Frequency dependence of the coercive field of 0.71Pb($Mg_{1/3}Nb_{2/3}$)O_3-0.29$PbTiO_3$ single crystal from 0.01 Hz to 5 MHz

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The frequency dependence of the coercive field E_c in $[001]_c$ poled 0.71Pb($Mg_{1/3}Nb_{2/3}$)O_3–0.29$PbTiO_3$ single crystals was investigated as a function of frequency f from 0.01 Hz to 5 MHz. E_c was found to be proportional to f^{β} as predicted by the Ishibashi and Orihara model, but our results showed two frequency regimes separated at around 1.0 MHz with different β values. This change of switching kinetics may be due to the presence of slower relaxation times for non–180° domain switching and heterogeneous nucleation of polar nanoregions, whose contribution to polarization reversal is frozen out beyond 1.0 MHz, leading to a larger β. *Published by AIP Publishing.*
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The coercive field (E_c) of ferroelectric materials is a critical parameter for the application of ferroelectric materials in random access memories (FRAMs) and medical ultrasonic transducers, which determines the lowest or maximum operating voltage of related devices.[1–3] In general, E_c is frequency dependent because polarization switching is associated with domain wall motions and/or opposite domain nucleation and growth, both processes are time and field dependent.[1,2,4] The frequency dependence of the coercive field of bulk ferroelectric single crystals or ceramics had been investigated by measuring the polarization hysteresis loops in the low frequency range of 0.01 Hz–1000 Hz.[5–7] There are two factors limiting the measurement frequency for the hysteresis loop. The first is the existence of a finite relaxation time for the domain switching process. If the electric field changes too fast, the domain switching process cannot be completed, which leads to partial polarization reversal and the hysteresis loop becomes distorted. The second is the heat generation during the hysteresis measurement at high frequencies, which will cause the change of polarization and the coercive field.[8] On the other hand, many practical devices, such as medical ultrasonic transducers, usually operate in the megahertz range. For example, the center frequencies of abdominal, obstetric, and cardiac imaging transducers are from 2 to 5 MHz. Therefore, it is very critical to investigate the frequency dependent E_c in the higher frequency range, particularly when the low frequency defined E_c is small, such as the (1-x)Pb($Mg_{1/3}Nb_{2/3}$)O_3-$x$$PbTiO_3$ (PMN-PT) single crystals. Transducer engineers and ultrasonic imaging system designers need to know if they could apply a field larger than E_c at higher frequencies to produce stronger signals.

For a ferroelectric system, the coercive field increases with frequency, which had been experimentally observed in single crystals,[4] bulk ceramics,[9,10] and thin films.[1,11,12] E_c was found to have a linear relationship with frequency in lead zirconate titanate (PZT) thin films.[12] A empirical correlation was established between log f and $1/E_c$ in PZT thin films[2] and $BaTiO_3$ single crystals.[13] The Kolmogorov-Avrami-Ishibashi (KAI) domain nucleation-switching model treats polarization reversal as a nucleation and growth process and a relationship was derived based on the Avrami nucleation model of crystal growth.[14] This model stated that E_c is proportional to f^{β} and the relationship has been verified in different ferroelectric materials, including triglycine sulphate (TGS) single crystals[15] and PZT thin films.[1,11] In recent years, different scaling regions of E_c vs f^{β} were observed in ferroelectric thin films,[16–19] but the reason for these different scaling regions is still a debating issue. There are numerous investigations on polarization switching in the time domain,[20–23] which is related to our results in the frequency domain. In particular, an investigation of Pb-based piezoelectric crystals also demonstrated the presence of multiple regions in the time domain, in particular near E_c.[22]

The relaxor–based (1-x)Pb($Mg_{1/3}Nb_{2/3}$)O_3-$x$$PbTiO_3$ (PMN-PT) ferroelectric single crystals have been extensively investigated owing to their giant piezoelectric coefficient, ultrahigh electromechanical coupling factor, large dielectric constant, and low dielectric loss. More complete picture about the superior functional properties can be seen from the complete set of elastic, piezoelectric, and dielectric constants.[24,25] However, there is one apparent disadvantage of the PMN-PT single crystals: it has a very low coercive field (E_c=1.8–2.5 kV/cm), about 1/5th of the traditional PZT piezoceramics, which limits their practical applications to relatively low field levels. Conventionally, the coercive field E_c is measured at very low frequencies (< 1 Hz). Because the coercive field increases with frequency, people are extremely eager to know the effective coercive field of PMN-PT single

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crystals at megahertz frequencies since medical imaging transducers are usually operated in the range of 2–5 megahertz.

