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Polarization reversal and dynamic scaling of $(Na_{0.5}K_{0.5})NbO_3$ lead-free ferroelectric ceramics with double hysteresis-like loops

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The polarization reversal and dynamic hysteresis of ferroelectrics specially with double hysteresis-like loops were investigated by using CuO-doped $(Na_{0.5}K_{0.5})NbO_3$ ceramics. The variation of the hysteresis area and current density clearly suggests three stages of the polarization reversal. It was found that the hysteresis behavior of the dynamics can be scaled as power law relationships apart from the second stage, where different numbers of domains can be rapidly activated. The main polarization mechanism was ascribed to the reversible domain wall motion (field amplitude $E_o < 0.5E_c$) and 180° domain switching ($0.5E_c < E_o < E_c$) for the first stage, and to the non-180° domain switching ($E_o > 3.5$ kV/mm) for the third stage. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4768270]

I. INTRODUCTION

Dynamic hysteresis of the ferroelectrics has gained extensive attention in the ferroelectric sensors, actuators, and ferroelectric random access memories.[1,2] This phenomenon in ferroelectric materials is intrinsically related to the dynamics of the polarization reversal under a cycle of time-varying electric field, where the hysteretic polarization reversal behavior is usually induced by the domain wall motion and domain switching. This is the nucleation and growth process of domains dependent on time and electric field.[3,4] As a consequence, the hysteresis area $\langle A \rangle$ that represents the energy dissipation within one cycle of polarization reversal was considered as a characteristic parameter of the dynamic behavior in ferroelectrics.[5] It was usually described as a function of signal frequency f and electric-field amplitude E_o.[6,7] A couple of studies have been reported in recent years on the polarization reversal dynamic behavior of ferroelectric materials, including thin film,[8] single crystal,[9] and bulk ceramics[10,11] generally with normal ferroelectric hysteresis loops. In these systems, it was found that the scaling relation between $\langle A \rangle$ and f, E_o obeys the power law relationship

$$\langle A \rangle \propto f^{\alpha} E_0^{\beta}, \tag{1}$$

where the exponents α and β depend on the dimensionality and symmetry of the system.[8–11] For example, non-180° domain wall motion is typically heavily clamped in thin films compared to bulk materials.[12] In addition, hysteresis loops tend to become asymmetric as the frequency of the driving field increases in some ferroic systems.[5]

By comparison, the polarization dynamics of another typical ferroelectric system with double hysteresis-like loops was rarely investigated. These ferroelectrics exhibit constrained hysteresis loops similar to those of antiferroelectrics, resulting from the restriction of spontaneous polarization by the defect dipoles that consist of the acceptor dopant ions and oxygen vacancies.[13,14] Such phenomena can be usually seen in "hard" piezoelectric ceramics with acceptor doping.[15] In fact, Yimnirun *et al.*[10] have reported the scaling behavior of "hard" lead zirconate titanate piezoelectric ceramics. However, only normal hysteresis loops in their study were mentioned. Kim *et al.*[16] and Chen *et al.*[17] have proposed the scaling behavior of antiferroelectrics with double hysteresis loops as follows:

$$\langle A \rangle \propto f^{\alpha} (E_0 - E_c)^{\beta}. \tag{2}$$

However, it is known that the double hysteresis loops in antiferroelectrics originate from the anti-parallel spontaneous polarization. Therefore, anti-ferroelectrics are in nature quite different from the "hard" piezoelectric materials.

