

Studies of structural and electrical properties of $\text{Pb}(\text{Li}_{1/4}\text{Eu}_{1/4}\text{Mo}_{1/2})\text{O}_3$ ceramics

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Abstract. Polycrystalline sample of $\text{Pb}(\text{Li}_{1/4}\text{Eu}_{1/4}\text{Mo}_{1/2})\text{O}_3$ was prepared by usual ceramic route. X-ray diffraction, SEM and EDAX were used to check the formation, homogeneity and elements present in the compound. The measurement of dielectric constant (ϵ), dielectric loss ($\tan \delta$), hysteresis loop parameters (e.g. spontaneous polarization) as function of frequency and temperature suggest that the compound is a ferroelectric one and has a ferro-paraelectric phase transition at 112 ± 2 C. The measurement of dc resistivity both as function of biasing electric field and temperature of the compound suggests that the compound has negative temperature coefficient (NTC) of resistance above 100 C.

Keywords. Distorted perovskite structure; dielectric anomaly; polarization reversal; phase transition; dc electrical resistivity.

1. Introduction

Some compounds of ABO_3 -type [A = mono, divalent, B = tri-hexa valent ions] such as YCrO_3 could be made (Keith and Roy 1954) which were not normal perovskite but heavily distorted perovskite. Normally the identification of this type of compounds can be made for any multicomponent oxygenous perovskite of general formula $(\text{A}_1, \dots, \text{A}_k)(\text{B}_1, \dots, \text{B}_l)\text{O}_3$ with satisfying following conditions:

$$(i) \quad \sum_{i=1}^k x_{\text{Ai}} n_{\text{Ai}} + \sum_{i=1}^l x_{\text{Bi}} n_{\text{Bi}} = 6, \quad (1)$$

where

$$\sum_{i=1}^k x_{\text{Ai}} = 1; \quad 0 \leq x_{\text{Ai}} \leq 1,$$

$$\sum_{i=1}^l x_{\text{Bi}} = 1; \quad 0 \leq x_{\text{Bi}} \leq 1,$$

$$n_{\text{Ai}} = 1, 2, 3;$$

$$n_{\text{Bi}} = 2, 3, 4, 5, 6;$$

and

$$(ii) \quad t = \frac{\bar{r}_A + r_O}{\sqrt{2}(\bar{r}_B + r_O)}, \quad (2)$$

where t is the tolerance factor, \bar{r}_A the average ionic radius of A site atoms, \bar{r}_B the average ionic radius of B site atoms and r_O the ionic radius of $\text{O}^{2-} = 1.32 \text{ \AA}$ (Goldschmidt).

For normal perovskite the value of t tends to unity ($0.8 \leq t \leq 1$). The compound having tolerance value less than 0.8 forms distorted perovskite structure. $\text{Pb}(\text{Li}_{1/4}\text{Eu}_{1/4}\text{Mo}_{1/2})\text{O}_3$

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is a member of distorted perovskites having tolerance value $t = 0.734$. Though a large number of Pb-based perovskite ferroelectrics have been synthesized and characterized for many electronic devices (Cross 1984; Deb 1988; Okuyama and Hamakawa 1991; Tandon *et al* 1991), not much work has been done on PbWO_3 , PbMoO_3 and their modified compounds. Some members of this family have shown very interesting behaviour which motivate us to carry out a systematic study of $\text{Pb}(\text{Li}_{1/4}\text{Eu}_{1/4}\text{Mo}_{1/2})\text{O}_3$ (here after PLEM) compound. In this paper we are reporting the structural, SEM, detailed dielectric, hysteresis loop/polarization reversal and resistive properties of PLEM.

