# Microheterogeneity and field-cooling effects on $Pb[(Zn_{1/3}Nb_{2/3})_{0.955}Ti_{0.045}]O_3$ single crystals probed by micro-Brillouin scattering

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Microheterogeneity and field-cooling effects were investigated on $Pb[(Zn_{1/3}Nb_{2/3})_{0.955}Ti_{0.045}]O_3$ (PZN-4.5%PT) single crystals by using a high-resolution micro-Brillouin scattering. The temperature dependence of Brillouin shift showed a typical relaxor behavior with marked softening on approaching the diffuse phase transition, but also revealed a clear microareal variation in a rhombohedral phase below 150 °C which means a heterogeneity exists over a length scale of at least a few microns in PZN-4.5%PT. These two features seem to correlate with the coexistence of both micronsized domains and irregular nanosized domains, recently confirmed by high-resolution domain studies. This complex domain structure may make each microdomain represent different relaxor behaviors due to its own polar nanoregions and their dynamics. When the crystal was cooled under the electric field along the [001] direction from a cubic phase, two field-induced changes were observed in the Brillouin shift at around 143 °C and 106 °C. This observation is in good agreement with the dielectric measurements, meaning a medium-range ordered phase exists between short-range ordered and long-range order phases. © *2005 American Institute of Physics*.
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Lead-based perovskite relaxor ferroelectrics are well-known functional materials for industrial applications such as high-permittivity capacitors, ultrasonic transducers and actuators, etc.[1] Physical properties of relaxor ferroelectrics are closely related to their complex perovskite structures and the existence of polar nanoregions (PNR). The dynamics of PNR causes a diffuse and frequency-dependent broad dielectric maximum, broad distribution of relaxation times and aging behaviors at low temperatures.[2] In spite of many experimental and theoretical efforts on relaxors, such as random-field model,[3] dipolar glass mode,[4] and recent spherical random bond-random field model,[5] understanding of the microscopic origin of their complex behaviors is still not enough up to the present.

Complex perovskite relaxor ferroelectric materials such as $Pb[(Zn_{1/3}Nb_{2/3})_{1-x}Ti_x]O_2$ (PZN-$x$%PT) and $Pb[(Mg_{1/3}Nb_{2/3})_{1-x}Ti_x]O_3$ (PMN-$x$%PT) single crystals are excellent candidates for electromechanical applications due to their huge piezoelectric properties. Concerning typical relaxors, $Pb(Zn_{1/3}Nb_{2/3})O_2$ (PZN) and $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN) crystals show a diffuse, frequency-dependent broad dielectric peak, broad distribution of relaxation times with divergent leading edge on cooling, and a formation of polar nanoregions below the Burns temperature, $T_B$, far above the temperature of dielectric maximum, $T_m$.[6] On the other hand, as the composition of Ti increases, PZN-$x$%PT and PMN-$x$%PT exhibit structural phase transitions from cubic to tetragonal or rhombohedral symmetries depending on the composition $x$.[7,8]

Recently, diffraction studies have clarified that the structures of PZN-$x$%PT and PMN-$x$%PT near the MPB are more complicated than our knowledge, and monoclinic and/or orthorhombic symmetries appear with and/or without biasing electric field depending on the composition.[9,10] Moreover, it was brought to light by high-energy x-ray and neutron diffraction studies that the ground state of parent PZN and PZN-$x$%PT with $x<8\%$ might be pseudo-cubic with an unknown phase "$X$" accompanied by a rhombohedral distortion limited to the outer surfaces of the crystals.[11,12]

Recently, Brillouin scattering has been performed on PZN and PZN-9%PT near the MPB,[13–15] while there is no systematic investigation on the PZN-4.5%PT crystals of which the composition is located at around the middle between the PZN-9%PT and pure PZN. Brillouin spectra of PZN showed typical relaxor behaviors such as a broad softening of the Brillouin shift of acoustic modes with an increase of phonon damping over a wide temperature range,[16] while PZN-9%PT exhibited clear two-step anomalies in both frequency shift and damping corresponding to two successive phase transitions from cubic to tetragonal and tetragonal to rhombohedral phases.[17] In this paper, we report our study on PZN-4.5%PT by using micro-Brillouin scattering in order to understand the field-cooling effects and spatial variation of elastic properties of this composition.

