Chapter VII:
Hysteresis response of pure and Modified PBN ceramic compositions
7.1 Introduction

Ferroelectric materials exhibit properties such as extremely large permittivities and possibility of retaining some residual electrical polarization after an applied voltage is switched off. These properties distinguish them from ordinary dielectrics the parameters, the state shifts and the resulting hysteric response for the primary ferroic ferromagnets, and ferroelectrics [1]. The ferroelectric character is established when the states can be transformed from one to another by suitably directed electric field and it also known that in ferroelectrics the domain states have different orientation of spontaneous electric polarization.

This reorientation of the domains state polarization distinguishes the ferroelectrics in the subgroup from the larger class of pyroelectric crystals in ten polar points symmetries [2]. An increase in potential difference \( V \) across the dielectric will result in a proportionate increase in the induced polarization ‘\( P \)’ or stored charge. The behavior of polarization on subsequent increase of voltage is not similar to subsequent decrease. The polarization which ferroelectrics exhibit at high field strength is saturation polarization (\( P_s \)) and remnant polarization (\( P_r \)) which is the retained value as \( V \) is reduced to zero after saturation. To reduce the polarization to zero, reverse field which is known as coercive field (\( E_c \)), is required. Application of an electric field across a ferroelectric changes the net polarization. This is due to the following
processes: (i) change in direction of polarization domain, (ii) the magnitude of 
P with each domain may be increased, especially if some randomness in 
dipole orientation is present before the field is applied and (iii) domain wall 
migration may occur so that favorable oriented domains grow in size at the 
expense of unfavorably oriented one. For a crystal to exhibit spontaneous 
polarization and become ferroelectric the necessary condition is that the space 
group should be non-centre-symmetric. Thus to characterize the material as 
ferroelectric, dielectric and hysteresis loop measurements are essential.

7.2 Material preparation

Conventional techniques are used in the preparation of polycrystalline 
solutions of the compositions of A-, B-, and C-series. Preparation of these 
ceramic compositions whose starting materials are analytical reagent grade 
PbO (lead oxide), BaCO₃ (barium carbonate), Ce₂O₃ (cerium oxide) and Nb₂O₅ 
(neobium pentoxide) is described in chapter III. To compensate for the lead 
loss arising due to the volatile nature of PbO at higher temperatures an excess 
of 3 wt% PbO is added. The compositions are sintered at 1280 °C for one 
hour. After polishing these sintered discs the surfaces are electroded by 
applying an electric field of 30 kV/cm is applied for poling the electrodes at a 
temperature of 120 °C for 30 minutes.

7.3 Experimental techniques

Prior to the measurement on the pure and Ce doped PBN ceramics at 
different phases, they were poled by Belding and McLaren (3). The samples
were heated in silicone oil bath to a temperature of 120°C in an applied field of about 40 kv/cm. The electric field was maintained for about 30 minutes while the temperature is kept at 120°C and then specimens were field-cooled to room temperature. Modified Sawyer Tower circuit [4] was used to study hysteresis of the above materials. The device used for this purpose is a full wave rectifier with maximum output voltage of 7 kv. Poling at high electric field was not tried due to possible occurrence of dielectric breakdown of the materials.