2. Experimental

Polycrystalline sample of PLEM was synthesized by high-temperature solid-state reaction technique from high purity oxides and carbonate: PbO (99.99%, M/s Aldrich Chemical Company Inc. USA), Eu_2O_3 (99.90%, M/s Indian Rare Earth Ltd.), MoO_3 (99.9%, John Baker Inc. USA) and Li_2CO_3 (99.99%, M/s S. D. Fine Chemical Pvt. Ltd.) in a suitable stoichiometry. These anhydrous oxides and carbonate powders were thoroughly mixed in an agate mortar for 4 h. The fine mixed powder was fired at 550°C for 12 h. The mixing and recalcination were completed at 600°C for 10 h and finally at 680°C for 10 h in air atmosphere. The homogeneous powder of PLEM was then used to make cylindrical pellets of diameter 10 mm and thickness 1–2 mm under an isostatic pressure of about $6 \times 10^7 \text{ kg/m}^2$. Polyvinyl alcohol (PVA) was used as binder to reduce the brittleness of the pellets. The pellets were finally sintered at 700°C for 6 h in a platinum plate.

The formation of the desired compound was checked by preliminary structural studies with the help of X-ray diffractogram (XRD) on calcined powder in the wide range of Bragg angle, 2θ ($20^\circ \leq 2\theta \leq 100^\circ$) at room temperature using X-ray diffractometer (Philips PW 1710, Holland) with FeK_α radiation ($\lambda = 1.9370 \text{ \AA}$). The surface morphology/grain distribution of the pellet and its compositional analysis (elements present) were carried out with scanning electron microscope (STEREOSCAN S-180). The dielectric constant and loss of PLEM were measured both as function of frequency (500 Hz–10 kHz) and temperature (-150°C – 180°C) using GR 1620 AP capacitance measuring assembly and laboratory made 3-terminal sample holder, which compensates stray capacitance.

The study of hysteresis loop was carried out using modified Sawyer and Tower circuit (Sinha 1965) with a dual trace oscilloscope (TESTATION–4444 APLAB) at a field 4.5 kV/cm. The temperature dependence of spontaneous polarization (P_s) was also measured from the hysteresis loop parameters.

The dc electric resistivity was measured both as function of biasing electric field (30–100 V/cm) at room temperature and temperature (RT– 300°C) at constant electric field (80 V/cm) with the help of KEITHLEY–617 programmable electrometer and laboratory made heating arrangement.

3. Results and discussion

3.1 Structural property

Figure 1 shows the XRD pattern of calcined powder of PLEM at three different calcine temperatures. It is clear from the X-ray diffraction profiles that the peaks of finally calcined powder are unsplit and different from the precursor, indicating the formation of desired compound. All the peaks were indexed with different configurations of seven

