Chapter VI: Pyroelectric response of pure and modified PBN ceramic compositions
6.1 Introduction:

Twenty one out of thirty two types of symmetries are made of crystals of non-centro symmetrical structure and of these twenty one, ten non-symmetric classes can exhibit spontaneous electric polarization. However, in case of a conductor, an external electric field will not be normally observed because its mobile charge carriers will assume a distribution, which neutralizes the internal moment. While stray charges will be attracted to and trapped on the surfaces until the surface charge associated with the polarization is neutralized, if the material is an insulator. The charge distribution produced in this way near the surface of an insulator is relatively stable, unable to respond quickly to sudden changes of the internal dipole moment and thus, in particular, if the temperature on the material is changed, the dipole moment may also change. An observable external electric field is produced due to this change.

Although the dipole moment is not directly observable its temperature co-efficient is observable and it is called the pyroelectric coefficient. The pyroelectric properties of substances are quantitatively described in terms of a pyroelectric co-efficient, \( P \) [1] which relates to a change in polarization \( P \) to the temperature \( t \) given by the relation,

\[
p = \frac{dP}{dt}.
\]  

A sensitive electrometer can detect a charge of about \( 5 \times 10^{-16} \) C. It is seen that the use of pyroelectric effect should enable change in temperature of
less than 1 micro-degree \([2,3]\). Any sensitive thermoelectric element can, in principle, be used as a thermal infrared detector. The applications of the pyroelectric effect were suggested as early as in 1938 by Ta \([4]\) and Chynoweth \([5]\). Cooper \([6]\) made a detailed analysis of the characteristics of the pyroelectric detector \([7]\) and showed that it should be possible to produce a pyroelectric detector of performance close to the limit set by the surroundings at room temperature. Unfortunately Cooper did not achieve this performance in practice due to the limitations of the pyroelectric materials then available. Subsequently several materials have been developed for the pyroelectric detection \([8-14]\).

Samples were prepared and rolled as described earlier in this thesis. The pyroelectric current was measured using the method described by Byer and Roundy \([15]\) as explained in Chapter III and the rate of heating is maintained at 4°C per minute. The pyroelectric coefficient in the present studies was estimated by the method suggested in by \([15]\). The Pyroelectric coefficient \(P_1(\theta)\) was evaluated using the relation

\[
P_1(\theta) = \frac{I}{A} \left[ \frac{d\theta}{dt} \right]
\]

where \(I\) is the pyroelectric current, \(A\) is the area of the sample and \(d\theta/dt\) is the rate of heating.

The quality of the pyroelectric material must be evaluated through different figures of merit. Taking the material into account.
(1) Voltage responsivity, \[ FM_{RV} = \frac{P}{\rho c_p k} \]

(2) Normalized detectivity, \[ FM_{RN} = \frac{P}{\rho c_p k} \] and

(3) Current responsivity, \[ FM_{Rt} = \frac{P}{\rho c_p} \]

Materials in general must have high \( P \) and low \( K \) to achieve high Figure of Merit. Especially significant are ferroelectric ceramics, which are suitable for the production of detectors of different sizes and shapes. It is easy to obtain a material with any specific curie point by varying the composition of solid ceramic solution in desired proportions and thereby achieve the required relationship between \( P \) and \( K \).

Ever since the pyroelectric detectors appeared in the 70’s \([16,17]\), they established themselves as the detectors of choice for numerous applications involving the detection of middle infrared (3.15 \text{rum}) radiation. These detectors are now indispensable in applications such as motion detector remote thermometers and moisture analysis, fire detectors, etc. To improve the proportion of the pyroelectric materials is the key for enhancing the performance of ferroelectric detectors. It is very important to make detailed study of the relation between pyroelectric parameters and proportions of the detectors in order to improve the available pyroelectric materials and develop new materials with high performance.

6.2 Material preparation
Conventional techniques are used in the preparation of polycrystalline solutions of the compositions of the 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. In order 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 of these sintered discs, the surfaces are electroded. And electric field of 30 kV/cm is applied for poling the electroded at a temperature of 120 °C for 30 minutes.

6.3 Experimental technique

Pyroelectric coefficient on the poled pure and Ce substituted PBN compositions was measured with the Microprocessor 8085 based temperature control furnace, Indian Instruments, Chennai and Keithly electrometer model 614.