The PZN-4.5%PT single crystals were grown by the Bridgman method and cut for obtaining pseudo-cubic crystal

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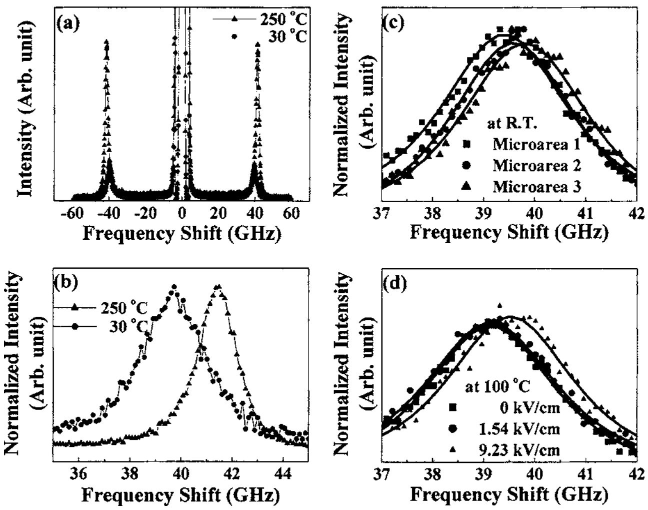


FIG. 1. (a) Brillouin scattering spectra of a PZN-4.5%PT crystal at two temperatures; (b) Brillouin peaks of longitudinal acoustic mode at 250 °C and 30 °C in an extended frequency scale; (c) the microareal dependence of the Brillouin peak at room temperature; (d) the dependence of the Brillouin shift on the biasing electric field at 100 °C. Solid lines in (c) and (d) denote fitting lines.

orientations of [100]/[010]/[001]. The crystal dimensions were approximately $6.5 \times 4.1 \times 0.65$ mm$^3$, and the two crystal surfaces perpendicular to the pseudo-cubic [001] direction were polished to the optical grade and coated by ITO. The micro-Brillouin scattering system with a 3+3 pass Sandercock-type tandem Fabry–Perot interferometer (FPI) was used to investigate the elastic properties.[17] A free spectral range and a scan range were 75 and ±60 GHz, respectively. When different microareas were investigated, one micro area was measured and the sample was translated by approximately $100 \sim 200$ $\mu$m by adjusting the X–Y translator. Since we used a backward scattering geometry, both the phonon propagating direction and the biasing electric field direction were along the [001] direction.

Typical Brillouin spectra of the PZN-4.5%PT crystal composed of a longitudinal acoustic (LA) mode and a weak central peak measured at 30 °C and 250 °C are shown in Fig. 1(a). Figure 1(b) shows a clear change of frequency shift and damping factor between 30 °C and 250 °C. Figure 1(c) shows the variation of Brillouin peaks at three different microareas measured at room temperature. Figure 1(d) shows the electric field dependence of the Brillouin peak at the same microareas at 100 °C. As the field increases, the frequency shift moves to higher position in the frequency window. At the field below about 3.0±0.5 kV/cm, Brillouin frequency shift is nearly same as the value measured without any bias field.

The temperature dependences of the Brillouin shift ($\Delta\nu$) measured at three different microareas on the same sample are shown in the Fig. 2(a), where $\Delta\nu$ shows the same value above 200 °C within experimental uncertainty. In contrast, it starts to exhibit slight differences below 200 °C and a relatively large microareal dependence below 150 °C near $T_m$. As a result, the maximum change of $\Delta\nu$ in microareal dependence at room temperature amounts to approximately 0.6 GHz within the investigated area. This means that rhombohedral phase in the low-temperature range below the diffuse phase transition temperature is characterized by a microheterogeneity. Each microregion probed by micro-

