Crossover from diffuse to sharp phase transition by electric field in 0.955Pb(Zn$_{1/3}$Nb$_{2/3}$)O$_3$-0.045PbTiO$_3$

To cite this article: Shinya Tsukada et al 2014 IOP Conf. Ser.: Mater. Sci. Eng. 54 012005

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Crossover from diffuse to sharp phase transition by electric field in $0.955\text{Pb(Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3-0.045\text{PbTiO}_3$

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Abstract. Effect of an electric field along [100] direction on diffuse phase transitions in a relaxor ferroelectric $0.955\text{Pb(Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3-0.045\text{PbTiO}_3$ (PZN-0.045PT) crystal is studied through dielectric properties and a longitudinal acoustic (LA) phonon. Compared with the diffuse phase transition observed in zero-field cooling in PZN-0.045PT, it shows two sharp phase transitions under field cooling. This result indicates that inhomogeneity is reduced by the electric field in the way that electric field grows the static polar nanoregions and microdomains into larger ferroelectric domains. From a thermodynamic point of view, the electric field enhances the relaxation from the nonequilibrium polymorphic states to the equilibrium homogeneous state. At the same time, ferroelectric tetragonal phase is stabilized with increasing an electric field along [100].

1. Introduction

A special class of ferroelectric materials, relaxor ferroelectrics, has attracted much attention due to their giant dielectric and electromechanical responses [1, 2]. The responses are as a result of polar fluctuations of intrinsic inhomogeneity. Such phenomena in inhomogeneous systems have attracted a great deal of research in the field of condensed matter physics, because intrinsic inhomogeneity in complex oxides sometimes induces some kinds of unusual behavior [3, 4]. In relaxor ferroelectrics, local polar regions of several nanometers wide, called polar nanoregions (PNRs), static nanodomain and microdomain structures are observed as intrinsic inhomogeneity; that is, relaxor ferroelectrics demonstrate structural hierarchy. Although the response of homogeneous inorganic dielectric materials to an external electric field is usually related to ionic displacements, relaxor ferroelectrics show high-order structures at a mesoscopic scale in addition to ionic displacements—so responses to an electric field are enhanced by their fluctuations. Thus, relaxor ferroelectrics are an intriguing
system in which intrinsic inhomogeneity can lead to a large-magnitude response to an external electric field. Pb(Zn\textsubscript{1/3}Nb\textsubscript{2/3})O\textsubscript{3} and its solid solution with typical ferroelectric PbTiO\textsubscript{3}, (1-x)Pb(Zn\textsubscript{1/3}Nb\textsubscript{2/3})O\textsubscript{3}-xPbTiO\textsubscript{3} (PZN-xPT), are one of the most extensively investigated relaxor systems, which are distinguished from normal ferroelectrics by the broad and frequency-dispersive maximum in the temperature dependence of dielectric constant \[1, 2\]. The crystal structure of PZN-xPT is characterised by inhomogeneous arrangement of Zn\textsuperscript{3+}, Nb\textsuperscript{5+}, and Ti\textsuperscript{4+} on crystallographically equivalent sites in the perovskite structure. The disorder due to the different ions at equivalent lattice sites generates PNRs at much higher temperatures than a ferroelectric phase-transition temperature, leading to structural hierarchy in relaxor ferroelectrics.

Various investigations of relaxor ferroelectrics have been undertaken to understand the curious phenomena. One intriguing macroscopic phenomenon is phase transitions. We have investigated the role of PNRs in the ferroelectric phase transition in relaxor ferroelectrics through dielectric and acoustic phonon measurements \[5–12\]. Our results indicate that the ferroelectric phase transition as well as the dynamics of PNR is sensitive to composition of PbTiO\textsubscript{3} and thermal treatments. Moreover, since Kutnjak \textit{et al.} pointed out the enhanced polarization fluctuation around a critical end point in temperature-electric field phase diagram, studies on the electric field induced phenomena have been performed by many researchers, which indicates that relaxor ferroelectrics also very sensitive to an electric field \[13–18\]. As most of works are on the static properties, at the present stage, it is necessary to investigate the phase transition from a dynamical point of view. Thus, relaxor dynamics are discussed in the present study by measuring Brillouin scattering and dielectric properties under an electric field in a PZN–0.045PT single crystal. By this complementary measurements enable us to discuss the dynamics in the broad frequency range up to the GHz range.

