Domain-Related Phase Transitionlike Behavior in Lead Zinc Niobate Relaxor Ferroelectric Single Crystals

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The relaxor ferroelectric lead zinc niobate (Pb(Zn$_{1/3}$Nb$_{2/3}$)O$_3$) has been intensively investigated, because of its large dielectric and piezoelectric properties for applications in actuators and transducers. In this study, the in-situ behavior of the domains in Pb(Zn$_{1/3}$Nb$_{2/3}$)O$_3$ single crystals has been observed using optical microscopy in combination with a charge-coupled device (CCD) camera. The temperature of the sample has been cycled between $-185 ^\circ$C and $+200 ^\circ$C, while applying an electric field of up to $\pm 10$ kV/cm. Many characteristics, such as the induction of birefringence, the transition between the microdomains and macrodomains, and the "freeze-in" of the macrodomains, have been optically observed. The optical and dielectric data have been collected and plotted as a function of temperature and electric field. An electric-field–temperature diagram showing five domain-related regions has been proposed. The microdomain-to-macrodomain phase transitionlike behavior seems to be an analog of a martensitic phase transition.

I. Introduction

Lead zinc niobate, Pb(Zn$_{1/3}$Nb$_{2/3}$)O$_3$ (PZN), single crystals have been studied intensively since it was suggested in 1981 that they would make good candidate materials for actuator and transducer applications, because of their large dielectric constant ($K_{r77} \approx 3000$) and piezoelectric coefficient ($d_{33}^\circ \approx 1050 \times 10^{-12}$ C/N). PZN has a disordered perovskite structure in which the Zn$^{2+}$ and Nb$^{5+}$ ions exhibit short-range ordering on the B site, resulting in regional composition variations on the nanometer scale. These compositional fluctuations not only broaden the phase transition but also introduce fine-scale inhomogeneities for the nucleation of microdomains.

The symmetry of PZN is cubic, $Pm3m$, above the Curie temperature and rhombohedral, $3m$, below the transition point. Because a broad phase transition occurs in PZN, a "Curie temperature range," $T_m$, occurs rather than a Curie temperature as in normal ferroelectrics. In this study, the Curie temperature range correlates to the "microdomain formation temperature," $T_c$. $K_{r3}$ and dielectric loss (tan $\delta$) values are strongly dependent on the measurement frequency (dielectric relaxation). At 1 kHz, $T_m$ occurs at $\sim 140 ^\circ$C with a $K_{r3}$ maximum of 56000 along the (111). The broad phase transition and frequency dispersion that are exhibited by relaxor ferroelectrics such as PZN have a strong link to the configurations of the ferroelectric microdomains.

Static ferroelectric domains have been observed by several methods, such as optical microscopy on acid-etched samples or transmission electron microscopy (TEM) on mechanically thinned samples. However, the dynamic observation of switching domains under an applied electric field or with changing temperature has been difficult experimentally, which has resulted in limited research efforts.

An optical technique has been used to explore the growth of macrodomains (>0.1 $\mu$m) from microdomains (~20 nm and 0.1 $\mu$m) in PZN single crystals along the (111) direction, as functions of temperature and applied electric field. The measured dielectric constant $d_{33}^\circ$ and tan $\delta$, as a function of temperature for a poled sample, are compared to the optically observed macrodomain motion in an attempt to develop a fundamental understanding of the relaxor behavior in PZN. The focus of this paper is to develop an electric-field–temperature diagram that describes the domain behavior in PZN. Optically and electrically measured characteristics will be used to develop the different phase fields.

II. Experimental Procedure

Single crystals of PZN were grown using a flux method with excess lead oxide. The crystals were light brown, with sizes ranging from 0.5 mm to 1 cm on an edge. The Laue X-ray technique was used to precisely determine the [111] directions in the crystals. The crystals were then sliced, ground to a thickness of 100 $\mu$m, and polished with diamond paste until a near-mirror finish was obtained on both surfaces. The samples were thinned to 200 $\mu$m, the temperature and rhombohedral, 3m, below the transition point. The broad phase transition and frequency dispersion that are exhibited by relaxor ferroelectrics such as PZN have a strong link to the configurations of the ferroelectric microdomains.

