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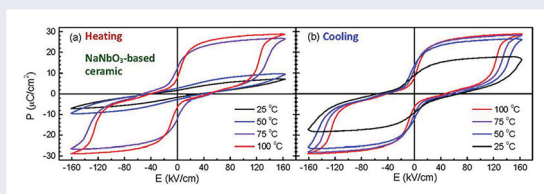
Double hysteresis loops at room temperature in NaNbO_3 -based lead-free antiferroelectric ceramics

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ABSTRACT

Polarization-field double hysteresis loops have hardly ever been observed at room temperature in polycrystalline NaNbO_3 , one of a few lead-free antiferroelectric compounds. In this Letter, it is shown that the exposure of a modified NaNbO_3 ceramic to bipolar electric fields of $\pm 160 \text{ kV/cm}$ at 100°C can preserve the double hysteresis loops at room temperature. These double hysteresis loops can still be observed after 125 days room temperature aging with some decay in maximum polarization. Frequency dependence analysis suggests that the double hysteresis loops originate from the antiferroelectric $\leftrightarrow$ ferroelectric phase transition, not the charged defects.



IMPACT STATEMENT

A novel electrical treatment of a NaNbO_3 -based polycrystalline ceramic to achieve double hysteresis loops at room temperature is reported for the first time.

ARTICLE HISTORY

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KEYWORDS

Double hysteresis loops;
 NaNbO_3 -based composition;
antiferroelectric ceramic

Perovskite PbZrO_3 is the prototypical antiferroelectric compound. At room temperature, the antiferroelectric phase in chemically modified PbZrO_3 ceramics can be readily transformed into a ferroelectric phase by electric fields, manifesting in the appearance of the polarization-field double hysteresis loops [1–5]. Polarization hysteresis loop is the most generally accepted method to characterize a ferroelectric material and has been considered as the fingerprint which contains information on the structures and properties of the material [6]. The existence of the double hysteresis loops in PbZrO_3 -based ceramics indicates a reversible phase transition, which forms the foundation for their device applications. In these lead-containing perovskite oxides, record-high energy storage densities ($> 50 \text{ J/cm}^3$) [7–9] and electrocaloric temperature changes ($> 45^\circ\text{C}$) [10] have been reported.

NaNbO_3 , known for its complex structures and phase transitions [11–15], is one of the very few lead-free antiferroelectric oxides. In contrast to PbZrO_3 -based

ceramics, double hysteresis loops are only observed in high quality NaNbO_3 single crystals with an electric field applied perpendicular to the orthorhombic c axis during initial cycles; in subsequent cycles square loops, characteristic of ferroelectrics, are seen [12,13]. Square polarization hysteresis loops are usually observed in polycrystalline NaNbO_3 ceramic samples at room temperature once large polarizations are developed [16,17]. This is explained by the argument that the NaNbO_3 polycrystalline ceramic is antiferroelectric at room temperature in the as-sintered state. Exposure to a strong electric field transforms the ceramic into a metastable ferroelectric phase, which remains after the applied field is removed and produces a large remanent polarization [11,18]. Recently, empirical rules on selecting chemical modifiers to destabilize the induced ferroelectric phase in NaNbO_3 have been put forward and tested [19–21]. In CaZrO_3 - and SrZrO_3 -modified ceramics [19,20], double hysteresis loops were observed at temperatures of 120°C

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and above. In CaHfO_3 -modified NaNbO_3 ceramics, the polarization-field plot at room temperature looks very similar to double hysteresis loops [21].

In this Letter, the $0.96\text{NaNbO}_3\text{--}0.04\text{CaZrO}_3$ composition reported in Ref. [19] is modified with minor additions of Li_2O and CuO . Double hysteresis loops are observed at room temperature after an electrical treatment of the ceramic.

Ceramic pellets with the composition of $(\text{Na}_{0.95}\text{Li}_{0.01}\text{Ca}_{0.04})(\text{Nb}_{0.96}\text{Zr}_{0.04})\text{O}_3$ were prepared with the solid state reaction method. In addition, 1 wt.% CuO was added as a sintering aid [22]. Starting materials include powders of Na_2CO_3 , CaCO_3 , Li_2CO_3 , Nb_2O_5 , ZrO_2 and CuO . The Na_2CO_3 and Li_2CO_3 powders were baked at 200°C for 10 h right before use. Powders in amounts according to the chemical formula were mixed and milled in ethanol for 7 h. The slurry was dried, pressed into a cylinder form, and then calcined at 1050°C for 3 h. After another 7-hour vibratory milling, sintering was carried out at 1280°C for 3 h. The phase purity and crystal structure of the sintered pellets were analyzed with X-ray diffraction using $\text{Cu K}\alpha$ radiation. The polarization hysteresis loops were measured using a standardized ferroelectric test system on polished pellets electroded with sputtered silver films. During room temperature aging, the two electrodes were short-circuited.

