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A micro-Brillouin scattering study of the acoustic properties of PLZT relaxor ceramics

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Abstract

Acoustic properties of the transparent relaxor ferroelectric ceramics of PLZT-10/65/35 and PLZT-7.6/72/28 were studied by the high-resolution micro-Brillouin scattering technique. The ceramics showed significant softening in the elastic constant and velocity of the longitudinal acoustic (LA) phonon mode, a broad anomaly in the attenuation of the LA mode, and a frequency-dependent dielectric maximum. The temperature dependences of the acoustic anomalies could be explained qualitatively by using electrostrictive coupling, quadratic in order parameter and linear in strain. The interaction between the polar micro regions is more pronounced at some percolation limit below the Burns temperature T_B , where the shear deformation develops due to polarization fluctuations, local electrostrictive strain fields and tilting of the oxygen octahedra.

1. Introduction

Lanthanum modified lead zirconate-titanate $\{(Pb_{1-x}La_x)(Zr_yTi_{1-y})O_3, \text{PLZT } x/(y/1-y)\}$ perovskite type ceramics are ferroelectric materials with a variety of technical applications owing to their unique properties, such as high dielectric permittivity and piezoelectricity [1]. Most investigations have been concentrated on the composition $x/65/35$ (x being the La content with 65/35 Zr/Ti ratio). In $x/65/35$ materials with a relative high La content ($7 < x < 12$) a typical relaxor character is observed. Relaxors are highly disordered materials showing a diffuse dielectric response with a broad maximum in the permittivity curves at the apparent Curie temperature, the absence of long-range order and existence of local polarization far above the freezing temperature [2, 3]. Such response of relaxors is taken to indicate a ferroelectric–paraelectric diffuse phase transition (DPT). In this composition range and with zero external electric field the crystal structure remains nearly cubic perovskite ABO_3 . It is believed [4], that the coupling of the ferroelectrically active oxygen octahedral containing B-site cations is broken by the addition of La ions and associated A-site vacancies, thus causing

the formation of locally polarized regions, rather than development of a long-range ordered ferroelectric state. However, the long-range ferroelectric state is formed only by cooling the relaxors in an electric field E higher than the critical field $E_C \sim 5 \text{ kV cm}^{-1}$ [5].

Many theoretical attempts have been made to explain the complex behaviour of relaxor ferroelectrics; a satisfactory picture is not yet clear. Among them are the superparaelectric model [2], the composition fluctuation model [6], the dipolar glass model [7], the random field model [8], and the spherical random-bond-random-field model [9, 10]. According to Smolenskii *et al* [11] the DPT is caused by the local compositional fluctuations arising from the aggregations of ions of one type, both in solid solutions and complex compounds. Cross [2] has proposed the coexistence of randomly oriented polar and non-polar micro regions, whose relative amount depends strongly on temperature, giving rise to relaxor properties in ferroelectrics. These polar micro regions (PMRs) are formed in the paraelectric phase and have the approximate linear dimensions of 10 nm. PMRs at lower temperatures have been shown to undergo a Vogel–Fulcher-like slowing down of the polarization fluctuations. According to Burns and Dacol [12] in their measurements on the refractive index of PLZT ceramics, the transition occurs first in regions which are deficient in lanthanum; the average value of the refractive index is lowered by the onset of local polarization (at Burns temperature, $T_B \approx 627 \text{ K}$ for PLZT- $x/65/35$). Darlington [13] observed a small discontinuity in the temperature factors of A-site atoms, and line widths of (220) and (321) reflections at 560 K in PLZT-8.7/65/35. Also a change in the line width of $\{h00\}$ reflections at 640 K was found, which was interpreted as the onset temperature of the growth of unconnected PMRs of sufficient size giving rise to co-operative shear in the structure at 560 K. Thus there appears to be consensus that a random or nearly random distribution of A- and/or B-site ions gives rise to PMRs, with slightly different Curie points for their ferroelectric–paraelectric phase transition. The broad dielectric anomaly is a result of size and composition fluctuations of PMRs.