The purpose of this work is to, thus, deal with the dynamics of the polarization reversal and its hysteresis behavior of a special ferroelectric family with double hysteresis-like loops by choosing CuO doped $(Na_{0.5}K_{0.5})NbO_3$ (NKN) lead-free ferroelectric ceramics. Cu^{2+} acts as a typical acceptor dopant. This lead-free composition has been extensively investigated as potential applications for piezoelectric ceramics.[14]

II. EXPERIMENT

The 1 mol. % CuO doped NKN ceramics (CuO-NKN) were manufactured via a conventional solid-state reaction method using high-purity raw materials such as K_2CO_3 (99.0%), Na_2CO_3 (99.8%), Nb_2O_5 (99.5%), and CuO (99.0%). The powders were weighed according to the stoichiometry and mixed in a planetary mill for 8 h. After calcination at 850 °C for 5 h, 1 mol. % CuO and 0.5 wt. % polyvinyl butyral (PVB) binder were added, followed by a ball milling process for 24 h. Disk samples were uniaxially pressed and then sintered in air at 1040–1120 °C for 3 h. The sintered ceramic disks with a diameter of 8.5 mm were ground and polished to a thickness of 0.70 mm. The more

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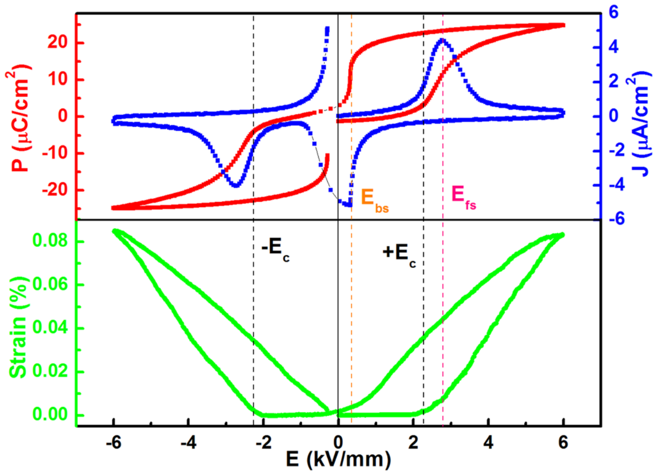

FIG. 1. The polarization and strain versus electric field loop and the corresponding current density of unpoled CuO-NKN ceramics at a fixed frequency f = 10 Hz.

detailed processing procedure can be further referred elsewhere.[18] The polarization versus electric field (P-E) hysteresis loops and the electric field induced strain curves (S-E) of unpoled specimens were measured at room temperature by using a ferroelectric measuring system (Precision LC, Radiant Technologies Inc., Albuquerque, NM) connected with a laser interferometric vibrometer (SP-S 120, SIOS Meβtechnik GmbH, Germany).

III. RESULTS AND DISCUSSION

Figure 1 shows room-temperature P-E and S-E loops and the corresponding polarization current density (J-E) curve of unpoled CuO-NKN ceramics at a field amplitude $E_o = 6$ kV/mm. It is found that different from typical ferroelectrics, the CuO-NKN ceramics exhibit pronounced antiferroelectric-like characteristics, as manifested by constricted and double hysteresis loops. These loops are characterized of four current peaks (two forward switching peaks at E_{fs} and two backward switching peaks at E_{bs}), and zero remanent polarization (P_r) and strain (S_r) after a bipolar cycle. E_{fs} is the field at the maximum forward switching current. E_{bs} is the field at the maximum backward switching current. This kind of typical loops was believed to stem from an internal bias field E_{bias} established by the defect dipoles $(Cu'''_{Nb} - V_O^{\bullet\bullet})$ along the spontaneous polarization direction.[14] In general, the domain switching process in a typical ferroelectric is irreversible due to the lack of driving force to reestablish the domain states after removal of the electric field,[13] characterized by obvious P_r and S_r values. Compared to normal ferroelectrics, the domain switching process in this study was believed to be reversible, because the defect dipoles can provide a restoring force (E_{bias}) to recover the switched polarization (i.e., the backward switching process of the polarization). As a result, the meaning of E_{bs} in this work is different from that for a typical antiferroelectric in which the E_{bs} value corresponds to the ferroelectric-antiferroelectric phase transition.[17]

Figure 2 shows the effect of the field amplitude E_o and frequency f on the P-E hysteresis loops of unpoled CuO-NKN specimens at room temperature. As the field amplitude E_o changes but its frequency f is fixed at 10 Hz (Fig. 2(a)), the evolution of the P-E loops can be divided into three stages with an increase of E_o. At the first stage, the accessible maximum polarization P_{max} is very limited ($P_{max} < 4\,\mu$C/cm^2) as the applied fields are lower than 2.2 kV/mm. It can be seen that a further increase of the applied fields will induce minor (unsaturated) hysteresis loops ($E_o = 2.2$–3.5 kV/mm). In the meantime, the P_{max} value and $\langle A\rangle$ rapidly increase with increasing the E_o value. Therefore, the coercive field E_c of the studied material, which is generally defined as a threshold field producing macroscopic polarization, should approximate to 2.2 kV/mm.