X-ray diffraction analysis of the sintered ceramic is displayed in Figure 1. It is clear that the ceramic is phase pure with a distorted perovskite structure. The inset shows the $\{21\frac{3}{4}\}$ superlattice peak [18], which is characteristic of the antiferroelectric phase in the base compound NaNbO_3 [15]. The other two low-intensity peaks at $\sim 36.8^\circ$ and $\sim 38.4^\circ$ can be indexed as $\{11\frac{3}{4}\}$ and $\{\frac{1}{2}\frac{1}{2}\frac{3}{2}\}$, respectively. The presence of $\{11\frac{3}{4}\}$ peak is in support of an antiferroelectric structure. Therefore, the as-sintered ceramic is antiferroelectric at room temperature.

In addition to serving as the sintering aid, CuO is also known to suppress the electrical conductivity of NaNbO_3 -based ceramics [22–24], allowing the application of strong electric fields for polarization measurements. The sintered ceramic was first tested at the peak field of 140 kV/cm at 25°C , then at temperatures in the sequence of 50, 75, 100, and 125°C . It is found that the ceramic remains antiferroelectric under the peak field up to 75°C with an almost linear dielectric response of minimum electric polarization. As shown in Figure 2(a), the hysteresis loop starts to open up at 100°C , suggesting an antiferroelectric to ferroelectric phase transition. At 125°C fully developed double hysteresis loops are observed with a maximum polarization of $20.5\text{ }\mu\text{C/cm}^2$ at the peak field of 140 kV/cm . Compared with the previously reported base composition

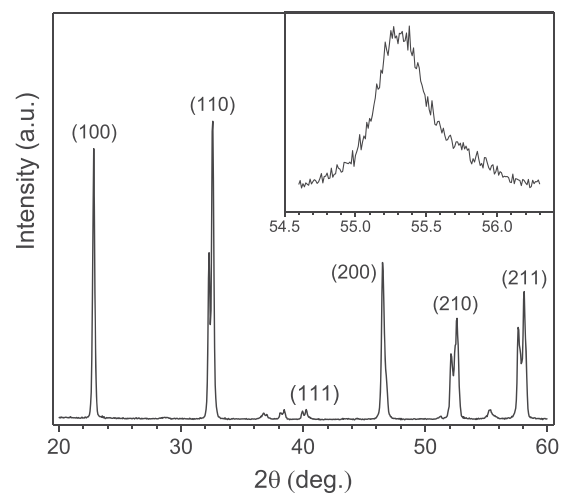


Figure 1. X-ray diffraction pattern of as the as-sintered $(\text{Na}_{0.95}\text{Li}_{0.01}\text{Ca}_{0.04})(\text{Nb}_{0.96}\text{Zr}_{0.04})\text{O}_3$ ceramic. The spectrum is indexed based on a cubic perovskite unit cell. The inset shows the close view of the characteristic antiferroelectric $\{21\frac{3}{4}\}$ superlattice peak.

$(\text{Na}_{0.96}\text{Ca}_{0.04})(\text{Nb}_{0.96}\text{Zr}_{0.04})\text{O}_3$ [19], 1 at.% replacement of Na^+ with Li^+ appears to facilitate the antiferroelectric to ferroelectric transition, which is consistent with the role Li^+ plays in $(\text{Na}_{1-x}\text{Li}_x)\text{NbO}_3$ solid solutions [25,26]. After testing at 125°C , the ceramic pellet was gradually cooled down to room temperature (25°C) and the polarization hysteresis loops recorded during cooling are displayed in Figure 2(b). It is noted that after exposure to bipolar fields of $\pm 140\text{ kV/cm}$ at 125°C , the ceramic shows a much higher polarization during the cooling sequence than that at the same temperature during the heating sequence. Double hysteresis loops are almost retained at 50°C and some distortions on the loop, reminiscent of high temperature phase transitions, can still be seen even at 25°C .