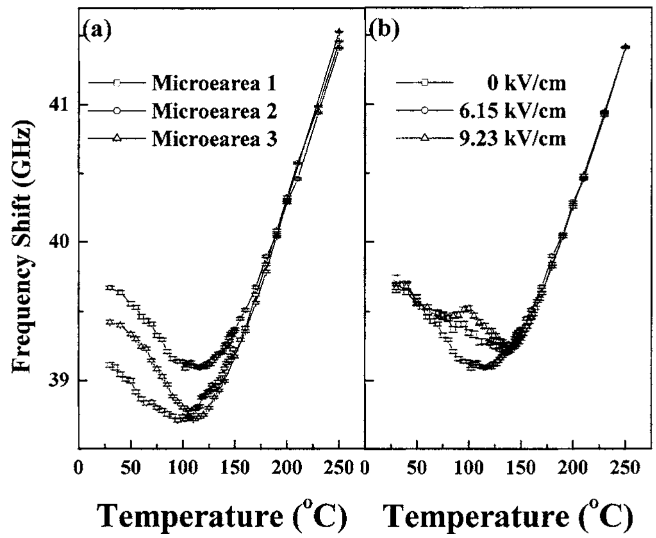


FIG. 2. Temperature dependences of the Brillouin shift of LA mode measured at three different microregions (a) and at three different biasing electric fields on the same microregion (b).

Brillouin scattering behaves as if it is an independent relaxor with its own dynamics. This feature cannot be detected by usual macroscopic measurements such as dielectric spectroscopy, since they get the average response from the whole surface of the sample.

In Fig. 2(b), one microregion was chosen for the investigation of field-cooling effects on PZN-4.5%PT using several biasing electric fields. As the electric field increases, Brillouin shift begins to become hardened below approximately 150 °C. In particular, $\Delta\nu$ exhibits a minimum just near 143 °C and a change of slope near 106 °C under the electric field of 6.15 and 9.23 kV/cm. Figure 2(b) points out the field-induced changes in the PZN-4.5%PT crystals at two distinct temperatures. Regarding the temperature dependence of the damping factor (not shown in this paper), it did not show any noticeable changes up to 10 kV/cm within the experimental accuracy.

Figure 3 reveals the microheterogeneity of PZN-4.5%PT in more details. The microregion for the Brillouin measurement was scanned across the surface of the crystal at selected temperatures. The spatial distance between neighboring microregions was approximately $100 \sim 200$ $\mu$m. It is found that

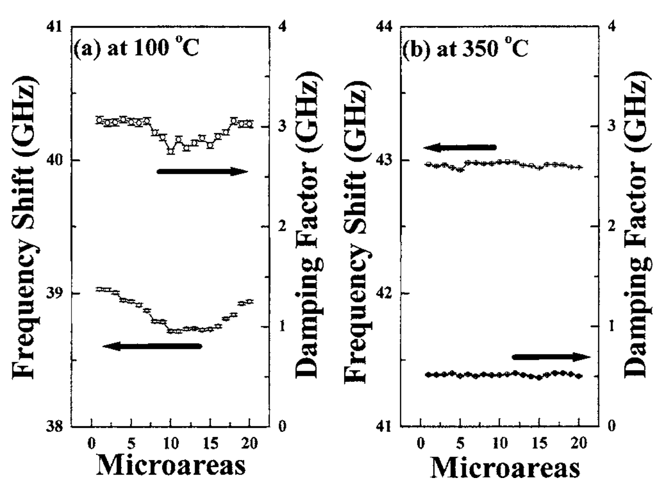


FIG. 3. Microareal dependences of Brillouin shift and damping factor at 100 °C (a) and 350 °C (b).

there is no microareal dependence in $\Delta\nu$ and damping factor in the cubic phase at 350 °C. On the other hand, we can see microheterogeneity clearly in $\Delta\nu$ and damping factor at 100 °C below the diffuse phase transition temperature of 150 °C, consistent with the temperature dependence of $\Delta\nu$ in Fig. 2(a). When we compare these results with those of PZN-9%PT,[18] the Brillouin spectrum itself does not show any noticeable signature for symmetry lowering. This result is in contrast to PZN-9%PT which showed coexistence of several phases such as tetragonal and rhombohedral symmetries depending on what microregion has been chosen.

