

## Coercive field of $0.955\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3-0.045\text{PbTiO}_3$ single crystal and its frequency dependence

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Domain switching behavior of  $0.955\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3-0.045\text{PbTiO}_3$  ferroelectric single crystal has been investigated using the ultrasonic technique in addition to the polarization hysteresis measurements. The ultrasonic technique makes it possible to extend the coercive field measurement to frequencies as low as  $10^{-5}$  Hz, revealing the existence of a saturated coercive field  $E_{sc}$ , which representing the intrinsic switching barrier. © 2002 American Institute of Physics.

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In recent years,  $(1-x)\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3-x\text{PbTiO}_3$  (PZN-PT) single crystal system has become one of the hottest materials of study due to its extremely high piezoelectric and electromechanical coupling coefficient that is produced by the domain engineering process.<sup>1,2</sup> It is also an interesting system for studying the domain switching mechanism since domains in this system can be easily manipulated by applying the electric field in different directions.<sup>3-5</sup>

It is well known that the polarization hysteresis loop depends strongly on the switching frequency.<sup>6</sup> However, the exact mechanism of the switching process is still not completely understood. One of the most fundamental questions is if there should be a switching threshold. Based on the continuum theory, one could define a definite coercive field, which reflects the switching energy barrier.<sup>7</sup> On the other hand, based on the random field model,<sup>6</sup> such a coercive field is only a reflection of the relaxation effect under a different field level. In other words, the switching could occur even under a very small field if one could wait long enough. Recent experiments seem to support the latter argument.<sup>6</sup> It is shown experimentally that the switching time versus coercive field curve could be fitted to an exponential relation derived from the random field mode,  $\tau = \tau_0 \exp[E_0/(E_c + E_{RF})]$ . This relation actually implies that the coercive field  $E_c$  may be arbitrarily small if the frequency is low enough.

Since the coercive field obtained from continuum theory is much too high compared to the experimental value, this idea of local random field induced nucleation is worth further investigation since it could change the traditional thinking of polarization switching. A natural test is to see if the relation could hold for very low frequency measurements. However, it is very difficult to measure the hysteresis loop for extremely low frequencies since the currently used method is based on the integration of the switching current, which becomes too small to measure for the low frequency process.

In order to overcome this limitation, we have constructed a system that can measure the polarization quasistatically. The material under study is a  $0.955\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3-0.045\text{PbTiO}_3$  [PZN-4.5% PT] single

crystal. The objectives of this study are twofold: (1) find the initial nucleation field level, and (2) find out if there is a saturated coercive field  $E_c$ . The information will help us to further understand the polarization switching mechanism.

We found that the ultrasonic phase velocity can be a powerful tool for probing the domain state in the PZN-4.5%PT system, since the ultrasonic wave velocity is directly related to the symmetry and orientation of the domain state and the switching process in this system is primarily through domain rotations.<sup>8</sup> The phase velocity is determined by the measurement of the time of flight of the ultrasonic waves propagating in the crystal sample. As reported by many other researchers, the  $0.955\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3-0.045\text{PbTiO}_3$  single crystals have rhombohedral  $3m$  symmetry at room temperature, and the dipoles are formed along the body diagonal of the parent cubic perovskite unit cell. Based on the parent cubic coordinates, the crystal used in our experiments has the orientations of  $[111]$ ,  $[1\bar{1}0]$ , and  $[11\bar{2}]$ , respectively, and the dimensions are  $3 \times 5 \times 5$  mm. Gold films were sputtered onto the  $[111]$  and the  $[\bar{1}\bar{1}\bar{1}]$  faces (or the  $C$  direction in the rhombohedral coordinates) to form the electrodes. A Bertan series 105 high voltage supply was used for the electric field generation. A 10 MHz longitudinal wave transducer driven by Parametrics 200 MHz pulser/receiver was used for both pulse launching and echo receiving of the ultrasonic waves. The wave forms were recorded using a Tektronix TDS460A digital oscilloscope and were then transferred to a personal computer for further data analysis. The schematic experiment setup is shown in Fig. 1. In the experiment, the field was changed slowly with small increments each time. The total period of the electric field cycle is from 20 min up to 7 h. Such a long period is not usually used for the hysteresis loop measurements because of the  $RC$  charging problem and the extremely low switching current, which prevent accurate measurements. The low frequency limitations, however, do not exist for the ultrasonic technique. For comparison, we have also measured the frequency dependence of the hysteresis loop from 0.1 to 100 Hz using a conventional technique, which corresponds to a period of 0.01–10 s. The measured  $P-E$  hysteresis loops are shown in Fig. 2. One can see that the 10 s cycle is obviously not long enough since the coercive field is still decreasing with decreasing frequency. In

