CHAPTER-4

Dielectric Study
Dielectric Study

4.1 Introduction

The characterization of dielectric ceramics has received considerable scientific interest because of their enormous applications in electronic devices such as resonators, actuators, multilayer capacitors, etc. The principal applications of dielectric materials are as capacitive elements in electronics circuits and electrical insulations. In contrast to electrical conductivity that involves long-range motion of charge carriers, the dielectric response results from the short-range motion of charge carriers under the influence of an externally applied electric field. The relative dielectric constant ($\varepsilon_r$), loss tangent (tan$\delta$) and dielectric strength (breakdown) are the three important characteristics of the dielectrics relevant to their suitability for device applications. The relative dielectric constant of the material determines the ability to store electrostatic energy. The loss tangent indicates the ability of dielectrics to support the electrostatic field, while dissipating minimal energy in the form of heat. The lower the dielectric loss (the proportion of energy loss as heat) the more effective is the dielectric material. Dielectric strength indicates the maximum voltage that the dielectric can safely withstand. Dielectric properties depend upon the chemical composition, structure and particle size of the material and various external factors such as temperature, humidity, mechanical stress, intensity and frequency of the electric field.

Ferroelectrics are non-linear dielectrics whose dielectric behavior changes appreciably with change of the electric field strength, pressure and temperature. Ferroelectric ceramics play a significant role in modern technology owing to their excellent dielectric, electro-optic, pyroelectric, piezoelectric, elasto-optic and electro-mechanical properties. These materials are used to design high permittivity capacitors, ferroelectric memory devices, pyroelectric sensors, piezoelectric transducers, PTC thermistors, actuators, resonators, printer logic circuit, light modulator and deflector, frequency changer, etc.
Ferroelectrics materials are considered important and useful for the following reasons:

1. high relative dielectric constant as compared to the ordinary dielectrics
2. relatively low dielectric loss
3. high specific electrical resistivity
4. moderate dielectric breakdown strengths
5. non-linear electrical behavior (hysteresis).

The measurement of dielectric parameters of the ferroelectrics over a wide range of frequency and temperature provides some useful information regarding the existence of ferroelectricity, the nature of phase transition and suitability of materials for device applications. It is also important to explore the dependence of dielectric properties on impurities, microstructure, grain size, porosity, etc.

The dielectric properties of ferroelectrics depend on the field strength at which it is measured. It is a consequence of non-linear relation between polarization and electric field. For ferroelectric materials the dielectric constant increase up to the transition temperature and after that it obeys the Curie-Weiss law.

In this chapter detailed studies of dielectric properties of all the proposed compounds as a function of frequency and temperature have been discussed, which may provide information regarding the existence of ferroelectricity, the nature of phase transition in them and the effect of substitution on dielectric properties of the proposed compounds.

4.1.1 Brief Review of the Previous Work

Dielectric properties ($\varepsilon_r, \tan\delta$) of $A\left(B'_{1/2}B''_{1/2}\right)O_3$ compounds depend on their crystal structure, tolerance factor, the type of the ions occupying the B-site, and the A-site. The pronounced effect of the radius of the A-site cation on the dielectric constant can be envisaged when $Ba\left(B'_{1/3}B''_{2/3}\right)O_3$ perovskites are compared to that of $Pb\left(B'_{1/3}B''_{2/3}\right)O_3$ compounds. Radii of lead and barium cation (in 12-fold coordination) are $R_{Pb}=0.172$ nm and $R_{Ba}=0.161$ nm and the dielectric constant 6500 and 24 for $Pb\left(Mg_{1/3}Ta_{2/3}\right)O_3$ and $Ba\left(Mg_{1/3}Ta_{2/3}\right)O_3$, respectively [230]. The dielectric constant of $Ba\left(Mg_{1/3}Ta_{2/3}\right)O_3$ [231,232] and $Ba\left(Mg_{1/3}Nb_{2/3}\right)O_3$[233] has different value. The niobates possess higher value of dielectric constants as compared to tantalates. Tantalates, in
general, have higher Q-factors than niobates. This is because the materials with higher $E$ have higher harmonic component of the lattice vibration energy [234]. Only two contributions into the dielectric constant of $\text{Ba(B}^1/3\text{B}^+2/3\text{)}_3\text{O}_3$ compounds come from ionic and electronic polarizations. Kawashima et al. [235] reported that improvement in the Q factor corresponds to increased ordering of Zn and Ta in $\text{Ba(Zn}_{\text{1/3}}\text{Ta}_{\text{2/3}}\text{)}_3\text{O}_3$. According to the literature, high degree of ordering and high density is the two most important factors determining the dielectric constant and loss for devices. Kinetics of cation ordering depends on the diffusion of the B-site cations from one oxygen octahedron to another. This is controlled by temperature, type of B-site cations, stoichiometry and impurities. The rate of ordering and densification of ceramics can be significantly increased with increase in temperature. In recent years, there has been a considerable amount of interest in the investigation of relaxor ferroelectrics (i.e., the ferroelectrics having a diffuse phase transition (DPT)) which is characterized by a broad maximum in the temperature dependence of the dielectric permittivity (real part) and the dielectric dispersion in the said transition region (Smolenskii 1970, 1984). Lead iron niobate, $\text{PbFe}_{0.5}\text{Nb}_{0.5}\text{O}_3$ (PFN), is known to be the most intensively investigated by Ivanov et al (2000), Lampis et al (1999), Darlington (1991), Yasuda and Ueda (1989a, 1989b). PFN is a ferroelectric of the disordered-type (Smolenskii et al 1958, Bokov et al 1962) having a ferroelectric transition temperature at $110^0\text{C}$ (Bhat et al 1974, Brunskill et al 1981). It is current interest as a component in commercial electroceramic materials, particularly as it is typically characterized by high relative permittivities and low sintering temperatures. The lead free BFN ceramic is synthesized by the solid-state reaction technique for the first time by Saha et al [136]. The phenomenon of the high value of the dielectric permittivity in ceramics $\text{AFE}_{1/2}\text{B}_{1/2}\text{O}_3$ (A=Ba, Sr, Ca; B=Nb, Ta, Sb) in a wide temperature interval is due to the Maxwell–Wagner relaxation was reported by Raevski et al [139].