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References

1. Development of Electric-Field–Temperature Diagram

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The microscope system was used to observe many characteristics of the PZN domain structure, such as the birefringence change, the microdomain-to-macrodomain transition, and the
“freeze-in” temperature. The magnitude of the electric field has been plotted against temperature using the optically observed characteristics and measured dielectric data, as shown in Fig. 2, which identifies five domain-related regions.

Because the birefringence changes were caused by the alignment of the microdomains and the peak in the permittivity (at 0.05 Hz) was caused by the onset of microdomains, it was assumed that these two anomalies marked the first phase transition when the temperature was decreased. It is the boundary between the paraelectric and ferroelectric microdomain regions, which will be discussed in Section III(1)(A).

The second transition occurs at the temperature where the macrodomains appear when field cooling is applied and disappear when field heating is applied, which will be discussed in Section III(1)(B). This transition separates the ferroelectric microdomain region from the ferroelectric macrodomain region and corresponds to the shoulderlike anomaly of the permittivity curve. Section III(1)(C) describes the behavior of the switching macrodomains, as a function of the electric field and temperature.

The third transition occurs at the domain freeze-in temperature, which will be discussed in Section III(1)(D). When the field heating is applied, the unfreezing temperature occurs at slightly higher temperatures. (The freeze-in temperature that is referenced in this study corresponds to the temperature when the electric field cannot switch the macrodomains anymore.) The transition temperature between the ferroelectric macrodomain region and the ferroelectric frozen domain region shifts to lower temperatures as the magnitude of the electric field increases. In the vicinity of this transition temperature, the dispersion of $\tan \delta$ is observed.

(A) Boundary between Paraelectric Region ↔ Ferroelectric Microdomain Region: The single crystals used in this study were beige in the paraelectric region and retained this
The ferroelectric microdomain behavior for an unpoled and poled PZN single crystal was observed. The ferroelectric microdomain boundary was characterized by the microdomains orienting with the electric field. As the magnitude of the electric field increased, the microdomain formation temperature (\(T_m\)) corresponded to the paraelectric; at the critical temperature (\(T_m\)), the color of the single crystal changed to a combination of blues and browns. The macroscopic birefringence that has been detected as color changes in the crystal was caused by the microdomains orienting with the electric field. The magnitude of the electric field increased, the microdomain formation temperature (the temperature at which the birefringence appeared) increased. The first boundary was determined by observing birefringence as a function of the electric field and temperature. No temperature hysteresis was observed at the paraelectric ↔ ferroelectric microdomain boundary, represented by solid triangles in Fig. 2.

The position of the paraelectric ↔ ferroelectric microdomain boundary was supported by the \(K_{BT}\) and tan \(\delta\) behavior for an unpoled (Fig. 3) and poled (Fig. 4) PZN single crystal. The dielectric behaviors were identical for both the poled and unpoled samples at temperatures of \(\geq T_m\). However, when \(T_m\) as a function of frequency, for the unpoled sample was plotted and then extrapolated to a frequency of 0.05 Hz, \(T_m\) was \(\sim 124^\circ C\). The frequency-dependent transition temperature corresponded to the paraelectric ↔ ferroelectric microdomain boundary, represented by a solid triangle at 124°C (for 0.05 Hz) in Fig. 2.

**Boundary between Ferroelectric Microdomains ↔ Ferroelectric Macrodomains:** The ferroelectric microdomain ↔ macrodomain boundary temperature was at which the macrodomains were first observed with an electric field, represented by solid circles in Fig. 2. This temperature (\(-110^\circ C\)) was almost constant for all applied electric fields. Macrodomains were not observed with fields below \(\pm 0.7\) kV/cm, the threshold field (\(E_0\)) of PZN. The threshold field is necessary to induce the microdomain-to-macrodomain transition. A threshold field also was observed in Pb(Mg\(_{1/3}\)Nb\(_{2/3}\))O\(_3\) (PMN). When field heating was applied, the ferroelectric microdomain ↔ macrodomain boundary, which was characterized by the disappearance of the macrodomains, occurred at slightly higher temperatures, represented by the open circles in Fig. 2. The boundary increased to higher temperatures as the electric field level increased.