In this letter, the frequency dependence of the effective coercive field in $[001]_c$ poled $0.71Pb(Mg_{1/3}Nb_{2/3})O_3$-$0.29PbTiO_3$ (PMN-0.29PT) single crystals was investigated in the frequency range of 0.01 Hz to 5 MHz. Two different measurement methods, namely hysteresis loop measurement and critical value method based on polarization degradation, were used to perform the task. The degradation of ferroelectric properties under a bipolar pulse electric field was analyzed to obtain a suitable parameter to define the effective coercive field at megahertz frequencies and the feasibility of this critical value method was validated.

The $[001]_c$ oriented PMN-0.29PT single crystal wafers were purchased from CTS Corp., USA, and were cut into $2.5 \times 2.5\,mm^2$ platelets with the thickness of 0.113 mm. All specimens were sputtered with gold on the larger surfaces and poled along the thickness direction $[001]_c$ at room temperature for 10 min under an electric field of 10 kV/cm. The ferroelectric hysteresis loops at low frequencies were measured using a modified Sawyer Tower circuit with the frequency range of 0.01 Hz to 500 Hz at room temperature. A high electric field of 9 kV/cm (larger than three times of the coercive fields of the samples) with a sinusoidal bipolar waveform at different frequencies was generated using a computer controlled high voltage amplifier (KEPCO Model BOP 1000M). The high frequency coercive field from 10 kHz to 5 MHz was measured using a critical value method based on ferroelectric degradation.[3] In this method, a pulse/function generator (Wavetek Model 81) was used to generate a sinusoidal pulse signal, and then, the signal was amplified using a RF broadband power amplifier (Electronics & Innovation 1040L, 10 kHz–5 MHz). The amplified signal was output to the samples and oscilloscope through a "T" connection. When the amplitude of the applied AC electric field reaches its critical value, some ferroelectric domains begin to switch in the reverse direction and the sample begins to depolarize. To characterize the degradation of the samples, the switching measurement was interrupted at a predetermined time interval at each given field level, and the electromechanical coupling factor k_t, dielectric constant ε_r (1 kHz), and dielectric loss D were measured using an impedance analyzer (HP 4194A).

Figure 1 summarizes the behavior of remnant polarization and coercive field as functions of frequency for the PMN-0.29PT single crystal at selected frequencies. We can see that the well-saturated P-E loops are strongly frequency dependent. Figure 2 shows a typical result of the degradation of k_t as a function of the number of cycles under a bipolar electric pulse of 2.5 MHz with different peak values E_p, and the pulse repetition frequency is 100. It can be seen that k_t keeps nearly a constant value within the investigated number of cycles when $E_p = 540$ V/mm but decreases with the number of cycles when $E_p = 620$ V/mm, indicating the onset of polarization switching. When $E_p = 660$ V/mm, a higher decreasing rate of k_t was observed as shown in Fig. 2. Also, we found that the loss D increases while ε_r and d_{33} decrease with the number of cycles when the electric field E_p is larger than 620 V/mm. Because it is much hard to get accurate

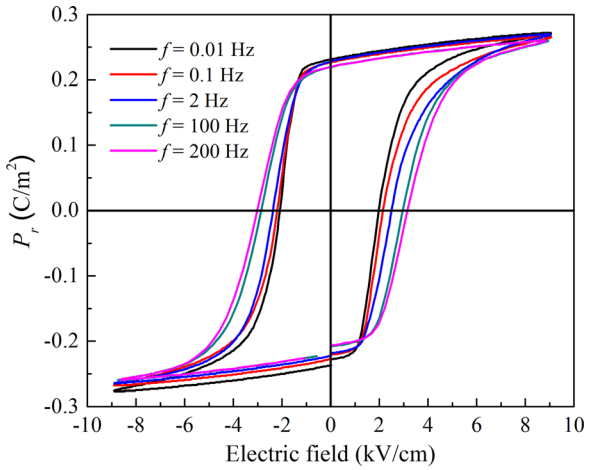

FIG. 1. Frequency dependence of hysteresis loops for the PMN-0.29PT single crystal at selected frequencies.

measurements on d_{33} and D, k_t was chosen to be the critical parameter to indicate the effective coercive field. When the applied field reached a critical value, the antiresonance peak began to shift toward lower frequencies, and we define this critical field level to be the effective coercive field at the given frequency. If the applied electric field maintained above E_c, the anti-resonance frequency would keep reducing with the number of cycles. This means that the PMN-0.29PT single crystal began to depolarize when the electric field is higher than the effective coercive field. The inset of Fig. 2 shows a typical change of impedance spectrum with the number of cycles when a 2.5 MHz bipolar pulse was applied with the field amplitude of 710 V/mm. One can see that the parallel frequency f_p directly reflects the change of k_t, while series resonance frequency f_s is nearly a constant.

