CHAPTER - 8

DIELECTRIC BEHAVIOUR OF BARIUM DOPED SODIUM FLUOROANTIMONATES

8.1 INTRODUCTION

When an external electric field is applied to an ionic solid, positive charges are displaced in the direction of field towards negative end whereas negative charges are displaced in the opposite direction. This displacement produces dipoles throughout the solid. The dipole moment per unit volume of the solid is the sum of all individual dipole moments within the volume and is called the polarisation $P$ of the solid.

The polarisation occurs due to several mechanisms. Electronic polarisation is the result of displacement of positively charged nucleus and electrons of an atom in opposite directions in the application of electric field. The electron cloud around the nucleus shifts towards positive end of the field when the field is applied. Such a shift results in a dipole moment within the atom equal to the product of charge and shift distance and proportional to field strength. The constant of proportionality is called electronic polarisability of the atom, which is independent of temperature.

During chemical bonding, atoms may acquire excess negative or positive charge and form an ionic bond. When the electric field is applied to an ionic solid, cations and anions get displaced in opposite directions. Ionic polarisation is also independent of temperature.
In some molecules, centre of positive and negative charges do not coincide and give rise to orientational polarisation. Even in the absence of electric field orientational polarisation exists. This polarisation depends upon temperature.

The fourth type of polarisation is called space charge polarisation which occurs due to accumulation of charges at the electrodes or at the interfaces in a multiphase material.

The total polarisation is the sum of the contributions from various components.

\[ P_{\text{TOT}} = P_e + P_i + P_o + P_s \]  \hspace{1cm} (8.1)

Ionic polarisation is slower than the electronic polarisation. Hence at optical frequencies, there is no ionic polarisation. Orientational polarisation is even slower than ionic polarisation and it occurs when the frequency of the applied voltage is in the audio range. Space charge polarisation is the slowest process. When all polarisation occur in a material, it follows that dielectric constant will decrease with increasing frequency of the applied voltage.

The effect of temperature on the relative dielectric constant of a material can be twofold. In orientational polarisation, the randomizing action of thermal energy decreases the tendency of permanent dipoles to align themselves in the applied field. This results in decrease in the dielectric constant with increasing temperature. The other effect of temperature is to facilitate the diffusion of ions in space charge polarisation (Raghavan 1991).
Close examination of dielectric constant and d.c. resistivity value of LaCr_{1-x}Ti_xO_3 show that high resistivity always exhibit low dielectric constant (Sujatha Devi and Subba Rao 1992). Bhagavantha Reddy and Venugopal Reddy (1991) measured dielectric constant and dielectric loss tangents of Li-Ti ferrites at different compositions and concluded that lower concentration of titanium had minimal effect on dielectric constant while higher concentration of titanium decreases the dielectric constant. Ovenston et al (1994) concluded that antimony doping on tin-antimony-oxide reduces the dielectric constant. Decrease of dielectric constant with Ag doping on Pb_0.6Ba_0.4O_6 is reported by Padmajarani et al (1990). Sinha (1991) concluded that static and optical dielectric constants for the entire range of compositions in twelve systems of mixed crystals of alkali and silver halides with NaCl structure. Fontella et al (1993) explained that the high value of dielectric loss in berlinite is due to presence of trace impurities. Bhagavantha Reddy and Venugopal Reddy (1991) concluded that variation of dielectric constant with composition and with temperature are in the same manner.

Shinichi Hirano et al (1990) studied the variation of dielectric constant of gadolinium orthophosphate single crystals and reported that variation of dielectric constant was independent of frequency at room temperature and the values increases with temperature from 310 to 500°C at 1 MHz. Sharma et al (1995) have studied the dielectric properties of Pb\left(\text{Mg}_{1/4}\text{Zn}_{1/4}\text{Nb}_{1/2}\right)\text{O}_{11/4} and concluded that both dielectric constant and dielectric loss decreases with increase of frequency. Decrease of dielectric constant and dielectric loss with aromatic polyamides was reported by Rangaswami et al (1993). Decrease of dielectric constant with frequency for Ni–Zn ferrites has been reported by Parvatheeswara Rao et al (1996).
The temperature dependence of dielectric parameter of $\text{Bi}_x\text{Ge}_{20}\text{Se}_{80-x}$ has been reported by Ibrahim et al (1990). Dielectric properties of oxide thin film capacitor is reported by Sivakumar and Subba Rao (1991).

Urbonavicious et al (1982) studied the complex permittivity of $(\text{NH}_4)_2\text{SbF}_5$. The dielectric measurements with frequency and temperature for various stoichiometric compounds of ammonium fluoride and antimony tri-fluoride $(\text{NH}_4\text{SbF}_4$, $(\text{NH}_4)_2\text{SbF}_5$, $(\text{NH}_4)_3\text{SbF}_9$) have been reported by Ranichristudas (1993). Reports of dielectric studies on sodium fluoroantimonates (NaSbF$_4$, Na$_2$SbF$_5$, NaSb$_3$F$_{10}$) single crystals (Bennet Charles 1992; Bennet Charles and Gnanam 1994) are seen in the literature. Scanning the literature reveals no earlier work on doped sodium fluoroantimonates.

