Elastic Properties of Lanthanum Modified Lead Zirconate Titanate Ferroelectric Ceramics

G. Shabbir

Central Diagnostic Laboratory, Physics Division, Directorate of Science, PINSTECH, Islamabad, Pakistan

Elastic properties of lanthanum-modified lead zirconate-titanate (PLZT) relaxor ceramic oxide used as optical shutters are required for device design, storage and field purposes. Therefore, acoustic phonon mode velocity and related elastic constant of PLZT ceramic were measured by the non-destructive high-resolution Brillouin light scattering technique in the temperature range from 700 K down to 200 K. Broad anomalies were observed in the acoustic phonon velocity and the elastic constant showing minimum between ~320 – ~240 K showing a typical relaxor ferroelectric character. A broad central peak was also observed at 200≤T≤500 K. The temperature dependence of the acoustic anomaly and central peak was associated to the fluctuations of the local polarization caused by the polar nanoregions.

Keywords: Brillouin light scattering, Elastic constant, PLZT, Relaxor ferroelectrics

1. Introduction

Lanthanum modified lead zirconate-titanate $(Pb_{1-x}La_x)(Zr_{1-y}Ti_y)O_3$ (PLZT x/1-y/y) perovskite relaxor ferroelectric (RFE) ceramics remain attractive for actuating and sensing technology owing to their unique dielectric, electrooptic and electromechancial properties [1]. Relaxor ferroelectrics are disordered materials both with respect to charge and site occupancy and are of much interest because of their resemblance with dipolar and/or spin glasses [2-4]. Although no structural phase transition exists in RFEs, they show ergodicity below the so called Burn's temperature (T_B). This ergodic relaxor (ER) behavior appears due to the development of randomly oriented polar nanoregions (PNRs) which exhibit slowing dynamics with decreasing temperature and ultimately freeze into a non-ergodic relaxor (NER) state at T_f (freezing temperature).

One of the most interesting characteristics of relaxor materials is that although no ferroelectricity is found but the normal ferroelectric state can be induced in them by the application of a sufficiently high electric field. This property reflects that some critical state exists in RFEs. Kutnjak *et al*. [5] have shown in their recent field induced investigations of thermodynamic properties of $Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ (PMN-PT) that such criticality really exists and is not limited to PMN-PT [6] but also seems to be found in PLZT RFEs also. Further exploration of this phenomenon may help to understand the peculiar nature of RFEs, central peaks phenomena, and giant electromechanical response near the morphotropic phase boundary (MPB) in these compounds.

PLZT-x/65/35 based ceramics (showing relaxor behavior for 7<x<14) have been studied extensively. As an example, capacitance of three ceramic compositions is plotted in Figure 1 exhibiting a broad maximum instead of sharp anomaly related to structural phase transition. In view of the technological importance of RFEs we have investigated elastic properties of PLZT ceramics in a broad temperature range [3, 4, 7-9]. This communication reports elastic constants and acoustic phonon mode velocity of the PLZT-9.4/65/35 relaxor ferroelectric ceramic as a function of temperature. This composition is important due to its specific applications as optical shutters [10] and temperature dependent study is necessary for device design, storage and field requirements.
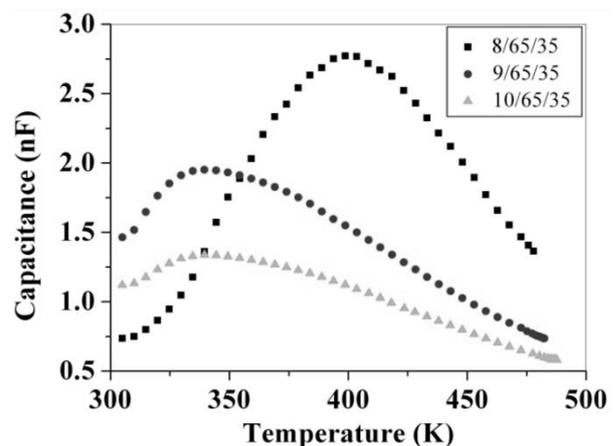

Figure 1. Capacitance of three PLZT ceramics as a function of temperature.