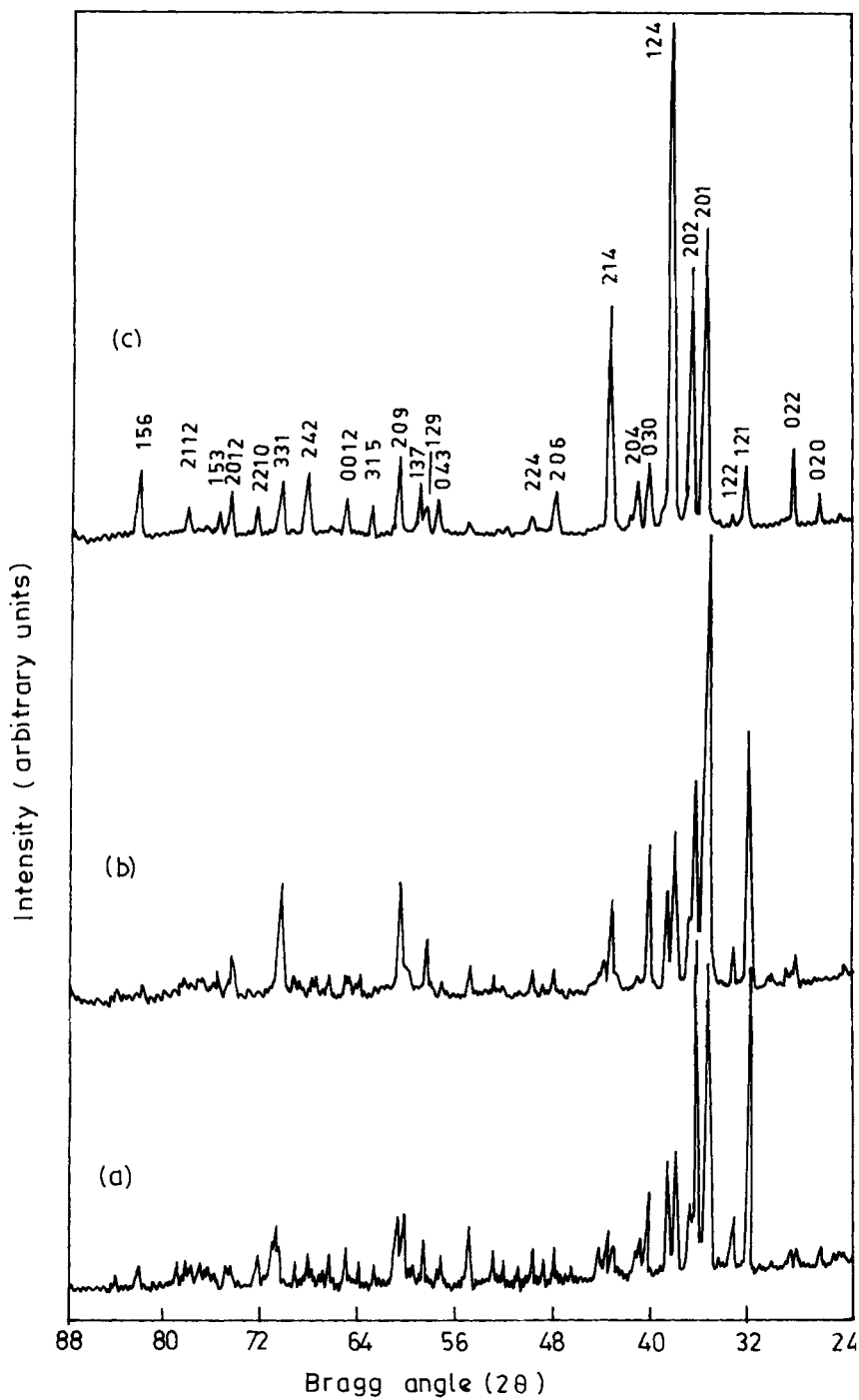


Figure 1. X-ray diffraction patterns of PLEM calcined powder (a) 550°C for 12 h, (b) 600°C for 10 h and (c) 680°C for 10 h.

crystal systems. The selected cell parameters in orthorhombic system at room temperature were refined by least-squares method. The refined cell parameters of distorted PLEM were found to be: $a = 6.3295 \text{ \AA}$, $b = 8.3398 \text{ \AA}$ and $c = 21.4751 \text{ \AA}$. The average linear particle size of the sample calculated from the peak broadening of XRD pattern over a wide 2θ range using Scherrer's equation

$$P_{hkl} = \frac{0.89\lambda}{\beta_{1/2} \cos \theta_{hkl}},$$

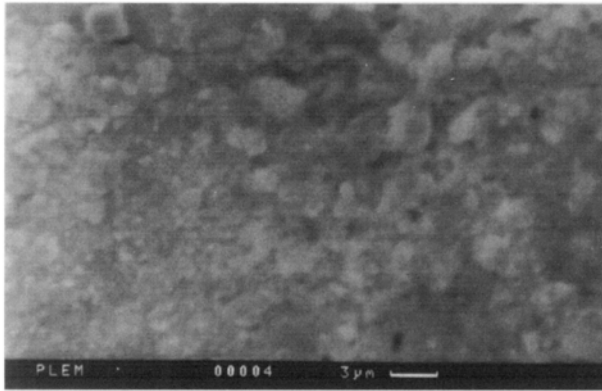


Figure 2. SEM micrograph of PLEM at $3 \mu\text{m}$ magnification.

