Hypersonic and dielectric anomalies of $(\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3)_{0.905}(\text{PbTiO}_3)_{0.095}$ single crystal

Chi-Shun Tu, F.-C. Chao, C.-H. Yeh, and C.-L. Tsai

Department of Physics, Fu-Jen University, Taipei, Taiwan 242, Republic of China

V. Hugo Schmidt

Department of Physics, Montana State University, Bozeman, Montana 59717

(Received 8 March 1999)

Both the longitudinal (LA) Brillouin backscattering spectra and dielectric permittivities along the [001] direction have been measured as a function of temperature for relaxor-ferroelectric single-crystal $(\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3)_{0.905}(\text{PbTiO}_3)_{0.095}$ (PZN-9.5%PT). A sharp ferroelectric phase transition (which is associated with a sharp Landau-Khalatnikov-like phonon damping maximum) was observed near 460 K. As the temperature decreases, a diffuse phase transition (which is associated with a broad acoustic phonon damping maximum) was detected near 340 K. This broad damping evolution is attributed to dynamic order-parameter fluctuations. In addition, the nature of the thermal hysteresis for the dielectric permittivity confirms that these transitions (near 340 and 460 K) are diffuse first order and first order, respectively. The frequency-dependent dielectric data $\epsilon''(f, T)$ prove the existence of an electric dipolar relaxation process below 360 K. The activation energy, the Vogel-Fulcher temperature, and attempt frequency corresponding to this relaxation process are also calculated. [S0163-1829(99)03030-1]

I. INTRODUCTION

In contrast to typical ferroelectric (FE) crystals such as PbTiO_3 (PT), relaxor ferroelectrics exhibit a broad and frequency-dependent phase transition (diffuse phase transition).¹⁻⁹ Lead zinc niobate, $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (PZN), is an example of a relaxor ferroelectric material which has a disordered complex structure in which the Zn^{2+} and Nb^{5+} cations exhibit only short-range order on the B site. PZN undergoes a diffuse phase transition around 410 K in the dielectric permittivity and has rhombohedral symmetry at room temperature with space group $R3m$.¹ The normal ferroelectric PbTiO_3 has tetragonal symmetry with space group $P4mm$ at room temperature and has a FE phase transition taking place at $T_c = 760$ K.¹

The mixed solid solution $(1-x)\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - $(x)\text{PbTiO}_3$ (PZN- x PT) naturally has a morphotropic phase boundary (tetragonal FE ordering $\leftrightarrow$ rhombohedral FE ordering) near room temperature in the range from 9 to 9.5 mol % of PT content, where huge dielectric and piezoelectric constants appear, as is similar to the case in the PbZrO_3 - PbTiO_3 (PZT) system.¹⁻³ For the PZN-PT system, the morphotropic phase boundary exists only for $x < 15\%$. The values of the piezoelectric constants and the electromechanical coupling factors so far reported for the PZN- x PT single crystals are larger than those in the PZT family of ceramics. Several papers have reported the large piezoelectric constants ($d_{33} \approx 1500 \times 10^{-12}$ C/N) and electromechanical coupling parameters ($k_{33} \approx 92\%$) of PZN-PT based single crystals.^{1,5} Moreover, single-crystal growth of PZN-PT by the flux technique is also considerably easier than for PZT, which makes PZN-PT a promising material for high-performance transducers. However, as far as we know, there is no study correlating the properties of acoustic phonons as a function of temperature for PZN-PT-type crystals. Especially, the understanding of dielectric anomalies near the morphotropic phase

boundary (tetragonal symmetry $\leftrightarrow$ rhombohedral symmetry) is still lacking. This motivated us to carry out measurements of both Brillouin scattering and dielectric permittivity on PZN-9.5%PT to look for both hypersonic and dielectric anomalies. Especially, direct evidence for an acoustic phonon soft mode near the phase transition (cubic paraelectric phase $\leftrightarrow$ tetragonal FE phase) in PZN-9.5%PT is presented.

