Polarization reversal study using ultrasound

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We found that the sound velocity changes drastically near the coercive field for a $0.955Pb(Zn_{1/3}Nb_{2/3})O_3$–$0.045PbTiO_3$ ferroelectric single crystal, which reflects that domain rotation occurred during polarization switching. This velocity change associated with polarization switching provides a powerful method to study the dynamics of polarization reversal process in nontransparent ferroelectric crystals. A complete phase velocity-electric field loop was measured quasi-statically in a switching cycle and compared with the polarization hysteresis loop. In addition, two attenuation peaks were found in the switching cycle, which indicates that two domain switching processes are involved in the polarization reversal. © *2001 American Institute of Physics.*
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The electronic applications of ferroelectric materials have intrigued more fundamental studies on these materials. In recent years, the polarization reversal process has been revisited[1–7] since the understanding of this process could help to build many devices using polarization reversal phenomena. The rich physical phenomena associated with the domain switching process have attracted many physicists and material scientists since the 1950's.[8–11] The experimental methods that have been used for studying the domain switching/polarization reversal are the measurements of ferroelectric hysteresis loop,[4] transient reversal current,[2,3,9,10] permittivity vs E-field[8,11] and domain observation using optical microscope.[7,8] Each method reveals a particular aspect of the polarization reversal process. In this work, we present an ultrasonic method to study the polarization reversal process, which is very useful for studying nontransparent systems and reveals average effects.

Because the velocity is a function of elastic stiffness coefficients, which are anisotropic, it can reflect the orientation of the domains. In addition, ultrasonic measurement could also reveal information on the attenuation of ultrasonic waves. Therefore, if polarization rotation is involved in the reversal process, we should be able to detect velocity variation based on the crystal symmetry. We show in this letter that this method is very effective for the study of the polarization reversal process in $0.955Pb(Zn_{1/3}Nb_{2/3})O_3$–$0.045PbTiO_3$ ferroelectric single crystals. Analogous to the ferroelectric hysteresis loop (P–E loop), a loop of the ultrasonic phase velocity versus electric field has been measured (v–E loop). We found that the coercive field E_c can be determined from both the P–E loop as well as from the v–E loop. Two peaks were found in the curve of the attenuation versus electric field. The peaks correspond to the critical field levels at which severe mechanical activities occur. The two attenuation peaks indicate that the polarization reversal in this crystal system is coupled strongly to two domain rotation processes.

The $0.955Pb(Zn_{1/3}Nb_{2/3})O_3$–$0.045PbTiO_3$ single crystals were grown using the high temperature flux technique[12] and their properties have been fully characterized.[13] The crystal orientations are $[111]/[1\bar{1}0]/[11\bar{2}]$ and the dimensions of the sample are $3\times5.3\times3.8$ (mm). Gold films were sputtered onto the $[111]$ and $[\bar{1}\bar{1}\bar{1}]$ faces to form the electrodes. A Bertan high voltage supply was used to apply the electric field to the samples and a 10 MHz longitudinal wave transducer, which was driven by a Parametrics Pulser/Receiver, was use for both pulse launching and echo receiving. The wave forms were recorded using a Tektronix digital oscilloscope and were then transmitted to a personal computer for analysis. The schematic of experiment setup is shown in Fig. 1. In the experiment, the applied field was changing very slowly. The total time for the cycle is about 4 h. This slow process allows the domains to have enough time settling into their new positions in each small increment of the field. The insert of Fig. 1 shows more details of the sample geometry and orientation. For convenience of discussion, coordinates for the cubic parent phase are used in this letter since the natural crystal coordinates will rotate during the switching process as will be discussed next. The initial state has a

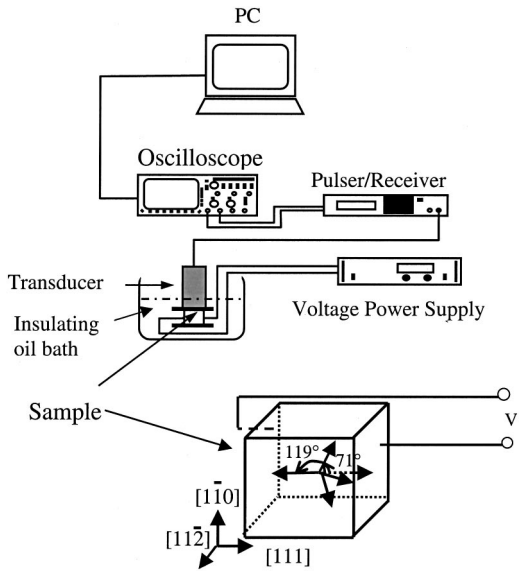

FIG. 1. Ultrasonic measurement system. The insert at the bottom shows the crystal orientation.

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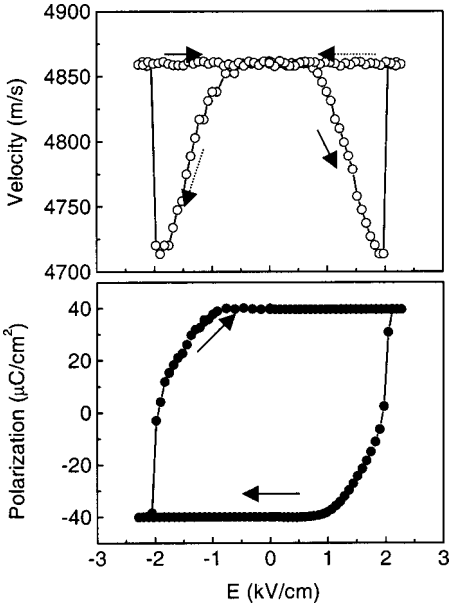

FIG. 2. Velocity–electric field loop and Polarization–Electric field loop. The longitudinal velocity is measured in [111] under an electric field also in [111].