### 4.1.2 Measurements of dielectric constant and loss tangent

Measurements of relative dielectric constant and loss tangent can be carried out using various methods depending upon the nature of specimen and frequency. To obtain relative dielectric constant and loss tangent the following methods are generally used.

- RF method (lump circuit method).
- Microwave method (distributed circuit method).
- Impedance method/LCR method.
In the present study, the impedance method has been used to investigate the dielectric and resistivity properties of the compounds. Capacitance of a sample is measured using impedance or LCR bridge, depending on frequency range, such as Schering bridge, transformer ratio bridge etc. Then the relative dielectric constant \((\varepsilon_r)\) of the sample is calculated from its capacitance and geometry.

### 4.1.3 Experimental

The dielectric properties \((\varepsilon_r\) and \(\tan\delta\)) of all the samples were measured at different temperatures and frequencies with the help of a computer-controlled LCR meter (4NL, Model: PSM-1735, UK) along with a laboratory-designed and fabricated sample holder and furnace [Fig. 2.7]. A chromel-alumel thermo-couple and a digital millivoltmeter (KUSAM MECO 108) were used to measure the temperature with accuracy of 0.1 mV (equivalent to 2.5 °C). The data were recorded in a temperature interval of about 2.5 °C after the sample attains steady state. Silica gel was put inside the sample holder to make the sample moisture free. The flow chart is given in Fig 4.1 for testing procedure of impedance meter.

![Fig. 4.1 Flow chart for testing procedure of impedance meter](image-url)
The observations were taken for every 0.1mV (approximately 2.5°C). The LCR meter simultaneously gives number of parameters such as quality factor (Q), tanδ, impedance (Z), phase angle (θ), parallel inductance (L), parallel capacitance (C) and parallel resistance (R) as a function of frequency. Before taking measurements the continuity of the silver coating and sample holder is checked. The offset voltage (the voltage of the applied signal) and the frequency range are optimized. By varying the variac attached to the furnace the heating rate is controlled and readings at different temperatures are noted down. All the above parameters of each pellet sample were recorded simultaneously as a function of frequency (1kHz to 5MHz) at different temperatures (25- 500°C). Here, after obtaining capacitance (C), the relative dielectric constant ($\varepsilon_r$) of the material was calculated using the formula $\varepsilon_r = C/C_0$, where $C_0$ is the value of air capacitance, and is equal to $\varepsilon_0A/t$ ($\varepsilon_0 = 8.85\times10^{-12}$ F/m, $A =$ surface area of the sample, $t =$ thickness of the pellet). Measurements are carried out in the frequency range of $10^3$ - $10^6$ Hz, and temperature range of room temperature to about 500°C.

4.1.4 Results and discussion

Variation of relative dielectric constant ($\varepsilon_r$) and loss tangent (tanδ) with temperature at different frequencies.