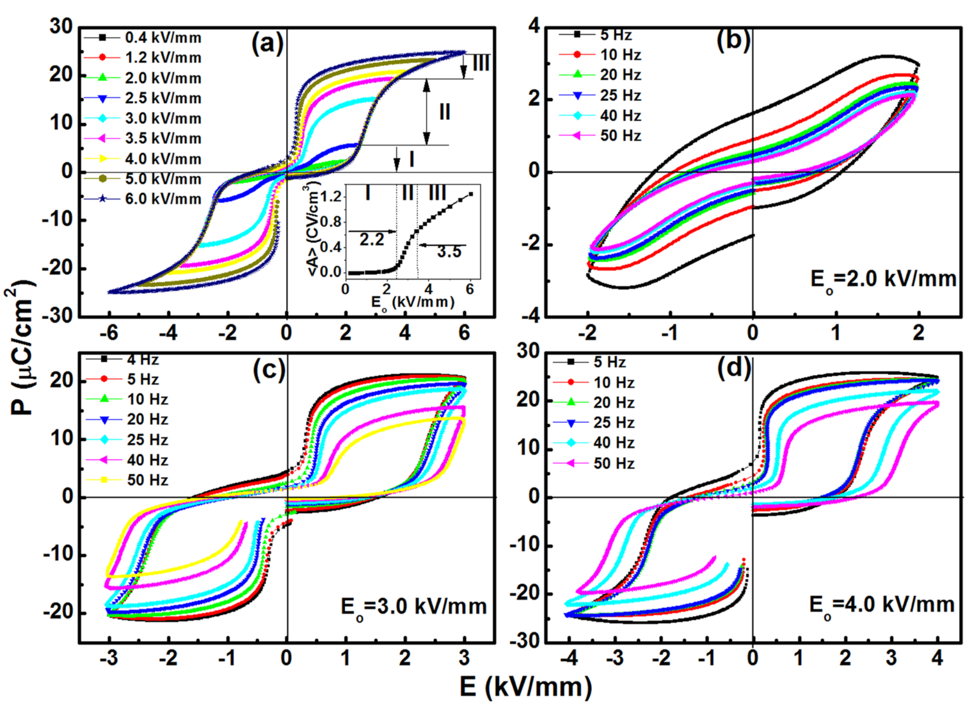

FIG. 2. (a) P-E hysteresis loops of CuO-NKN ferroelectric ceramics under different amplitudes of electric fields at a fixed frequency f = 10 Hz, and under three fixed-amplitude fields but with various frequencies: (b) $E_o = 2$ kV/mm, (c) $E_o = 3$ kV/mm, and (d) $E_o = 4$ kV/mm.

The coercive field E_c seems to be a critical field between the first and the second stages. As $E_o < E_c$, the field induced strain is nearly zero (Fig. 1), meaning that only domain wall motion and 180° domain switching could participate in the first stage. At the third stage, the saturated double hysteresis-like loops with large P_{max} values (more than 20 $\mu C/cm^2$) can be developed under fields far above E_c ($E_o > 3.5$ kV/mm). The above phenomenon looks similar to that observed in an antiferroelectric, except that the P_r values are near zero in antiferroelectrics,[16] which exhibit small non-zero values for CuO-NKN specimens. The three stages of P-E loops can be more clearly distinguished in the inset of Fig. 2(a). As the field amplitude E_o is fixed, the shape of P-E loops also relies on the signal frequency. Figs. 2(b)–2(d) indicate the frequency dependent loops under three certain E_o values corresponding to the above-mentioned three different stages, respectively. It can be seen that P_r, P_{max} as well as $\langle A \rangle$ decrease, whereas E_c increases with an increase of f. This phenomenon is universal in ferroelectrics owing to the fact that domain switching is the time dependent nucleation-growth process under a certain E_o.[19] In addition, the switching time under a lower E_o should be larger than under a higher E_o because the domain nucleation rate increases with an increase of the applied field strength.