2. Experimental
A single crystal of PZN–0.045PT was grown using the high-temperature flux technique with PbO-based fluxes (Microfine Materials Technologies). Each surface of the crystals was a (100) plane of pseudo-cubic orientation. The LA phonon close to the \( \Gamma \) point of reciprocal space was observed through inelastic light scattering. The light scattering was measured with a high-contrast 3+3-pass tandem Fabry–Pérot interferometer (JRS Scientific Instruments) combined with an optical microscope (Olympus). The PZN–0.045PT single crystal was placed inside a cryostat cell (Linkam Scientific Instruments) to allow the sample temperature to be adjusted between 80 K and 873 K. The measurements were performed on cooling with and without applying an external electric field by using a DC power source (Matsusada Precision). A diode-pumped solid-state laser (Coherent Inc.) with single-frequency operation at 532 nm and an output power of 100 mW was used. A 180°-scattering geometry without a polarizer was adopted for observing the LA phonon.

The complex dielectric constant \( \varepsilon^*=\varepsilon'+j\varepsilon'' \) of a PZN–0.045PT single crystal was measured using an LCR meter (HP) in the [100] direction. The measurements were performed while cooling at a rate of 2 K min\(^{-1}\) in a homemade furnace. An external field was applied for the dielectric measurements by a DC power supply (Matsusada Precision). To avoid applying an electric field on the LCR meter, a homemade circuit containing condensers as low-frequency filters was set between the sample and the LCR meter \[19\].

3. Results and Discussion

3.1 Brillouin scattering
Figure 1 (a) shows the light scattering spectra at three temperatures with and without an electric field of 500 V/cm. The spectrum consists of a longitudinal acoustic (LA) phonon at 42 GHz, which is related to the complex elastic stiffness constant \( c_{11}^\prime = c_{11} - j c_{11}'' \), and a central peak at 0 GHz, which is related to relaxation in the GHz range. The LA phonon is apparently temperature and electric field dependent, and the dependences are shown in Figure 1 (b). Figure 1 (b) shows the contour map of light scattering spectra as functions of the frequency shift and temperature. The data on ZFC shows a clear
anomaly in the LA phonon around 400 K: the LA phonon softens toward \( T_C \). At the same time, the peak broadens towards \( T_C \). The anomalous behavior is typical of ferroelectric phase transitions in perovskite ferroelectrics through strain–polarization coupling of free energy [20, 21]. However, the temperature range over which the phonon anomaly observed in a paraelectric phase is especially large for the cubic perovskite structure, reflecting the characteristics of relaxor ferroelectrics. The LA phonon on FC shows different phase transition behaviors: two anomalies appear at 420 K and 363 K, which correspond to the phase transitions from cubic phase to tetragonal one, then to rhombohedral. Note that the electric field at critical end point in PZN–0.045PT is around 1000 V/cm \( (E_{\text{CEP}}) \). To extract the frequency shift and the width of the LA phonon from the light scattering spectra, we used the Voigt function. The width of a Gaussian component in the Voigt function was fixed as an instrumental function. The computed parameters of the acoustic phonons, including Brillouin shift, \( \nu_B \), and full-width at half-maximum (FWHM), \( \Gamma \), are shown in Figure 1 (c) as a function of temperature for the PZN–0.045PT under \( E = 0 \), 100, and 500 V/cm, respectively. The \( \nu_B \) and \( \Gamma \) represent the characteristic tendencies of the LA phonon (i.e., softening and broadening over a wide temperature range more clearly than Figure 1 (b). Above \( T_C \), typical perovskite ferroelectrics do not show an anomaly in the LA phonon, or only show anomalies in a narrow temperature range less than 10 K wide, because the piezoelectric coupling is prohibited in their paraelectric phases due to the symmetry restriction [21]. Consequently, the LA phonon anomaly in the relaxor ferroelectric PZN–0.045PT indicates that strong coupling between strain fluctuation and polarization fluctuation exists in the relaxor ferroelectrics [11, 22]. This characteristic behavior does not change with the application of an
electric field. On the other hand, marked changes are seen below the ferroelectric phase transition temperature. Even a small electric field of 100 kV/cm (~ 0.1 $E_{\text{CEP}}$) makes the diffuse phase transition sharp and two jumps and a plateau appear around 400 K in both $\mu_B$ and $\Gamma$. The plateau denotes the electric-field-induced tetragonal phase. With increasing the electric field, the tetragonal phase is stabilized as evidenced by the broadening plateaus. Despite the PZN–0.045PT approaches the critical end point by applying electric field, the amount of changes in $\mu_B$ and $\Gamma$ at the phase transition does not enhanced, which must be attributed to the dynamics up to the GHz range.