8.2 THEORY

In an anisotropic material polarisation $P$ and electric field $E$ is related to electric displacement vector $D$ as

$$D = \varepsilon E + P$$

(8.2)

Where $\varepsilon$ is the permittivity of the medium. For a parallel plate capacitor with dielectric introduced in between the plates capacitance $C$ is related to Area $A$ and spacing $d$ as

$$C = \frac{\varepsilon A}{d} = \varepsilon_0 \varepsilon_r \frac{A}{d}$$

(8.3)
where \( \varepsilon_r \) is the dielectric constant of the material. \( \varepsilon_r \) depends on external factors such as frequency, voltage, temperature, pressure and humidity.

In a periodic potential

\[
E = E_0 \cos \omega t \tag{8.4}
\]

Therefore \( D = D_0 \cos (\omega t - \phi) \)

\[
D = D_0 \cos \phi \cos \omega t + D_0 \sin \phi \sin \omega t \tag{8.5}
\]

i.e., \( D = D_1 \cos \omega t + D_2 \sin \omega t \)

where \( D_1 = D_0 \cos \phi \) \hspace{1cm} (8.6)

\( D_2 = D_0 \sin \phi \) \hspace{1cm} (8.7)

Since \( \frac{D_0}{E_0} \) depends on frequency, two different dielectric constants \( \varepsilon_1(\omega) \) and \( \varepsilon_2(\omega) \) are introduced as follows

\[
D_1 = \varepsilon_1 E_0
\]

\[
D_2 = \varepsilon_2 E_0
\]

\[
\therefore \tan \phi = \frac{\varepsilon_1}{\varepsilon_2} \tag{8.8}
\]

The complex dielectric constant

\[
\varepsilon = \varepsilon_1 - i\varepsilon_2
\]
\[ \varepsilon_1(\omega) \rightarrow \varepsilon_s \text{ (static dielectric constant)} \]

and \[ \varepsilon_2(\omega) \rightarrow 0 \text{ when } \omega \rightarrow 0 \]  \tag{8.9}

\[
\tan \phi \text{ is referred as dielectric loss.}
\]

**8.3 EXPERIMENTAL**

The dielectric measurements are carried with a same set up that of conductivity measurement (Fig. 5.1). The temperature dependence is determined by placing the specimen in a wire wound furnace. The temperature is controlled using temperature controller to an accuracy of ± 1°C. Rectangular specimen of thickness approximately 1.0 mm and area of cross section 1.0 cm\(^2\) are subjected to dielectric measurements. Since the specimen dimensions, flaws and water content of the grown crystals significantly influence the measurement (Shinichi Hirano et al 1990), care has been taken to polish the samples such that thickness variation along the surfaces is seen to be less than 10 \(\mu m\). Samples are mounted over the conductivity cell. The upper and lower faces of the sample are coated with silver paste and I-V characteristics are tested to check the ohmic contact. Both the dielectric constant and dielectric loss are studied as a function of frequency for all barium doped samples in the temperature range 30° to 200°C for NaSbF\(_4\) crystals and 30 to 250 °C for Na\(_2\)SbF\(_5\) crystals. ANDO Type AG 4311B LCR meter is used for measurement. The LCR meter has 31 inbuilt frequencies ranging from 100 Hz to 100 KHz which are approximately equally spaced in logarithmic scale. Prior to the measurement, the samples are heated to 100°C and cooled for few cycles. From the DSC measurements, it is concluded that there is no water of hydration present hence heating and cooling does not alter the value of dielectric constant as usually suspected. The dielectric constant is calculated using the expression 8.3
8.4 RESULTS AND DISCUSSION

Figs. 8.1 and 8.2 show the variation of dielectric constant with frequency for barium doped samples of NaSbF$_4$ and Na$_2$SbF$_5$. The variation of dielectric loss with frequency is shown in Figs. 8.3 and 8.4 for the samples.