6.4 Results and Discussions

From literature survey it is found that very brief dielectric and structural studies have been made on this material, PBN. Data available on pyroelectric behavior of PBN (Lead Barium Niobate) are very sparse. Pyroelectric response of pure PBN and cerium modified PBN ceramic composition are giving in this section. Figures 6.1A, 6.1B and 6.1C shows temperature variation of pyroelectric coefficient on pure and Ce substituted PBN composition on
different phases. Maximum pyroelectric coefficient is observed at a particular temperature and then decreases as the temperature increases. The temperature ($P_{TC}$) at which the maximum pyroelectric coefficient in all compositions of the series, which almost coincides with $T_C$, the values obtained from dielectric studies (chapter IV) and resistivity measurements ($P_{TC}$) (chapter VIII). Such behavior has been observed in similar type of materials such as PBN [18] and SBN [19,20].

It is found that the room temperature pyroelectric coefficients $P_{RT}$ vary from (142 – 177) $\mu$C/m$^2$K for A- series, (264 – 291)$\mu$C/m$^2$K for B- series, and (138 – 166)$\mu$C/m$^2$K for C- series. It has been reported by Lane that the value of $P_{RT}$ in pure PBN ceramic compositions is 270$\mu$C/m$^2$K [21]. The value of $P_{RT}$ observed in all PBN compositions is nearly equal to the one reported by Lane et al [21] and lead based perovskite-type structures ferroelectric thin films of Pb (Zr, Ti) O$_3$ [22]. The observed values of pyroelectric coefficients $P_{RT}$ of all compositions are possibly due to the fact that the compositions are ceramic in nature.

It is observed that in all pure and Ce modified PBN compositions there is an increase of an order of magnitude in the pyroelectric coefficients at $P_{TC}$ compared with $P_{RT}$ value [23] reported by Guo et al in PBN single crystals. The Figure of Merit and voltage responsivity (FMR$_v$) normalized responsivity values of Figure of Merit or in the order of $10^{-12}$ CM/J, $10^{-11}$ CM/J, $10^{-11}$ CM/J.
for FM_{RV}, FM_{RN} and FM_{RI} respectively. These values are of the same order when compared with the lead based perovskite-type structure ferroelectric thin film of PZT reported by Shi et al [22].

i) Compositions of A-series

Temperature variation of pyroelectric coefficient of Ce substituted PBN compositions near orthorhombic side of phase boundary are shown in Fig 6.1A. The pyroelectric coefficient of all compositions is nearly equal to pure PBN composition reported by Lane et al [21]. The value of $P_{RT}$ is in the order of $\mu$C/m$^2$K, which is the same order when compared with pure PBN compositions [21]. However the magnitudes of $P_{RT}$ are slightly enhanced in A-series when compared with pure composition ($A_o$). Further it is observed that the $P_{RT}$ value varies from 142 to 177 $\mu$C/m$^2$K. The $P_{max}$ value in compositions is one order of magnitude higher when compared with value at $T_c$ reported by Guo et al [23]. It is observed that the $P_{TC}$ values 347, 342, 305, 295, 277 and 270°C corresponding to $P_{max}$ in all compositions are well matched with $T_c$ from dielectric measurements (Chapter IV) and resistively studies (Chapter VIII).

The values of Figures of Merit FM_{RV}, FM_{RN} and FM_{RI} are calculated and found in the order of $10^{-12}$ CM/J, $10^{-11}$ CM/J and $10^{-10}$ CM/J respectively. These values are of same order when compared with the lead based perovskite-type structure ferroelectric thin films of PZT reported by Shi et al [22]. The values of $P_{RT}$, $P_{max}$, $P_{TC}$, FM_{RV}, FM_{RN}, FM_{RI} and $T_c$ are given in the Table 6.1A.
Table 6.1A: Pyroelectric data for compositions of A series