Email Address : gshabbir@gmail.com

2. Experimental

Transparent ceramics of nominal composition PLZT-9.4/65/35 were prepared by the hot-pressed solid state sintering in oxygen atmosphere from the high purity (>99.9%) oxides of PbO, La_2O_3, ZrO_2 and TiO_2.
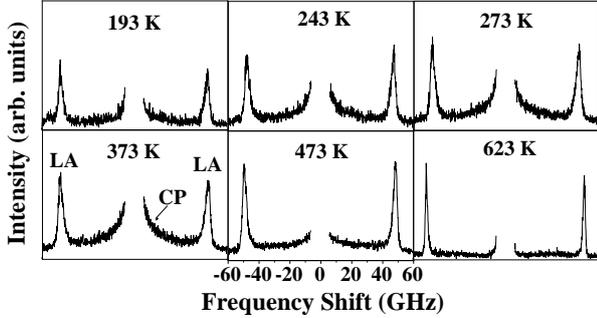

Figure 2.   Brillouin spectra of the PLZT-9.4/65/35 ceramic at some selected temperatures.

The starting powders were ball milled for 12 hrs in alcoholic media and the green pallets were prepared and sintered repeatedly at ~1150 ^{o}C in excess PbO atmosphere to compensate lead loss. Transparent ceramic specimen polished to optical quality was put in a LINKAM Stage (THMS 600) placed on *X-Y* adjustable stage of a microscope for temperature dependent measurements by a non-destructive Brillouin light scattering system in the backscattering geometry. The acoustic phonon modes were excited by a single mode Ar^+ -laser with a wavelength of 514.5 nm and a power of ~100 MW and a free spectral range (FSR) of 75 GHz. The sample temperature was first raised to ~750 K and Brillouin spectra were then recorded in cooling the sample to ~200 K with a temperature accuracy of ±1 K and a stability of ±0.1 K. Capacitance of the ceramic samples was measured by an Agilent 4294A Impedance analyzer and LINKM THMSE 600 heating stage.

3. Results and Discussion

In order to clarify the concept of relaxor nature of these ceramics, capacitance measurements were performed in a limited temperature range on three compositions and the data are shown in Figure 1. It can be seen that with increasing lanthanum contents, the maximum peak position (T_m) shifts towards lower temperatures along with decrease in peak value.

This behavior is characteristics of RFEs and the results are in very good agreements to the original studies on PLZT ceramics [1]. Typical Brillouin light scattering spectra of PLZT-9.4/65/35 ceramic are shown in Figure 2 at some selected temperatures. These spectra consist of a Brillouin doublet arising from the longitudinal acoustic (LA) mode and a strong elastic peak. No transverse acoustic (TA) phonon modes were observed in present measurements in the temperature range of interest. The measured spectra were analyzed using the peak fitting module (PFM) for Origin version 6.0 (Microcal^{TM} Software, Inc.). The Brillouin frequency shifts ($\Delta\nu$) and full width at half maximum (FWHM) of the Brillouin peak of the LA phonon mode were thus obtained from the observed spectra and their temperature dependences are plotted in Figure 3. Acoustic velocity of the LA phonon mode (V_{LA}) is related to $\Delta\nu$ through the elastic stiffness coefficient (c_{11}) as given below :

$$\frac{2\pi\Delta\nu}{q} = V_{LA} = \sqrt{\frac{c_{11}}{\rho}}$$

(1)

where ρ= 7863 (kg.m^{-3}) is density of the sample and q (~0.062 nm^{-1}) is the scattering wave vector. The temperature dependences of the calculated values of V_{LA} and c_{11} are plotted in Figure 4.
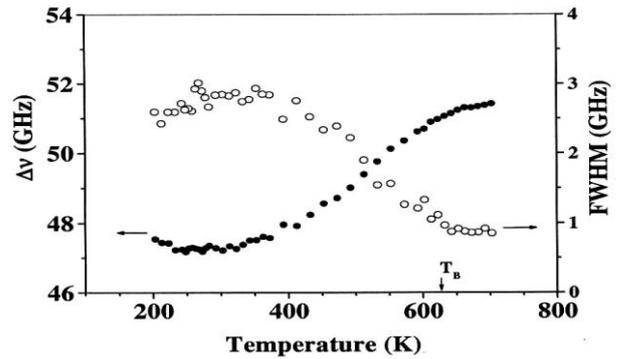