The polarization reversal process is usually accompanied by the formation of the polarization current. The J-E curves under various E_o values are shown in Figs. 3(a)–3(i). It can be found that the J values increase linearly with increasing the electric field when $E_o \leq 1.2$ kV/mm. As the E_o value is above 1.2 kV/mm, J values start to rapidly increase. The current density J is known to reflect the change of the dielectric displacement, which should change drastically when the polarization direction switches along the direction of the applied electric field (i.e., domain switching). That is to say, a rapid increase of J under E_o above 1.2 kV/mm means that the domain switching starts to take part in the polarization reversal process. By comparison, the polarization reversal is dominated by the domain wall motion in the field range of $E_o < 1.2$ kV/mm. However, the critical field between the first and the second stages is located at E_c rather than at the field approximately equal to $E_o = 0.5E_c$ (1.2 kV/mm), which hints that the dynamic of domain switching under subcoercive field should be similar to that of the domain wall motion but different from that of domain switching under a field value beyond E_c. The difference should be attributed to the different polarization mechanism between $E < E_c$ and $E > E_c$, which will be later discussed in detail. Moreover, a sharp J peak starts to appear at $E_o \sim E_{fs}$ (2.7 kV/mm) (Figs. 3(f)–3(i)), which should correspond to the maximum switching rate of the domains. This means that the switching rate of domains changes drastically in the second stage of the polarization reversal. This is also the reason why the increase of P_{max} and $\langle A \rangle$ is very fast in the second stage, as seen from Fig. 2(a). It is worthy of note that the value of E_{fs} (2.7 kV/mm) is larger than that of E_c (2.2 kV/mm) here probably owing to the existence of an internal bias field. There is another J peak for most of P-E loops even for the case, where E_o is less than 1.2 kV/mm. As the applied field is decreased, a small J peak at E_{bs} starts to appear as shown by pink arrows in Fig. 3. As we mentioned above, the appearance of this J peak is also related to the existence of the internal bias field E_{bias}, which is estimated to be 0.55 kV/mm from Fig. 3 and can make the domain wall motion reversible in the first stage. None of any other J peaks can be observed

