that all these different forms of relaxation should obey the
same laws, but it is possible to see a certain commonality of behaviour.

The characterization of the dielectric behavior is very important not only to the
theory of polarization mechanism but also to applications. With regard to applications,
what is important for the dielectric behaviour characterization of a relaxor ferroelectric is
the temperature dependence of the dielectric constant, the frequency dependence of \( T_m \),
etc. With regard to research on the polarization mechanism of relaxor ferroelectrics
(REFs), there has been intensive investigation, and various models have been proposed,
such as the inhomogeneous microregion model [25] the microdomain–macrodomain
transition model [26,27], the superparaelectric model [28], the dipolar glass and the new
glass model [29, 30], the order–disorder model [31, 32] and the local electrical field
model [33]. However, some basic features and the polarization mechanisms are still not
clear for the RFEs.

With regard to the dielectric characterization of relaxor ferroelectrics, the
temperature dependence of the dielectric constant for the materials at temperatures higher
than \( T_m \) has been widely studied, and the results have been widely used to characterize
the degree of dielectric relaxation [25]. Moreover, the phenomenon has been widely
studied at temperatures lower than \( T_m \). The results of the degree of dielectric relaxation
observed from the dielectric behaviour at high temperatures does not characterize well
the relaxation degree [34]. Moreover, there are some contradictory results on the
temperature dependence of the dielectric constant at high temperatures. Thus, the relaxation between the temperature and the dielectric constant is still an open problem for RFE's. Also a reasonable and complete method is still needed to describe the degree of dielectric relaxation of the material. For the characterization of the frequency dependence of $T_m$, these relationships can be used. It has been found that the Vogel–Fulcher (V-F) relationship and a new super-exponential relationship are more suitable than the Debye relationship for the RFEs [29].

6. 11 References

ION IRRADIATION AND IMPLANTATION EFFECTS IN FERROELECTRIC CERAMICS

7.1 Introduction
This chapter reviews the fundamentals of penetration of energetic ions into solids. It describes the basic physics of how the ions lose energy to the solid, creating damage and the final distribution of these ions after they stop within the solid. In this chapter, we first present a typical theoretical distribution of ion implantation as calculated by the computer programme TRIM (TRansport of Ions in Matter), which is widely used in ion implantation studies. By reviewing this program, and its many description of the physics of ion penetration of matter, we understand the details necessary to understand various phenomena associated with ion penetration and stopping. Results obtained on ion irradiation studies on SBN and BNN ceramics are presented later in the chapter.

7.2 Calculation of implantation range and damage distribution
The calculation of ion implantation distribution can be made using many computer programs. These programs mostly use fitted curves to experimental data, and generate simple distributions for use in very large scale integration (VLSI) calculation. The first unified approach to stopping and range calculation theory was made by Lindhard, Scharff and Schiott and their approach is commonly called the LSS theory [1]. This work brought together the pieces and, bridging approximations were made so that calculations of stopping and range distributions could be made within a single model. The remarkable achievement was the result of over a decade of study by Lindhard and collaborators [1, 2, 3, 4, 5, 6] with the later publications deriving in detail some of the major equations of LSS theory. LSS theory was the peak of stopping and range theory based on statistics of atoms. With this theory it was possible to predict the range of ions in solids-a remarkable achievement considering it was applicable over the entire range of atomic species and energies up to the stopping power maximum [7, 8, 9, 10, 11, 12]. Since it was based on