CHAPTER IV

DIELECTRIC CONSTANT

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CHAPTER - XIV
DIELECTRIC CONSTANT

4.1 Introduction:

Dielectrics are the materials in which electric field persists. When a flat slab of any solid dielectric is placed in a uniform field of strength $\mathbf{E}_o$, with its normal parallel to the field, the dielectric displacement $\mathbf{D}$ in CGS system of units is given by

$$\mathbf{D} = \varepsilon \mathbf{E} = \varepsilon_0 \mathbf{E}_o = \varepsilon \mathbf{E}_o + 4\pi \mathbf{P}$$

(4.1)

Where $\mathbf{E}_o$ is the field strength outside the dielectric.

$\mathbf{E}_o$ is the field strength in the dielectric.

$\varepsilon_0$ is the dielectric constant of surrounding medium.

$\varepsilon$ is the dielectric constant of the solid dielectric.

and

$\mathbf{P}$ is the polarization. (Electric moment per unit volume).

The dielectric constant is defined by the ratio of the capacitance of a capacitor filled with the substance under test to that of empty capacitor. It is a dimensionless parameter.

Thus far, few investigators except Rupprecht et al (1961) and Diamond (1961) have attempted to give an explicit relationship between dielectric constant and the externally applied field. Rupprecht's theory (based on Salter's theory)
is valid for small fields only. Diamond developed his theory to apply to polycrystalline materials which are inherently more lossy. Stern and Lurio (1964) applied the phenomenological theory of Devonshire (1945, 1954) to determine the change in dielectric constant with applied field.

The dielectric constant measured along a ferroelectric axis increases in the paraelectric phase when the Curie temperature is approached. In many ferroelectrics, this increase can be approximated by the Curie-Weiss law.

\[ \epsilon = \frac{C}{T - T_0} \quad (4.2) \]

Here \( T \) designates the temperature of sample, \( T_0 \) is the temperature which does not coincide with Curie point, it is somewhat smaller than the transition temperature. \( C \) is so called Curie constant (Merz, 1953, Drougard and Young, 1954).

Considerable effort has been devoted to understanding the behaviour of the dielectric constants of barium titanate single crystals and to the explanation of the behaviour of the dielectric constant of ceramic barium titanate in terms of the single crystal values (Jona and Shirane 1962), particularly in tetragonal phase. The dielectric properties of \( \text{BaTiO}_3 \) single crystals were first investigated by Merz (1949). Subsequently, Cross (1953) and a number of other authors extended and improved the results obtained by Merz.
Robert (1947) and Mason (1948) have studied separately the dielectric properties of polarized ceramic BaTiO$_3$ and reported that dc bias causes a marked decrease of the dielectric constant measured with small ac field. The high value of dielectric constant was computed by Merutake (1956). Measurements of the dependence of dielectric constant on grain size, as a function of temperature were described by Miller (1967). The dependence of the dielectric constant of BaTiO$_3$ single crystals on applied ac field and crystal temperature was studied by Deshpande et al (1977). The maximum value of dielectric constant of BaTiO$_3$ was reported to be 4000 at room temperature by Merz (1949). Later on Benedict and Durand (1958) have reported this value as 4100 at room temperature.

The effect of different factors on the dielectric constant of SrTiO$_3$ was studied by Sawaguchi et al (1962), Hegenberth (1964) and Samara and Giardini (1965). A peak in the dielectric constant of ceramic SrTiO$_3$ around 20 - 30 °K was in fact reported by Smolenskii (1950). The value of the dielectric constant at room temperature was reported to be 250. These results, however, are in sharp contrast with those of Hulm (1950), who observed the value of the dielectric constant as 1300 in the temperature range between 4 °K and 1.3 °K and appears to be practically temperature independent.
Granicher's (1958) dielectric measurements on single crystals of SrTiO₃ indicate that the Curie - Weiss law is obeyed down to 95 °K. At lower temperatures, deviations from this law are observed but the dielectric constant keeps increasing monotonously up to a value of 20,000 at 20 °K.

For CaTiO₃ the dielectric constant has reached a value of 167 at room temperature (Von Hippel et al, 1946). The variation of the dielectric constant of CaTiO₃ with temperature was studied by Linz and Herrington (1958).

The effect of temperature on the dielectric constant of ceramic (Ba,Sr)TiO₃ was studied by Somlenskii and Rozgachev (1954). Mitsui and Westphal (1961) have reported that the dielectric constant of (Ba,Ca)TiO₃ not only varies with temperature but also varies with calcium concentration.

In the present study we have determined the dielectric constants of the solid solution systems (Baₓ-Sr₁₋ₓ)TiO₃ and (Baₓ-Ca₁₋ₓ)TiO₃ at various temperatures.