7.4 Results and discussions

The coercive field is related to the ease with which polarization reversal is produced by an applied field [5]. The coercive and remnant fields are related to the domain structure [5-8]. The region in which spontaneous polarization points in the same direction is called domain. The symmetry of the crystal determines the allowable direction of spontaneous polarization. It is along the [001], [110], and [111] direction or tetragonal, orthorhombic and rhombohedral structures respectively [9]. In a ceramic material the size of the domain is limited by the grain size and hysteresis in the results of polarization reversal, which occurs by re-orientation. The grain structure [8] influences the domain orientation, which takes place by nucleation and growth phenomena. Techniques of preparation and sintering condition differ considerably in the grain structure. Significant re-orientation of domains along the direction of the applied field is not the consequence of poling at room temperature. Thus saturation polarization on the samples poled at room temperature is calculated.
Figures 7.1A, 7.1B and 7.1C shows that the hysteresis loops obtained pure and Ce modified PBN poled at 120 °C. It is evident that most materials exhibit saturation. The \( P_s \), \( P_r \) and \( E_c \) values are calculated and tabulated in Tables 7.1A, 7.1B and 7.1C. The reported values of \( P_s \) at room temperature in a lanthanum doped PBN ceramics was 10.9 \( \mu \)C/cm\(^2\) by Neurgaonkar et al [10] and 43.34 \( \mu \)C/cm\(^2\) for Ba doped PLZT by Sinha et al [11]. Table 7.1B shows that values of spontaneous polarization vary from 6.75 \( \mu \)C/cm\(^2\) to 9.33 \( \mu \)C/cm\(^2\). The values of \( P_r \) and \( E_c \) are nearly equal in the materials with composition of La doped PBN ceramics and Ba doped PLZT compositions as reported by [8-9]. The values of \( P_r \) and \( E_c \) are 1.4 \( \mu \)C/cm\(^2\) and 18.3kV/cm reported by Cheng et al [12] in Ba\(_{0.98}\) Sr\(_{0.2}\) TiO\(_3\) thin films fabricated using a precursor 0.05 M solution by a sol-gel process at temperatures of 550 to 600°C. The Sr Ba Nb\(_2\)O\(_6\) composition having the same tungsten bronze structure has lower curie temperature than PBN composition and can be easily poled by applying an electric field of kv/mm at room temperature. To draw a contrast of LiNbO\(_3\), with a high \( T_c \) of 1230 °C, is very difficult to completely pole at room temperature as the samples were very thin (<500um). An extremely high electric field of around 20 kV/mm in applied [13, 14]. It was reported by Czchrlai-growth Pb\(_{0.33}\) Ba\(_{0.70}\) Nb\(_{1.95}\) O\(_5\) can be poled by applying an electric field of 100 to 200 V/mm while it is slowly cooled from a high temperature field cooling method [15]. However, the optimum poling
conditions for the Pb$_{1-x}$Ba$_x$Nb$_2$O$_6$ crystals grown in this study were unknown. The electric field required for poling of PBN is estimated to be several kilovolts per millimeter. The crystals suffered breakdown at high electric fields before reaching polarization saturation. The reason for hysteresis loop remains ambiguous and requires further study. Thus we conclude, that basing on the requirements, this particular set of PBN crystals could not be poled into a single domain state at low temperatures by applying an electric field.

i) Compositions of A-series

The modified PBN compositions having the value of $P_n$, $P_s$, $E_c$ and Ce lie in the orthorhombic side of phase boundary calculated from the hysteresis loops of Fig 7.1A and the data in the Table 7.1A. The concentration of Ba for all compositions is kept at 35 mole %. It is seen from Fig 7.1A that on Ce substitution of the compositions also effects the values of $P_n$, $P_s$ and $E_c$. An increase in Ce concentration from 0.02 to 0.1 increases the coercive field $E_c$ by 3.57 to 5.95 kV/cm while results in the decrease of the other parameters 3.90 to 1.95 $\mu$C/cm$^2$, 4.98 to 2.48 $\mu$C/cm$^2$. The values given above are nearly equal to La doped PBN compositions reported by Neurogonkar et al [10] and are lower than the tungsten bronze structure of non-lead composition SBN. The report by Maciolek and Liu [16] showed the value at room temp is 30 $\mu$C/cm$^2$. The composition $A_o$ requires higher electric field of polarization. The ceramic sample breaks down before reaching polarization saturation which explains the occurrence of hysteresis loop instability in PBN composition [17].
Table 7.1A: Ferroelectric data for compositions of A series

<table>
<thead>
<tr>
<th>Composition</th>
<th>P, µC/cm²</th>
<th>E, kV/cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.49</td>
<td>5.95</td>
<td>A³</td>
</tr>
<tr>
<td>2.44</td>
<td>5.36</td>
<td>A³</td>
</tr>
<tr>
<td>2.92</td>
<td>4.76</td>
<td>A³</td>
</tr>
<tr>
<td>4.53</td>
<td>3.40</td>
<td>A²</td>
</tr>
<tr>
<td>4.98</td>
<td>3.90</td>
<td>A¹</td>
</tr>
</tbody>
</table>
Fig. 7.1A Hysteresis Loops Data for Compositions of A-Series
ii) Compositions of B- series