All the components of polarizations (i.e., electronic, ionic, dipolar and interfacial polarization) are present in the audible range. In contrast to electronic and ionic polarization, dipolar polarization occurs at lower frequencies and is thus important because it can greatly affect the capacitive and insulating properties of glasses and ceramics for low frequency applications. From the nature of variation of $\varepsilon_r$ with frequency, it is possible to find out the contribution of polarization predominantly present in the compound in a particular frequency range [236]. In the frequency range under investigation only the polar contribution to the total dielectric constant undergoes dispersion. All the spontaneously polarized regions make a contribution to the dielectric constant only at temperatures below the transition point. The space charge contribution depends upon the purity and perfection of the crystal and exhibits itself prominently at low frequencies. The increase in space charge polarization increases the value of relative dielectric constant and loss tangent. The space charge polarization arises due to defects and impurities present either in the bulk or at the surface of the crystal or both [237]. Generally pressed ceramic samples contain voids, grain boundaries and other defects.
The value of the dielectric constant decreases with the increase in the number of voids. The number of polarizable entities will be enhanced due to the increase in density or packing fraction. The loss tangent in pellet samples is mostly due to the scattering mechanism of charge carriers or defects [237]. The scattering cross section depends on the grain size, inter grain space and grain boundaries. Since the pellets are pressed at high pressure (4 \times 10^6 N/m^2) and sintered at high temperature, the packing fraction of the pellets is high. As a result, the inter-grain space as well as the grain boundaries in the pellet was reduced considerably by means of reducing the scattering cross section. Hence, the tan\(\delta\) decreases with increase in frequency due to the high packing fraction of the pellet. Also, the dielectric loss decreases as the frequency of the applied ac electric field increases because the jumping frequency of charge carriers cannot follow the frequency of the applied field after certain frequency [238].

Fig. 4.2 Temperature dependence of (a) \(\varepsilon_r\) and (b) \(\tan\delta\) of \(\text{Ba(Bi}_{0.5}\text{Nb}_{0.5})\text{O}_3\) at different frequencies.

Fig. 4.2 shows the variation of relative dielectric constant (\(\varepsilon_r\)) and loss tangent (tan\(\delta\)) of \(\text{Ba(Bi}_{0.5}\text{Nb}_{0.5})\text{O}_3\) with temperature at different frequencies. It is also observed that both \(\varepsilon_r\) and tan\(\delta\) decrease on increasing frequency, which is a general feature of dielectric materials. Again, \(\varepsilon_r\) increases gradually on increasing temperature to its maximum value (\(\varepsilon_{\text{max}}\)) and then decreases. The increase in \(\varepsilon_r\) in all the samples can be ascribed to the electron-phonon interaction. [239,240]. The dielectric anomaly observed around 317\(^\circ\)C may be due to the ferroelectric-paraelectric phase transition [223]. Above this anomaly further increase of \(\varepsilon_r\) may be considered due to space charge polarization which comes from mobility of ions and imperfections in the material. These combined
effects produce a sharp increase in the relative dielectric constant on increasing temperature. Similar trend of variation is observed in tan\(\delta\) (as in \(\varepsilon_r\)). The rate of increase in tan\(\delta\) in the material at low temperatures is slow, whereas at higher temperatures the increase is relatively sharp. This sharp increase in tan\(\delta\) at higher temperatures may be due to scattering of thermally activated charge carriers and presence of some unknown defects including oxygen vacancies in the sample. At higher temperatures, the conductivity begins to dominate, which in turn, is responsible for rise in tan\(\delta\). At the same time, the defect structure along with the presence of Nb\(^{5+}\) ions accounts for its high temperature ferroelectrics [241-243]. The higher value of tan\(\delta\) at high temperatures may be due to space charge polarization and ferroelectric domain wall contributions.

The variation of relative dielectric constant (\(\varepsilon_r\)) and loss tangent (tan\(\delta\)) with temperature of Ba\((\text{Bi}_{0.5}\text{V}_{0.5})\text{O}_3\) at different frequencies is shown in Fig.4.3. The value of \(\varepsilon_r\) increases on increasing temperature up to a temperature (referred as transition temperature (\(T_c\))), and then decreases. It is also observed that both \(\varepsilon_r\) and tan\(\delta\) decrease on increasing frequency, which is a general feature of dielectric materials [244]. The maximum value of \(\varepsilon_r\) and tan\(\delta\) decreases with rise in frequency. Such characteristic is found in a normal ferroelectric material. Additionally, dispersion in tan\(\delta\) at the higher temperatures has been observed in the titled compound. This trend is also observed in some similar-type of compounds [245–248]. It is associated to ionic conductivity of the material, which is related to the loss of oxygen during high-temperature sintering. Dielectric constant decreases with increase in frequency, which is a general characteristic of dielectric

Fig. 4.3 Temperature-frequency dependence of (a) \(\varepsilon_r\) and (b) tan\(\delta\) of Ba\((\text{Bi}_{0.5}\text{V}_{0.5})\text{O}_3\)

