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# Hysteresis in acoustic properties of ferroelectric relaxor $\text{Pb}[(\text{Zn}_{1/3}\text{Nb}_{2/3})_{0.955}\text{Ti}_{0.045}]\text{O}_3$ single crystals studied by Brillouin and dielectric spectroscopies

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Acoustic and dielectric properties of  $\text{Pb}[(\text{Zn}_{1/3}\text{Nb}_{2/3})_{1-x}\text{Ti}_x]\text{O}_3$  (PZN- $x$ PT) single crystals with  $x = 0.045$  have been studied by the high-resolution micro-Brillouin scattering and dielectric spectroscopy in a wide temperature range. The softening of the Brillouin shift and the increase of dielectric relaxation time upon cooling indicated the formation of polar nanoregions (PNRs) and the slowing down of their dynamics. In contrast to the acoustic properties of typical model relaxors such as lead magnesium niobate, the change in the Brillouin shift near its minimum became sharper on heating compared to the change on cooling, pointing to the clear existence of hysteresis in the dynamics of the diffuse phase transition in PZN-4.5%PT. Since the number of PNRs will increase upon cooling, it may be expected that the kinetics of the phase transition would become slower, the lower the transition temperature resulting in the more sluggish, broad feature of the Brillouin shift observed during cooling. This result may indicate that the number and size of polar nanoregions, which are dependent on temperature, play an important role in the development of the mesoscopic ferroelectric order in PZN-4.5%PT. © 2006 American Institute of Physics.

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Relaxor ferroelectrics are promising materials for technological applications as high-permittivity capacitors, piezoelectric devices, electro-optic devices, etc.<sup>1</sup> They are characterized by complex dynamic behaviors such as a frequency-dependent diffuse dielectric maxima, a broad distribution of relaxation times with a divergent leading edge on cooling, and the existence of nanosized polar clusters below the so-called Burns temperature.<sup>2,3</sup> Several theoretical studies have been carried out in order to understand the microscopic origin of the complex behaviors of relaxors including the random-field model,<sup>4</sup> the dipolar glass mode,<sup>5</sup> and the spherical random-bond-random-field model,<sup>6</sup> but the exact nature of ferroelectric relaxors still remains an open question.

Recently, relaxor-based complex perovskite single crystals have attracted great attention as promising materials in various electromechanical applications owing to their superior piezoelectric properties.<sup>7</sup>  $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$  (PZN) is one of typical relaxors exhibiting a diffuse ferroelectric phase transition into a rhombohedral symmetry at  $\sim 413$  K.<sup>8</sup> As the Ti concentration increases towards the morphotropic phase boundary (MPB) at  $x \sim 9\%$ , PZN- $x$ PT shows a different phase sequence upon cooling. The phase diagram of PZN- $x$ PT for  $0 \leq x \leq 9\%$  is under intense study for a better understanding of complex structural and dynamical behaviors of these compounds.<sup>9,10</sup>

Brillouin scattering can probe acoustic properties arising from various couplings between the order parameter and elastic strain caused by acoustic waves.<sup>11</sup> Brillouin scattering has been applied to pure PZN,<sup>12,13</sup> PZN-9%PT,<sup>14,15</sup> and recently on PZN-4.5%PT crystals<sup>16</sup> in the temperature ranges around the diffuse phase transitions. Longitudinal acoustic (LA) mode of PZN showed typical relaxor behaviors such as a very broad softening of the Brillouin shift  $\Delta\nu$  accompanied by an increase of hypersonic damping due to order parameter fluctuations.<sup>12,13</sup> In contrast, PZN-9%PT clearly exhibited two-step anomalies in both  $\Delta\nu$  and damping, corresponding to two successive phase transitions.<sup>14,15</sup> In a previous Brillouin study on a PZN-4.5%PT crystal grown by the Bridgmann method, microheterogeneity and electric-field-induced changes have been clearly observed.<sup>16</sup> However, the temperature range of the previous study was too narrow to fully probe the dynamics of PZN-4.5%PT.

In the present study, acoustic properties of a PZN-4.5%PT crystal grown by the flux method have been examined in a wide temperature range between 80 and 873 K on both cooling and heating runs. The purpose of this study is first to investigate the phase transition behaviors of the PZN-4.5%PT single crystal, which is located in the middle of the rhombohedral composition range of PZN- $x$ PT, by both dielectric and Brillouin light scattering spectroscopies and then to compare the results with those of typical relaxors such as  $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$  (PMN).

