Dielectric and pyroelectric characteristics of PZT doped with gadolinium

H. D. Sharma, A. K. Tripathi, Vijayaraghavan Chariar, T. C. Goel and P. K. C. Pillai

Department of Physics, Indian Institute of Technology, New Delhi 110016 (India)

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Abstract

This paper reports on the dielectric and pyroelectric properties of Gd\textsuperscript{3+} modified PZT ceramic (Pb\textsubscript{1–x/2}Gd\textsubscript{x/2})Zr\textsubscript{0.95}Ti\textsubscript{0.05})O\textsubscript{3} (x in the range 0.0–0.1). It is found that Gd\textsuperscript{3+} modified PZT ceramic has a low dielectric constant and high pyroelectric coefficient. It is shown that the PGZT ceramic possesses the characteristics required by a good IR detector. The calculated parameters of interest, based on measured properties, are comparable with those of other ceramic and pyroelectric materials.

1. Introduction

There is a great need for the development of suitable pyroelectric detectors for a variety of applications. Pyroelectric detectors using ferroelectric ceramics are simple in construction and do not require cooling. They are robust and non-hygrosopic, and their useful temperature range can be tailored. The ferroelectric properties of PbTiO\textsubscript{3}, and PZT ceramics modified by partial substitution of La\textsuperscript{3+}, Sm\textsuperscript{3+}, Nd\textsuperscript{3+}, and Gd\textsuperscript{3+} have been investigated by several workers and interesting results have been reported [1–5].

Pyroelectric studies of PZT incorporating the trivalent rare earth Gd\textsuperscript{3+} have not been reported in the literature. Therefore, it was thought worthwhile to investigate the dielectric and pyroelectric properties of PGZT.

2. Experimental details

(Pb\textsubscript{1–x/2}Gd\textsubscript{x/2})Zr\textsubscript{0.95}Ti\textsubscript{0.05})O\textsubscript{3} samples with x = 0, 0.025, 0.05, 0.075 and 0.1 were prepared using PbO, ZrO\textsubscript{2}, TiO\textsubscript{2} and Gd\textsubscript{2}O\textsubscript{3} obtained from Aldrich Chem. Co., USA. The oxides were wet mixed in stoichiometric proportions in a solution of alcohol, and ball milled using zirconia balls for 16 h. Extra lead oxide (4% by weight over and above the stoichiometric ratio) was also added to the mixture during ball milling. This is to counteract lead losses during calcination and sintering. The mixture was dried and calcined at 850°C for 2 h. 4% by weight polyvinyl alcohol was added as a binder to the calcined powder and mixed thoroughly. The mixture was compacted to form pellets of 1 cm diameter using a die and hydraulic press under a load of 10 tons. The pellets were then heated very slowly (at 2°C min\textsuperscript{−1}) up to 600°C to avoid bending or cracking of the samples. The samples were then taken to a final sintering temperature of 1200°C at a heating rate of 5°C min\textsuperscript{−1} and were maintained at that temperature for 2 h. The sintering was done in a closed alumina crucible in lead atmosphere. An atmosphere of lead was generated by smearing the inner surface of the crucible with a layer of lead oxide powder.

X-ray diffractograms of these samples were taken using CuK\textalpha radiation on Rigaku diffractometer. The voltage and current ratings used for the present experiment were 40 kV and 30 mA respectively and the X-ray scan speed was 10° min\textsuperscript{−1}. Dielectric measurements were taken using an LF Hewlett Packard impedance analyzer (model 4192A). Quick drying silver paint was used for these and other electrical measurements. Charge field hysteresis phenomena were studied using a Sawyer Tower circuit [6]. Samples were corona poled at a voltage of 7 kV cm\textsuperscript{−1} and current of 50 μA for measurement of the pyroelectric coefficient. The pyroelectric current was measured at a heating rate of 4°C min\textsuperscript{−1} on a Keithley 610C electrometer. The pyroelectric coefficient was calculated using the relation

$$P_i = \frac{(I/A)(d\theta/dT)^{−1}}{2}$$

where I is the pyroelectric current, A is the electrode area of the sample and dθ/dT is the heating rate.
3. Results and discussions

X-ray diffractograms of PZT and PGZT with different percentages of Gd$^{3+}$ doping are shown in Fig. 1 and the peaks are identified. The presence of well resolved peaks due to (002) and (200) planes indicates that the material is in tetragonal form. It can be observed from the diffractograms that the heights of the peaks due to the different planes increase at 5% Gd$^{3+}$ doping and decline at 7.5% Gd$^{3+}$ doping without any appreciable change in peak position. The lattice parameters were calculated and are tabulated in Table 1. Some peaks due to titanium oxide and zirconium oxide are also observed in the diffractograms. This suggests the presence of trace quantities of unreacted TiO$_2$ and ZrO$_2$ in the samples, as has been reported by others [7].