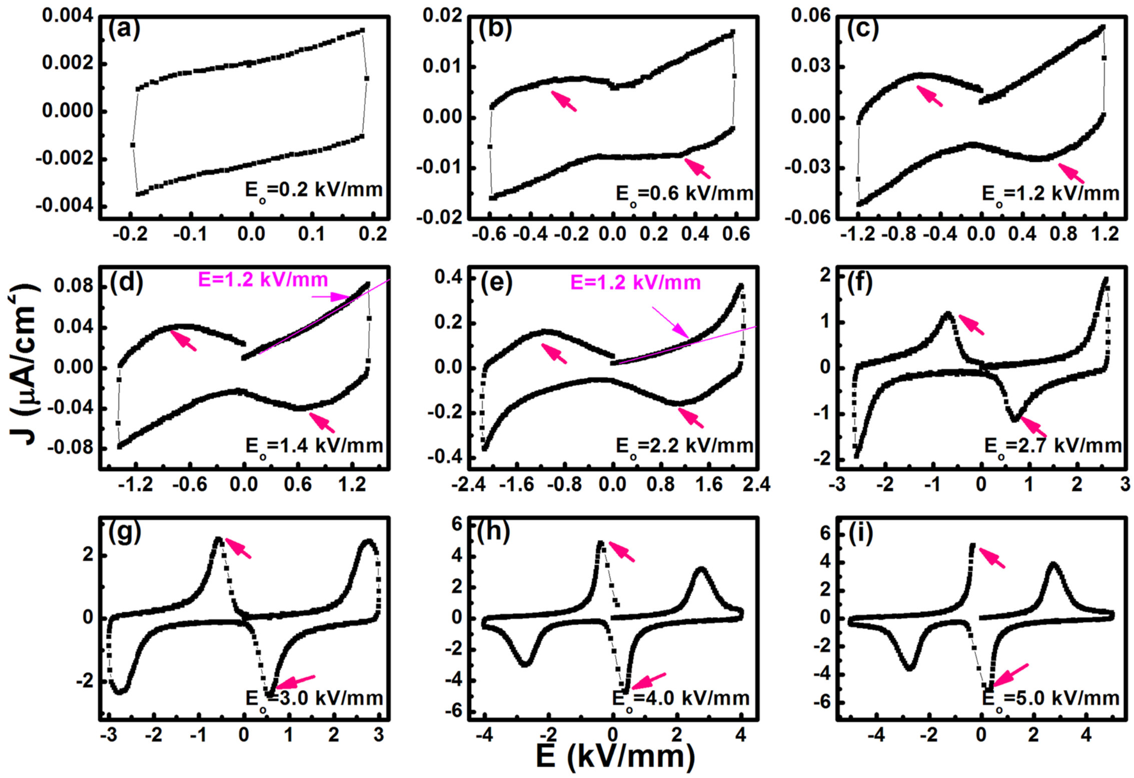

FIG. 3. The polarization current density versus electric field curves under selected electric field amplitudes.

as E_o is less than E_{bias} and the variation of the current density is probably due to the capacitance effect (Fig. 3(a)). It is obvious that as E_o is below E_c, no macroscopic strains can be observed. With further increasing the electric field amplitude, the S-E curves exhibit typical butterfly loops but without S_r. As we know, the type of the domains walls in ferroelectrics depends on their crystal symmetry. In the present study, CuO-doped NKN ceramics persist an orthorhombic symmetry.[14] This gives 12 possible directions of the spontaneous polarization with 180°, and non-180° (90°, 60° and 120°) domain walls, where non-180° domain walls are both ferroelastically and ferroelectrically active but 180° domain walls are only ferroelectrically active. It means that the electric field induced strain mainly stems from the non-180° domain switching in ferroelectrics. Therefore, this could illustrate that the 180° and non-180° domain switching are the main polarization mechanisms in the field range of 1.2 kV/mm < E_o < 2.2 kV/mm and E_o > 2.2 kV/mm, respectively. This critical electric field determined by the S-E curve is also considered as the point separating the first stage from the second stage, indicating that the dynamic of the 180° and non-180° domain switching should be different from each other. This coincides with the analysis from the J-E curves. However, we cannot exclude the possibility that the 180° domain switching exists as E_o is just above 2.2 kV/mm, i.e., in the second stage. By comparison, the polarization reversal mechanism can be assigned to the non-180° domain switching only as E_o > 3.5 kV/mm because the field value far above E_c should be strong enough to finish the orientation of all 180° domains before 3.5 kV/mm. This can be further supported by the following quantitative analysis.

The dynamic scaling behavior of the polarization reversal induced by domain wall motion and reversible domain switching can be quantitatively analyzed by using not an antiferroelectric mode (i.e., Eq. (2)), owing to that $\langle A\rangle$ is not zero when $E_o < E_c$, but a ferroelectric mode (i.e., Eq. (1)), where the exponent β can be determined directly by plotting $\ln\langle A\rangle$ against E_o at a fixed f. Considering that the slope of $\ln\langle A\rangle$ versus $\ln E_o$ does not show an obvious change with the variation of f, only one curve between $\ln\langle A\rangle$ and $\ln E_o$ at