The procedure of measuring the effective coercive field at megahertz frequencies based on the change of k_t can be summarized as follows: First, a bipolar pulse of certain frequency with certain amplitude is applied to the sample for a certain number of cycles. Then, the field is removed and the impedance spectrum is measured to see whether there is a change of the anti-resonance frequency. If not, increase the

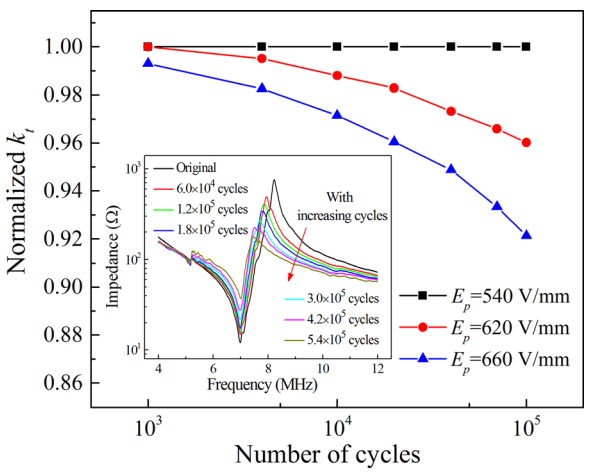

FIG. 2. Degradation of electromechanical coupling factor k_t of the PMN-0.29PT single crystal sample under 2.5 MHz bipolar electric field with different amplitudes. The inset shows the impedance spectrum change of a sample after applying a 2.5 MHz electric field of different numbers of burst cycles.

electric field level and repeat the measurement until the anti-resonance frequency begins to decrease. The critical field level at which the anti-resonance frequency began to decrease is defined as the coercive field at that frequency. Figure 3 shows the variation of k_t under a bipolar electric field of 11.5 kHz with different field amplitudes. When the amplitude of the electric field reached 292 V/mm, k_t begins to decrease, indicating that partial depoling occurred, so that 292 V/mm is defined as the effective coercive field at 11.5 kHz.

The f-dependence of E_c for PZT ceramics had been investigated by some researchers.[2,15] The theoretical model of the frequency dependent coercive field developed by *Ishibashi* and *Orihara* based on the Avrami model is widely used to analyze such experimental results.[1,10] According to the model, the f-dependence of E_c obeys the following power law

$$E_c = Kf^{\beta} \tag{1}$$

Equation (1) indicates a linear relation between $\log(E_c)$ and $\log(f)$.

The inset of Fig. 3 shows the frequency dependence of the coercive field of our sample based on the hysteresis loop measurements. From the linear fitting line (red), the E_c data can be well described by the relationship of $E_c = 1.926f^{0.04522}$ (kV/cm). Using this relationship, we can predict that the coercive field of the sample at 11.5 kHz should be 2.94 kV/cm, in good agreement with the direct measurement result (2.92 kV/cm) using our critical value method. This validated the high frequency effective coercive field measurement method we developed based on the change of the electromechanical coupling coefficient k_t.

We further verified if the relationship Eq. (1) is valid in the higher frequency range from 10 kHz to 5 MHz for the PMN-0.29PT single crystal. Figure 4(a) shows a log–log plot of the effective coercive field versus frequency f from 0.01 Hz to 5 MHz. When the measurement frequency was increased from 0.01 Hz to 800 kHz, the coercive field increased about 122%. At 5 MHz, the effective E_c increased by 234%. As shown in Fig. 4(a), the E_c data can be well fitted to Eq. (1), but one can see that the log–log plot of E_c and

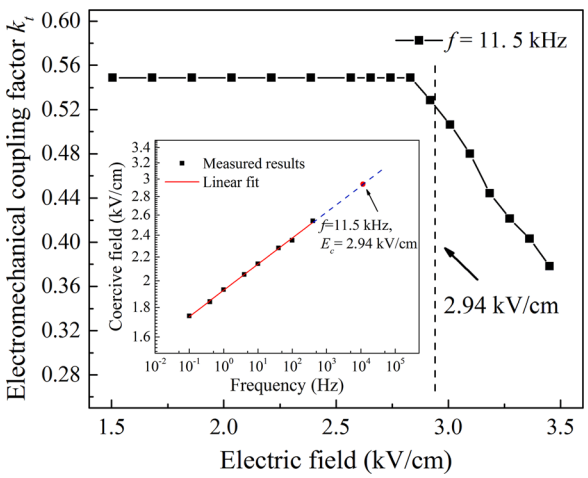

FIG. 3. Electromechanical coupling factor k_t of PMN-0.29PT single crystal sample vs. field amplitude at $f = 11.5$ kHz. The inset shows the frequency dependence of the coercive field from 0.1 Hz to 400 Hz.