II. EXPERIMENTAL PROCEDURE

The lead zinc niobate-lead titanate single crystal PZN-9.5%PT was grown by the high-temperature flux solution method without electric poling. The sample was cut out of the crystals along the c axis, and the size is about $5 \times 5 \times 2$ mm³. The Brillouin spectra were obtained from the backscattering geometry with configuration $z(yu)\bar{z}$. “ u ” means that the collection was not polarization discriminated. Here y and z correspond to the crystal b and c axes, respectively. The sample was illuminated along [001] with an Innova 90 plus-A3 argon laser with wavelength $\lambda = 514.5$ nm, so the longitudinal phonons with wave vector along [001] were studied. The laser line half-width (for $\lambda = 514.5$ nm) is about 0.02 GHz determined by the spectrometer. Scattered light was analyzed by a Burleigh five-pass Fabry-Pérot (FP) interferometer. The free spectral range (FSR) of the FP interferometer was determined from measuring the longitudinal acoustic phonon shift of fused quartz with the S/N ratio greater than 70. The Brillouin scattering data were taken during a step heating process. To avoid sample heating, the laser power incident on the sample was kept less than 120 mW. For measurements (including both heating and cooling runs) of dielectric permittivities, the sample surfaces were coated with silver paste electrodes and a Wayne-Kerr Precision Analyzer model PMA3260A with four-lead connections was used for the frequency range from

FIG. 1. Stokes components of the LA[001] Brillouin scattering spectra for PZN-9.5%PT. The solid lines are fits to the damped harmonic oscillator model.

300 Hz to 2.5 MHz. A Janis model CCS-450 closed-cycle refrigerator (which is designed for the temperature range 10–475 K) was used with a Lakeshore model 340 temperature controller for both of the above temperature-dependent measurements.

III. RESULTS AND DISCUSSION

Actual temperature-dependent LA[001] phonon spectra of the Stokes Brillouin component are shown in Fig. 1. The solid lines are fits to the damped harmonic oscillator model,¹⁰ from which the frequency shift and half-width (damping) were obtained. The phonon frequency exhibits a strong negative coupling (softening) near 460 K. Figure 2(a)–2(c) show the temperature dependences (heating run) of the phonon frequency shift, half-width, and the real part ϵ'_c of dielectric permittivity, respectively. Due to the weak intensity factor (the S/N ratio of Brillouin scattering spectra is about 2 for PZN-9.5%PT) and the uncertainty of the collection angle which can appreciably broaden and distort the Brillouin line shape, the frequency shift and half-width data [Figs. 2(a) and 2(b)] show scatter. The phonon frequency shows two successive minimum dips near 340 and 460 K (which is more pronounced with a reduction about 5%), associated with a strong broad damping peak and a sharp damping peak, respectively.

Figures 3(a) and 3(b) show the temperature dependences of both the real and imaginary parts (ϵ'_c and ϵ''_c) of the dielectric permittivity for the frequency range from 300 Hz to 2.5 MHz upon cooling. The insets of Fig. 3 are enlargements of both ϵ'_c and ϵ''_c for temperatures below 450 K to clarify the dispersion behavior. Compared with the prototypical relaxor ferroelectric crystal $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$, which has a dif-

FIG. 2. (a) Brillouin frequency shift (open circles), (b) half-width (solid circles), and (c) the real part ϵ'_c of dielectric permittivity (heating run) vs temperature for PZN-9.5%PT. The dashed lines are guides for the eye.

fuse phase transition near 410 K, PZN-9.5%PT exhibits a much narrower frequency dispersion and weaker maximum of dielectric constant near 460 K due to the PT content. For temperature below 360 K, a broad dispersion anomaly (with much weaker dielectric constant) appears in both ϵ'_c and ϵ''_c . Figure 4 shows the temperature-dependent data of ϵ'_c from both cooling and heating runs at measuring frequency $f = 50$ kHz. Two clear thermal hystereses were observed near 300 ± 40 and 455 ± 5 K, respectively. The inset of Fig. 4 shows the reciprocal of ϵ'_c in which a typical first-order-type FE phase transition appears near 460 K.¹¹

What are the origins of the temperature-dependent Brillouin spectra and dielectric phenomena shown in Figs. 2–4 for PZN-9.5%PT near 460 K? For a typical FE phase transition, the transition temperature occurs where the frequency shift curve of acoustic phonon has an abrupt change.^{11,12} In PZN-9.5%PT, the acoustic phonon frequency [Fig. 2(a)] reaches a sharp turning point near 460 K. The real part ϵ'_c of dielectric permittivity [Fig. 2(c)] exhibits a steep change (with narrow frequency dispersion) and an obvious thermal hysteresis near 460 K. In addition, a sharp damping maximum [Fig. 2(b)], which is associated with a Landau-Khalatnikov-like maximum, was detected near 460 K. Such a damping anomaly is usually attributed to a rapid growth of long-range electric ordering. Thus we conclude that the PZN-9.5%PT single crystal possesses a sharp first-order ferroelectric phase transition at $T_c \approx 460$ K. This value is consistent with the transition temperature 460 ± 5 K (cubic paraelectric phase $\leftrightarrow$ tetragonal FE phase) predicated from the

FIG. 3. Temperature dependences of (a) the real part ϵ'_c and (b) the imaginary part ϵ''_c of the dielectric permittivity for PZN-9.5%PT, taken from frequencies from 300 Hz to 2.5 MHz upon cooling (cooling rate=1.5 K/min). The insets are enlargements for both (a) ϵ'_c and (b) ϵ''_c below 450 K.

morphotropic phase boundary (MPB) in Ref. 1.