The results shown in Figure 2(a) and (b) suggest that the ceramic exposed to fields higher than 140 kV/cm at elevated temperatures may potentially retain the double hysteresis loops after it is cooled back to room temperature. This is indeed the case, as shown in Figure 2(c) and (d) where the same pellet was exposed to $\pm 160\text{ kV/cm}$. During the heating sequence, well-developed double hysteresis loops are observed at 75 and 100°C . A maximum polarization of $28.9\text{ }\mu\text{C/cm}^2$ is recorded at 100°C . During the cooling sequence, the double hysteresis loops are almost completely preserved at 50°C , with a maximum polarization of $26.5\text{ }\mu\text{C/cm}^2$ at the peak field. It is quite striking that double hysteresis loops are still seen at 25°C with a maximum polarization of $18.1\text{ }\mu\text{C/cm}^2$. Therefore, an electrical treatment of the NaNbO_3 -based antiferroelectric ceramic is shown to stabilize the double hysteresis loops at room temperature.

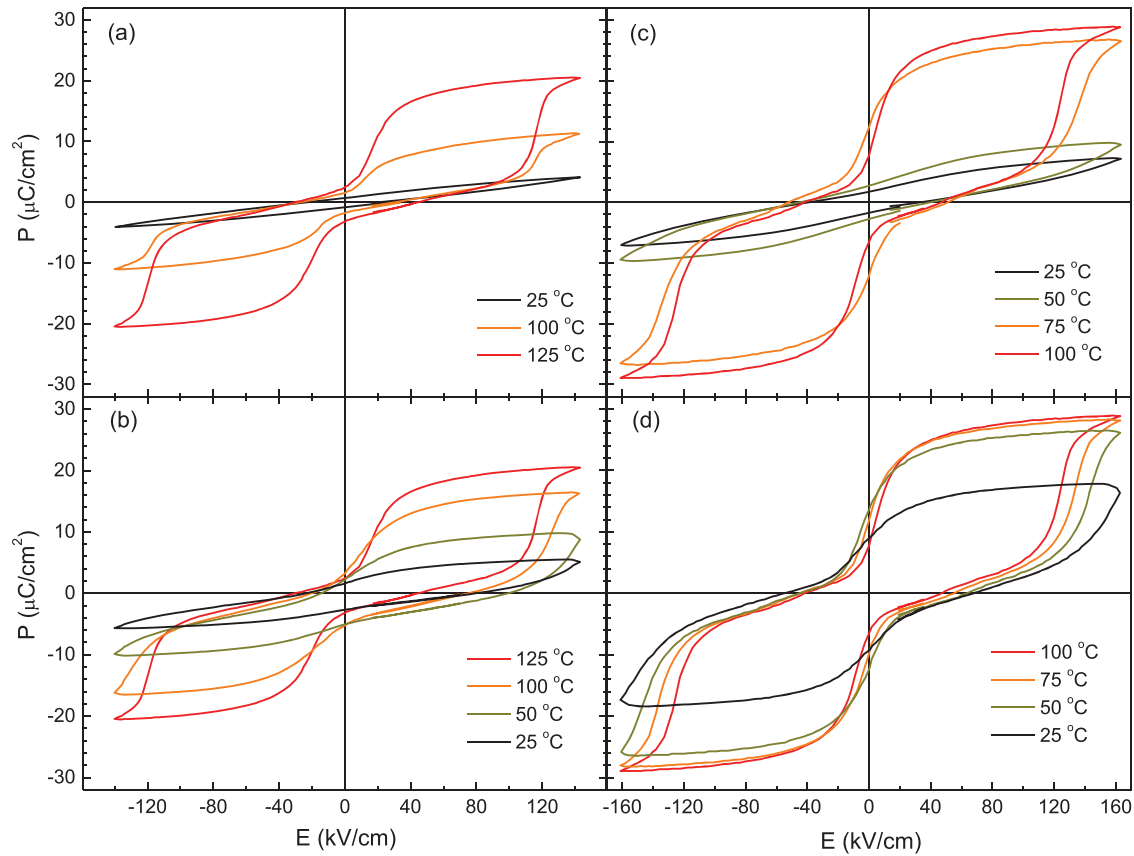


Figure 2. The polarization hysteresis loops assessed at 4 Hz under (a), (b) ± 140 kV/cm and (c), (d) ± 160 kV/cm. (a) Hysteresis loops recorded during the heating sequence at 25, 100, and 125 °C. The loops at 50 and 75 °C (not shown) are almost identical to that at 25 °C. (b) Hysteresis loops recorded during the cooling sequence. (c) Hysteresis loops recorded under ± 160 kV/cm during the heating sequence. (d) Hysteresis loops recorded during the cooling sequence.