The variation of relative dielectric constant (\(\varepsilon_r\)) and loss tangent (tan\(\delta\)) with temperature of Ba\((\text{Bi}_{0.5}\text{V}_{0.5})\text{O}_3\) at different frequencies is shown in Fig.4.3. The value of \(\varepsilon_r\) increases on increasing temperature up to a temperature (referred as transition temperature (\(T_c\))), and then decreases. It is also observed that both \(\varepsilon_r\) and tan\(\delta\) decrease on increasing frequency, which is a general feature of dielectric materials [244]. The maximum value of \(\varepsilon_r\) and tan\(\delta\) decreases with rise in frequency. Such characteristic is found in a normal ferroelectric material. Additionally, dispersion in tan\(\delta\) at the higher temperatures has been observed in the titled compound. This trend is also observed in some similar-type of compounds [245–248]. It is associated to ionic conductivity of the material, which is related to the loss of oxygen during high-temperature sintering. Dielectric constant decreases with increase in frequency, which is a general characteristic of dielectric
materials. This is because of the absence of dipolar and ionic polarizations in the material at higher frequency. A dielectric anomaly was observed around 295°C that may be related to the ferroelectric-paraelectric phase transition. This assumption has been confirmed by appearance of hysteresis loop. It is also observed that the value of \( \varepsilon'_{\text{max}} \) (dielectric constant at \( T_c \)) at 1, 10, 100, and 1000 kHz is found to be 280, 206, 182, and 173 respectively [224]. Above this anomaly, further increase of \( \varepsilon' \) (at lower frequency) may be considered due to space charge polarization which comes from mobility of ions and imperfections in the material. These combined effects produce a sharp increase in the relative dielectric constant above transition temperature. The rate of increase in \( \tan\delta \) in the material at low temperature is slow, whereas at higher temperatures the increase is relatively sharp. This sharp increase in \( \tan\delta \) at higher temperatures may be due to scattering of thermally activated charge carriers and presence of some unknown defects including oxygen vacancies in the material. At higher temperatures the conductivity begins to dominate, which in turn, is responsible for the rise in \( \tan\delta \). At the same time, the defect structure along with the presence of \( V^{5+} \) ions accounts for its high-temperature ferroelectrics [241-242]. The reason for higher value of \( \tan\delta \) at high temperatures is generally considered due to space charge polarization and ferroelectric domain wall contribution [249].

Fig. 4.4 Temperature dependence of (a) \( \varepsilon' \) and (b) \( \tan\delta \) of \( \text{Ba(Bi}_{0.5}\text{Ta}_{0.5}\text{)}\text{O}_3 \) at different frequencies.
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Fig. 4.4 shows the variation of relative permittivity ($\varepsilon_r$) and loss tangent ($\tan \delta$) of Ba(Bi$_{0.5}$Ta$_{0.5}$)O$_3$ as a function of temperature at different frequencies. It reveals that the values of both $\varepsilon_r$ and $\tan \delta$ decrease on increasing frequency, which is a general feature of dielectric materials [244]. Again, $\varepsilon_r$ increases gradually on increasing temperature to its maximum value ($\varepsilon_{\text{max}} = 3937$ at 1kHz) and then decreases. The dielectric anomaly observed at 315$^\circ$C suggests a phase transition from the ferroelectric to the paraelectric phase [226], and, usually referred as transition temperature (Tc). Above the temperature of dielectric anomaly, the value of $\varepsilon_r$ (at lower frequency) increases on further increase in temperature. The fast increase in relative dielectric constant may be considered due to space charge polarization that comes from mobility of ions and/or imperfections in the material. Similar trend of variation in $\tan \delta$ (as in $\varepsilon_r$) is observed. The rate of increase in $\tan \delta$ in the material in the low-temperature region is slow, whereas at higher temperatures the increase is relatively sharper. This sharp increase in $\tan \delta$ at higher temperatures along with the observed dispersion may be due to (i) scattering of thermally activated charge carriers, (ii) some inherent defects in the sample, and (iii) creation of oxygen vacancies during sample preparation. As a result, the electrical conductivity dominates at high temperatures that may also be responsible for sharp rise in $\tan \delta$. The defects, structural deformation and the presence of Ta$^{5+}$ ions may account for the high-temperature ferroelectric phase of the material [241-243]. For the higher value of $\tan \delta$ (at high temperatures), both space charge polarization as well as ferroelectric domain wall contributions are responsible.