The dielectric behavior that is represented in Figs. 3 and 4 also supports the ferroelectric microdomain ↔ macrodomain boundary. Frequency dispersion, which is exhibited by the unpoled sample, did not occur in the poled sample below this temperature. The temperature region (\(\sim 100^\circ C\) to \(-120^\circ C\)) where \(K_{BT}\) had a nondispersive frequency behavior appeared as a "shoulder" in the poled sample, as shown in Fig. 4. Also, the dielectric loss (tan \(\delta\)) decreased drastically in this temperature region. The decrease in tan \(\delta\) and the shoulder in the poled sample were caused by the macrodomain generation by the \(+15\) kV/cm poling field. However, in the unpoled sample, the macrodomains had not aligned and the variation in the orientations of the macrodomains caused frequency dispersion in the dielectric data. This temperature region, from the start of the frequency dispersion (\(-124^\circ C\)) to 100°C, corresponds to the ferroelectric microdomain region. The shoulder corresponds to the critical temperature (100°C) that signifies the ferroelectric microdomain ↔ macrodomain boundary.

**Ferroelectric Macrodomain Behavior:** The macrodomain region occurs at temperatures of \(<110^\circ C\) at \(>0.7\) kV/cm and remains until the macrodomains are not switchable with the electric field anymore. Several interesting macrodomain behaviors were observed as a function of the electric field and temperature.

Figures 5(A)–(D) are micrographs of the domain patterns of PZN single crystal at 100°C as the electric field increased. The domain wall density increased as the electric field was increased from 1.3 kV/cm to 5 kV/cm. The length of macrodomains elongated and narrowed as the electric field increased. The domain modulations were \(-5\) \(\mu m\) in size and lenticular in shape. The domain walls oriented along [011] directions. None of the samples that were examined achieved a monodomain state, even when a dc bias of up to +15 kV/cm was applied, which is similar to monodomain behavior that has been reported in PMN single crystals by several interesting macrodomain behaviors. However, in the unpoled sample, the macrodomains had not aligned and the variation in the orientations of the macrodomains caused frequency dispersion in the dielectric data. This temperature region, from the start of the frequency dispersion (\(-124^\circ C\)) to 100°C, corresponds to the ferroelectric microdomain region. The shoulder corresponds to the critical temperature (100°C) that signifies the ferroelectric microdomain ↔ macrodomain boundary.

**Frozen Ferroelectric Macrodomains:** At temperatures that were electric-field dependent, the macrodomains became non-switchable. This temperature is referred to as the macrodomain freeze-in temperature, represented by solid squares in Fig. 2.
Fig. 4. Permittivity versus temperature for a poled PZN single crystal at 100 Hz, 1 kHz, 10 kHz, and 100 kHz.

Fig. 5. Four frames from the videotape that represent changes in domain density at 100°C with increasing electric field ((A) 1.3, (B) 2.5, (C) 3.8, and (D) 5.0 kV/cm).
The dispersion of the tan δ value that is observed below −70°C in Fig. 3 may be attributed to the domain freeze-in phenomenon. The freeze-in temperature marked the ferroelectric macro-domain → frozen macrodomain boundary. When field heating was applied, the thawing or “unfreezing” temperature, represented by open squares in Fig. 2, occurred at temperatures slightly higher than the freeze-in temperature, indicating a slight temperature hysteresis. The unfreezing temperature represented the ferroelectric macrodomain ← frozen macrodomain boundary. The behavior of the electric-field dependence was approximately the same when field heating and cooling were applied.

At temperatures just above the freeze-in temperature, the single crystal seemed to undergo a domain structural transition. The domains split into narrower domain segments. The width of each segment decreased as the temperature decreased. The segments switched synchronistically. At ±3 kV/cm, the domain switching was “frozen in” at −50°C. However, at ±5 kV/cm, the freeze-in temperature occurred at −150°C. Figures 7(A)–(D) show the domain configuration at ±5 kV/cm (ac field of ±5 kV/cm) as the temperature was decreased from 26°C down to −154°C. For this sample, as the temperature decreased, the number density of domains also decreased.

The polarization-versus-electric-field (P vs E) data, shown in Fig. 8, supported the optically observed freeze-in temperature for PZN single crystals. For a normal ferroelectric, the P vs. E curve has an “S”-shaped hysteresis. With PZN, the P vs. E curve developed a rounded rhombic loop as the temperature decreased. As the electric field increased, the rhombic loop was maintained to lower temperatures, as shown in Figs. 8(A)–(D). At the freeze-in temperature, the loop closed as spontaneous polarization vanished. From Fig. 8, it can be observed that, at ±5 kV/cm, the rhombic loop closed between −125°C and −175°C, which is in the same temperature range as the optically observed domain freeze-in temperature of −150°C plotted in Fig. 2. However, even at −175°C, the P vs. E curve for ±10 kV/cm has a slight rhombic shape, which signifies that the sample was still able to switch.