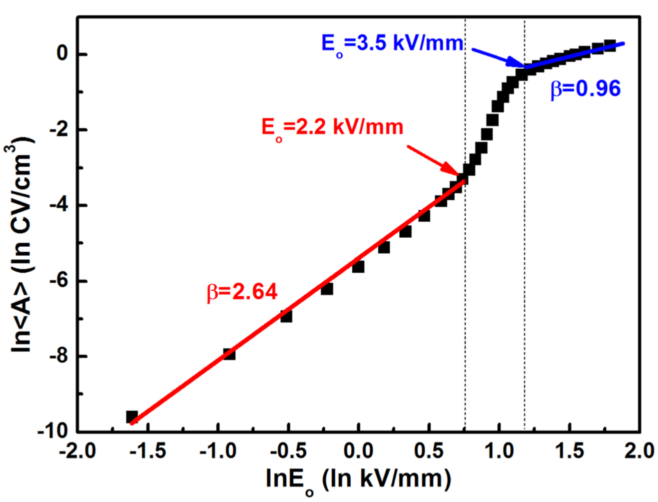

FIG. 4. The curve of $\ln\langle A\rangle$ as a function of $\ln E_o$ in the case of the signal frequency f = 10 Hz.

$f = 10$ Hz was given as an example (Fig. 4). It is evident that two perfectly linear relations were identified exactly in the E_o ranges for the first and third stages, respectively. At the same time, the exponent β values were determined to be $\beta = 2.64$ and 0.96 for these two stages, respectively. These values are much larger than those in antiferroelectrics ($\beta = 2.12$ and 0.50, respectively),[16] but smaller than those in many normal ferroelectrics.[8,9] The possible reason might be related to the fact that CuO-NKN is ferroelectric in nature but its polarization switching suffers from the restriction of the defect dipoles. Compared with NKN single crystals, the lower β values in both first and third stages for CuO-NKN ferroelectric ceramics also suggest that the domain switching is constricted because the exponent β represents the ability of domains following the electric field direction.[9] As mentioned above, although the domain wall motion and 180° domain switching can be distinctly distinguished in the first stage, they obey the same power raw relation. By comparison, the scaling behavior between the domain wall motion and the domain switching is different in a normal ferroelectric,[11] possibly due to the restricted polarization orientation by the dipole defects in this work.

On the other hand, the exponent α, i.e., the slope of the $\ln\langle A\rangle$ versus $\ln f$ curve, shows a strong electric-field dependence as can be seen from Fig. 5. The $\ln\langle A\rangle$ value was plotted as a function of $\ln f$ for different E_o values (Fig. 5(a)). It is obvious that the exponent α (the slope of the curve) increases with the increase of the electric fields. The exponent α values calculated for various electric fields can be further plotted as a function of E_o, as shown in Fig. 5(b). We can clearly find that there are two perfectly linear sections in the α versus E_o curve. These two linear sections ($\alpha = 0.16E_o$-0.85 and $\alpha = 0.008E_o$-0.21) also exactly correspond to the first and third stages as far as the dynamic behavior is concerned. On the contrary, not only the $\ln\langle A\rangle$ values with respect to $\ln E_o$ but also the α values with respect to E_o vary dramatically in the second stage and cannot be linearly fitted, because in this stage the increase in the number of the activated domains should not be the same with any increment of E_o.[11] Moreover, the polarization reversal mechanism in this stage is not as simple as in the first and third stages. The nucleation and growth of both 180° and non-180° domains are probably involved. The explanation can be further supported by the fact that there is a J peak corresponding to the maximum domain switching rate in the field range of 2.2 kV/mm < E_o < 3.5 kV/mm.

If Figs. 4 and 5(a) are compared, one can clearly find that the hysteresis area $\langle A\rangle$ decays slowly with f but increases rapidly with E_o for both first and third stages. This is mainly because the nucleation and growth process during the domain wall motion and domain switching show much more dependence on the electric field than the frequency.[7] It is also interesting to note that the β value in the case of the saturated loops under E_o far above E_c (stage 3) is much less than that in the case of $E_o < E_c$ (stage 1) for CuO-NKN ferroelectric ceramics (Fig. 4), similar to the normal ferroelectrics.[5–9] Generally, domains in ferroelectrics ceramics can be divided into 180° and non-180° domains. It was believed that larger β values at $E_o < E_c$ in normal ferroelectrics are