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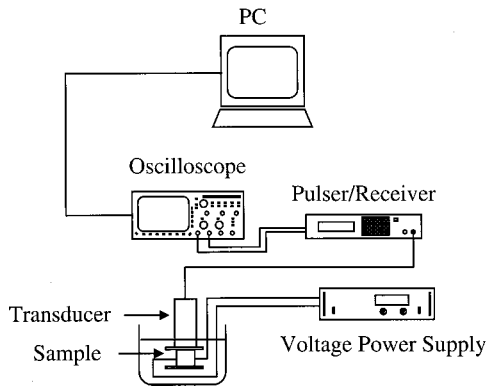


FIG. 1. Scheme of ultrasonic measurement system.

fact, the coercive field change is still noticeable even for a 100 s cycle as indicated in Ref. 6.

Using the ultrasonic method we were able to perform coercive field measurements at much lower frequencies. This is based on our earlier report that the sound velocity in the PZN-4.5%PT system has a strong dip at the coercive field,<sup>8</sup> which provides us with a powerful tool to measure the coercive field without having to measure the polarization at such low frequencies. In other words, we only need to measure the velocity versus field and find the velocity minimum to define the coercive field.

Figure 3 shows a typical loop of ultrasonic phase velocity versus electric field measured using the system described in Fig. 1. This measurement cycle took about 4 h to complete in order to achieve a quasistatic condition. Starting from a  $-C$  direction poled single domain state, the velocity is almost unchanged when the electric field level  $E$  is less than 0.6 kV/cm, which means that no other domain nuclei were activated under such a low field. When the field level reaches 0.6 kV/cm, the phase velocity started to decrease, indicating that domains having dipoles of orientations other than up and down directions start to nucleate. The velocity reaches its minimum value at the coercive field  $E_c$ . Further increase of the field level will cause the velocity to drastically increase from the minimum value back to its original level at zero field, implying that the reverse polarized domains are formed much more quickly under higher field (Note: waves in the

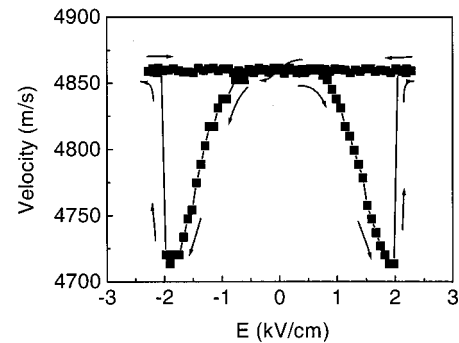
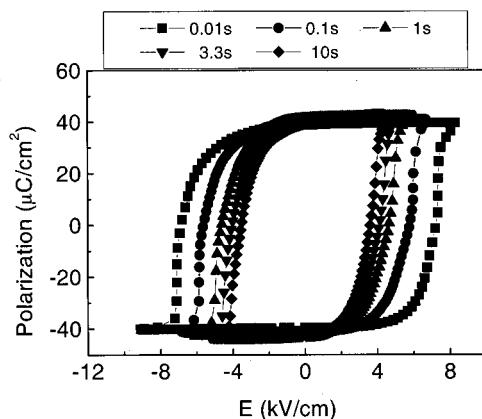
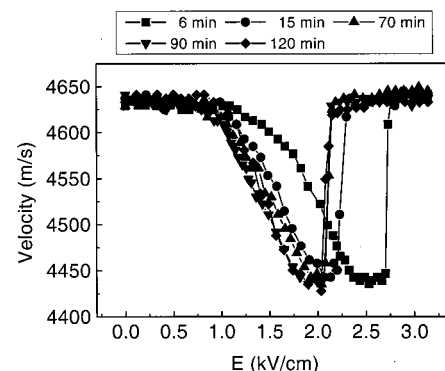


FIG. 3. Phase velocity along [111] under an electric field in the same direction.

up-polarization domains have the same velocity as those propagating in the down-polarization domains).

As shown in Fig. 3, the switching process indicated two critical electric field levels. The first is near 0.6 kV/cm, at which domains having different polarization axes nucleate at multiple sites inside the crystal and the process follows an exponential relationship. The second critical field is the coercive field  $E_c$  ( $\sim 2$  kV/cm), at which the bulk starts to switch. Obviously, there exist localized nucleation agents, which cause the nucleation to start at a very low field level. On the other hand, there is definitely an energy barrier for the bulk material. We will further analyze this situation below.