<table>
<thead>
<tr>
<th>Composition Density</th>
<th>( p_i )</th>
<th>( T_{2873} )</th>
<th>( \bar{E}_{\text{FMR}} \times 10^{-1} )</th>
<th>( Q_{\text{CM}} )</th>
<th>( p_{\text{max}} )</th>
<th>( T_{\text{OC}} )</th>
<th>( p_{\text{OC}} )</th>
<th>( T_{\text{OC}} )</th>
<th>( p_{\text{OC}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>A_0</td>
<td>0.52</td>
<td>0.164</td>
<td>8.66</td>
<td>0.063</td>
<td>0.056</td>
<td>0.225</td>
<td>0.223</td>
<td>0.000</td>
<td>0.386</td>
</tr>
<tr>
<td>A_1</td>
<td>0.57</td>
<td>0.174</td>
<td>13.47</td>
<td>0.050</td>
<td>0.054</td>
<td>2.787</td>
<td>2.785</td>
<td>3.024</td>
<td>5.979</td>
</tr>
<tr>
<td>A_2</td>
<td>0.92</td>
<td>0.190</td>
<td>19.87</td>
<td>0.093</td>
<td>0.106</td>
<td>3.32</td>
<td>3.30</td>
<td>3.35</td>
<td>3.32</td>
</tr>
<tr>
<td>A_3</td>
<td>0.95</td>
<td>0.196</td>
<td>25.67</td>
<td>0.068</td>
<td>0.064</td>
<td>3.25</td>
<td>3.22</td>
<td>3.20</td>
<td>3.24</td>
</tr>
<tr>
<td>A_4</td>
<td>0.53</td>
<td>0.106</td>
<td>1.56</td>
<td>2.570</td>
<td>2.570</td>
<td>1.77</td>
<td>1.75</td>
<td>0.050</td>
<td>0.175</td>
</tr>
<tr>
<td>A_5</td>
<td>0.38</td>
<td>0.142</td>
<td>2.22</td>
<td>2.22</td>
<td>2.22</td>
<td>1.70</td>
<td>1.75</td>
<td>0.050</td>
<td>0.175</td>
</tr>
<tr>
<td>A_6</td>
<td>0.35</td>
<td>0.257</td>
<td>2.57</td>
<td>2.57</td>
<td>2.57</td>
<td>1.77</td>
<td>1.75</td>
<td>0.050</td>
<td>0.175</td>
</tr>
<tr>
<td>A_7</td>
<td>0.48</td>
<td>0.252</td>
<td>2.22</td>
<td>2.22</td>
<td>2.22</td>
<td>1.70</td>
<td>1.75</td>
<td>0.050</td>
<td>0.175</td>
</tr>
<tr>
<td>A_8</td>
<td>0.85</td>
<td>1.42</td>
<td>2.565</td>
<td>3.47</td>
<td>3.47</td>
<td>2.77</td>
<td>2.77</td>
<td>3.52</td>
<td>3.52</td>
</tr>
</tbody>
</table>
Fig. 6.1A Pyroelectric Coefficient Vs Temperature for Compositions of A-series
<table>
<thead>
<tr>
<th>Composition</th>
<th>Density (gm/cm^3)</th>
<th>FMR (x 10^11 C/m/V)</th>
<th>Tc (°C)</th>
<th>Pmc (C/m^2)</th>
<th>Pmax (C/m^2)</th>
<th>Bz (T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bx</td>
<td>0.93 0.145</td>
<td>0.053 0.93 0.023</td>
<td>92 112</td>
<td>2820 2932</td>
<td>264 275</td>
<td>5.90</td>
</tr>
<tr>
<td></td>
<td>0.99 0.94 0.0177</td>
<td>0.020 0.032 0.226</td>
<td>204 226</td>
<td>3940 340</td>
<td>284 291</td>
<td>5.97</td>
</tr>
<tr>
<td></td>
<td>0.99 0.186 0.036</td>
<td>0.240 0.036 0.226</td>
<td>239 282</td>
<td>3902 278</td>
<td>5.91 278</td>
<td>5.95</td>
</tr>
</tbody>
</table>

Table 6.1B: Pyroelectric data for compositions of B series
Fig. 6.1B Pyroelectric Coefficient Vs Temperature for Compositions of B-series
ii) **Compositions of B- series**

Temperature versus pyroelectric coefficients near MPB region have been shown in the Fig 6.1B. The value of $\mathbf{P_{RT}}$ is in the order of $\mu\text{C/m}^2\text{K}$ that is of the same order when compared with pure PBN composition [21]. However, the magnitude of $\mathbf{P_{RT}}$ are slightly enhanced in B- series when compared with compositions of A- series. Further it is observed that $\mathbf{P_{RT}}$ value varies from (264-291) $\mu\text{C/m}^2\text{K}$. The $\mathbf{P_{max}}$ value in composition is one order of magnitude higher when compared with the $\mathbf{T_c}$ value as reported by Guo et al [23]. It is observed that the $\mathbf{P_{TC}}$ values 281, 239, 26, 204, 112 and 92°C corresponding to $\mathbf{P_{max}}$ in all compositions are well matched with $\mathbf{T_c}$ from dielectric measurements (chapter IV) and resistively studies (chapter VIII).