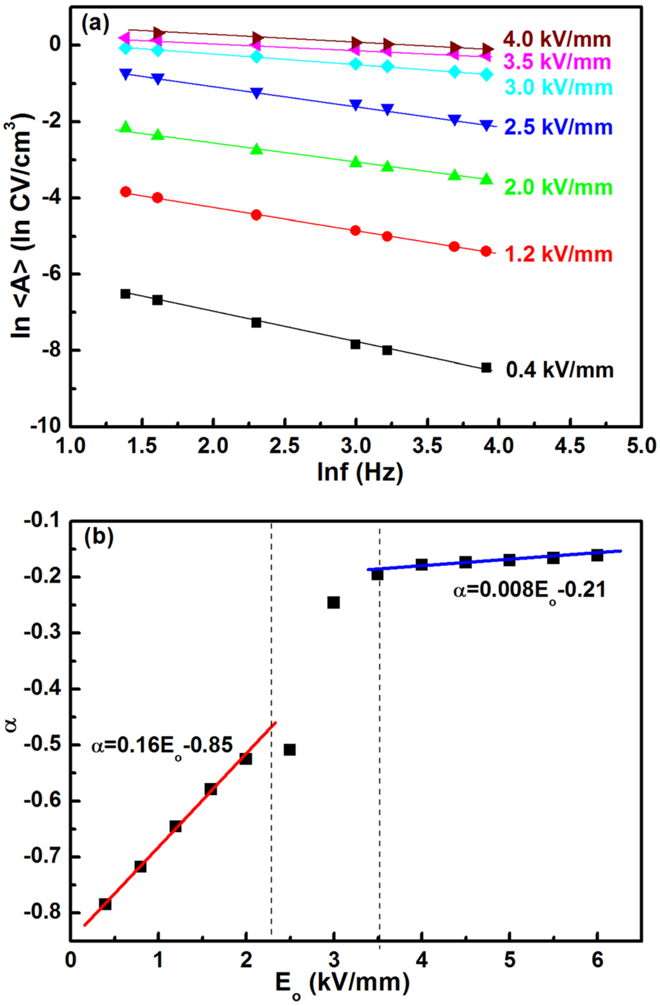

FIG. 5. (a) The curves of $\ln\langle A\rangle$ as a function of $\ln f$ in the case of different E_o values, and (b) the variation of the exponent α with an increase of E_o.

due to the fact that the main polarization mechanisms under the sub-coercive field conditions originate from the domain wall motion and the 180° domain switching. However, the non-180° domain switching, which was usually accompanied by mechanical strains, should occur under much higher electric fields than E_c. As a result, the β values in the case of $E_o < E_c$ and $E_o > 3.5$ kV/mm for CuO-NKN ceramics are likely to be related to the domain wall motion and 180° domain reversible switching, and the non-180° domain reversible switching, respectively. Meanwhile, the α value should be based on the same mechanism as the β value, considering their similar electric field dependence.

IV. CONCLUSIONS

The dynamic scaling behavior of 1 mol. % CuO doped NKN lead-free ferroelectric ceramics with double hysteresis-like loops has been well established by using a ferroelectric mode. It was indicated that the scaling behavior obeys the power law relationships as follows: $\langle A\rangle \propto f^{0.16E_0-0.85} E_0^{2.64}(E_o < E_c)$ and $\langle A\rangle \propto f^{0.008E_0-0.21} E_0^{0.96}(E_o > 3.5\,\text{kV/mm})$ in the first and third stages, respectively. In addition, the power-law relation does not fit in the second stage as the applied field E_o is between E_c and 3.5 kV/mm because the different numbers of domains can be activated by the driving fields in this stage. Owing to the restricted polarization orientation by the dipole defects, it was believed that the exponents in the power law relations are likely related to the domain wall motion ($E_o < 0.5E_c$) and 180° domain switching ($0.5E_c < E_o < E_c$) for the first stage and the non-180° domain switching for the third stage.

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