The PZN-4.5%PT single crystals were grown by the flux method<sup>17</sup> and cut normal to the pseudocubic orientations of

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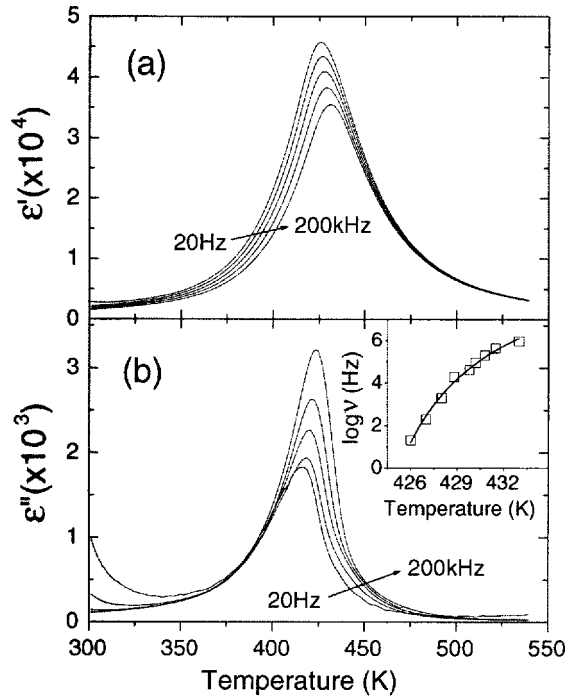


FIG. 1. Real (a) and imaginary (b) parts of the complex dielectric permittivity of PZN-4.5%PT as a function of temperature. (Inset: Characteristic relaxation frequencies as determined from the maximum temperature of the real part and the frequencies, along with the best-fitted result using the Vogel-Fulcher law.)

[100]/[010]/[001]. Micro-Brillouin scattering system with a 3+3 pass Sandercock tandem Fabry-Pérot interferometer (FPI) was used to measure the Brillouin spectra at a backward scattering geometry. The sample was first heated to 873 K, cooled to 80 K, and then heated to 873 K again. During the last cooling and heating runs, the Brillouin spectrum was recorded.

Figure 1 shows the real and imaginary parts of the complex dielectric permittivity of PZN-4.5%PT measured on cooling. It shows typical relaxor behaviors with a broad, frequency-dependent dielectric maximum which shifts to higher temperatures with increasing frequency. The position of the dielectric maximum in Fig. 1(a),  $T_{\max}$ , along with the corresponding probe frequency  $\nu$  was used to determine the temperature dependence of the characteristic relaxation frequency of PZN-4.5%PT, according to the Vogel-Fulcher law of the form  $\nu = \nu_0 \exp[-E/k_B(T_{\max} - T_f)]$ , where  $\nu_0$ ,  $E$ , and  $T_f$  denote the attempt frequency, activation energy, and freezing temperature, respectively. The fitting result is shown in the inset of Fig. 1(b) with  $\nu_0 = 3.6 \times 10^{10}$  Hz,  $E/k_B = 137 \pm 32$  K, and  $T_f = 419 \pm 2$  K. It is interesting to note that this freezing temperature is very similar to the temperature at which a field-induced phase transition occurs in PZN-4.5%PT.<sup>16,18</sup>

Typical Brillouin spectra consist of the LA mode and a strong elastic Rayleigh peak. The frequency shift  $\Delta\nu$  and the full width at half maximum (FWHM) of LA mode are shown in Figs. 2(a) and 2(b), respectively. For comparison,  $\Delta\nu$  and FWHM of PMN measured on cooling are also plotted in the same figure.

$\Delta\nu$  of PZN-4.5%PT, which corresponds to the elastic stiffness coefficient  $c_{11}$ , measured on cooling exhibits a

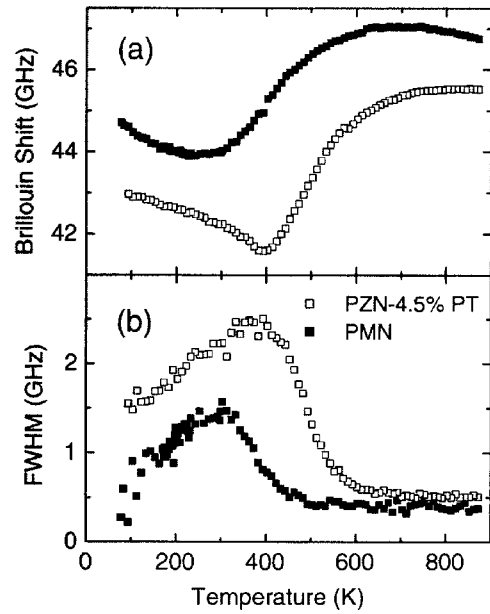


FIG. 2. Brillouin shift (a) and FWHM (b) of PMN and PZN-4.5%PT as a function of temperature.

broad minimum near  $\sim 395$  K. This behavior has also been observed in other typical relaxor crystals.<sup>11–13,19–22</sup> The interactions of the PNRs inherently present in relaxors with the strain induced by the acoustic wave through the electrostrictive coupling are believed to be responsible for the softening of the Brillouin shift as the temperature decreases from high temperature to the diffuse phase transition point.<sup>23</sup>

The quadratic coupling between the polarization and deformation usually accompanies order parameter fluctuations, which are responsible for the growth of acoustic damping on cooling. Figure 2(b) shows the temperature dependences of FWHM of PMN and PZN-4.5%PT. Consistent with the temperature dependences of  $\Delta\nu$ , the location of maximum of FWHM of these two crystals shows a temperature difference of about 100 K. As PZN-4.5%PT undergoes a diffuse phase transition on cooling, the damping decreases because of the freezing of ferroelectric microdomains.<sup>12</sup>