To clarify if the preservation of the double hysteresis loops at room temperature is a transient effect, this same pellet was kept at room temperature with two electrodes short-circuited for an aging process. The polarization hysteresis loops were recorded for a series of aging times. The results, shown in Figure 3, indicate that the double hysteresis loops at room temperature are still observed after 36 days of aging. However, the maximum polarization decreases from the initial value of $18.1 \mu\text{C}/\text{cm}^2$ to $9.7 \mu\text{C}/\text{cm}^2$ during this period. It should be noted that the results shown in Figures 2 and 3 are reproducible in other pellets of the ceramic. The longest aging time conducted for this ceramic is 125 days and the double hysteresis loops are still observed in that pellet.

It was previously reported that minor addition of CuO to $\text{K}_x\text{Na}_{1-x}\text{NbO}_3$ ceramics can lead to double hysteresis loops at room temperature without antiferroelectric-ferroelectric phase transitions [23,24]. The interpretation is that Cu^{2+} occupies Nb^{5+} lattice and symmetry-conforming defect dipoles are then formed with oxygen vacancies [23,27]. Such defect dipoles provide a restoring force for domain polarization back switching during

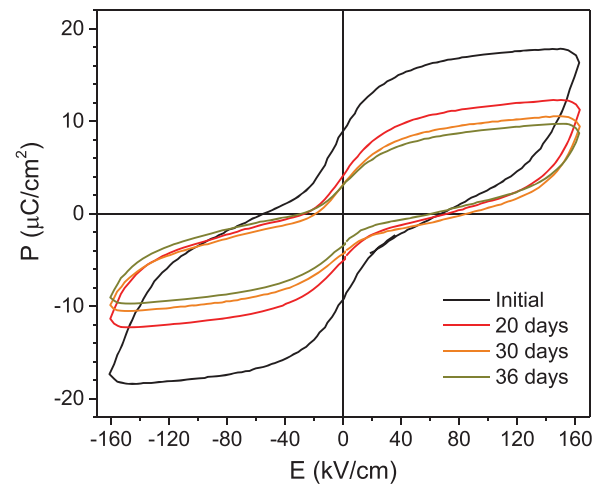


Figure 3. The double hysteresis loops recorded at room temperature and 4 Hz from the same pellet as Figure 2 after room temperature aging.

electric field unloading, producing the double hysteresis loops. The important characteristics of defect dipole originated double hysteresis loops are their strong frequency

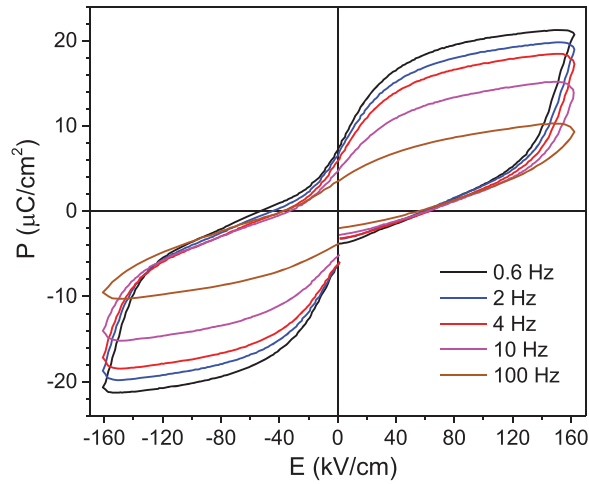


Figure 4. The double hysteresis loops recorded at room temperature and a series of frequencies in a pellet that had been exposed to ± 160 kV/cm at 100°C .

and temperature dependence. Double hysteresis loops are prominent at high frequencies (100 Hz) and low temperatures (20°C), but become a single hysteresis loop at low frequencies (0.1 Hz) and high temperatures ($> 160^\circ\text{C}$) [23]. In order to check if the double hysteresis loops observed in our ceramic have the origin from defect dipoles, the frequency effect is evaluated. As shown in Figure 4, a ceramic pellet was exposed to ± 160 kV/cm at 100°C , then the polarization loops were recorded at a series of frequencies after it was cooled to 25°C . It is observed that the double hysteresis loops are even more prominent at lower frequencies, which is the opposite of those originating from defect dipoles. Furthermore, another measurement at 170°C under ± 160 kV/cm still reveals fully developed double hysteresis loops. Therefore, the double hysteresis loops observed in our ceramic cannot be a direct result of the presence of defect dipoles, they are from the electric field-induced antiferroelectric-ferroelectric phase transitions. Defect dipoles can only play an assisting role to producing the double hysteresis loops.