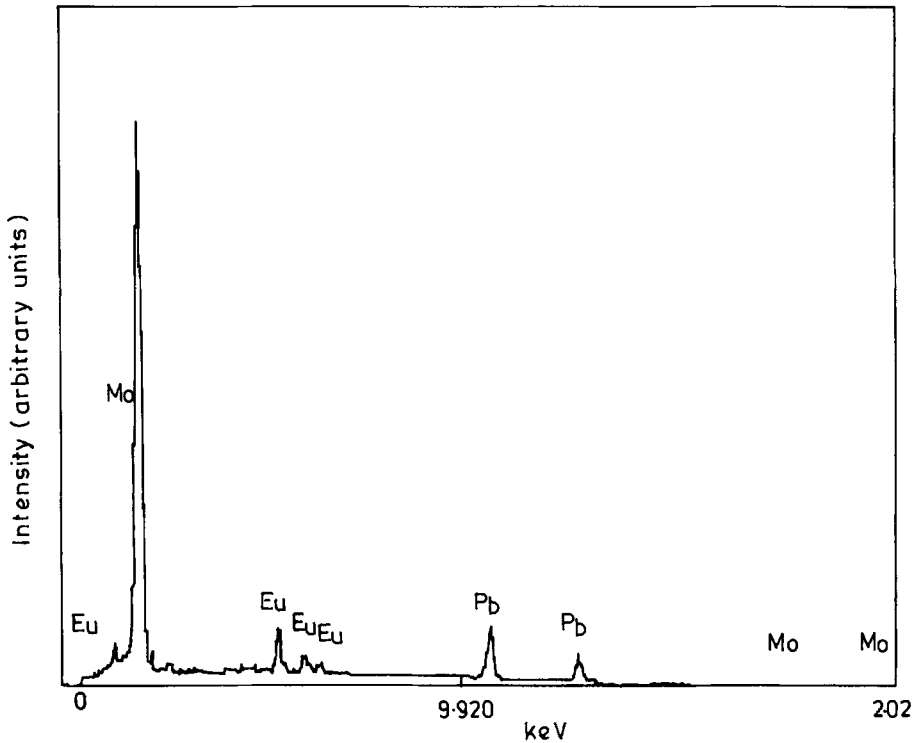


Figure 3. Energy dispersive X-ray profile of PLEM.

where $\beta_{1/2}$ = half-peak width in radian, was found to be 350 Å. Here broadening due to instrument has been neglected. The result is consistent with the result obtained from particle size analyzer.

3.2 SEM and EDAX studies

Figure 2 shows the SEM micrograph of PLEM at 3 μm magnification. The tiny grains are closely distributed and results in a high density ceramic. The elemental analysis was also carried out from the SEM studies. Figure 3 shows the energy dispersive X-ray spectrum of PLEM, which confirms the elements present in the compound. The light elements such as lithium and oxygen could not be detected as expected.

3.3 Dielectric properties

Figure 4 shows the variation of dielectric constant (ϵ) and dielectric loss ($\tan \delta$) as a function of frequency. The nature of variation of these parameters shows the normal behaviour of dielectrics. Dielectric constant of PLEM significantly decreases with increasing frequency. This is due to presence of all types of polarization (viz. electronic,