There exist numerous studies in the $x/65/35$ series of compositions [1, 5, 14–16]. In recent investigations, attention is being paid to the problem of freezing, nonlinear phenomena and effects of the dc bias field [5, 17–22]. As to the case of acoustic properties of PLZT ceramics, only sound velocity data of PLZT- $x/65/35$ ceramics have been reported previously by ultrasonic methods [23, 24] but over a limited temperature range. Internal strain relaxation and the glassy behaviour of PLZT ceramics have been studied by a nonlinear technique [7]. But no detailed study exists on acoustic properties of PLZT ceramics by the Brillouin scattering technique. In this work, we present our recent results on the sound velocities and elastic stiffness constants of two PLZT ceramic samples of slightly different composition measured by the micro-Brillouin scattering technique. The two compositions are named hereafter in this work as PLZT-10/65/35 and PLZT-7.6/72/28, respectively. In these compositions electrostriction (a quadratic effect) is dominant, so they are well suited for purely electrostrictive devices where small but precise movements are required, for example telescope mirror correctors, phase modulators, microscope stage translators and mask aligners. As the electrostriction coefficients, elastic strain and the macroscopic elastic stiffness constants are interrelated, the investigation of the elastic properties of PLZT ceramics may improve our physical understanding of relaxors, and advance their applications in engineering.

2. Experimental details

Transparent PLZT samples were grown by hot pressing in an oxygen atmosphere. Polished samples of approximate dimensions $2.1 \times 3.6 \times 0.32 \text{ mm}^3$ were used for present measurements. Micro-Brillouin scattering experiments were performed by using a Sandercock 3 + 3 pass tandem Fabry–Pérot interferometer in backscattering geometry with a free spectral range (FSR)

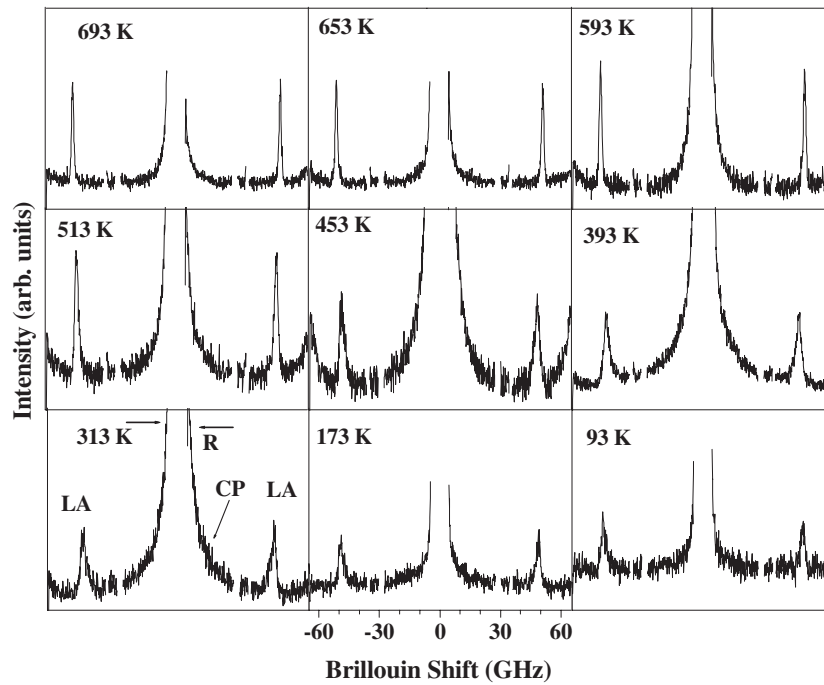


Figure 1. Brillouin spectra of PLZT-10/65/35 ceramic at some selected temperatures.