Ferroelectric transitions are known to be associated with a soft mode of lattice motion. Lines and Glass pointed out that if the transition is strongly first order, mode softening may not be detectable.¹¹ Thus, with the temperature-dependent dielectric results, the phase transition near 460 K (paraelectric phase $\leftrightarrow$ FE phase) for PZN-9.5%PT should be weakly first order. We note that a zone-center ($q=0$) acoustic soft mode in the reduced Brillouin zone of the reciprocal sublattice always has, for a second-order transition, a zero frequency on approaching T_c from the ordered phase, i.e., $T \rightarrow T_c^-$. Therefore, the nonzero minimum of phonon frequency shift at ≈ 460 K implies either a first-order transition or that the structural instabilities (as $T \rightarrow T_c^+$) in PZN-9.5%PT must be associated with a more complicated mode.

In the lower-temperature region (below 360 K), the acoustic phonon frequency [Fig. 2(a)] reaches a weak turning point near 340 K. The real part ϵ'_c of dielectric permittivity [Figs. 2(c) and 3] exhibits a gradual change with a notably extensive frequency dispersion (or diffuse phase transition) and an obvious thermal hysteresis near 340 K. Correspondingly, the imaginary part ϵ''_c of dielectric permittivity also shows a relatively pronounced frequency dispersion. Instead of a sharp maximum (near 460 K), the acoustic phonon damping [Fig. 2(b)] of PZN-9.5%PT exhibits a gradual growth with a maximum located near 340 K. Such a slowly

FIG. 4. Thermal hysteresis of the real part $\epsilon'_c(f, T)$ of the dielectric permittivity taken at measuring frequency $f = 50$ kHz. The inset is the reciprocal of ϵ'_c .

rising damping anomaly reveals that order-parameter fluctuations are the dominant dynamic mechanism. Qualitative estimates of this fluctuation contribution are given by the dashed curve in Fig. 2(b). The dynamic fluctuation contribution is a characteristic of an $\eta^2 \mu$ -type electrostrictive coupling, squared in order parameter and linear in strain.¹² A similar acoustic damping anomaly was also seen in other mixed systems such as $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (PMN) and $\text{Rb}_{1-x}(\text{ND}_4)_x\text{D}_2\text{AsO}_4$ (DRADA- x) in which a local short-range order or a coexistence of two different phases was found.^{12,13} According to previous x-ray diffraction (XRD) data, the PZN-10%PT crystal possesses a mixed phase of rhombohedral and tetragonal symmetries around the morphotropic phase boundary.¹ Thus one can conclude that the PZN-9.5%PT composition has a diffuse transition near 340 K which is triggered by the local structural fluctuation between rhombohedral and tetragonal symmetries. We call this a first-order transition only because the thermal hysteresis in the permittivity shows that the system is metastable in this temperature region. The usual distinctions between first- and second-order transitions, such as discontinuity in dP/dT , do not apply for diffuse transitions.

In addition to the acoustic anomalies near 340 K, there is another similar frequency shift dip near 410 K with a corresponding damping maximum (Fig. 2). The imaginary part ϵ''_c of dielectric permittivity also shows a frequency dispersion which is relatively weaker than that which appears below 360 K [inset of Fig. 3(b)]. These occur close to the diffused phase transition temperature of pure PZN.¹ These anomalies (near 410 K) could be due to unmixed regions of pure PZN within the sample.

Precise measurements at temperatures below 360 K proved the existence of frequency dispersion in both the real $\epsilon'_c(f, T)$ and imaginary $\epsilon''_c(f, T)$ parts of the dielectric permittivity, which are illustrated in the insets of Figs. 3(a) and 3(b), respectively. These dispersion phenomena of both ϵ'_c and ϵ''_c confirm that the relaxation process begins to be evidenced below 360 K. As shown in Fig. 5, it was found that

FIG. 5. $\ln(f)$ vs $1000/T$. f is the measuring frequency and T is the temperature corresponding to the maximum value of ϵ''_c below 360 K. The solid line is the fit of Eq. (1) with the parameters mentioned in the text.