The polarisation and hence the dielectric constant in any direction of the medium can be considered as a measure of the energy associated with the electrostatic binding strength between the ions in the direction. The higher the dielectric constant lower the electrostatic binding. Hence large energy is required to move the charge carriers along the direction of large dielectric constant compared to direction of small dielectric constant. Comparing the results with that of the undoped samples (Table 8.1 and 8.2), the nature of variation of dielectric constant with respect to frequency remains the same. But for a fixed frequency dielectric constant decreases very much. The values are tabulated in Tables 8.3 and 8.4. The phenomena can be explained as follows. Owing to doping more impurity is incorporated into this lattice. Due to easiness of polling of impurities, both dielectric constant and dielectric loss decreases. In the case of Pb$_{0.6}$Ba$_{0.4}$Nb$_2$O$_6$, introduction of Ag in the lattice produces similar effect (Padmaja Rani et al 1990). They reported that decrease of grain size and dielectric loss with the introduction of Ag in the lattice. The dielectric constant of a material at low frequencies depends on the electronic, ionic, dipolar, orientation and space charge polarisations. At very low frequencies all the four contributions may be active. The contribution of space charge will depend on purity and perfection of the crystals. Its influence is negligible at very low frequency region. The dipole orientational effect in some materials can be seen even up to $10^{13}$Hz. The ionic and electronic polarisations always exist below $10^{15}$Hz. However electronic and atomic polarization are dependent on beta barium borate (Ramachandra Raja et al 1993). Increase of
### Table - 8.1

**Dielectric constant of undoped sodium fluoroantimonates along (100) orientation**

<table>
<thead>
<tr>
<th>Crystal</th>
<th>Frequency 0.1 KHz</th>
<th>Frequency 100 KHz</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaSbF₄</td>
<td>29.2</td>
<td>11.10</td>
</tr>
<tr>
<td>Na₂SbF₅</td>
<td>32.0</td>
<td>12.10</td>
</tr>
</tbody>
</table>

### Table - 8.2

**Dielectric loss for undoped sodium fluoroantimonates**

<table>
<thead>
<tr>
<th>Crystal</th>
<th>Frequency 0.1 KHz</th>
<th>Frequency 100 KHz</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaSbF₄</td>
<td>0.014</td>
<td>0.0053</td>
</tr>
<tr>
<td>Na₂SbF₅</td>
<td>0.020</td>
<td>0.0040</td>
</tr>
</tbody>
</table>
### Table - 8.3

Dielectric constant of barium doped NaSbF$_4$ and Na$_2$SbF$_5$ Crystals

<table>
<thead>
<tr>
<th>Crystal</th>
<th>Dopant concentration in ppm</th>
<th>Frequency</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>0.1 KHz</td>
</tr>
<tr>
<td>NaSbF$_4$</td>
<td>55</td>
<td>27.5</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>26.4</td>
</tr>
<tr>
<td></td>
<td>68</td>
<td>25.1</td>
</tr>
<tr>
<td>Na$_2$SbF$_5$</td>
<td>65</td>
<td>30.1</td>
</tr>
<tr>
<td></td>
<td>71</td>
<td>29.4</td>
</tr>
<tr>
<td></td>
<td>79</td>
<td>27.0</td>
</tr>
</tbody>
</table>

### Table - 8.4

Dielectric loss of barium doped NaSbF$_4$ and Na$_2$SbF$_5$ Crystals

<table>
<thead>
<tr>
<th>Crystal</th>
<th>Dopant concentration in ppm</th>
<th>Frequency</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>0.1 KHz</td>
</tr>
<tr>
<td>NaSbF$_4$</td>
<td>55</td>
<td>0.0053</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>0.0055</td>
</tr>
<tr>
<td></td>
<td>68</td>
<td>0.0060</td>
</tr>
<tr>
<td>Na$_2$SbF$_5$</td>
<td>65</td>
<td>0.0020</td>
</tr>
<tr>
<td></td>
<td>71</td>
<td>0.0019</td>
</tr>
<tr>
<td></td>
<td>79</td>
<td>0.0018</td>
</tr>
</tbody>
</table>
Figure 8.1 Variation of dielectric constant for barium doped NaSbF$_4$ crystals in the frequency range 0.1 KHz to 100 KHz
Figure 8.2 Variation of dielectric constant for barium doped Na$_2$SbF$_5$ crystals in the frequency range 0.1 KHz to 100 KHz.
Figure 8.3 Variation of dielectric loss for barium doped NaSbF$_4$ crystals in the frequency range 0.1 KHz to 100 KHz
Figure 8.4 Variation of dielectric loss for barium doped Na$_2$SbF$_5$ crystals in the frequency range 0.1 KHz to 100 KHz
atomic distances influences the electronic and ionic polarization. The influence of defects and impurities will also depend upon temperature. Hence there is a variation of $e^1$ and $e^H$ with temperature and composition for sodium fluoroantimonate single crystals. The large value of $e^1$ and $\tan \phi$ at lower frequencies may be considered to be due to space charge polarisation of lattice defects. The low values of $\tan \phi$ suggest that the grown crystals are of moderately good quality. In the low frequency region, dielectric loss shows larger value due to loss associated with ionic mobility (Shinichi et al 1990).

8.5 CONCLUSION

The dielectric constant of NaSbF$_4$ and Na$_2$SbF$_5$ crystals doped with barium for different concentrations are determined over frequency range from 100 Hz to 100 KHz. It is found that both dielectric constant and dielectric loss decrease with increase in frequency and attains a constant value at high frequency. Due to doping the dielectric constant decreases for all crystals.