of 75 GHz and finesse of 75–80. The samples were excited with a diode-pumped solid-state laser (DPSS532) with a wavelength of 532 nm and a power of 100 mW. A conventional photon counting system was used to detect and average the signals. An optical microscope (OLYMPUS BH-2) was combined with the interferometer to achieve a focal point of 1–2 μm , which has been very effective in studying the acoustic properties of ferroelectric relaxors [25, 26]. For the temperature variation studies, the sample was put in a cryostat cell (THMS 600) with X – Y adjustments, placed on the stage of microscope. The Brillouin spectra were recorded with 300–500 time repetitions of accumulation. The sample temperature was first raised to 700 K and then measurements were done in cooling cycle down to 85 K with a stability of ± 0.1 K. The sample was slightly tilted by less than 5° with respect to the plane perpendicular to the incident laser light in order to reduce the strong reflection from the sample surface. The Brillouin spectra thus obtained consisted of only the longitudinal acoustic (LA) mode.

To examine the exact value of the dielectric maximum temperature (T_m) the linear dielectric constant was measured by using a Solartron impedance analyser (SI1260). A closed-cycle helium refrigerator (RMC LTS-22) and a home-made high-temperature furnace were combined to cover a temperature range from ~ 550 K down to 20 K. The temperature was monitored either by a silicon diode sensor or a chromel–alumel thermocouple by using a digital temperature controller (SI9650/LakeShore331). Measurements were done in a cooling run at a rate of 1 K min^{-1} and with a 1 V probing ac-signal.

3. Results and discussion

Typical Brillouin spectra of PLZT-10/65/35 at various temperatures are shown in figure 1. These spectra consist of a Brillouin doublet arising from the LA mode and a strong elastic peak. No transverse acoustic phonon modes were observed in present measurements in the

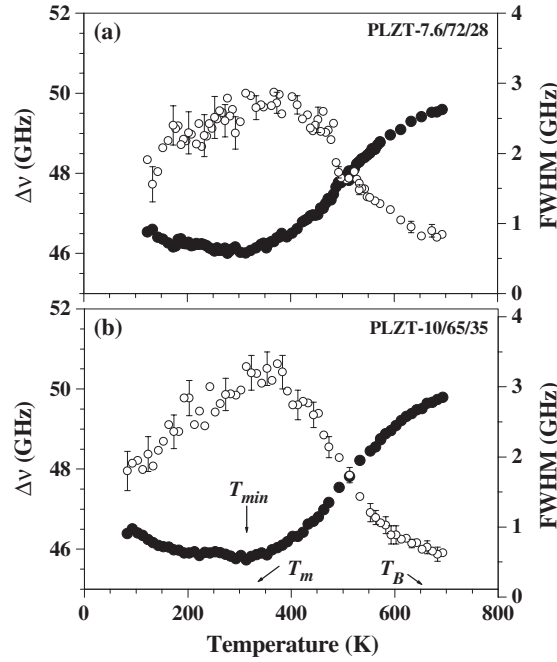


Figure 2. Temperature dependences of the Brillouin frequency shift $\Delta\nu$ (full circles), and FWHM (open circles) of (a) PLZT-7.6/72/28 and (b) PLZT-10/65/35 ceramics. Typical error bars are also shown for FWHM.

temperature range of interest. The Brillouin spectra of PLZT-7.6/72/28 were similar and hence are not shown. The Brillouin frequency shifts ($\Delta\nu$) related to the velocity (V_L) of the LA phonon mode were calculated relative to the elastic peak and the results are plotted in figure 2 for both ceramics. Figure 2 also shows the temperature dependence of the full width at half maximum (FWHM) of the Brillouin peak, which is a measure of the attenuation of the acoustic phonon.

In Brillouin scattering, acoustic modes produce strain which leads to spatial variation in the polarization (P) and consequently $\varepsilon^*(\omega, T)$ or the refractive index of the medium is modulated. In a linear elastic body the elastic stiffness constants c_{mn} , stresses (σ_m) and strains (ε_n) are related (tensorially) by $\sigma_m = c_{mn}\varepsilon_n$. In an isotropic material, such as polycrystalline aggregates and ceramics (as in the present case of PLZT) the 81 components of the fourth-order stiffness tensor are reduced to only two, i.e., c_{12} and c_{44} , usually known as *Lamé constants* λ and μ , respectively. The velocities of the bulk elastic waves are controlled by these constants as defined by the following equations:

$$c_{11} = \rho V_L^2 \quad (1)$$

$$c_{12} = \rho(V_L^2 - 2V_T^2) = \lambda \quad (2)$$

$$c_{44} = \rho V_T^2 = \mu \quad (3)$$

where ρ is the sample density, 7863 kg m^{-3} , and V_L and V_T are the velocities of the longitudinal and transverse acoustic phonon modes, respectively. As we could observe only one LA phonon mode in the present measurements, therefore, from the calculated values of $\Delta\nu$, only V_L and c_{11} could be obtained whose temperature dependences are shown in figures 3 and 4 for the two compositions, respectively.

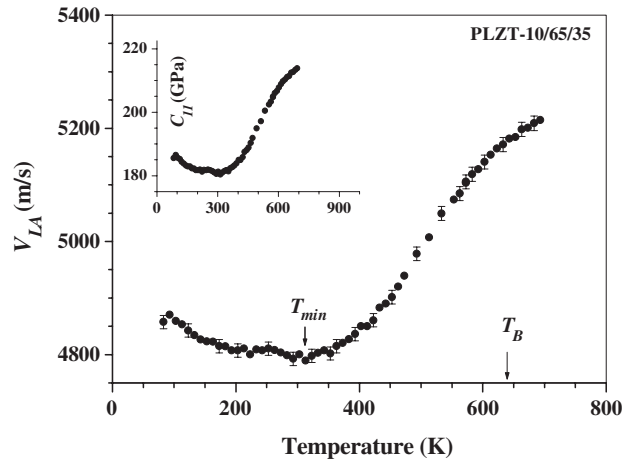


Figure 3. The acoustic phonon velocity V_L (with typical error bars) of the longitudinal mode and the elastic constant c_{11} (inset) of PLZT-10/65/35 ceramic as a function of temperature.

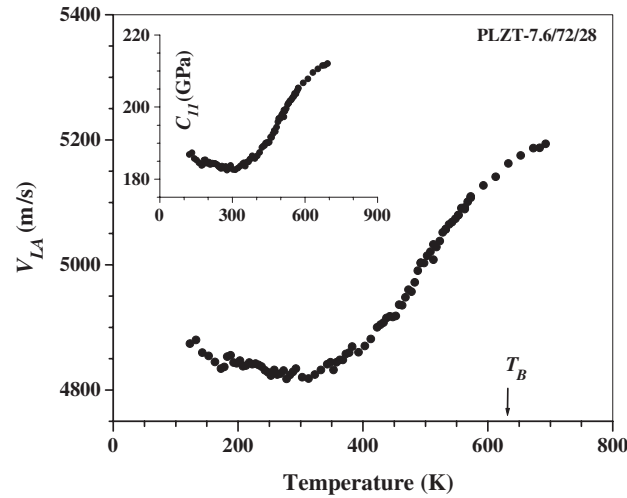


Figure 4. Temperature dependences of the LA phonon velocity V_L , and the elastic constant c_{11} (inset) of PLZT-7.6/72/28 ceramic.

From figure 2 it can be seen that for both ceramics $\Delta\nu$ shows a marked softening on cooling from $T \geq T_B$, which is accompanied by an increase in attenuation of the phonon mode. There is no sharp anomaly in temperature dependences of $\Delta\nu$ and attenuation for both samples. Instead, we see a very broad dip in $\Delta\nu$ spreading over a wide temperature range with a minimum at temperature $T_{min} \sim 313$ K, and a hump in attenuation at ~ 340 K. Unlike $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (PMN) [27], a Landau–Khalatnikov-type sharp anomaly in attenuation could not be observed in the present measurements. A similar softening behaviour in $\Delta\nu$ with increasing attenuation on cooling has also been observed in PMN and $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (PZN) relaxor crystals [27, 28]. However, it is worth mentioning that in PMN, the maximum softening is coincident with the dielectric maximum, whereas in the present case $T_{min} \leq T_m$ where T_m is the temperature of maximum dielectric permittivity. The value of T_m for both samples was determined separately from the temperature dependence of the real part $\varepsilon'(T)$ of the complex