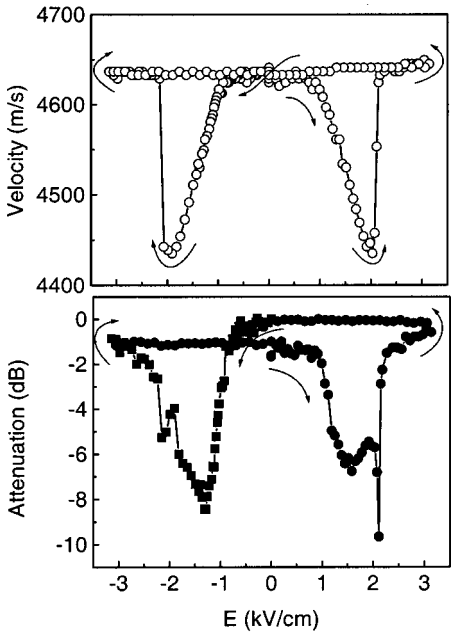

FIG. 3. Velocity and attenuation versus electric field, with the longitudinal wave propagating in $[1\bar{1}0]$ under an electric field along [111].

polarization along [111] with the crystal symmetry of $3m$. There are a total of eight possible domain states for this system.

Figure 2 shows a loop of ultrasonic phase velocity versus electric field measured using our system. As a comparison, a ferroelectric hysteresis loop obtained at the same time is also shown. The crystal sample was poled before the measurement so that the starting point is not from the origin. The electric field was applied to the sample along the [111] of the cubic coordinates, or the C axis of the trigonal coordinates, and the phase velocity of ultrasound in [111] direction was measured.

The electric field is applied opposing the polarization at the beginning. When the field is gradually increased, the velocity is almost unchanged until the electric field amplitude reaches 0.6 kV/cm for negative field direction and 0.75 kV/cm for positive field direction. After this critical point, velocity begins to decrease with increasing field amplitude at faster speed. The velocity reaches a minimum near the coercive field E_c and then drastically increases back to its original value with further increase of the field level. Little change of the velocity was found after the sample being poled into a single domain state with the polarization either along [111] or $[\bar{1}\bar{1}\bar{1}]$. Compared to the electric hysteresis loop, one can see that the velocity minimum appears at the point of $P=0$, $E=E_c$. There are two reasons that might cause the velocity to decrease: one is the reduction of piezoelectric contribution, which softens the effective elastic constant along the poling direction, and the other is due to the rotation of domains, which reduces the velocity due to elastic anisotropy. Our analysis showed that the change observed in this system corresponds to domain rotation.[14]

Figure 3 shows the velocity and attenuation of ultrasound in the $[1\bar{1}0]$ direction under an electric field in [111] direction (longitudinal wave perpendicular to the field direction). The cycle period is also about 4 h. The dependence of the velocity on the electric field is similar to the v–E loop shown in Fig. 2, which confirmed that the velocity change is due to domain rotation since the piezoelectric effect has no influence on the effective elastic constant in the direction perpendicular to the polarization. One important finding is the change of acoustic attenuation during polarization reversal. The attenuation level represents the degree of mechanical motion involved in the polarization reversal process, similar to the case in ferromagnetic system when it is coupled to the elastic strain.[15]

There are two characteristics in the field–attenuation curve, which differ from the field–velocity curve.

(1) Asymmetry of the attenuation for positive and negative fields. It indicates that the domain motion is not symmetric since the domain pattern changes may be controlled by nonsymmetric defect pinning centers. This asymmetry is also reflected in the velocity versus electric field curve, but not as so obviously as in the attenuation versus field curve.

(2) Instead of one minimum in the velocity curve, there are two downward peaks in the attenuation versus field curve. The first peak appears at $E=E_c$ and the second peak appears at the half-way point of the decreasing path of the velocity–field curve. This is a convincing evidence that the polarization switching in the PZN–4.5%PT crystal is via the path of $0°\rightarrow71°\rightarrow180°$ as illustrated in the insert of Fig. 1. Such a switching path is quite different from the conventional $0°\rightarrow180°$ domain flipping mechanism. This point has been discussed in detail in another paper.[14] The two attenuation peaks correspond to the critical field for the $0°\rightarrow71°$ and $71°\rightarrow180°$ domain switching, respectively.

In summary, we have demonstrated that the ultrasonic method can be used to probe the polarization reversal process through the study of a 3m symmetry system, for which there are eight possible domain states. The method is not

restricted to transparent materials and can probe the interior averaging change occurred during switching. In addition, it can be performed in a quasi-static manner so that the domains can have enough time to relax to equilibrium position responding to the field change. We found that the polarization switching process is directly correlated to the velocity variation with a minimum appears at the coercive field. Most importantly, the attenuation peaks indicate the intensity of mechanical activities involved in the polarization reversal process. The two peaks appeared in the attenuation imply that the polarization switching process in the $0.955Pb(Zn_{1/3}Nb_{2/3})O_3-0.045PbTiO_3$ system is via $0° \rightarrow 71° \rightarrow 180°$ domain rotation rather than the $0° \rightarrow 180°$ domain flipping. Another important advantage of the ultrasonic method is that the measurements could be carried out in any direction, resulting more information on the anisotropic nature of the crystal.

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