Fig. 4.5 Temperature dependence of (a) $\varepsilon_r$ and (b) $\tan \delta$ of Sr(Bi$_{0.5}$Nb$_{0.5}$)O$_3$ at different frequencies.
The variation of relative dielectric constant ($\varepsilon_r$) and loss tangent ($\tan\delta$) with temperature of Sr(Bi$_{0.5}$Nb$_{0.5}$)O$_3$ at different frequencies is shown in Fig.4.5. It is observed that both these parameters decrease on increasing frequency that is a general feature of dielectric materials. Again, $\varepsilon_r$ increases gradually on increasing temperature. In the high-temperature region, higher value of $\varepsilon_r$ may be due to space charge polarization which comes from mobility of ions and imperfections in the material. These combined effects produce a sharp increase in the relative dielectric constant on increasing temperature. This trend is also observed in some similar-type of compounds [250, 251].

The variation of $\tan\delta$ follows the same behavior as that of $\varepsilon_r$. The value of $\tan\delta$ increases on increasing temperature [227]. It is associated with ionic conductivity of the material, which is related to the loss of oxygen during high-temperature sintering. This sharp increase in $\tan\delta$ at higher temperatures may be due to scattering of thermally activated charge carriers and presence of some unknown defects including oxygen vacancies in the sample. At higher temperatures, the conductivity begins to dominate, which in turn, is responsible for rise in $\tan\delta$. As the above material does not have ferroelectric properties, space charge polarization only may be considered for higher value of tangent loss in the high-temperature region.

![Fig. 4.6 Temperature dependence of (a) $\varepsilon_r$ and (b) $\tan\delta$ of Sr(Bi$_{0.5}$V$_{0.5}$)O$_3$ at different frequencies.](image)

Fig. 4.6 shows the variation of relative dielectric constant ($\varepsilon_r$) and loss tangent ($\tan\delta$) of Sr(Bi$_{0.5}$V$_{0.5}$)O$_3$ with temperature at a few selected frequencies. It is observed that both $\varepsilon_r$ and $\tan\delta$ decrease on increasing frequency. The dielectric anomaly observed around 258°C may be due to the phase transition [228]. All the peaks appear at the same
temperature irrespective of the frequency. Further, above the phase transition
temperature, the relative dielectric constant at low frequency increases with increase in
temperature, which could be due to space charge polarization and conductivity of the
sample. The observed variation of dielectric constant with temperature at different
frequencies is analogous with that of the report by Kim et al [252]. Similar trend of
variation is observed in tanδ (as in ε_r) as a function of temperature. It is observed that
the tangent loss (tan δ) increases with increase in temperature at all the said frequencies. The
small increase in the value of tan δ is up to 300°C and above this temperature there is a
sudden increase in tan δ on further increase in temperature. The peak position is observed
to be in the temperature range of 250 and 260°C. The increasing trend in tan δ at higher
temperature regions (for all frequencies) may be due to space charge polarization [253].

Fig. 4.7 shows the variation of ε_r, tanδ, and Sr(Bi_{0.5}Ta_{0.5})O_3 as a function of
temperature and frequencies. It is also observed that both ε_r and tanδ decrease on
increasing frequency, which is a general feature of dielectric materials [244]. Again, ε_r
increases gradually on increasing temperature. In the high-temperature region, higher
value of ε_r may be due to space charge polarization, which comes from mobility of ions
and imperfections in the material. These combined effects produce a sharp increase in the
relative dielectric constant on increasing temperature. The variation of tanδ follows the
same behavior as that of ε_r. The value of tanδ increases on increasing temperature. It is
associated to ionic conductivity of the material, which is related to the loss of oxygen during high-temperature sintering. This sharp increase in tanδ at higher temperatures may be due to scattering of thermally activated charge carriers and presence of some unknown defects including oxygen vacancies in the sample. At higher temperatures the conductivity begins to dominate, which in turn, is responsible for rise in tanδ.

To summarize, (Figs. 4.2-4.7) show the variation of relative dielectric constant and loss tangent of all the studied compounds as a function of temperature at different frequencies. Ba(Bi₀.₅Nb₀.₅)O₃, Ba(Bi₀.₅V₀.₅)O₃, Ba(Bi₀.₅Ta₀.₅)O₃ and Sr(Bi₀.₅V₀.₅)O₃ exhibit ferroelectric-paraelectric phase transition. In normal ferroelectrics, relative dielectric constant increases with increase of temperature up to transition temperature (T_c) then it decreases. The temperature dependence of ε_r and tanδ at different frequencies (1 kHz, 10 kHz, 100kHz and 1MHz) of above compounds are shown in the above figures. It is observed the value of ε_r increases on increasing temperature up to a temperature (referred as transition temperature (T_c)), and then decreases. Such characteristic is normally found in normal ferroelectric materials. The transition temperature is found to be 317, 295, 315, and 258°C of Ba(Bi₀.₅Nb₀.₅)O₃, Ba(Bi₀.₅V₀.₅)O₃, Ba(Bi₀.₅Ta₀.₅)O₃ and Sr(Bi₀.₅V₀.₅)O₃ respectively. The value of ε_max and loss tangent at 1, 10,100 kHz and 1 MHz is compared in Table 4.1. This has been confirmed by appearance of hysteresis loops at different temperatures (below T_c). Similar trend of variation is observed in tanδ (as in ε_r) as a function of temperature in all the sample may be due to scattering of thermally activated charge carriers and some defects in the sample. The rate of increase in tanδ in the material at low temperature is slow, whereas at higher temperature the increase is relatively sharp. In comparison to ε_r, negligible increase in tanδ is observed up to T_c. Above T_c the sharp increase in tanδ at higher temperatures may be due to scattering of thermally activated charge carriers and presence of some unknown defects including oxygen vacancies in the samples.

