

Double hysteresis loop in Cu-doped $K_{0.5}Na_{0.5}NbO_3$ lead-free piezoelectric ceramics

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In this letter the authors report the observation of double hysteresis loops in Cu-doped $K_{0.5}Na_{0.5}NbO_3$ (KNN) ceramics. Unlike other ferroelectric titanates (e.g., $BaTiO_3$), aging is not required for the ceramic to exhibit the double-loop-like characteristics. Based on the symmetry-conforming principle of point defects, it is suggested that defect dipoles are formed by the acceptor dopant ions- Cu^{2+} and O^{2-} vacancies along the polarization direction after the diffuse tetragonal-orthorhombic phase transition of the ceramic. Because of the low migration rates of defects, the defect dipoles remain in the original orientation during the P - E loop measurement, providing a restoring force to reverse the switched polarization. The defect dipoles also provide “pinning” effects in the normal piezoelectric activities. As a result, the ceramic becomes “hardened,” exhibiting an extraordinarily high mechanical quality factor (2500), while the other piezoelectric properties remain reasonably good: electromechanical coupling coefficients $k_p=39\%$, $k_t=47\%$, and piezoelectric coefficient $d_{33}=82$ pC/N. © 2007 American Institute of Physics.
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Double polarization hysteresis (P - E) loop is a typical feature exhibited by antiferroelectric materials, such as $PbZrO_3$ and high-Zr-content $Pb(Zr,Ti)O_3$ ceramics.¹ It is caused by the antiferroelectric-ferroelectric phase transformation. However, it has been known that after aging, a number of ferroelectric titanates also exhibit a double P - E loop.²⁻⁶ It is generally believed that aging is a process involving gradual stabilization of ferroelectric domains by defects, and the double P - E loops are caused by the resulting constriction of the polarization.²⁻⁶ Various stabilization theories such as the grain-boundary theory, surface-layer model, domain-wall theory, and volume theory have been proposed.⁶ Recently, based on the symmetry-conforming principle of point defects, it has been shown that the domain stabilization is a volume effect.^{3-5,7} Although double P - E loops are frequently observed in ferroelectric titanates, there is little work reporting similar characteristics in other ferroelectrics. In this letter, we will report the observation of double P - E loops in $K_{0.5}Na_{0.5}NbO_3$ (KNN)-based ceramics and the resulting effects on the electromechanical properties of the ceramics.

KNN and KNN doped with 1 mol % Cu (KNN-Cu) ceramics were used for the present investigation. The ceramics were prepared by a conventional ceramic fabrication technique. The powders in the stoichiometric ratio of $K_{0.5}Na_{0.5}NbO_3$ were first mixed and calcined at 880 °C for 6 h. The calcined powders were then ball milled and mixed thoroughly with a polyvinyl alcohol (PVA) binder solution. For preparing the KNN-Cu ceramic, CuO was added to the calcined KNN powders before mixing with the PVA binder solution. The mixtures were then pressed into disk samples. After removal of the binder, the disk samples were sintered at 1090–1120 °C for 4 h in air.

The XRD patterns of the KNN and KNN-Cu ceramics are shown in Fig. 1. Both ceramics exhibit a single-phase perovskite structure with orthorhombic symmetry. A small

change in their lattice parameters is found; for KNN, $a=5.6398$ Å, $b=3.9444$ Å, and $c=5.6709$ Å, while $a=5.6355$ Å, $b=3.9411$ Å, and $c=5.6678$ Å for KNN-Cu. This suggests that Cu^{2+} has entered the lattices of KNN to form a normal ferroelectric. The temperature dependence of ϵ for the ceramics is shown in Fig. 2. Similar to KNN, the KNN-Cu ceramic undergoes the cubic-tetragonal phase transition at T_C (421 °C) and the tetragonal-orthorhombic phase transition at T_{O-T} (201 °C).