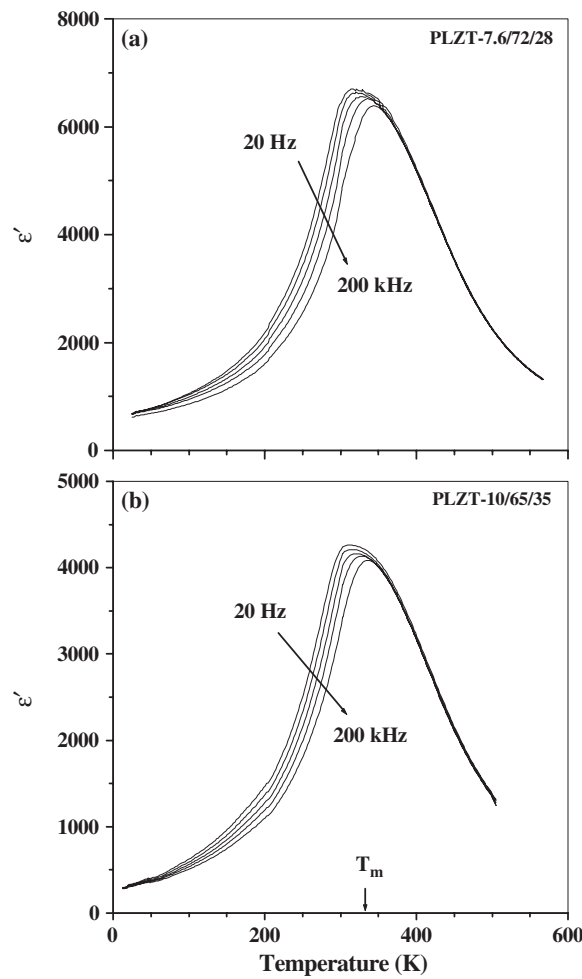


Figure 5. The temperature variation of the real permittivity (ϵ') of (a) PLZT-7.6/72/28 and (b) PLZT-10/65/35 ceramics at various frequencies.

permittivity measured in the frequency range from 20 Hz up to 200 kHz (figure 5). These ceramics show a typical relaxor behaviour exhibiting broad frequency-dependent maxima of the temperature-dependent complex dielectric permittivity $\epsilon^*(\omega, T) = \epsilon'(\omega, T) + i\epsilon''(\omega, T)$. The maximum in $\epsilon'(T)$ occurs at temperature $T_m \sim 329$ K (at 10 kHz). The peaks of $\epsilon'(T)$ and $\epsilon''(T)$ (not shown) in PLZT-10/65/35 are shifted ~ 6 K to lower temperatures than in PLZT-7.6/72/28.

The DPT in relaxors is characterized by the existence of PMRs at temperatures higher than the dielectric maxima (T_m). The growth of PMRs and the coupling between them seem to control the relaxor properties. The growth of attenuation is a manifestation of the order parameter fluctuations induced by the dynamics of PMRs and very broad frequency softening originates from the electrostrictive coupling between the squared order parameter and the strain. From the anomalies in c_{11} and V_L for both ceramics (figures 3 and 4) we see that PMRs with local polarization P_d (random in orientation) appear at temperature $T \geq T_B$, and their volume fraction is increased on cooling. The appearance of PMRs and their subsequent thermodynamical effects on the elastic properties of PLZT ceramics can be understood

qualitatively in the framework of phenomenological Landau theory for ferroelectrics. For this purpose we start with writing the free energy expression in terms of order parameter components P_i as follows.