The values of ε_r and tanδ, at room and transition temperature (at 10 kHz) for Ba(Bi₀.₅Nb₀.₅)O₃, Ba(Bi₀.₅V₀.₅)O₃, Ba(Bi₀.₅Ta₀.₅)O₃ and Sr(Bi₀.₅V₀.₅)O₃ and the values of ε_r and tanδ, at room and 300°C of Sr(Bi₀.₅Nb₀.₅)O₃ and Sr(Bi₀.₅Ta₀.₅)O₃ are compared in Table 4.1.
Table 4.1 Comparison of dielectric properties, $T_c$ at 10 kHz of $A(B'_0.5B''_0.5)O_3$ where $A=(Ba, Sr), (B'=Bi, B''=Nb, V, Ta)$ compounds.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>$\varepsilon_{RT}$</th>
<th>$\varepsilon_{max}$</th>
<th>$\tan\delta_{RT}$</th>
<th>$\tan\delta_{max}$</th>
<th>$T_c$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba(Bi$_0.5$Nb$_0.5$)O$_3$</td>
<td>451</td>
<td>580</td>
<td>0.01</td>
<td>3.93</td>
<td>317</td>
</tr>
<tr>
<td>Ba(Bi$_0.5$V$_0.5$)O$_3$</td>
<td>174</td>
<td>206</td>
<td>0.02</td>
<td>0.303</td>
<td>295</td>
</tr>
<tr>
<td>Ba(Bi$_0.5$Ta$_0.5$)O$_3$</td>
<td>1023</td>
<td>1319</td>
<td>0.10</td>
<td>1.76</td>
<td>315</td>
</tr>
<tr>
<td>Sr(Bi$_0.5$Nb$_0.5$)O$_3$</td>
<td>264</td>
<td>290</td>
<td>0.01</td>
<td>0.134</td>
<td>------</td>
</tr>
<tr>
<td>Sr(Bi$_0.5$V$_0.5$)O$_3$</td>
<td>185</td>
<td>221</td>
<td>0.07</td>
<td>0.729</td>
<td>285</td>
</tr>
<tr>
<td>Sr(Bi$_0.5$Ta$_0.5$)O$_3$</td>
<td>349</td>
<td>381</td>
<td>0.01</td>
<td>0.130</td>
<td>------</td>
</tr>
</tbody>
</table>

4.2 Polarization study

Ferroelectrics are a class of pyroelectric materials in which the spontaneous polarization ($P_s$) can be reversed by the application of electric field ($E$) in opposite direction. The hysteresis loop (polarization ($P$) vs. field ($E$)) that can be observed in certain temperature region is one of the most important characteristics of ferroelectric materials [236]. The $P$-$E$ loop is very similar to the magnetic hysteresis loop ($B$ vs. $H$). Ferroelectric hysteresis loop describes the non-linearity between the polarization and electric field. The hysteresis loop is generally taken using a disc shape ferroelectric specimen. The electric field across the specimen is varied and corresponding values of charge stored on the large capacitor (in series with the sample) are recorded. The charge on the capacitor is proportional to the charge on the specimen and hence a continuous plot of polarization as a function of electric field is obtained. The hysteresis loops obtained in different size and shape helps to identify the material. A considerable amount of information can be obtained from the hysteresis loop such as high remanent polarization ($P_r$) relates to high internal polarizibility, strain, electromechanical and electro-optic activity. A very strong field could lead to the reversal of the polarization in the domain known as domain switching. With the reversal of the electric field the domains start to align in the positive direction giving rise to a rapid increase in polarization. At some higher field, domain switching occurs abruptly and a significant increase in effective polarization takes place within the material [254, 6]. At very high field all the domains are aligned in the direction of field and the polarization attains a saturation value ($P_s$). Reducing the field to zero leaves the material with a net polarization known as remanent polarization ($P_r$). In order to remove the remanent
polarization a minimum field in opposite direction is to be applied. This field is termed as coercive field $E_c$. At full reversal field, the final $P_s$ will have in magnitude equal to the original field $P_s$ but opposite in sign. If the field increases to a more negative value, the direction of polarization flips and hence hysteresis loop is obtained. The value of $P_s$ is obtained by extrapolating the curve onto the polarization axis. The hysteresis thus observed is a function of the work required to displace the domain walls and is closely related to the defect distribution in the crystal and to the energy barrier separating the different orientation states. When the $E_c$ value is large the loop is of square-type and the material is useful for memory applications. When temperature increases the area of the loop decreases and becomes a straight line at Curie temperature ($T_c$). Thus the prominent features of ferroelectric properties are hysteresis and nonlinearity in the relation between polarization and electric field.