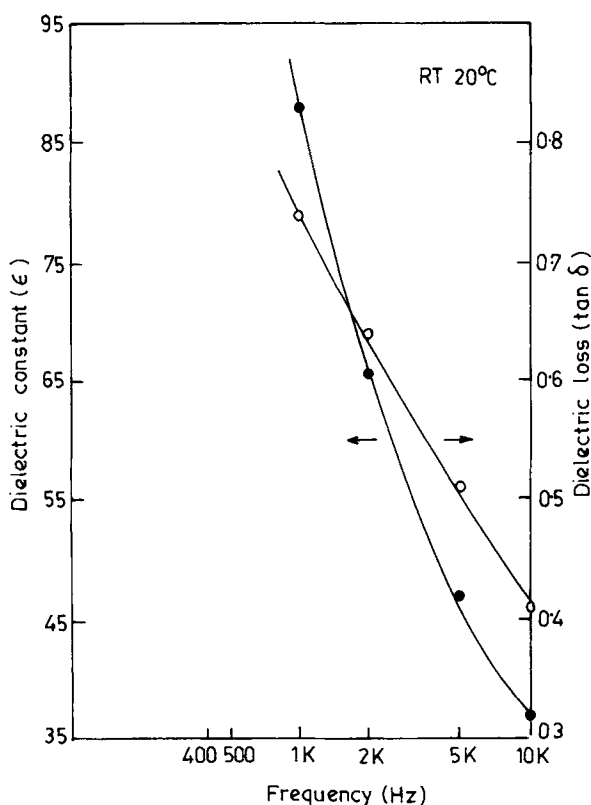


Figure 4. Variation of dielectric constant (ϵ) and dielectric loss ($\tan \delta$) as a function of frequency at room temperature of PLEM.

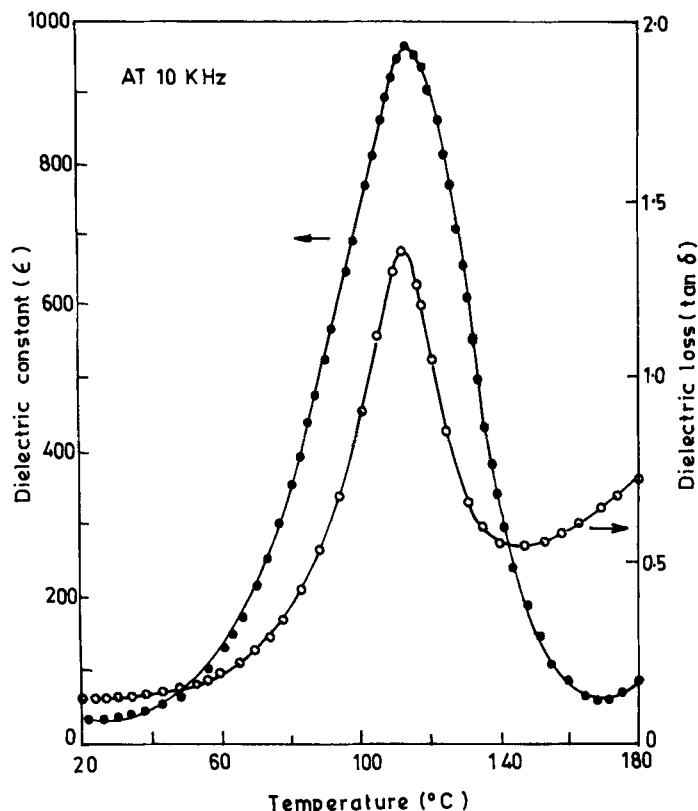


Figure 5. Variation of dielectric constant (ϵ) and dielectric loss ($\tan \delta$) of PLEM as a function of temperature at 10 KHz.

dipolar, interfacial, orientational etc) at room temperature and at low frequencies (Lines and Glass 1977). The variation of dielectric constant (ϵ) and dielectric loss ($\tan \delta$) as a function of temperature (20°C – 180°C) have been shown in figure 5. The dielectric constant and loss are almost independent of temperature (-150 – 20°C) (not shown in figure 5), but start increasing slowly up to 60°C and then rapidly to its maximum value around 114°C . Above 114°C , ϵ decreases sharply. The dielectric loss also varies in similar way. A strong dielectric anomaly was found at 114°C which may be considered as transition temperature of PLEM.