3. 2 Dielectric properties

The dielectric properties probing lower frequency dynamics are shown in Figure 2. In common with the LA phonon, the tetragonal phase is induced by an electric field. The two peak temperatures in $\varepsilon'$ under an electric field (360 K and 425 K) are in good agreement with two anomaly temperatures in the LA phonon, however, the peak temperature in $\varepsilon''$ (421 K at 250 Hz) on zero-field cooling is different from the anomaly temperature in the LA phonon (403 K). It is because the complex elastic stiffness constant $c_{11}$ is connected with $\varepsilon''$ at 0 Hz when we assume that acoustic anomaly is a result of single relaxation process at the GHz range [11, 22].

As expected from the critical phenomena, the low frequency $\varepsilon'$ is enhanced: a peak $\varepsilon'$ at 250 Hz increases from 55000 to 65000, while $\varepsilon'$ at 100 kHz increases from 45000 to 48000 by applying 500 V/cm (~ 0.5$E_{\text{CEP}}$). The increase in $\varepsilon'$ indicates that $\varepsilon'$ at only low frequency is enhanced markedly at the critical end point. This idea is consistent with the LA phonon at the GHz range shown in Figure 1. Because the Brillouin scattering probes around the 42 GHz, little enhancement in $\varepsilon''$ is detected through the strain-polarization coupling. In other words, the enhanced relaxation is located below the GHz range.

3. 3 Effect of electric field on phase transitions

Effect of an electric field on diffuse phase transitions in a relaxor ferroelectric PZN-0.045PT single crystal is studied through dielectric properties and a longitudinal acoustic (LA) phonon. Compared with the diffuse phase transition observed in zero-field cooling in PZN-0.045PT, it shows two sharp phase transitions under field cooling. According to our previous work on thermal hysteresis in PZN-0.07PT [12], the present data is analyzed.

From a mesoscopic point of view, the phase transition diffuseness is attributed to inhomogeneous structure from the static PNRs, nanodomains, and microdomains. When the relaxor ferroelectrics are cooled across $T_c$ from the highest temperature, the size of the inhomogeneity just below $T_c$ must be distributed, which smears the phase transition. When the relaxor ferroelectrics is cooled with an

![Figure 2](image-url)
electric field, the static PNRs, nanodomains, and microdomains unite with others, and thus the ferroelectric domains grow in size and in polarization. Therefore, the complex inhomogeneous structure is eliminated, making the phase transitions sharp. The effect of inhomogeneity on a phase transition behavior is not so large in normal ferroelectrics. However, in the case of PZN–0.045PT, the cubic, tetragonal, and rhombohedral phases are in such competition around 400 K, in addition to the inhomogeneous structure, that the inhomogeneity can have a greater influence on the phases.

In general, more than one minimum in the free energy is thought to explain a first-order phase transition, but in the present case, at least three phases–cubic, tetragonal, and rhombohedral–should be taken into account as shown Figure 3. These phases adopt similar free energies around the phase transitions; as a result, nonequilibrium states can be easily achieved through supercooling, leading to the appearance of the drastic change by applying an electric field. When the sample is cooled without an electric field from the high temperature, the paraelectric cubic phase transforms to the supercooled ferroelectric rhombohedral state. On the field cooling, the electric field enhances the relaxation from the nonequilibrium polymorphic states to the equilibrium phase. Thus, each phase transition can be clearly distinguished.

4. Conclusion
The LA phonon and dielectric properties under an electric field in a PZN–0.045PT single crystal were measured to investigate the phase transition in relaxor ferroelectrics. The diffuse phase transition in PZN–0.045PT becomes sharp by applying the electric field during the phase transition, which is the result of reduced inhomogeneity in the complex relaxor system by an electric field. An external electric field grows the static PNRs and microdomains into larger ferroelectric domains.

By the complementary measurements of the LA phonon and dielectric properties, we discuss the phase transition dynamics in a broad frequency range up to the GHz range. The results indicate that enhanced dielectric property due to the applied electric field appears only in a low frequency region, which is necessary to be confirmed by measuring at various conditions in the future work.

Acknowledgments
This work was supported by JSPS KAKENHI Grant Number 30150981.

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