Our major findings on PZN-4.5%PT single crystals can be summarized as follows: (1) hypersonic frequency $\Delta\nu$ measured without poling field shows typical relaxor behaviors, but it clearly shows a microareal dependence below the diffuse phase transition temperature; (2) two anomalies in $\Delta\nu$ occur at ~143 °C and ~106 °C during field cooling under the bias field of 5~9 kV/cm.

That is, the elastic properties of pure PZN showed a difference between the cooling and heating processes.[14,16] However, PZN-4.5%PT in the present study shows a clear microareal dependence, i.e., the Brillouin shift becomes sensitive to what microregion we choose when the temperature is lower than the diffuse phase transition point. It is noteworthy that this kind of microareal dependence has been reported in the Brillouin studies of other common relaxor single crystals. PMN-35%PT[13] and PZN-9%PT[18] are exceptional because they are located at MPB, which is characterized by quasidegenerate energy states and prone to show different symmetries depending on different microregions. In case of PZN-4.5%PT, each microregion seems to show its own relaxor behavior different from each other near and below the diffuse phase transition temperature. The overall shape of $\Delta\nu$ as a function of temperature is very similar to that of PZN, reflecting relaxor nature of PZN-4.5%PT. Softening of $\Delta\nu$ accompanied by phonon damping over a wide temperature range reveals the order parameter fluctuation owing to the dynamics of PNRs, which is governed by quenched random electric fields and random interactions.

Recent high-resolution domain studies revealed that the domain structure of PZN-4.5%PT is composed of both normal micron-sized domains and irregular nano-sized domains.[19] Irregular domain patterns with the typical sizes 20–100 nm, mainly observed on the (001)-oriented surfaces of unpoled PZN-4.5%PT, was interpreted to be related to the relaxor nature of this composition. It is believed that the coexistence of both the relaxor nature and microheterogeneity from our Brillouin study reflects the complex domain structure in PZN-4.5%PT, where the significant softening in $\Delta\nu$ is related to the dynamics of irregular nanosized domains while the microareal dependence is due to the formation of micronsized ferroelectric domains in which their own irregular nanodomains are incorporated. Therefore, each microdomain represents its own relaxor behavior that is slightly different from one another at low temperatures.

Regarding the field cooling effects in Fig. 2(b), it is worth comparing the present result with previous measurements.[20,21] Figure 2(b) revealed that field-induced successive transitions occur at two critical temperatures around 143 °C and 106 °C. Shen *et al.* observed two anomalies in the dielectric constant under field-cooling and suggested these two anomalies are related to field-induced changes from high-temperature short-range ordered phase to the medium-range ordered phase and then to the long-range ordered ferroelectric state at low temperatures. Two-step changes in the remanent polarization were also observed at the same temperatures. These two critical temperatures correlate well with those of two anomalies in $\Delta\nu$ as can be confirmed from Fig. 2(b). These two temperature ranges are also in good agreement with the phase diagram suggested by Lu *et al.*[21] Shen *et al.* reported that a small bias field of 0.65 kV/cm was enough for inducing the above two phase transitions, since the direction of the electric field was along the polar direction [111] of the rhombohedral phase. In our study, the biasing field was applied along the [001] direction, and an electric field one order of magnitude higher than 0.65 kV/cm was necessary to induce two clear anomalies in the acoustic properties of PZN-4.5%PT crystal.

In summary, Brillouin spectrum of PZN-4.5%PT showed both a typical relaxor behavior and a microheterogeneity. This was ascribed to the coexistence of micron-sized domains and irregular nano-sized domains.[19] This complex domain structure may make each microdomain, which begins to form near the diffuse phase transition temperature at ~150 °C, experiences its own freezing dynamics owing to the interactions of PNRs in the environment of quenched random fields and complex domain configurations in which orthorhombic, monoclinic, or even triclinic symmetry might be expected.[22] Two anomalies were induced at ~143 °C and ~106 °C under the poling field along [001]. These two temperatures are in good agreement with previous dielectric studies and seem to indicate the medium-range ordered state between the high-temperature short-range and low-temperature long-range ordered phases.[20]


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