3.4 Hysteresis loop and measurement of spontaneous polarization

Figures 6 a–c show the ferroelectric hysteresis loop at 32°C (RT), 100°C and 112°C respectively. As the ceramic sample has lower density than that of its single crystal, therefore, higher electric field is required to obtain saturation polarization. On the other hand at higher field the ceramic sample breaks into small pieces. So, we have optimized a maximum field 4.5 kV/cm at which we have got the above loops. At 100°C the loop area reduces and becomes zero at 112°C . The variation of spontaneous

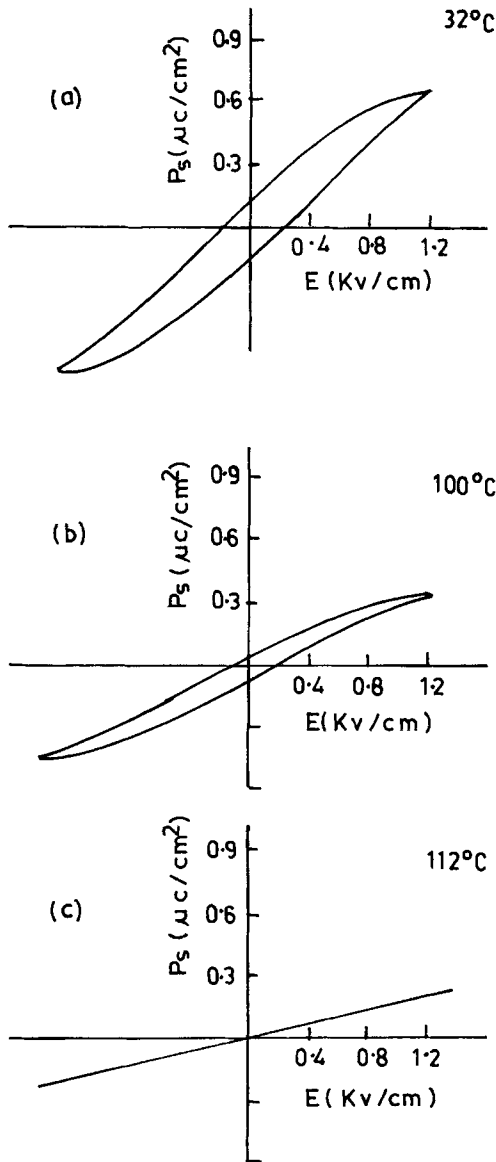


Figure 6. Trace of typical hysteresis loops of PLEM ceramics (a) at $32^\circ C$, (b) at $100^\circ C$ and (c) at $112^\circ C$ at an ac field 4.5 kv/cm.

polarization (P_s) as a function of temperature has been shown in figure 7. The spontaneous polarization decreases with increasing temperature until it reaches to a constant non zero value. The temperature at which the spontaneous polarization sharply falls is called the Curie temperature or in other words transition temperature ($T_c = 112^\circ C$). This transition temperature is confirmed from both the experimental evidences: (i) dielectric anomaly ($T_c = 114 \pm 2^\circ C$) and (ii) sharp fall in spontaneous polarization ($T_c = 112 \pm 2^\circ C$). Usually, for ceramic sample it has been found that there remains a constant spontaneous polarization instead of zero above T_c . This can be

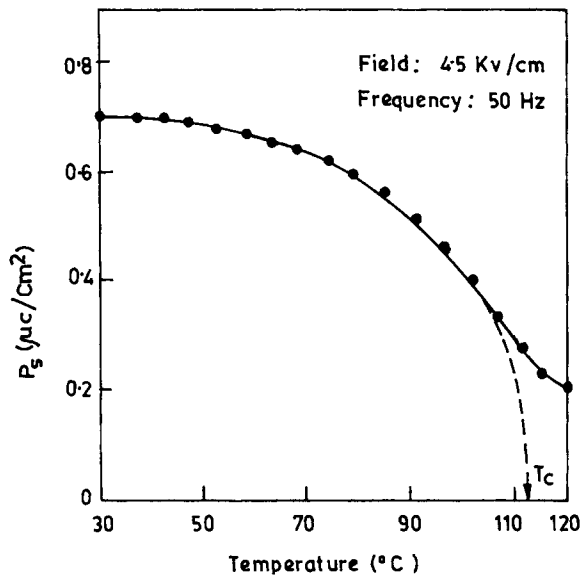


Figure 7. Variation of spontaneous polarization (P_s) of PLEM as a function of temperature.