4.2 Experimental:

The usual methods of measuring the dielectric constant are based on a comparison of the capacity C of a capacitor filled with the substance and the capacity C' of the empty capacitor. The ratio \( \frac{C'}{C} = \varepsilon \), the dielectric constant. The determination of the value of the capacitance may in
principle be accomplished by an LC resonant circuit as shown in fig. 4.1, where $C_s$ is a calibrated variable capacitor and $C$ is the capacitor in which the specimen may be placed. The experimental set-up used for the measurement of dielectric constant at various temperatures is shown in fig. 4.2. The experimental set-up consists of an electrically heated furnace with a temperature controller arrangement and a capacitance bridge (Marconi Universal Bridge TF 2700). Pellets of the solid solutions having thickness of about 0.15 cm are placed in a sample holder and heated in a furnace. Dielectric constant measurements are based on the method of comparison of capacitance. The variation of dielectric constant of $(\text{Ba}_{0.8} \text{Sr}_{0.2})\text{TiO}_3$, $(\text{Ba}_{0.6} \text{Sr}_{0.4})\text{TiO}_3$ and $(\text{Ba}_{0.5} \text{Sr}_{0.5})\text{TiO}_3$ are shown in figures 4.3, 4.4 and 4.5 respectively. Figures 4.6, 4.7 and 4.8 show the variation of dielectric constant with temperature for $(\text{Ba}_{0.8} \text{Ca}_{0.2})\text{TiO}_3$, $(\text{Ba}_{0.6} \text{Ca}_{0.4})\text{TiO}_3$ and $(\text{Ba}_{0.5} \text{Ca}_{0.5})\text{TiO}_3$ respectively.

4.3 Results and Discussion:

From the figures it is clear that the dielectric constant for the solid solution system $(\text{Ba}_x \text{Sr}_{1-x})\text{TiO}_3$ and $(\text{Ba}_x \text{Ca}_{1-x})\text{TiO}_3$ depends upon the temperature. The maximum dielectric constants are observed at 223 °C, 322 °C and 377 °C for $(\text{Ba}_{0.8} \text{Sr}_{0.2})\text{TiO}_3$, $(\text{Ba}_{0.6} \text{Sr}_{0.4})\text{TiO}_3$ and $(\text{Ba}_{0.5} \text{Sr}_{0.5})\text{TiO}_3$ respectively. For $(\text{Ba}_{0.8} \text{Ca}_{0.2})\text{TiO}_3$, $(\text{Ba}_{0.6} \text{Ca}_{0.4})\text{TiO}_3$ and $(\text{Ba}_{0.5} \text{Ca}_{0.5})\text{TiO}_3$ (peaks in) the maximum
Fig 4.1 - SCHEMATIC DIAGRAM OF APPARATUS FOR THE MEASUREMENT OF DIELECTRIC CONSTANT.
FIG 4.2 : Experimental set-up to measure the dielectric constant.
Fig. 4.3 THE VARIATION OF DIELECTRIC CONSTANT WITH TEMP. IN \((\text{Ba}_{0.5}\text{Sr}_{0.5})\text{TiO}_3\).
Fig. 4.4 THE VARIATION OF DIELECTRIC CONSTANT WITH TEMP. IN (Ba$_{0.6}$Sr$_{0.4}$)TiO$_3$. 

SCALE — TEMP. 20°C = 1 CM. ALONG X-AXIS.
DIELECTRIC CONSTANT 0.5 = 1 CM. ALONG Y-AXIS.
The variation of dielectric constant with temp. in $(Ba_{0.5}Sr_{0.5})TiO_3$.
Fig. 4.6 THE VARIATION OF DIELECTRIC CONSTANT WITH TEMP. IN \((\text{Ba}_{0.8}\text{Ca}_{0.2})\text{TiO}_3\).
Fig. 4.7 THE VARIATION OF DIELECTRIC CONSTANT WITH TEMP. IN 
$\text{(Ba}_{0.6}\text{Ca}_{0.4})\text{TiO}_3$. 
Fig. 4.8 THE VARIATION OF DIELECTRIC CONSTANT WITH TEMP. IN \( (\text{Ba}_{0.5}\text{Ca}_{0.5})\text{TiO}_3 \).
dielectric constants are observed at 125 °C, 129 °C and 133 °C, respectively. This indicates that these are the transition temperatures of the respective solid solutions. Further the figures show that the dielectric constant decreases with increasing Sr and Ca concentrations. The peak values of the dielectric constants observed for the solid solution systems \((\text{Ba}_x\text{-Sr}_{1-x})\text{TiO}_3\) and \((\text{Ba}_x\text{-Ca}_{1-x})\text{TiO}_3\) are \(11.5 \times 10^3\) and \(9.6 \times 10^3\) respectively.

The higher atomic polarizability of strontium and calcium ion in the solid solutions of \((\text{Ba}_x\text{-Sr}_{1-x})\text{TiO}_3\) and \((\text{Ba}_x\text{-Ca}_{1-x})\text{TiO}_3\) respectively, may raise the Curie temperature. The dielectric constant follows the Curie-Weiss law at and above the Curie temperature. The spontaneous polarization decreases as temperature increases. At Curie temperature the spontaneous polarization becomes zero giving rise to a maximum dielectric constant.

The following conclusions can be drawn.

1) Curie temperature varies with Sr and Ca concentration in the respective solid solutions.

2) The Curie temperatures of \((\text{Ba}_{0.8}\text{-Sr}_{0.2})\text{TiO}_3\), \((\text{Ba}_{0.6}\text{-Sr}_{0.4})\text{TiO}_3\) and \((\text{Ba}_{0.5}\text{-Sr}_{0.5})\text{TiO}_3\) seems to be 223 °C, 322 °C and 377 °C respectively and that of \((\text{Ba}_{0.8}\text{-Ca}_{0.2})\text{TiO}_3\), \((\text{Ba}_{0.6}\text{-Ca}_{0.4})\text{TiO}_3\) and \((\text{Ba}_{0.5}\text{-Ca}_{0.5})\text{TiO}_3\) seems to be 125 °C, 129 °C and 133 °C respectively.
3) There is a negligible change in the height of dielectric peak with change in Sr and Ca concentration.

4) The slight broadening of the dielectric peak with Sr and Ca concentration is observed.
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