The value of Figure of Merit $\mathbf{F_{MRV}}, \mathbf{F_{MRN}}$ and $\mathbf{F_{MRI}}$ are calculated and found in the order of $10^{-12}$ CM/J, $10^{-11}$ CM/J and $10^{-10}$ CM/J respectively. These values are of the same order when compared with lead based perovskite-type structured ferroelectric thin films of PZT as reported by Shi et al [22]. The values of $\mathbf{P_{RT}}, \mathbf{P_{max}}, \mathbf{P_{TC}}, \mathbf{F_{MRV}}, \mathbf{F_{MRN}}, \mathbf{F_{MRI}}$ and $\mathbf{T_c}$ are given in the Table 6.1B.

iii) **Compositions of C- series**

Temperature versus pyroelectric coefficients of pure and Ce substituted PBN composition in tetragonal phase are shown in Fig 6.1C. The values of $\mathbf{P_{RT}}$ are in the order of $\mu\text{C/m}^2\text{K}$, which is of the same order when compared with pure PBN composition [21]. However, the magnitudes of $\mathbf{P_{RT}}$ are nearly equal
<table>
<thead>
<tr>
<th>Composition</th>
<th>Density (g/cm³)</th>
<th>P E (pm/V⁻¹)</th>
<th>Tc (°C)</th>
<th>p max (μm²/cm²)</th>
<th>fmax (Hz)</th>
<th>fmin (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.50</td>
<td>5.82</td>
<td>1.943</td>
<td>0.041</td>
<td>203</td>
<td>138</td>
<td>5.75</td>
</tr>
<tr>
<td>0.50</td>
<td>5.88</td>
<td>0.133</td>
<td>0.035</td>
<td>223</td>
<td>2542</td>
<td>141</td>
</tr>
<tr>
<td>0.63</td>
<td>5.68</td>
<td>0.136</td>
<td>0.037</td>
<td>231</td>
<td>221</td>
<td>166</td>
</tr>
<tr>
<td>0.53</td>
<td>5.80</td>
<td>0.131</td>
<td>0.038</td>
<td>256</td>
<td>2259</td>
<td>178</td>
</tr>
<tr>
<td>0.50</td>
<td>5.88</td>
<td>0.132</td>
<td>0.036</td>
<td>251</td>
<td>221</td>
<td>166</td>
</tr>
<tr>
<td>0.50</td>
<td>5.82</td>
<td>0.134</td>
<td>0.042</td>
<td>221</td>
<td>2542</td>
<td>141</td>
</tr>
<tr>
<td>0.53</td>
<td>5.80</td>
<td>0.131</td>
<td>0.038</td>
<td>256</td>
<td>2259</td>
<td>178</td>
</tr>
<tr>
<td>0.50</td>
<td>5.88</td>
<td>0.132</td>
<td>0.036</td>
<td>251</td>
<td>221</td>
<td>166</td>
</tr>
</tbody>
</table>

Table 6.1C: Pyroelectric data for compositions of C series
Fig. 6.1C Pyroelectric Coefficient Vs Temperature for Compositions of C-Series.
in C series when compared with the composition of A series. Further it is observed that \( P_{RT} \) value varies from 138 to 166 \( \mu \)C/m\(^2\)K. The \( P_{max} \) values in the compositions are one order of magnitude higher when compared with values at \( T_c \) as reported by Guo et al [23]. It is observed that the \( P_{TC} \) values 304, 287, 268, 251, 220 and 201°C corresponding to \( P_{max} \) in all compositions are well matched with \( T_c \) from dielectric measurements (chapter IV) and resistivity studies (chapter VIII).

The value of Figures of merit \( F_{MRV}, F_{MRN} \) and \( F_{MRU} \) are calculated and found in the order of \( 10^{-12} \) CM/J, \( 10^{-11} \) CM/J and \( 10^{-10} \) CM/J, respectively. These values are of the same order when compared with lead based pervoskite-type structure ferroelectric thin films of PZT reported by Shi et al [22]. The values of \( P_{RT}, P_{max}, P_{TC}, F_{MRV}, F_{MRN}, F_{MRU} \) and \( T_c \) are listed in Table 6.1C.

**6.5 Summary**

The values of \( P_{RT} \) and \( P_{TC} \) are high for most of the B-series compositions when compared with the rest of the compositions. Also light values of Figure of merit of \( F_{MRV}, F_{MRN} \) and \( F_{MRU} \) have been found in the compositions indicating that the materials are useful for pyroelectric detectors. The values of \( P_{RT} \) obtained in all series of compositions combined with low values of \( \varepsilon_{RT} \) and \( \tan \delta \) indicating the materials under study would be useful for pyroelectric detectors.
In the present study temperature dependence of pyroelectric coefficients of pure and Ce modified PBN ceramic compositions are obtained with large pyroelectric coefficients near MPB region. Near morphotropic phase boundary pure and modified PBN compositions are therefore interesting for pyroelectric device applications.
References

12. L.S.Kremenchugskii, A.P.Malnev and V.V.Samoilov, Probony I Tehhn Eksperim 6,169 (1966) [Instr and experiment techniques (English Trans!.) 6,1460 (1966)].