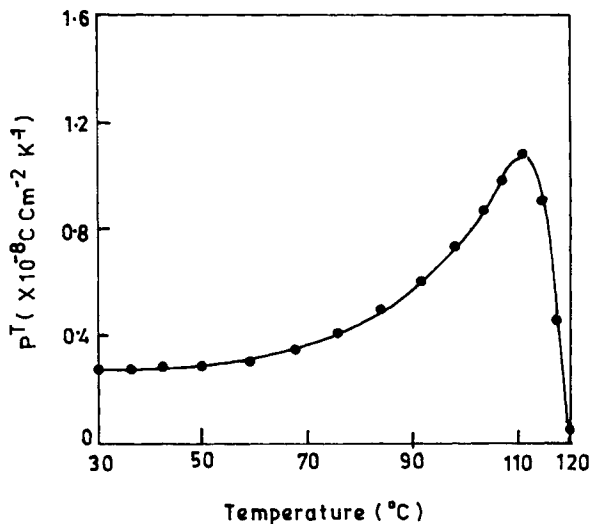


Figure 8. Variation of pyroelectric coefficient (P^T) as a function of temperature of PLEM.

explained by the nature of domains present in the ceramics. The ceramic sample has a large number of domains having different direction of polarization in spite of a single polar axis as it has in a single crystal. Due to application of external ac electric field the dipoles in each and every domain experience a force to oscillate about their mean position of rest with the frequency of applied field (50 Hz). When thermal energy is supplied to it the dipole may agitate and rearrange randomly. But some of them still show a definite dipole moment, which results in a small value of spontaneous polarization above T_c .

3.5 Pyroelectric property

The temperature derivative of spontaneous polarization (P_s) at constant stress (θ) and electric field (E) is called the pyroelectric coefficient P^T (Lang 1974)

$$P^T = \left[\frac{\partial P_s}{\partial T} \right]_{\theta, E}$$

Figure 8 shows the variation of P^T as a function of temperature. The value of P^T is maximum at T_c .

3.6 Resistive property

At room temperature variation of dc resistivity as a function of biasing field is shown in figure 9. It has been observed that the resistivity of PLEM decreases with increasing biasing electric field. This may be due to the following reasons: (i) ionization occurs in inhomogeneous ceramic dielectric mainly through the mechanism of partial discharge of gases or moistures from the pores or cracks present in the ceramics. The supplied electric field results in the generation of local heat which results in the generation of thermal stresses and increasing of local conduction. The stresses can generate more cracks leading to further ionization up to certain field (Buchanan 1986) and (ii) electrons may be ejected from electrodes and accelerated through the sample. During acceleration they collide with other ions or atoms in the solid and knock out other electrons. Hence ionization takes place. So, resistivity comes down as biasing field increases (Buchanan 1986).

The temperature dependence of dc resistivity of PLEM at constant biasing field (80 V/cm) has been shown in figure 10. The dc resistivity decreases with increasing temperature. The reason is as follows: Due to addition of thermal energy the electrons

