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Local Polarization and Field Induced Anomaly in PLZT Relaxor Ferroelectric Ceramics

G. Shabbir

Central Diagnostic Laboratory, Physics Division, PINSTECH, Islamabad, Pakistan

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ABSTRACT

Lanthanum doped lead zirconate titanate $(Pb_{1-x}La_x)(Zr_yTi_{1-y})O_3$ *(PLZT x/y/1-y) relaxor ferroelectric ceramics show no macroscopic polarization down to low temperatures as shown by the present dielectric and Raman scattering measurements on PLZT-10/65/35. The measured inverse dielectric constant exhibited a broad minimum that was associated to the randomly oriented local polarization due to appearance of polar nanoregions (PNRs) below the Burns temperature* (T_B)*. The temperature dependence of such kind of local polarization was successfully calculated from the classical Landau theory of ferroelectric phase transitions. Electric field induced Brillouin scattering data also exhibited an abnormal shift at ~249 K that confirmed the switchable character of local polarization in relaxor ferroelectrics.*

1. Introduction

Lanthanum doped lead zirconate titanate $(Pb_{1-x}La_x)(Zr_yTi_{1-y})O_3$ (PLZT x/y/1-y) solid solutions are transparent ceramics which have many potential applications in high-speed scanning, micro electro-mechanical devices, optical switches and shutters, eye protecting devices [1, 2]. The ceramics with compositions x/65/35 and La contents between 5 and 14 at. % show anomalous relaxor-like dynamics and have been a subject of much interest for researchers due to excellent electromechanical properties. PLZT relaxor ceramics are typically characterized by a frequency dependent broad complex dielectric constant, by the lack of macroscopic crystal symmetry changes near and below the dielectric anomaly in zero electric field, by slim-loop hysteresis character near the dielectric maxima (T_m ~350 K for PLZT) and slowing dynamics [3, 4]. It is believed that coupling of the ferroelectrically active oxygen octahedra is broken by the La ions resulting in *A*-site vacancies giving rise to polar fluctuations in intrinsically inhomogeneous matrix that in turn produce local polar entities known as polar nanoregions (PNRs). It is this unusual behavior induced by intrinsic inhomogeneities (disorder in the cation sublattices) in relaxor materials due to which long-range ferroelectric order cannot be stabilized.

In the thermally depoled state, PLZT relaxor ceramics have nearly cubic perovskite ABO_3 type lattice symmetry at room temperature and the long range ordered ferroelectric state can only be established by applying a sufficient *dc*-bias field higher than a threshold value E_c ~5 kV/cm as shown in electric field-temperature phase diagram (Fig. 1) [5]. After switching off the field the polarization remains stable only below a certain temperature called the freezing temperature T_f which is much lower than the maximum temperature T_m of the complex dielectric ac susceptibility $\chi \sim \varepsilon^* = \varepsilon' - j\varepsilon''$. However, in the measurements on refractive index of these ceramics, Burns and Dacol [6] reported that the anomalous behavior exists up to temperatures well above T_m. This so called the Burns temperature T_B for PLZT x /65/35 is ~ 620 K. It was attributed to the

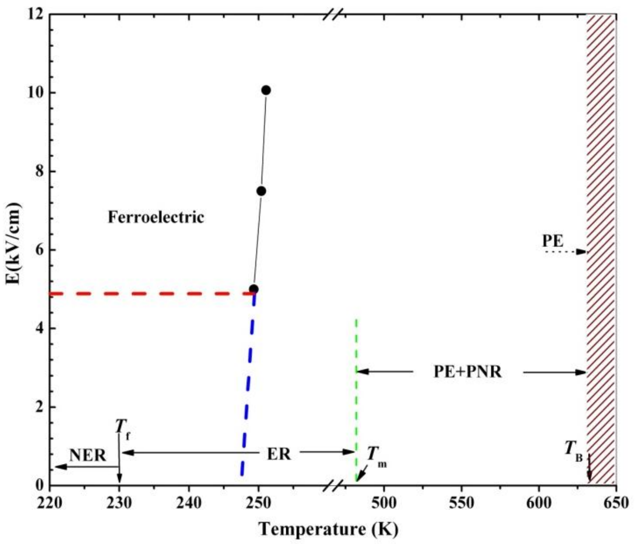

Fig. 1. Temperature-electric field phase diagram of PLZT-*x*/65/35 ceramics [5], abbreviations used are explained in the text.