Hysteresis loops observed on Ce doped PBN composition near MPB region are shown in Fig 7.1 B and the values are given in the Table 7.1 B. The concentration of Ba is kept at 40 mole % for all compositions. Thus it is noted from Fig 7.1 B that Ce substituted compositions also effect the values of $P_r$, $P_t$, and $E_c$. As the Ce concentration increases the coercive field $E_c$ increases 7.73 to 10.71 $\mu$C/cm$^2$ and the rest of the parameters 8.09 to 5.60 $\mu$C/cm$^2$ and 9.33 to 6.75 $\mu$C/cm$^2$ are decreased. These values are nearly equal to that of La doped PBN compositions reported by Neurgaonkar et al [10]. The above values are nearly equal to those of Lanthanum doped PBN compositions reported Ref. [10] and Ba$_{0.08}$Sr$_{0.2}$TiO$_3$ (BST) thin films reported by Cheng et al [12]. In Pb$_{0.9}$La$_{0.1}$Ti$_{0.975}$O$_3$ (PLT10) thin films the values of $P_r$ and $E_c$ are 12.6 $\mu$C/cm$^2$, 9.95kV/cm respectively as reported by Song et al [18]. When compared with other series the values of B- series are higher.

iii) Compositions of C- series

The hysteresis loops obtained for Ce doped PBN compositions in tetragonal side of phase boundary are shown in Fig 7.1C and the values are given in the Table 7.1C. The concentration of Ba is kept constant at 45 mole % for all compositions and the Ce concentration increases from 0.02 to 0.1. Thus from the Fig 7.1C that Ce substituted in compositions also effect the values of $P_r$, $P_t$, and $E_c$. As the concentration of Ce increases coercive field increases 4.8-
<table>
<thead>
<tr>
<th>Composition</th>
<th>E, kV/cm</th>
<th>P, μC/cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>B₅</td>
<td>5.60</td>
<td>6.75</td>
</tr>
<tr>
<td>B₄</td>
<td>9.52</td>
<td>6.22</td>
</tr>
<tr>
<td>B₃</td>
<td>8.93</td>
<td>6.84</td>
</tr>
<tr>
<td>B₂</td>
<td>8.33</td>
<td>7.38</td>
</tr>
<tr>
<td>B₁</td>
<td>7.73</td>
<td>8.09</td>
</tr>
</tbody>
</table>

Table 7.1B: Ferroelectric data for compositions of B series
Fig. 7.1B Hysteresis Loops Data for Compositions of B-Series
Table 7.1C: Ferroelectric data for compositions of C series

<table>
<thead>
<tr>
<th>Composition</th>
<th>P, μC/cm²</th>
<th>E, MV/cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₁</td>
<td>4.80</td>
<td>7.30</td>
</tr>
<tr>
<td>C₂</td>
<td>5.04</td>
<td>8.20</td>
</tr>
<tr>
<td>C₃</td>
<td>5.65</td>
<td>9.80</td>
</tr>
</tbody>
</table>
Fig. 7.1C Hysteresis Loops Data for Compositions of C-Series.
7.3 kv/cm and the other parameters 5.65 to 3.60 μC/cm² and 7.20 to 4.10 μC/cm² are decreased. These values are nearly equal to Lanthanum doped PBN compositions reported by Neurgaonkar et al [10]. The above values are lower than the tungsten bronze structure of non-lead composition SBN. As reported by Maciolek and Lie [14] the value at room temperature was given by 30 μC/cm². The ceramic sample breaks down before reaching the polarization saturation at higher electric field, which is the reason for hysteresis loop instability in PBN composition [17].

7.5 Summary

Thus we observe that the values of $P_r$, $P_s$ and $E_s$ in the B-series compositions are higher than the corresponding values in the A and C-series. Also the values of $P_s$ in the B-series are much higher than in other series. The values of $P_r$ and $P_s$ decrease with increase of Ce concentration.
References

   John Wily & Sons Inc (1980).


8. J. C. Burfoot and G. W. Taylor “Polar dielectrics and their applications”