Figure 4 shows the dependence of ultrasonic phase velocity on electric field ( $v$  versus  $E$ ) for a PZN-4.5%PT crystal measured in a time period from 6 to 120 min. The longitudinal phase velocities were measured in the  $X$  direction of the crystal axes or  $[1\bar{1}0]$  of the cubic coordinates, which is perpendicular to the polarization direction. One can see that the nucleation starts near 0.6 kV/cm for all cases, but the field corresponding to the minimum velocity decreases as the time of the measurements becomes longer. The two critical fields are clearly seen for all cases, although the locations of the velocity minimum are different. The coercive field  $E_c$  determined from the minimum point of the  $v-E$  curves shift to lower value for longer measurement time, or lower frequency. One can see that the coercive field  $E_c$  for the case of 90 and 120 min are very close, indicating that the  $E_c$  value is approaching a saturated value. The continuous change of the  $E_c$  field, even at such long period measurements, indicates that slow processes such as domain growth are involved in

FIG. 2. Frequency dependence of the  $P-E$  hysteresis loops.FIG. 4.  $v-E$  curves under electric field with different period. Phase velocity is along  $[1\bar{1}0]$  and the electric field is applied along  $[111]$ .

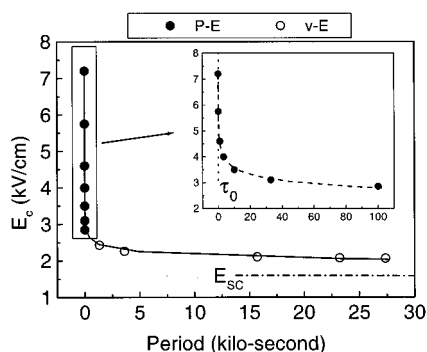


FIG. 5. Coercive field vs measurement period under electric field. Note: the scale for the horizontal axis of the insertion is second.

the later stage of the switching process. The uniqueness of the ultrasonic method is its capability of performing super slow switching measurements (as low as  $10^{-5}$  Hz).

Although the time dependence of  $E_c$  has been observed before by others, the relatively fast switching field used could not provide sufficient evidence for the existence of a saturated value for the coercive field. With only limited frequency data, a slight error could change the fitting parameter value substantially, and may even lead to a totally different conclusion. As an example, if we use the exponential relation of random field model  $\tau = \tau_0 \exp[E_0/(E_c + E_{RF})]$  for the switching field and the switching period, the fitting from the limited polarization hysteresis measurements would give a curve indicated by the dashed line in the inclusion of Fig. 5. The fitting parameters are:  $\tau_0 = 6.65 \times 10^{-10}$  s,  $E_0 = 205.8$  kV/cm, and  $E_{RF} = 5.21$  kV/cm. On the other hand, if we use the entire data available now to fit the relation, the parameters become:  $\tau_0 = 5.35 \times 10^{-5}$  s,  $E_0 = 22.8$  kV/cm, and  $E_{RF} = 0.45$  kV/cm (solid line in Fig. 5). The much longer relaxation time  $\tau_0$  would lose its original physical meaning.

On the other hand, if we only use the long time ultrasonic data, we could obtain the following set of parameters:  $\tau_0 = 22.6$  s,  $E_0 = 3.54$  kV/cm, and  $E_{SC} = 1.56$  kV/cm for the

exponential relation  $\tau = \tau_0 \exp[E_0/(E_c - E_{SC})]$ . Here the  $\tau_0$  represents a slow domain relaxation process or the domain growth rate and the  $E_{SC}$  represents the saturated coercive field, which is related to the intrinsic bulk switching energy barrier between domain states. However, the new relation could not account for the higher frequency switching data.

From our experiments, the following conclusions could be derived:

- (1) There is a saturated coercive value that corresponding to the intrinsic switching energy barrier.
- (2) There is a critical field at which localized nucleation starts. But the total switched volume through the initial nucleation process is very limited.
- (3) Domain process is involved in the later stage of the switching process and becomes the dominant process near the end. Its relaxation time is rather slow.

The observed facts indicate that two different processes exist for the polarization reversal. One is a fast process, mainly the formation of multiple nuclei. Their formation can be sped up greatly with high electric field. The other is a much slower process that mainly involves the growth of these nuclei via the movements of interfaces and domain walls. The change of coercive field with switching time (inverse of frequency) is shown in Fig. 5. There is a saturation value  $E_{SC}$  as the switching time increases, representing the energy barrier between different domain states.

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