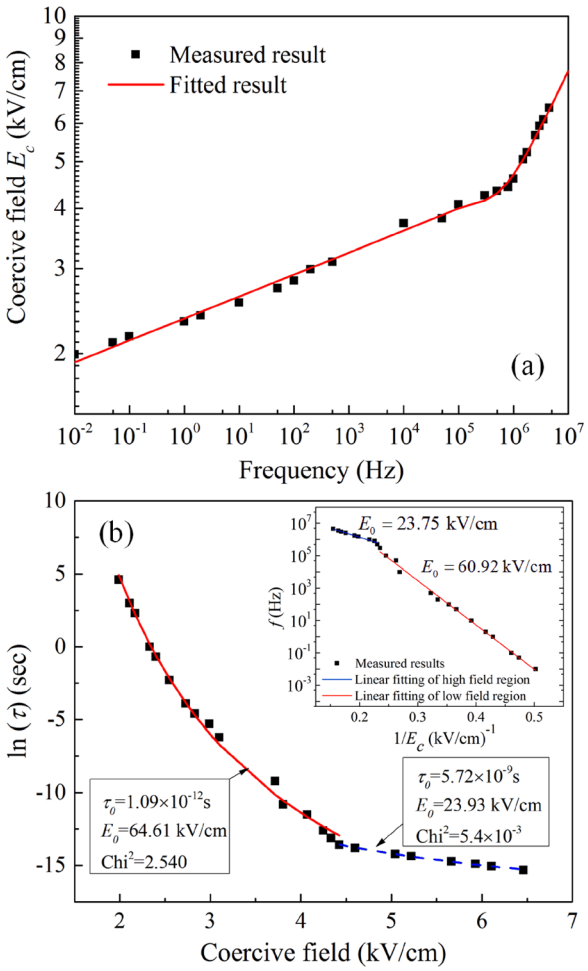

FIG. 4. (a) Frequency dependent coercive field E_c of the PMN–0.29PT single crystal sample from 0.01 Hz to 5 MHz. (b) Plot of the inverse of the measurement frequency as a function of the coercive field for the data shown in (a). The inset in (b) shows fitting of the same data using the Merz equation. The standard deviation Chi^2 is also given to show the fitting errors.

f displays two scaling regimes with a dividing point at about 1 MHz. This inferred that there should be two types of switching domain kinetics involved in the polarization reversal process.[26] Accordingly, we propose the following empirical formula to fit the experimental data in Fig. 4(a):

$$E_c = K_1 f^{\beta_1}\left[1 - \exp\left(-\frac{T}{\tau_1}\right)\right] + K_2 f^{\beta_2}\exp\left(-\frac{T}{\tau_2}\right). \tag{2}$$

Here, T is the period of the ac pulse field and τ_1 and τ_2 are the two critical relaxation times for two different domain reorientation processes. The first term is dominant when $T \gg \tau_1, \tau_2$, which represents the relationship of log–log E_c–f in the low frequency range. The second term becomes dominant when $T \ll \tau_1, \tau_2$, representing the high frequency part of the curve. In our case, the values of K_1, β_1, τ_1, K_2, β_2, and τ_2 obtained by least squares fitting are: $K_1 = 2.351$, $\beta_1 = 0.047$, $\tau_1 = 1.707 \times 10^{-7}$, and $K_2 = 1.105$, $\beta_2 = 0.116$, $\tau_2 = 2.767 \times 10^{-7}$, where τ_1 and τ_2 are in the same order of magnitude as the reciprocal of the inflection point on the E_c-f curve. The fitting curve using Eq. (2) is shown in Fig. 4(a) as indicated by the red solid line. One can see that Eq. (2) can satisfactorily describe the entire experimental data from 0.01 Hz to 5 MHz.