the relaxation occurring in the temperature region (100–360 K) obeys the exponential Vogel-Fulcher equation that has been used to describe other relaxation process, especially for mixed systems:

$$f = f_0 e^{-E_a/k_B(T_g - T_0)}, \quad (1)$$

where f is the measured frequency, f_0 is the attempt frequency, and E_a is the activation energy for orientation of electric dipoles. T_0 is the Vogel-Fulcher temperature, and T_g is the temperature where the imaginary part ϵ''_c of the dielectric permittivity reaches its maximum value. The results of the activation energy, attempt frequency, and Vogel-Fulcher temperature for PZN-9.5%PT are $E_a \approx 125$ meV (1446 K), $f_0 \approx 1.4 \times 10^{13}$ Hz, and $T_0 \approx 191$ K. What is the significance of these parameters? First, the attempt frequency is in the

usual range for lattice vibration frequency. Second, E_a is an average activation energy for various clusters in this partly disordered system to reorient, perhaps between rhombohedral and tetragonal local symmetries. Third, T_0 is the temperature at which, based on an unjustified extrapolation of the Vogel-Fulcher formula beyond the range of the data, all reorientation would cease. The fact that the Vogel-Fulcher formula fits better than the Arrhenius formula for many disordered systems reflects the fact that, as temperature decreases, a greater number of cooperative steps must occur in the course of a typical reorientation event.

IV. CONCLUSIONS

From the temperature-dependent Brillouin scattering LA[001] spectra and dielectric permittivities (ϵ'_c and ϵ''_c) of PZN-9.5%PT, two successive phase transitions are evidenced near 460 K (cubic paraelectric phase $\leftrightarrow$ tetragonal ferroelectric phase) and 340 K (a diffuse phase transition), respectively. A broad acoustic phonon damping evolution and a sharp Landau-Khalatnikov-like damping maximum were observed correspondingly. These two hypersonic damping anomalies imply that a diffuse phase transition (which is associated with a coexistence of both tetragonal and rhombohedral symmetries) and a rapid growth of FE ordering take place near 340 and 460 K, respectively. The behaviors of dielectric permittivity thermal hysteresis confirm that both phase transitions are first order. The frequency-dependent dielectric data $\epsilon''_c(f, T)$ of PZN-9.5%PT proved the existence of an electric dipolar relaxation process below 360 K. The activation energy, Vogel-Fulcher temperature, and attempt frequency corresponding to this relaxation process are also calculated.

ACKNOWLEDGMENTS

The authors would like to express sincere thanks to L.-F. Chen for help on experiments. This work was supported by NSC88-2112-M-030-002 (R.O.C.), NSF Grant No. DMR-9805272, and DOD EPSCOR Grant No. N00014-99-1-0523.

¹M. L. Mulvihill, S. E. Park, G. Risch, Z. Li, and K. Uchino, *Jpn. J. Appl. Phys., Part 1* **35**, 3984 (1996).

²J. Kuwata, K. Uchino, and S. Nomura, *Ferroelectrics* **37**, 579 (1981).

³J. Kuwata, K. Uchino, and S. Nomura, *Jpn. J. Appl. Phys., Part 1* **21**, 1298 (1982).

⁴S. Nomura, H. Arima, and F. Kojima, *Jpn. J. Appl. Phys.* **12**, 531 (1973).

⁵Y. Yamashita, *Jpn. J. Appl. Phys., Part 1* **33**, 5328 (1994).

⁶S. E. Park, M. L. Mulvihill, G. Risch, and T. R. Shrout, *Jpn. J. Appl. Phys., Part 1* **36**, 1154 (1996).

⁷S.-E. Paek and T. R. Shrout, *J. Appl. Phys.* **82**, 1804 (1997).

⁸S. Nomura, T. Takahashi, and Y. Yokomizo, *J. Phys. Soc. Jpn.* **27**, 262 (1969).

⁹J. Kuwata, K. Uchino, and S. Nomura, *Ferroelectrics* **37**, 579 (1981).

¹⁰C.-S. Tu, R. S. Katiyar, V. H. Schmidt, R. Guo, and B. S. Bhalla, *Phys. Rev. B* **59**, 251 (1999).

¹¹M. E. Lines and A. M. Glass, *Principles and Applications of Ferroelectrics and Related Materials* (Oxford University Press, London, 1977).

¹²C.-S. Tu and V. H. Schmidt, *Phys. Rev. B* **50**, 16 167 (1994).

¹³C.-S. Tu, V. H. Schmidt, and I. G. Siny, *J. Appl. Phys.* **78**, 5665 (1995).