4.2.1 Brief Review of the previous work:

In 1920, Valasek discovered that the polarization of Rochelle salt could be reversed by an externally applied electric field. From the nature of loop Valasek [4] recognized the similarities between the dielectric properties of Rochelle salt and ferromagnetic properties of iron. Literature survey reveals that some authors have reported regarding the nature of hysteresis loop in the similar type compounds. Rehring et al. [255] reported the polarization BZT-O$_{4.5}$ and BZT-O$_{5.0}$ crystals oriented along the pseudocubic <100> as a function of electric field at room temperature. The compounds have remanent polarization ($P_r$) and coercive fields ($E_c$) of approximately 13 $\mu$C/cm$^2$ and 1 kV/cm respectively. Z.Yu et al. [256] reported the polarization hysteresis loops of Ba(Ti$_{0.7}$Zr$_{0.3}$)O$_3$ at low temperature and observed near square P-E loops with high remanent polarizations ($P_r=10\mu$C/cm$^2$ at 175 K). From the above information it appears that no work has been done on polarization behavior of the proposed compounds as a function of electric field and temperature. In view of the above, we have carried out the polarization study of a few compounds under present study.

4.2.2 Experimental

The polarization is defined as the electric dipole moment per unit volume, which can be obtained from hysteresis loop parameters. Before tracing the hysteresis loops the ferroelectric materials are poled by applying an electric field. Poling is done to align the
randomly oriented electric dipoles in a specified direction. The process of poling of ferroelectrics is to switch reverse domains below $T_c$ with higher electric fields than coercive field. The hysteresis loop of the sample was obtained on the poled (for 24 h in the silicon oil shown in Fig. 2.9) samples. The DC poling unit consists of a regulated power supply, sample holder immersed in silicon oil and a small furnace. After poling in controlled environment and with an optimized electric field for sufficiently long duration, the hysteresis loops were obtained at room temperature using a P-E loop tracer (M/s Marine India, New Delhi) (Fig. 2.10). The P-E loop tracer consists of a computer-controlled regulated power supply, sample holder immersed in silicon oil and a small furnace. For the initialization, the sample thickness, area, tentative resistance and capacitance of the sample, and a tentative field is applied. By permutation and combination of sample capacitance and resistance, applied filed strength and frequency the loops are optimized at room temperature.

4.2.3 Results and discussion

As mentioned earlier, the non-linear relationship between $P$ and $E$ (hysteresis loop) is one of the essential characteristics of a ferroelectric material. Since the ceramics samples of this family have dielectric breakdown at low electric field, the saturation polarization could not be obtained with the given field; but due to the fixture arrangement inside the P-E loop tracer we have measured polarization of our samples of different thickness and area. The dielectric anomaly in the studied compounds was assumed to be related to the ferroelectric-paraelectric phase transition. This assumption was confirmed by appearance of hysteresis loop. The room temperature hysteresis loops of the samples are shown in Figs.4.8-4.11. Remanent polarization (i.e., $2P_r$) of all the samples at different electric field is shown in Table 4.2.
Fig. 4.8 P-E hysteresis loop \( \text{Ba(Bi}_{0.5}\text{Nb}_{0.5})\text{O}_3 \) at room temperature.

Fig. 4.8 shows the variation of polarization (P) as a function of electric field (E) on poled samples of \( \text{Ba(Bi}_{0.5}\text{Nb}_{0.5})\text{O}_3 \) at room temperature. The remanent polarization (\( 2P_r \)) and coercive field (\( 2E_c \)) of the compound at room temperature were found to be 0.44\( \mu \text{C/cm}^2 \) and 0.081\( \text{kV/cm} \) respectively [223]. It is clear that the compound has lower electric field and smaller remanent polarization. This confirms the existence of ferroelectricity in the sample.

Fig. 4.9 P-E loop of \( \text{Ba(Bi}_{0.5}\text{V}_{0.5})\text{O}_3 \) at room temperature.