$$F(P_i, \varepsilon_k; T) = F_0(T) + \frac{1}{2}\alpha(T)f_2(P_i) + \frac{1}{4}\beta f_4(P_i) + \frac{1}{6}\xi f_6(P_i) + \dots + F_m(\varepsilon_k) + F_c(P_i, \varepsilon_k) \quad (4)$$

where F_0 is the free energy when $P = 0$ (in the paraelectric phase), $f_n(P)$ are the n th-order components of the order parameter, F_m is the pure elastic contribution, α, β, ξ are considered as weakly temperature dependent except α , which goes through zero like $\sim(T - T_0)$ at the transition temperature T_0 , and F_c is the interaction term between the strain and the order parameter that is expressed in powers of P_i and ε_k :

$$F_c(P_i, \varepsilon_k) = \delta_{ij}P_i\varepsilon_j + \gamma_{ijk}P_iP_j\varepsilon_k + \zeta_{ijkl}P_i\varepsilon_i\varepsilon_j + \dots \quad (5)$$

where δ, γ , and ζ are nonzero symmetry-dependent coefficients. The adiabatic elastic constants under the action of strain are usually defined by the following relation:

$$c_{mn} = \frac{\partial^2 F}{\partial \varepsilon_m \partial \varepsilon_n} \quad \text{such that} \quad \frac{\partial F}{\partial P_k} = 0, \quad (k = 1, 2, 3). \quad (6)$$

From equations (4) and (5), the change in elastic constant due to motion of the order parameter, driven by the strain, and its reacting stress can be written as [29]

$$c_{mn}(T) - c_{mn}^\infty(T) = - \sum_{k,l} \left(\frac{\partial^2 F_c}{\partial P_k \partial \varepsilon_m} \right) \chi_{kl} \left(\frac{\partial^2 F_c}{\partial \varepsilon_n \partial P_l} \right) \quad (7)$$

where the clamped susceptibility $\chi_{kl} = (\partial^2 F / \partial P_k \partial P_l)^{-1}$ is the response of the order parameter and $c_{mn}^\infty(T)$ is the high-frequency limit of the elastic constant independent of the order parameter. If only the electrostrictive interaction is considered, the coupling term $F_c(P_i, \varepsilon_k)$ in the free energy expression contains only even powers of polarization ($\sim \gamma \varepsilon P^2$); then the change in elastic constant in terms of the local polarization P_d ($P^2 = \langle P_d^2 \rangle$) as an order parameter can be approximated as

$$c_{mn}(T) - c_{mn}^\infty(T) = -g^2 \langle P_d^2 \rangle \chi \quad (8)$$

where the coefficient γ in equation (5) is replaced by the electrostrictive constant g .

In the light of the above phenomenology, for $T \geq T_B$ (in the paraelectric phase) the local polarization P_d is absent, and, thus, there is no change in the order parameter. Therefore, the system easily follows on the mechanical perturbations in the elastic waves, so the elastic constant and the velocity of the phonon mode should be linear functions of T . At the transition temperature, a step-like anomaly is expected in the elastic constant. But it is anticipated that due to strong thermodynamical fluctuations in the order parameter, caused by the complex dynamics of PMRs, the step-like transition might be spread over a wide temperature range (figures 3 and 4). Moreover, equation (8) depicts that the quadratic contribution of the local polarization P_d , even if small in volume, and the temperature dependence of $c_{mn}^\infty(T)$ due to lattice anharmonicity, will cause the elastic constant to deviate from high-temperature linear behaviour well above T_m . Therefore, the acoustic anomalies are not abrupt as in the case of conventional phase transitions. The broad hump in the attenuation cannot be interpreted by the quadratic coupling in the order parameter as assumed above. This may be rather a reflection of dynamic fluctuations in the order parameter which are pronounced at some percolation limit below T_B [6]. This may be the reason that T_{\min} and maxima in the attenuation occur at slightly different temperatures (figure 2). The negative temperature coefficient of acoustic velocity at $T < T_{\min}$ may be associated with lattice anharmonicity in the ordered phase.

The apparent reason might be that at high frequency the polarization fluctuations could not follow the deformation in the matrix and the acoustic velocity should be similar as in the paraelectric phase. It is interesting to note that the minimum in V_L for both samples occurred in the same temperature range as detected by ultrasonic experiments [23, 24] within the limits of accuracy. The elastic stiffness response of PLZT-10/65/35 measured by a nonlinear method [6] also showed maximum softening at $T \sim 310$ K, consistent with the present results. A strong dielectric dispersion was also observed in the same temperature range (figure 5).