appearance of local PNRs, first in La deficient regions and growing with further decreasing temperature and saturate to ~10 nm below ~370 K as revealed by high resolution TEM

*email address: gshabbir@gmail.com

investigations [7]. PLZT ceramics are interesting materials because of their non-equilibrium glassy dynamics like multiple aging, memory, and rejuvenation, demonstrating hierarchical structure [8]. In this study, estimated local polarization and field induced changes in PLZT-10/65/35 relaxor ceramic are reported in a specific temperature range. The results are further complimented with the temperature dependent Raman scattering measurements.

2. Experimental

Brillouin scattering spectra were recorded by using a high-contrast 6 pass tandem Fabry-Pérot Interferometer (M/S JRS Scientific Instruments). Details about the PLZT-10/65/35 transparent ceramic sample and measurement procedure are described elsewhere [9]. The ceramic specimen was polished to optical quality and silver electrodes were evaporated on surface of the sample to apply electric field. It was then placed in a LINKAM Stage (THMS 600) fixed on *X-Y* adjustable stage of a microscope (Olympus, BH-2) for temperature dependent Brillouin spectra measurements in the backscattering geometry. Dielectric constant of the ceramic sample was measured by an Agilent 4294A Impedance analyzer and LINKM THMSE 600 heating stage. Temperature dependent Raman spectra were also measured by a high-resolution triple grating spectrometer (Jobin Yvon, T64000).

3. Results and Discussion

The dielectric constant exhibited a broad anomaly at T_m as shown in Fig. 2 (inverse plot of ε'). This broad dielectric anomaly can be qualitatively explained in the framework of

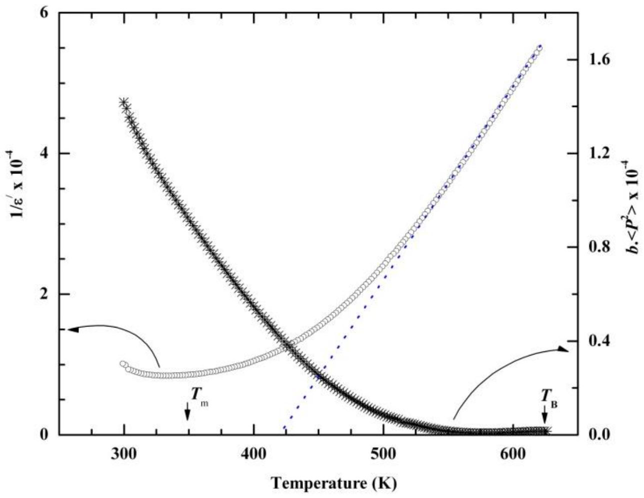

Fig. 2. Plot of inverse dielectric constant (ε') and calculated local polarization compounded with dielectric nonlinearity coefficient (b) as a function of temperature for PLZT-10/65/35 ceramic.

Landau Free Energy theory [10] which is based on the idea of an *order parameter* (spontaneous polarization $\boldsymbol{P}_s$ for normal ferroelectrics). The simplest expression for free energy in terms of $\boldsymbol{P}_s$ as an *order parameter* may be written as:

$$F(T,P) = F_o(T,0) + \frac{1}{2C}(T - T_o)P^2 + \frac{1}{4}\beta P^4 + ..F_C + .. \quad (1)$$

where F_o is the free energy in the paraelectric state ($\boldsymbol{P}_s$=0) and F_C is coupling term representing interaction between elastic strain and *order parameter*. In terms of dielectric susceptibility (χ), solving the above equation under the stability conditions of usual thermodynamics and taking lattice susceptibility (χ_o) and $\boldsymbol{P}_s$ as parameters alongwith g_{ijkl} as coupling constant we get:

$$\frac{1}{\chi_{ij}} - \frac{1}{\chi_{oij}} = \sum g_{ijkl} P_k P_l \quad (2)$$

The symmetry changes in normal ferroelectrics depicted by the coupling constant g_{ijkl} can be detected but in relaxor ferroelectrics like PLZT, it is hard to apply above formulation because of the absence of symmetry breaking in zero external electric field. Broad anomaly in the dielectric constant of relaxor materials can alternatively be explained by adopting the concept of local polarization [6] in which the term $\boldsymbol{P}_l\boldsymbol{P}_k$ would be replaced by mean squared polarization $\langle P^2\rangle$ (an *order parameter* in relaxor ferroelectrics). To accommodate isotropic nature of local polarization g_{ijkl} would become effective isotropic coupling constant (g_{eff}):

$$\frac{1}{\chi} - \frac{1}{\chi_o} = g_{eff} \left\langle P^2 \right\rangle \quad (3)$$

This local polarization is associated to the PNRs with random orientation that appears at T_B and can be roughly estimated from the dielectric constant data by considering the relationship between the static dielectric constant and the homogeneous ferroelectric polarizability similar to that of normal ferroelectric materials. The $\langle P^2\rangle$ may be approximated from the above relationship (Eq. 3) by incorporating real part of dielectric constant (ε') instead of dielectric susceptibility and neglecting higher order terms we get:

$$\frac{1}{\varepsilon'(T)} = \frac{T - T_o}{C} + 3b\left\langle P^2 \right\rangle \quad (4)$$

where C is the Curie-Weiss constant and b is the dielectric nonlinearity coefficient.

Although the local polarization is difficult to extract from above equation as an independent parameter, however, its temperature dependence can be understood as a product of coefficient b, ($b\langle P^2\rangle$), and thus calculated results are plotted in Fig. 2. The Curie-Weiss constant was of the same order of magnitude (~10^5) to that of normal ferroelectrics with displacive phase transition. It is clear in

Fig. 2 that $b\langle P^2\rangle$ appears at $T \leq T_B$ with decreasing temperature from the high temperature paraelectric state and increases markedly with further decrease in temperature. This indicates that broad dielectric anomaly at T_m in PLZT (and other relaxors) is clearly related to ferroelectricity. Although there is no macroscopic structural phase transition at T_B but for $T<T_B$ it shows different physical behavior as compared to that for $T>T_B$.

As measured Raman spectra of the PLZT-10/65/35 ceramic sample at some selected temperatures are shown in Fig. 3. The Raman spectrum for relaxor ferroelectric ceramics is forbidden due to their average cubic symmetry,

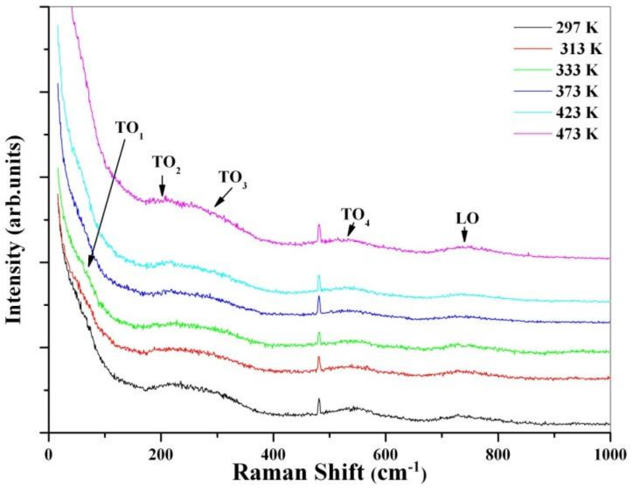

Fig. 3. Raman spectra of PLZT-10/65/35 ceramic specimen measured at some selected temperatures. Presence of different optical phonon modes is indicated by arrows.

however broad bands are observed due to glass-like disordered structure of these materials. This is most probably connected with second order type processes which result from coupling of hard polar modes with fluctuating local polarization associated with PNRs detectable at $T \leq T_B$. The observed broad band modes were fitted to the classical damped-harmonic-oscillator (DHO) function to understand their temperature dependent characteristics [11]. It can be observed that one longitudinal optical (LO) and four transverse optical (TO) modes are present at all temperatures with no detectable change in their positions and intensities at least in the investigated temperature range.