The hysteresis loop of \( \text{Ba(Bi}_{0.5}\text{V}_{0.5})\text{O}_3 \) recorded at room temperature\( (30^0\text{C}) \) is shown in Figure 4.9. The remanent polarization (\( 2P_r \)) and coercive field (\( 2E_c \)) of the
compound at 30°C are 0.43µC/cm² and 0.081kV/cm respectively [224]. However, even with smaller remanent polarization, the existence of ferroelectric properties in the compound can be concluded.

![P-E hysteresis loop Ba(Bi₅ Ta₅)O₃ at room temperature.](image1)

The hysteresis loop of Ba(Bi₅ Ta₅)O₃ recorded at room temperature(30°C), is shown in Figure 4.10. The remanent polarization (2Pᵣ) and coercive field (2Eᵣ) of the compound at 30°C are 8.13µC/cm² and 0.078kV/cm respectively. It is observed from the loop compound is lossy in nature [226]. The observed hysteresis loop confirms the existence of ferroelectric properties in the material at room temperature.

![P-E hysteresis loop Sr(Bi₅ V₅)O₃ at room temperature.](image2)
Fig. 4.11 shows the hysteresis loops of Sr(Bi\textsubscript{0.5}V\textsubscript{0.5})O\textsubscript{3}. Remanent polarization was found to be $2P_r = 0.38\mu\text{C/cm}^2$ and coercive field ($2E_c$) is 0.53kV/cm respectively. However, even with smaller remanent polarization, it confirms the existence of ferroelectricity in the sample.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>$2P_r$ ((\mu\text{C/cm}^2))</th>
<th>$2E_c$ (kV/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba(Bi\textsubscript{0.5}Nb\textsubscript{0.5})O\textsubscript{3}</td>
<td>0.44</td>
<td>0.081</td>
</tr>
<tr>
<td>Ba(Bi\textsubscript{0.5}V\textsubscript{0.5})O\textsubscript{3}</td>
<td>0.43</td>
<td>0.081</td>
</tr>
<tr>
<td>Ba(Bi\textsubscript{0.5}Ta\textsubscript{0.5})O\textsubscript{3}</td>
<td>8.13</td>
<td>0.078</td>
</tr>
<tr>
<td>Sr(Bi\textsubscript{0.5}V\textsubscript{0.5})O\textsubscript{3}</td>
<td>0.38</td>
<td>0.53</td>
</tr>
</tbody>
</table>

From the above hysteresis loop and table we are clear that the value of remanent polarization and coercive electric field are small. But in case of Ba(Bi\textsubscript{0.5}Ta\textsubscript{0.5})O\textsubscript{3} the value is more due to lossy nature. The polarization curves are lossy. The tangent loss of these materials has high tangent loss at high temperature. This may be due to presence of bismuth because it has volatile nature. Also the tantalum is lossy in nature. The observed hysteresis loop confirms the existence of ferroelectric properties in the compounds at room temperature.

### 4.3 Conclusion

On the basis of the above results the following conclusion can be drawn:

- It is observed that with increase in frequency, the values of dielectric constant and loss tangent decreases.

- Only four compounds Ba(Bi\textsubscript{0.5}Nb\textsubscript{0.5})O\textsubscript{3}, Ba(Bi\textsubscript{0.5}V\textsubscript{0.5})O\textsubscript{3}, Ba(Bi\textsubscript{0.5}Ta\textsubscript{0.5})O\textsubscript{3} and Sr(Bi\textsubscript{0.5}V\textsubscript{0.5})O\textsubscript{3} show dielectric anomaly (i.e. ferroelectric to paraelectric phase transition out of all samples).

- The variation of tan\(\delta\) with temperature nearly follows the nature of \(\varepsilon_r\) variation with temperature and the anomaly in tan\(\delta\) is also observed near the transition temperature.
- Ba(Bi_{0.5}Nb_{0.5})O_3 and Ba(Bi_{0.5}Ta_{0.5})O_3 have high value of \( \varepsilon_r \) at room temperature and at transition temperature as well. All the samples show low tangent loss but it increases suddenly at high temperature.

- The difference between \( \varepsilon_{\text{max}} \) and \( \varepsilon_{\text{min}} \) in the studied samples is found to be small implying lower variation of \( \varepsilon_r \) with temperature, which supports the diffuseness of the dielectric peak.

- Only four samples show polarization, i.e. the observed hysteresis loop confirms the existence of ferroelectric properties in the compounds at room temperature and the value of remanent polarization and coercive electric field is small.

- Ba(Bi_{0.5}V_{0.5})O_3 having highest remnant polarization and Sr(Bi_{0.5}V_{0.5})O_3 sample having maximum coercive field.