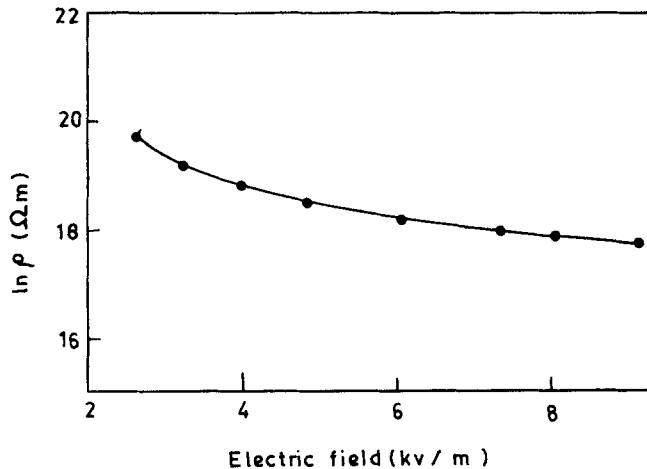


Figure 9. Variation of dc resistivity ($\ln\rho$) of PLEM as a function of biasing electric field at room temperature.

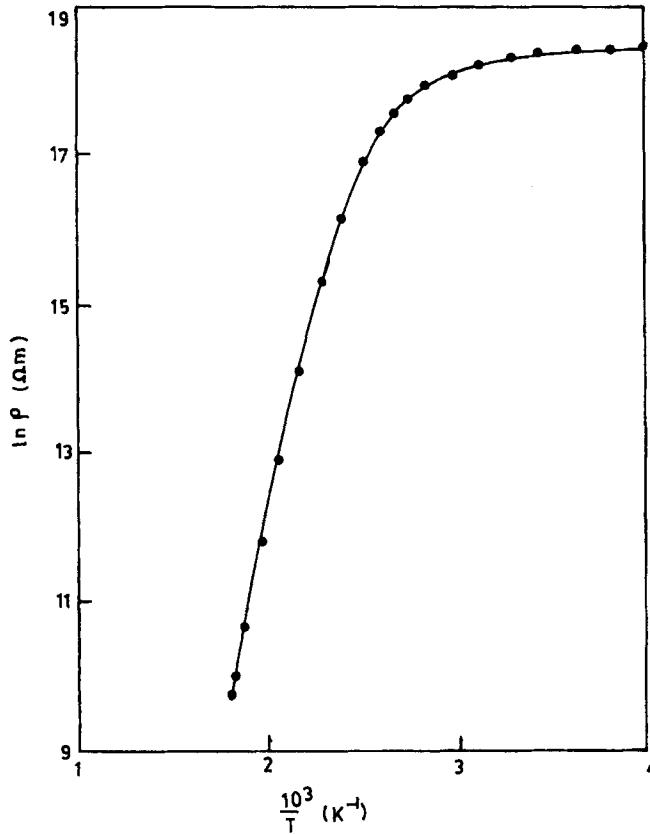


Figure 10. Variation of dc resistivity ($\ln \rho$) as a function of inverse of absolute temperature ($10^3/T$) of PLEM at 80 V/cm.

could be set free from O^{2-} ions. When an electron is introduced in the sample it might be associated with cations which results in unstable valence state (Buchanan 1986). This type of resistive behaviour has also been found in many semiconductors (Hanny 1959).

4. Conclusion

Finally, it has been concluded that PLEM is a ferroelectric material ($T_c = 112 \pm 2^\circ\text{C}$) and have negative temperature coefficient of resistance (NTC).

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References

- Buchanan R C 1986 *Ceramic materials for electronics* (New York and Basel: Marcel Dekker Inc.)
- Cross L E 1984 *Ferroelectrics* **76** 214
- Deb K K 1988 *Ferroelectrics* **82** 45
- Hanny N B 1959 *Semiconductors* (New York: Reinhold Publishing Corporation)
- Keith M L and Roy R 1954 *Am. Min.* **39** 1
- Lang S B 1974 *Source book of pyroelectricity* (London: Gordon and Breach Science Publishers)
- Lines M E and Glass A M 1977 *Principles and applications of ferroelectrics and related materials* (Oxford: Oxford Univ. Press)
- Okuyama M and Hamakawa Y 1991 *Ferroelectrics* **118** 261
- Sinha J K 1965 *J. Sci. Instrum.* **42** 696
- Tandon R P, Singh R, Singh R D P and Chandra S 1991 *Ferroelectrics* **120** 293