Figure 3.   Brillouin frequency shift ($\Delta\nu$) (filled circles) and full width at half maximum (FWHM) (open circles) of the LA mode as a function of temperature.
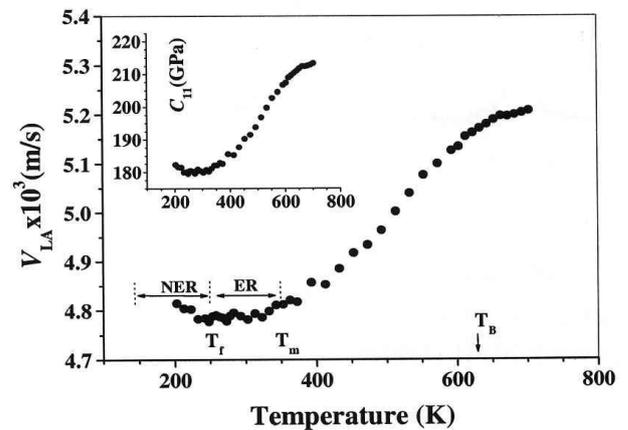

Figure 4.   Temperature dependence of the sound velocity (V_{LA}) of LA mode and related elastic stiffness coefficient (inset) of the PLZT-9.4/65/35 ceramic.

From Figure 3 it can be seen that $\Delta\nu$ shows broad softening and a corresponding rise in FWHM (related to phonon damping) with decreasing temperature. A similar softening also appears in V_{LA} and c_{11} (Figure 4) in accordance with relation 1. The large value of elastic constant (present data and ref. 7) depicts the high load bearing capability of the actuating devices fabricated from PLZT-x/65/35 ceramics. The observed temperature dependence of V_{LA} and c_{11} is similar to that reported in our earlier experiments on other PLZT relaxor ferroelectric ceramics [7, 8]. An increase in FWHM at $T{\leq}T_B$ with decreasing temperature and a maximum near the dielectric maximum temperature (T_m) seems to be related to the dynamics of PNRs. V_{LA} and c_{11} also have a broad minimum extending from ~320 K to ~240 K. It seems that this region is pre-dominated by fluctuations of the local polarization (P_d) induced by the PNRs that ultimately freeze at T_f but still they can be put to order by applying a sufficiently high electric field. But complete freezing of polarization fluctuations of PNRs (it must be kept in mind that there exists no macroscopic polarization in the RFEs rather a local polarization, $\boldsymbol{P}_d$, appears at $T{\leq}T_B$ such that, $P^2 = \left\langle P_d^2 \right\rangle$) occur at the Vögal-Fulcher temperature (T_{VF}) where the maximum relaxation time (τ) diverges and polarization fluctuations cannot be put into order even by applying an external electric field [7].

Another important observation is the appearance of a broad central peak (CP) below $T{\leq}500$ K (as seen in Brillouin spectra shown in Figure 2) and existing up to the lowest measured temperature (~200 K). A qualitative comparison of the Brillouin spectra observed at different temperatures to that already reported [9] shows that the CP temperature dependence is similar to that observed for other PLZT RFE ceramics although the present data is taken with a narrow FSR.

4. Summary

High-resolution Brillouin light scattering experiments were performed on PLZT-9.4/65/35 relaxor ferroelectric ceramic in the temperature range from ~700 to ~200 K to measure the velocity of low energy acoustic phonon modes and related elastic constant. Broad anomalies were observed in the acoustic phonon velocity and the related elastic constant in the measured temperature range indicating presence of relaxor ferroelectric character down to low temperatures. A broad central peak was also observed at temperature $200{\leq}T{\leq}500$ K. The temperature variations of the acoustic mode anomaly and the central peak were attributed to the dynamics of the PNRs. The acoustic mode velocity and elastic constant data in a broad temperature range would be useful to solve device design issues under mechanical loading of ceramic plates.

Acknowledgements

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