Figure 3 shows the polarization hysteresis (P - E) loops measured at different frequencies for the ceramics. The KNN ceramic exhibits a well-saturated and squarelike P - E loop at 100 Hz. The loop remains almost unchanged as the frequency decreases to 0.25 Hz. At 0.1 Hz, the loop becomes slightly “swelled.” This should be due to the increase in elec-

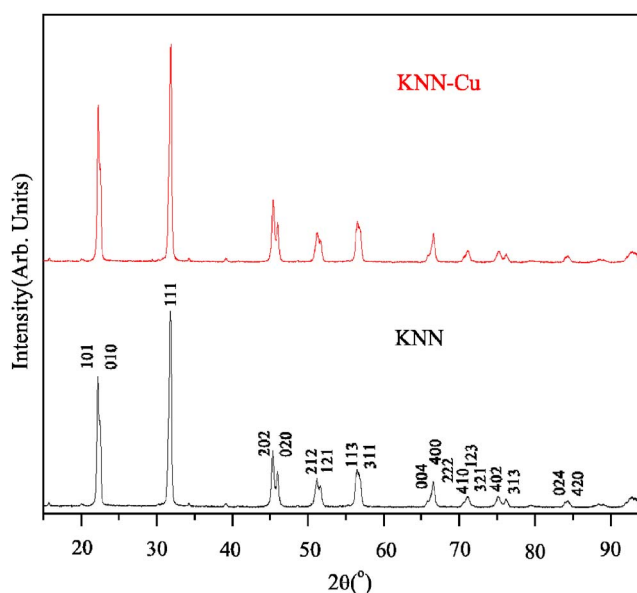


FIG. 1. (Color online) XRD patterns of the KNN and KNN-Cu ceramics.

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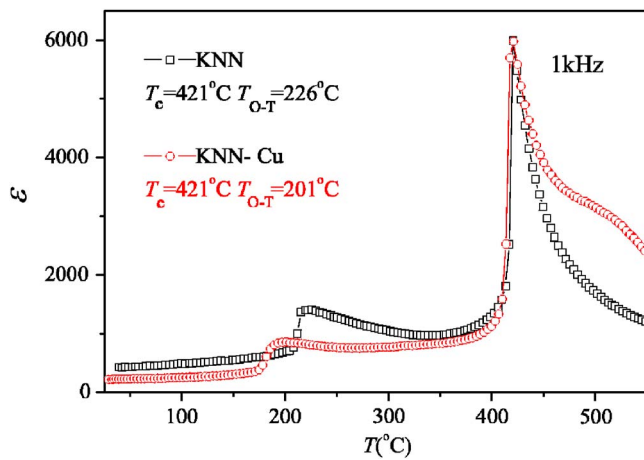


FIG. 2. (Color online) Temperature dependence of ϵ for the KNN and KNN-Cu ceramics at 1 kHz.

trical conduction at low frequencies. Unlike KNN, the KNN-Cu ceramic exhibits a double P - E loop at 100 Hz. The loop is constricted completely at $E=0$ kV/mm. However, as the frequency decreases, the loop “opens” gradually and becomes a normal single loop at 0.1 Hz. Indeed, electrical conduction at low frequencies would contribute to the opening and swelling of the P - E loops, in particular, at 0.1 Hz.

In order to provide additional evidence for the net polarization produced after the P - E loop measurements, the piezoelectric coefficient d_{33} of the ceramic has been measured. Prior to the measurement, the sample has been short-circuited for 24 h to remove the conducting charges. Because of the large remanent polarization (Fig. 3), the observed d_{33} of the KNN ceramic is large (~ 100 pC/N) and does not change with the frequency (for the P - E measurements). For the KNN-Cu ceramic, the observed d_{33} remains almost zero as the frequency decreases from 100 to 1 Hz. This is in agreement with the completely constricted P - E loop. As the frequency decreases from 1 to 0.1 Hz, d_{33} increases from 0 to ~ 30 pC/N. This clearly indicates that there is a net polarization after the low-frequency P - E measurement.

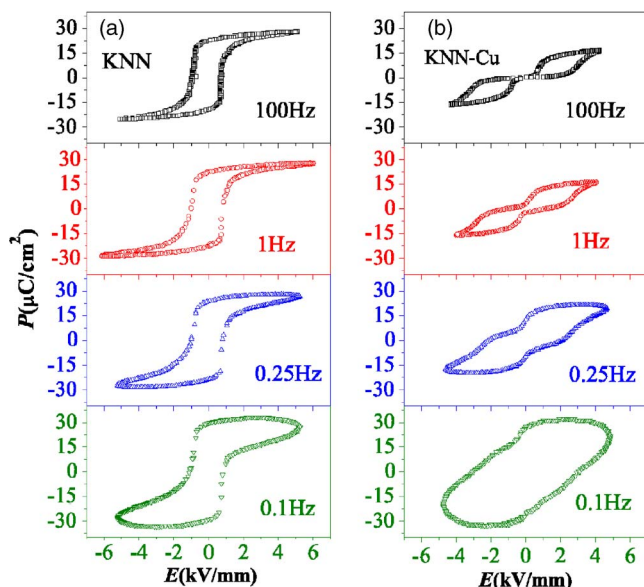


FIG. 3. (Color online) P - E loops of the KNN and KNN-Cu ceramics measured at different frequencies.