Table 1 shows the variation of lattice parameters $a$ and $c$ as a function of Gd$^{3+}$ concentration in PZT. As can be seen from the table, the substitution of Pb$^{2+}$ by Gd$^{3+}$ leads to a strong reduction in $a$ and $c$ parameters. A similar effect is observed on the parameters $c/a$ and $(a^2c)^{1/3}$. These results indicate that a solid solution was formed in the Gd$_2$O$_3$–PZT system. It is pertinent to note here that although 4% by weight extra lead was introduced in the samples prior to sintering, the possibility of the creation of lead vacancies due to evaporation cannot be ruled out. This is essential to maintain charge neutrality in the ceramic and can explain the decrease in unit cell volume and bulk density with increase in Gd$^{3+}$ concentration. A decrease in bulk density with increasing La content in PLZT for all Zr-to-Ti ratios has also been reported by Haertling and Land [8]. Further, our observations of a decrease in bulk density can be explained by the difference in ionic radii of Pb and Gd. Since the ionic radius of Gd$^{3+}$ (0.94) is smaller than that of Pb$^{2+}$ (1.20), the intralattice porosity in Gd modified PZT increases with increasing Gd$^{3+}$ doping in the PZT sample.

The differential scanning calorimetry (DSC) thermogram (Fig. 2) of the PGZT sample was obtained using a DuPont DSC meter at a heating rate of 10°C min$^{-1}$. The transition temperature of the Gd modified PZT sample is found to be 323.97°C.

Figures 3(a) and 3(b) show typical plots of the variation in dielectric constant and dielectric loss tangent with temperature for (Pb$_{1-3x/2}$Gd$_{3x/2}$)(Zr$_{0.6}$Ti$_{0.4}$)O$_3$, where $x = 0.05$ at several frequencies. It is observed that the value of $\varepsilon'$ increases gradually with temperature, while the value of tan $\delta$ decreases up to 60°C and then increases slightly. It is also observed that at lower frequencies (up to 1 kHz), the rise in tan $\delta$ is significant.

<table>
<thead>
<tr>
<th>Lattice parameter ($\text{nm}$)</th>
<th>Pure PZT</th>
<th>PGZT with 5% Gd</th>
<th>PGZT with 7.5% Gd</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$</td>
<td>4.058</td>
<td>4.026</td>
<td>4.024</td>
</tr>
<tr>
<td>$c$</td>
<td>4.171</td>
<td>4.126</td>
<td>4.120</td>
</tr>
<tr>
<td>$c/a$</td>
<td>1.0278</td>
<td>1.0243</td>
<td>1.0239</td>
</tr>
<tr>
<td>$(a^2c)^{1/3}$</td>
<td>4.095</td>
<td>4.059</td>
<td>4.058</td>
</tr>
</tbody>
</table>

Fig. 1. X-ray diffractograms of (a) PZT, (b) PGZT, Gd$^{3+}$ concentration 5%, and (c) PGZT, Gd$^{3+}$ concentration 7.5%.
above 100 °C. Importantly, it is seen that the value of \( \varepsilon' \) is low and does not vary much with frequency. This property of the ceramic is central to obtaining a higher and fairly constant pyroelectric voltage responsivity and detectivity over a wide frequency range.