The softening of  $\Delta\nu$  in a wide temperature range below  $\sim 700$  K accompanying the growth of the acoustic damping is in correlation with the temperature dependence of dielectric constant. The onset of softening of  $\Delta\nu$  near the Burns temperature indicates the appearance of PNRs. The growth of PNRs in their sizes and increasing interactions among them lead to the slowing down of their dynamics, which is reflected in the diverging characteristic of the dielectric relaxation time represented by the Vogel-Fulcher behavior. However, in contrast to PMN, PZN-4.5%PT exhibits a moderately diffused ferroelectric phase transition near 420 K resulting in mesoscopic polar domains owing to the addition of ferroelectrically active lead titanates, instead of being transformed into nonergodic relaxors. This transition behavior is reflected in the much sharper minimum in  $\Delta\nu$  than that of PMN, indicating the ferroelectric instability in PZN-4.5%PT. It should be noted that it is usually difficult to clearly reveal the mild, but distinct structural changes occurring in PT-doped relaxors by measuring only the temperature depen-

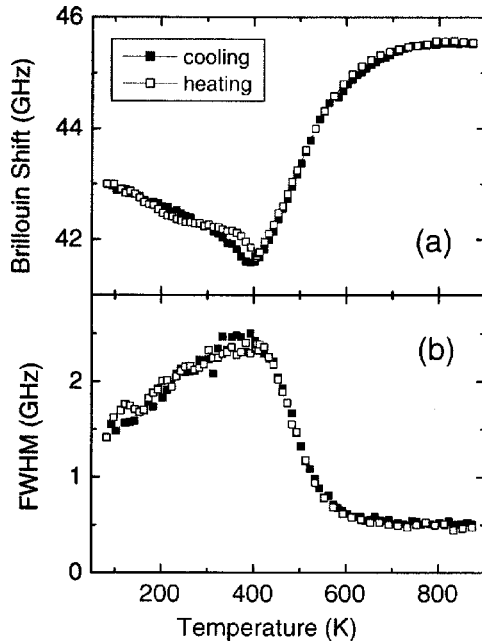


FIG. 3. Brillouin shift (a) and FWHM (b) of PZN-4.5%PT measured upon successive cooling and heating.

dence of the dielectric constant.<sup>24</sup> In this context, acoustic properties probed by Brillouin scattering might be more sensitive to the mild structural changes due to the ferroelectric instability, because the PT doping to PZN would enhance the local strain field in the crystal that will couple to the acoustic wave.

The  $\Delta\nu$  and FWHM of PZN-4.5%PT measured at both cooling and heating processes are plotted in Fig. 3 as a function of temperature. Upon heating from 80 K,  $\Delta\nu$  exhibits a different temperature dependence from that of cooling. Clear thermal hysteresis was also observed in PZN.<sup>12,13</sup> Moreover, the change in  $\Delta\nu$  recorded on heating became sharper at about 405 K compared to the relatively broad minimum of  $\Delta\nu$  obtained on cooling.

Algueró *et al.*<sup>25</sup> reported the low-frequency Young's modulus and the associated mechanical losses of PMN-20%PT measured through successive heating and cooling, and found strong thermal hysteresis in the phase transition behavior, i.e., the sharp transition that appeared on heating was not observed on cooling, similar to our results in Fig. 3.

The major finding of this study may be explained qualitatively by the two-stage model based on the intrinsic compositional inhomogeneities.<sup>25,26</sup> According to this model, the diffuse phase transition is influenced by the number of PNRs at the phase transition temperature. The growth of a ferroelectric nucleus is restricted by the existing neighboring PNRs that cannot be collapsed with the growing nucleus for some reasons, for example, due to the local random fields. Since the kinetics of the phase transition is influenced by the number of the PNRs at the second stage, it is expected that the kinetics would become slower at lower temperatures.<sup>25</sup> In this context, the sluggish, broad feature of  $\Delta\nu$  observed during cooling in Fig. 3(a) can be ascribed to the larger number of PNRs which would tend to interrupt the growth of the

ferroelectric nuclei. In contrast, at the higher phase transition temperature of PZN-4.5%PT upon heating, the fewer polar clusters would allow the ferroelectric nuclei to grow faster, resulting in a sharper phase transition.

In summary, the dielectric and acoustic properties of PZN-4.5%PT single crystals have been examined in a wide temperature range. The phase transition behavior of PZN-4.5%PT differed from that of typical relaxors such as PMN in two respects. First, the temperature dependence of  $\Delta\nu$  was much sharper than that of PMN, which may be ascribed to the ferroelectric instability owing to the enhanced local strain field formed by the doping of lead titanate. Second, the temperature dependence of the Brillouin shift showed a thermal hysteresis between the cooling and successive heating processes. The more sluggish kinetics of the phase transition at lower temperatures observed on cooling indicated that the characteristic time scale of the ferroelectric fluctuations became longer upon cooling and that the number of polar nano-clusters plays an important role in the development of the mesoscopic ferroelectric order in PZN-4.5%PT.

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