Although KNN and BaTiO₃ have different crystal symmetries (orthorhombic versus tetragonal), they have the same perovskite structures. It is hence expected that the symmetry-conforming principle of point defects³ proposed for BaTiO₃ is also applicable to KNN ceramics. After the doping of Cu²⁺ (for the B -site ions Nb⁵⁺), O²⁻ vacancies are formed (for satisfying the requirement of charge neutrality). In the ferroelectric phase, the B -site ion is not located in the center of the oxygen octahedral. As a result, the (statistical) distribution of O²⁻ vacancies around a dopant ion Cu²⁺ is not symmetric and affected greatly by the lattice symmetry. At equilibrium, the symmetry of short-range order distribution of defects (or defect symmetry) follows the crystal symmetry of KNN.³ The resulting noncentric distribution of defects (positively charged O²⁻ vacancies and negatively charged dopant ions Cu²⁺) forms defect dipoles along the spontaneous polarization direction. In the high-frequency P - E loop measurements (e.g., >1 Hz), the polarization is switched (abruptly) by the external field. Probably due to insufficient time for the ions/vacancies to migrate, the defect dipoles remain in the original orientation, thus providing a restoring force to reverse the switched polarization upon removal of the external field. However, in the low-frequency measurements (e.g., ≤ 0.1 Hz), the ions/vacancies may have enough time to migrate. As a result, the defect dipoles rotate with the polarization (probably at a lower rate), the restoring force decreases, and the reversal of the switched polarization cannot be completed, thus giving a small P_r .

Unlike BaTiO₃, the double P - E loop is observed in an “unaged” KNN-Cu ceramic, instead of an aged ceramic. This should be attributed to their different phase transitions. BaTiO₃ undergoes a cubic-tetragonal phase transition at ~ 128 °C. The transition is diffusionless and does not involve any exchange of ions.³⁻⁵ As a result, the distribution of the charged defects remains in the cubic symmetry even though the crystal has transformed to a tetragonal symmetry. It takes time (called aging) for the defect symmetry to correct into a polar tetragonal symmetry. The aging time for BaTiO₃ is usually long, e.g., 5 days at 80 °C or 28 days at room temperature.³⁻⁵ On the other hand, KNN-Cu undergoes a tetragonal-orthorhombic phase transition at 201 °C (Fig. 2). It is a diffuse phase transition,⁸ suggesting that ions/vacancies may migrate during the crystal transformation, and settles in a distribution with the same symmetry as the crystal after the transformation. Accordingly, aging is not required for the ceramic.

Figure 4 shows the P - E loops measured at 100 Hz and different temperatures for the KNN-Cu ceramic. The constricted P - E loop starts to open at 130 °C and becomes fully open at 190 °C. This suggests that the defect dipoles can respond to the external field at high temperatures (≥ 130 °C) and switch even along with the polarization at temperatures ≥ 190 °C. This also provides evidence that the defects can migrate during the diffuse phase transition (Fig. 2). It should be noted that at temperature ≥ 190 °C, the distribution of defects may be in a tetragonal symmetry.

To provide additional evidence for the defect migration, the KNN-Cu ceramic was annealed at 350 and 150 °C, respectively, for 2 h and then quenched to room temperature. It is expected that because of fast cooling, the defects can be frozen in the original distribution. The P - E loops measured at 100 Hz for the quenched sample are shown in Fig. 5. There is only a slight constriction in the P - E loop for the