The variation of the dielectric constant with temperature and frequency shows the normal behavior of a dipolar material. The low value of the dielectric constant compared with that of undoped PZT which was prepared under conditions similar to those for the PGZT ceramic (\( \varepsilon' = 8.50 \) at room temperature, 10 kHz) can be understood in terms of the anisotropy in the material. The \( c/a \) ratio in \( \text{PbTiO}_3 \) is 1.06 while in PZT with 60% Zr it is 1.03. The \( c/a \) ratio for the PGZT samples as calculated from the X-ray data is found to be 1.0243 for 5% Gd doping and 1.0239 for 7.5% Gd doping. This indicates that the structure in Gd modified PZT is less tetragonal than those of \( \text{PbTiO}_3 \) and PZT. The decrease in tetragonality may be one of the reasons for the decrease in the dielectric constant of the PGZT ceramic. Among the various factors that determine the dielectric constant of a ceramic are the dipole moment, domain wall mobility and internal stresses in the material. We would also like to point out that the lattice parameters obtained by us are slightly different from those reported by Jaffe et al. [9]. This appears to be due to the presence of traces of unreacted TiO\(_2\) and ZrO\(_2\), which could alter the exact composition of the sample.

Figures 4(a) and 4(b) show the variation in dielectric constant \( \varepsilon' \) and imaginary component of the dielectric constant \( \varepsilon'' \) for different concentrations of Gd\(^{3+}\) for various temperatures at 10 kHz. It is observed that the dielectric constant increases gradually as the Gd\(^{3+}\) doping increases up to 7.5%, and at 10% Gd\(^{3+}\) doping the dielectric constant actually decreases at all frequencies. The behavior of \( \varepsilon'' \) is similar. This type of behavior has also been observed for Yb\(^{3+}\) doping in PZT [10].

A charge field hysteresis curve of a Gd\(^{3+}\) doped sample is shown in Fig. 5. As can be seen from the figure, the hysteresis loop is symmetric about the origin. The values of saturation polarization \( P_s \) and remnant polarization \( P_r \) are found to be 8.3 \( \mu \text{C cm}^{-2} \) and 5.839 \( \mu \text{C cm}^{-2} \) at room temperature. The coercive field at room temperature is found to be 5.9375 kV cm\(^{-1}\).
Figure 6 shows the variation in pyrocurrent and pyrocoefficient with temperature. It is observed that both the pyrocurrent $I$ and pyrocoefficient $P_i$ increase initially with temperature up to 55°C and then remain constant up to 125°C. Above 125°C, both increase linearly with temperature. The variation in pyroelectric coefficient with temperature for four different concentrations of Gd$^{3+}$ is shown in Fig. 7. It is seen that the maximum value of pyroelectric coefficient for PGZT ceramic is between 5% and 7.5% doping. However, the pyrocoefficient increases almost linearly for the 2.5% Gd$^{3+}$ doped sample and as such can be used for detection from 40°C to 125°C [11-13].

The important characteristics of pyroelectric detectors are (a) the current responsivity $F_i$, (b) the voltage responsivity $F_v$, and (c) the detectivity $F_D$. The current and voltage responsivity are given by

$$F_i = \frac{p_i}{c'}$$
$$F_v = \frac{p_i}{c'\varepsilon'}$$

respectively, where $p_i$ is the pyroelectric coefficient of the ceramic, $c'$ is the volume specific heat and $\varepsilon'$ is the dielectric constant of the material. The detectivity $F_D$ is given by

$$F_D = \frac{p_i}{c'\varepsilon''}$$

where $\varepsilon'' = \varepsilon'\tan\delta$, $\tan\delta$ being the loss tangent in the dielectric. The values of these pyroelectric parameters are plotted in Fig. 8.

Fig. 4. (a) Variation of the dielectric constant $\varepsilon'$ with temperature for different Gd$^{3+}$ concentrations at 10 kHz. (b) variation of the imaginary component of the dielectric constant $\varepsilon''$ with temperature for different Gd$^{3+}$ concentrations at 10 kHz.

Fig. 5. Hysteresis loop for PGZT with 5% Gd$^{3+}$ doping.

Fig. 6. (a) Variation of pyrocurrent with temperature, 5% Gd; (b) temperature dependence of the pyroelectric coefficient, 5% Gd.
It is seen that $F_1$, $F_2$, and $F_D$ for PGZT are almost independent in the temperature range 40–125 °C. Above 125 °C, $F_1$, $F_2$, and $F_D$ increase linearly with temperature. This suggests that the material can be used as a pyroelectric detector in the temperature range up to 125 °C. Another useful advantage of doping PZT with Gd$^{3+}$ is that it relieves the internal stresses in the ceramic and thereby facilitates poling. Work is now in progress with respect to optimizing the Gd$^{3+}$ doping concentration with varying proportions of Zr and Ti.

Acknowledgments

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