Fig. 4 shows a clear anomaly in the Brillouin frequency shift (ν_B) and full width at half maximum (FWHM) related to damping factor (Γ) of observed acoustic phonon mode having angular frequency ω in PLZT-10/65/35 ceramic sample under external applied electric field. For these measurements, in order to know the approximate value of electric field sufficient to switch over to ferroelectric state from the ergodic relaxor (ER) state first the Brillouin

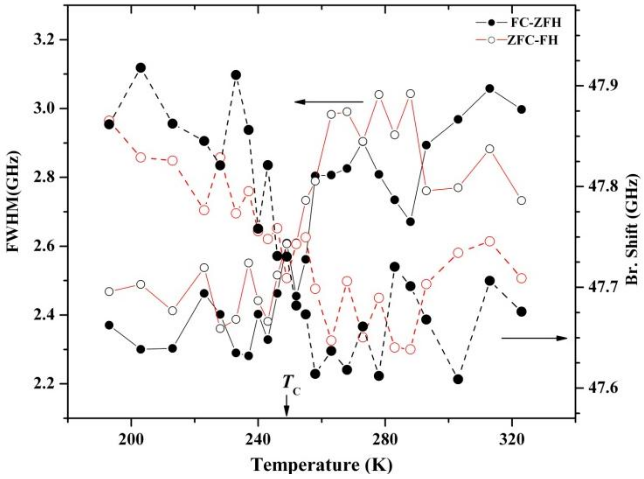

Fig. 4. Temperature dependent Brillouin spectra parameters measured under: (i) zero-field heating (ZFH) condition after field cooling (FC), (ii) field heating (FH) after zero-field cooling (ZFC) of the specimen.

spectra were recorded at T~220 K according to temperature-electric field phase diagram shown in Fig. 1. The temperature dependent Brillouin spectra were again recorded keeping the applied field constant at 1.2 kV (determined in previous run). The two Brillouin parameters, ν_B ($\sim\omega/2\pi$) and Γ, represent the real and imaginary parts of the complex elastic stiffness constant $c^*=c'-jc''$ in analogy with the complex dielectric constant. In the absence of external electric field, PLZT relaxor ceramics exhibit a broad minimum in ν_B corresponding to dielectric maximum at T_m [9]. This typical relaxor state can be transformed to long-range ordered ferroelectric state by the application of external *dc* electric field as evident (Fig. 4) from abrupt changes both in ν_B and Γ at T_C. In this figure, T_C (~249 K) indicates the onset of field induced transformation from ER to ferroelectric state (instead of changing to non-ergodic relaxor (NER) state below the freezing temperature T_f). It is clear from these data that both ν_B and Γ are unchanged during two measurement conditions, zero-field heating after field cooling (FC-ZFH) and field heating after zero-field cooling (FH-ZFC). This is in excellent agreement with the temperature-field phase diagram shown in Fig. 1. This electric-field induced property of PLZT relaxors has very unique electro-optic applications in the field of defense sciences.

4. Summary

Dielectric and Raman scattering experiments were performed on PLZT-10/65/35 relaxor ferroelectric ceramics as a function of temperature. A broad minimum was observed in the inverse dielectric constant exhibiting typical relaxor behavior due to development of randomly oriented local polarization associated with PNRs at $T \leq T_B$. The local polarization, $\langle P^2\rangle$, was estimated by neglecting the higher order terms in the frame work of classical Landau theory that showed a marked rising behavior with decreasing temperature ($T \leq T_B$). The Raman spectra showed only broad bands with no temperature dependence in the investigated temperature range. Field induced Brillouin spectra showed that it was possible to transform relaxor state to normal ferroelectric state under the application of external *dc*-electric field as predicted by the field-temperature phase diagram of PLZT relaxor ferroelectric ceramics.

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