According to the modified Arrhenius relation,[5] the rate of domain switching can be described by the following equation,

$$\tau = \tau_0 \exp(-E_0/E) \tag{3}$$

where τ is a characteristic relaxation time, τ_0 is a constant, E is the applied field, and E_0 is the activation field. Figure 4(b) shows the relaxation time ($1/f$) as a function of E_c for the data in Fig. 4(a), which show two different regions. Our analysis yielded the values of $\tau_0 = 1.09 \times 10^{-12}$s and $E_0 = 64.61$kV/cm in the low frequency region and $\tau_0 = 5.72 \times 10^{-9}$s and $E_0 = 23.93$kV/cm in the high frequency region. According to a similar equation given by Merz,[27] a plot of $(1/E_c)$ as a function of $\log f$ should yield a straight line having a negative slope E_0. Such a plot provides an evaluation of the activation field from the E_c–f data. Based on the fitting in the inset of Fig. 4(b), $E_0 = 60.92$kV/cm in the low frequency region and $E_0 = 23.75$kV/cm in the high frequency region.

Similar changes of the coercive field and activation field had been observed in PZT thin films[16] but no literature reports so far for bulk materials. It is believed that domain kinetics might be different in the low and high field regions. Yang *et al.* observed that domain wall dynamics around E_c plays an important role in the f–dependent shape of the hysteresis loop.[17] They think that thermally activated creep motion is more dominant to polarization switching at low f while viscous flow motions become more important at high f, which can lead to the coercive field E_c to be proportional to f^{β} with two scaling regions. However, the model is only suitable for pinning dominated ferroelectric domains and the frequency turning point of different scaling regions was relatively small. We believe that 180° and non-180° domain switching processes may result in the two E_c scaling regions and activation fields observed in Fig. 4. In $[001]_c$ oriented PMN-0.29PT rhombohedral single crystals, 109° and 71° ferroelastic and 180° ferroelectric domains can exist. Therefore, ferroelectric (180°) or ferroelastic (71° and 109°) domain switching processes are allowed in the system.[28,29] 180° domains can be reversed without strains involved while the switching of non–180° domains requires significantly larger strain.[30] Consequently, the switching of 180° domains is much faster than the switching of non–180° domains so that the non–180° domain switching will be more sensitive to the frequency of the applied field due to its relatively longer relaxation time. As a result, when a higher frequency field is applied, there will be less non–180° domains involved in the polarization switching process and they could become totally inactive if the frequency is too high, which leads to change of slope in the high frequency region as shown in Fig. 5(a).

On the other hand, the change of switching kinetics may have a relation with hierarchical relaxation of PMN-0.29PT single crystal which contains significant disorder due to the relaxor nature of PMN. The dynamics of polarization switching had been investigated over extremely broad time scale ($10^{-8} < t < 10^{2}$ s) and field ranges for various modified Pb-based perovskite ferroelectrics.[22] The results unambiguously demonstrated the presence of extremely broad relaxation time distributions for switching and the existence of multiple regions in the time domain near E_c. Stretched exponential functions[22,31] had been used to fit current transients and more than one average relaxation time (i.e., short-time, intermediate-time, and long-time relaxation times) were found. This strongly suggests the fact that heterogeneous nucleation (nucleation of polar nanoregions[31,32]) occurring in the vicinity of defects and/or random fields plays an important role during polarization switching. Following the explanation in Ref. 22, it may be inferred that when the frequency of the bipolar electric field was larger than 1.0 MHz, the process of intermediate-time and long-time transient polarization switching could not happen in the PMN-0.29PT single crystal samples. As a result, a larger electric field will be needed to increase the domain-switching rate of short-time polarization transients, which may also be partially responsible for the change of β in Fig. 4(a).

In summary, the frequency dependence of the coercive field of $[001]_c$ poled $0.71Pb(Mg_{1/3}Nb_{2/3})O_3$–$0.29PbTiO_3$ single crystals has been investigated in the frequency range from 0.01 Hz to 5 MHz by combining the hysteresis loop measurement and the critical value measurement. Our results showed that the coercive field E_c is proportional to f^{β} and the frequency dependent coercive field could be divided into two scaling regions with the turning point at about 1.0 MHz. We believe that the occurrence of the two scaling regions may come from two origins. The first one is related to the 180° and non-180° domain switching processes. In the high frequency range, there will be only 180° domain switching involved, which leads to the increase in the β value. The other is attributed to the presence of broad relaxation time distributions of polarization switching in relaxor ferroelectrics. If the frequency of the bipolar electric field is high enough, heterogeneous nucleation with intermediate characteristic relaxation times could not occur in the vicinity of defects or random fields, which may also cause the increase of the β value. The good news from our results is that in the megahertz range, the PMN-PT single crystals can be safely driven at a field level 2–3 times of conventionally defined E_c without depoling and property degradation, which is a very important information for medical transducer engineers and for the design of other high field high frequency applications.

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