(E) Ferroelectric Frozen Microdomain Region: At temperatures of <100°C and electric fields between +0.7 kV/cm and −0.7 kV/cm, a fifth domain-related region is proposed. This region is called the ferroelectric frozen microdomain region. Because the size of the microdomains is below the resolution of the optical microscope, this region has been extrapolated; therefore, it is represented by the dashed lines in Fig. 2.

(2) Phase Transition Analogy between PZN Microdomains and Plate like Martensite Regions

The optically observed domain behavior in PZN seems to be analogous to a martensitic phase transition (MPT). This idea was suggested for the domain behavior of PMN. The MPT is dispersive and initiates at a temperature M_e, which is the martensite start, and stops at a temperature M_s, which is the martensite finish. The martensite phase begins far above the
global transition temperature by the formation of platelike martensitic regions in the parent phase. The platelike martensitic regions form randomly in the structure. The growth of these regions occurs by the formation of new plates as temperature decreases rather than by increasing the size of already-formed plates. The $M_s$ temperature of a MPT can be shifted to higher temperatures with increasing stress, which could be understood from the formation of the local stress concentration. Another property of a MPT is a large temperature hysteresis between heating and cooling.

The behavior of PZN microdomains that form between the paraelectric region and macrodomain region under applied electric field seems to be an analog of the platelike martensitic regions in a MPT. In Section III(1)/(A), the onset of birefringence, as well as the peak in the permittivity, were the first sign of the alignment of the microdomains in the nonpolar region. The microdomains and nonpolar regions correspond to the platelike martensite regions and parent phase, respectively. The temperature of the observed birefringence (beginning of microdomains) as a function of electric field, shown in Fig. 2, is analogous to the $M_s$ temperature (beginning of platelike regions) in a MPT. Also, the temperature at which birefringence occurs notably increases as the electric field increases, which also is similar to a stress-induced increase of the $M_s$ in a MPT. The temperature where the first macrodomains are observed at a particular electric field is analogous to the $M_s$ temperature in a MPT where all the parent phase has been transformed. The transition temperature range ($M_s$ to $M_f$) and the dispersion of a MPT are similar to a dispersive and broad relaxor ferroelectric transition. Figure 2 shows a temperature hysteresis between the microdomain ↔ macrodomain transition when heating and cooling is applied. A temperature hysteresis also is a property of a MPT. Short-range order exists in each microdomain; however, the microdomains are randomly distributed over the entire structure, similar to the random formation of the platelike martensitic regions.

There are many observed behaviors of the microdomains in PZN that seem to be analogous to martensite regions in metal alloys. Further study is necessary to determine if this MPT modeling can be applied to the relaxor ferroelectric microdomain behavior.

**IV. Summary**

Five domain-related regions have been shown to exist in PZN in an electric-field–temperature diagram. The boundaries of these regions were determined by optical observations of the domain configurations. These results suggest that the temperature at which the initial birefringence occurs increases as the electric field increases. This temperature can be considered as the border between the paraelectric and ferroelectric microdomain regions. The transition from ferroelectric microdomains to ferroelectric macrodomains when field cooling is applied occurs at $\sim 130^\circ$C and is independent of the electric field. When
the dielectric constant of an unpoled PZN single crystal is compared to that of a poled sample, a shoulder occurs in the dielectric constant of the poled sample. The shoulder at 100°C for the poled sample is caused by the microdomain alignment. This temperature corresponds to the optically observed microdomain-to-macrodomain transition. The freeze-in temperature, when field cooling is applied, and the unfreezing temperature, when field heating is applied, is optically observed and decreases in temperature as the electric field increases. This observation is confirmed by the $P$ vs. $E$ curves at various temperatures and electric fields. As the freeze-in temperature is attained, the shape of the $P$ vs. $E$ curve changes from a ferroelectric “$S$” shape to a closed loop, which was accompanied by the disappearance of spontaneous polarization. The microdomain region behaves analogously to the platelike martensite regions; therefore, one might explore the possibility of using some of the well-documented studies on martensite to study the ferroelectrics relaxor systems.

References

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