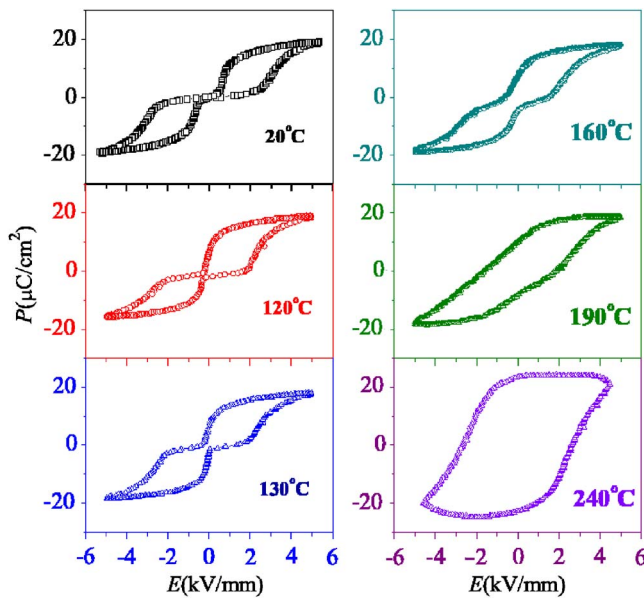


FIG. 4. (Color online) P - E loops for the KNN-Cu ceramic measured at 100 Hz and different temperatures.

sample quenched from 350 °C [Fig. 5(a)], suggesting that the restoring force for reversing the switched polarization is weak. As the defect symmetry is frozen in a cubic or tetragonal symmetry, there are few defect dipoles aligned with the orthorhombic crystal symmetry and hence the restoring force is weak. The P - E loop for the sample quenched from 150 °C is completely constricted at $E=0$ [Fig. 5(c)], suggesting that the defect symmetry is the same as the crystal symmetry. This also implies that the defect symmetry has transformed to the orthorhombic symmetry after the diffuse phase transi-

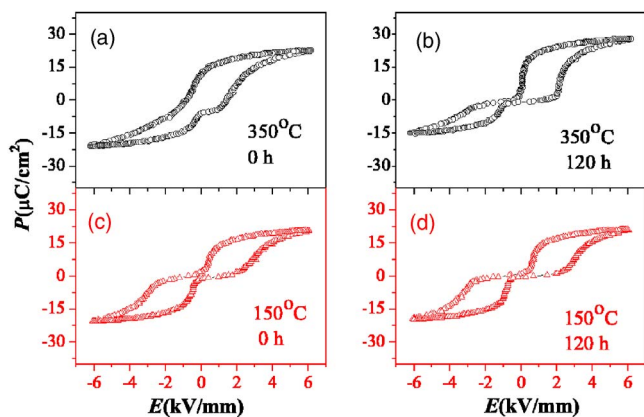


FIG. 5. (Color online) P - E loops measured at 100 Hz for the quenched ceramics and the aged ceramics.

tion of the ceramic at 201 °C. The quenched samples were then aged at room temperature for 5 days. As shown in Fig. 5, all the aged samples exhibit a constricted P - E loop. This clearly shows that after aging, the defect symmetry for the sample quenched from 350 °C has corrected to the orthorhombic symmetry. It should be noted that the aging time for KNN-Cu ceramics (5 days) is much shorter than that for BaTiO₃ (28 days). This may be the reason that the defect dipoles of the KNN-Cu ceramic can respond to an electric field at a relatively high frequency as compared to BaTiO₃ (1 Hz vs 0.1 Hz).⁴

It is also noted that after the poling with a dc field of 6 kV/mm at 200 °C for 30 min, the KNN-Cu ceramic exhibits an extraordinarily high mechanical quality factor Q_m (2500) and reasonably high electromechanical coupling coefficients k_p (39%), k_t (47%), and d_{33} (82 pC/N). During the dc poling at 200 °C, the defects migrate easily and form defect dipoles along the direction of the aligned polarization. Similar to the switching process, they provide restoring forces to the deformed polarization during the piezoelectric activities. As a result, the ceramic is “hardened,” giving a large Q_m .

In conclusion, the double P - E loop observed in the KNN-Cu ceramic is caused by a constriction of the polarization. Because of the symmetry-conforming property, the acceptor dopant ions Cu²⁺ and O²⁻ vacancies form defect dipoles along the polarization direction after the diffuse tetragonal-orthorhombic phase transition of the ceramic. As a result of the low defect migration rates, the defect dipoles remain in the original orientation and provide restoring forces to reverse the switched polarization. The defect dipoles also provide “pinning” effects in the normal piezoelectric activities, making the ceramic become hardened and exhibit an extraordinarily high mechanical quality factor (2500).

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