An important observation in the present investigations is that the softening in elastic anomalies is slower for $T \gtrsim T_B$ while it is faster in the temperature range $T_{\min} \leq T \lesssim T_B$ (figure 2). This indicates that for $T \gtrsim T_B$, only polarization fluctuations exist, whereas at $T \lesssim T_B$ the inhomogeneity in shear deformation starts to develop due to complex interaction of polarization fluctuations, local electrostriction fields and tilting of the oxygen octahedra. These arguments are consistent with x-ray diffraction experiments for PLZT-8.7/65/35 [13] where the change in line shape of the (200) reflection at 640 K, and at 560 K for (220) and (321) reflections, was observed with decreasing temperature. A small discontinuity in temperature factors for atoms on A-sites was also detected at 560 K. The former was interpreted as a result of the onset of local polarization in lanthanum-deficient regions whereas at 560 K the polarized regions grow to sufficient size so that co-operative shear of the structure can occur. Selected area electron diffraction (SAED) results [30] showed that in PLZT- x /65/35 superlattice spots became clearly visible only below 573 K for $x \geq 7$ at.%. However, weaker intensities were observable even at $T \geq T_B$. The origin of superlattice spots was associated to the staggered tilting of oxygen octahedra. Kirsch *et al* [31], in their low-frequency permittivity experiments, determined the onset of local polarization at 650 K, and the Curie–Weiss law ceases to be obeyed at $T \approx 570$ K. All these findings support the idea [6] that at $T \approx T_B$ local distortions occur in the stiff matrix. With further lowering of temperature, a percolation limit at temperature $560 \leq T < T_B$ may be reached, where deformation in the matrix can occur in response to sufficient fluctuations in the local polarization.

Although T_m is slightly different, the acoustic anomalies occur at almost the same temperature in both compositions (similar T_{\min}). It is expected that both T_m and T_{\min} have a common origin. What determines their values? From the phase diagram or temperature-dependent dielectric constant measurements [32] it is found that T_m occurs at ~ 633 K for PLZT-0/65/35 and ~ 609 K for PLZT-0/72/28, respectively. Since La addition decreases T_m , it is expected that it would be higher for PLZT-7.6/72/28 than for PLZT-10/65/35. But lowering in T_m with increasing La also depends on the Zr/Ti ratio, and it is faster in 72/28 than in 65/35 so the average effect seems to be compensated, resulting in very close T_m for both samples. This is the most plausible scenario, that both dielectric and acoustic anomalies occur in the same temperature range for both ceramics.

Another interesting phenomenon observed is the broad Rayleigh wing commonly known as central peaks (CPs) (see figure 1) which grows with decreasing temperature below 500 K. CPs have also been observed in other relaxor ferroelectrics (see [33] and references therein) and seem to be common features of relaxors. Since no soft optic modes have been observed in relaxor materials [34], the microscopic origin of CPs in relaxors may be other than coupling of the soft optic modes to the relaxation modes. The detailed study of CPs in PLZT ceramics will be reported separately.

4. Conclusions

Acoustic properties of PLZT ceramics were investigated in a wide temperature range from 85 to 700 K, by a micro-Brillouin technique. The temperature dependences of the elastic constant

and velocity of the phonon mode for both the compositions showed broad anomalies close to the temperature of dielectric maximum. The results were explained qualitatively by the phenomenological Landau theory. Since the polarization P_d appears gradually, the acoustic anomalies are extended over a wide temperature range. From these findings it is suggested that

- (i) T_B is an approximate temperature where the presence of microscopic local polarization can be seen, and it does not necessarily reflect the onset of the relaxation process and relaxor properties;
- (ii) the cooperative characteristic of PMRs is more visible below T_B , where the shear deformation develops due to fluctuations in the polarization, local electrostrictive strain fields (orientation), and tilting of the oxygen octahedra (elastic).

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