Figure 2 shows that the double hysteresis loops can be stabilized at room temperature in our NaNbO_3 -based ceramic after an electrical treatment at the peak field of 160 kV/cm, but not at 140 kV/cm. We then maintained the field level of 140 kV/cm and treated the ceramic differently to test if the double hysteresis loops can be realized at room temperature. The results are displayed in Figure 5. The first condition tested is exposing the ceramic to ± 140 kV/cm at even higher temperatures (up to 170°C). After the ceramic is cooled down to 25°C , a linear dielectric response that is almost identical to the virgin state is observed, as shown in Figure 5(a). The second condition tested is applying 60 cycles of ± 140 kV/cm

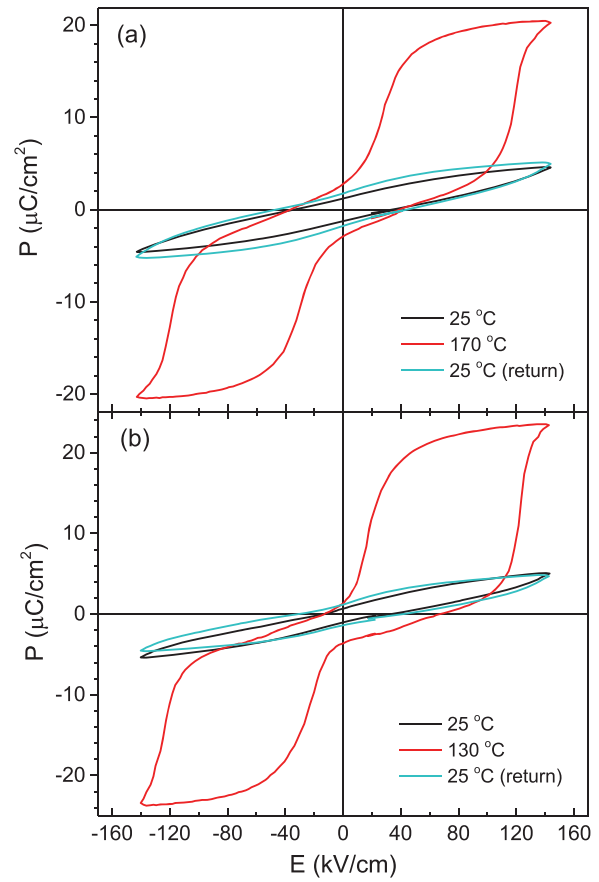


Figure 5. Different electrical treatments at 140 kV/cm cannot achieve double hysteresis loops at room temperature. (a) ± 140 kV/cm AC field exposure at 170°C . '25°C (return)' indicates that the curve is measured after the specimen is cooled down to 25°C from 170°C . (b) ± 140 kV/cm AC field exposure at 130°C for 60 cycles. '25°C (return)' indicates that the curve is measured after the specimen is cooled down to 25°C from 130°C .

bipolar fields at 130°C . Again, such a treatment is not able to retain the double hysteresis loops at room temperature [Figure 5(b)].

The experimental results reported here indicate that the ground state of the ceramic is antiferroelectric. The antiferroelectric order is so strong at room temperature that the critical field for a transition to a ferroelectric phase is in the range of breakdown strength. Without any heating or cooling, the ceramic started to develop double hysteresis loops at a peak field of 180 kV/cm. However, when the peak field is reduced to 160 kV/cm, no double hysteresis loops are observed. The purpose of adding Li^+ to the composition is to strengthen the ferroelectric order and to decrease the critical field. It is shown previously that the $(\text{Na}_{1-x}\text{Li}_x)\text{NbO}_3$ solid solution is an antiferroelectric up to $x = 0.02$, a mixture of antiferroelectric and ferroelectric for $0.02 \leq x \leq 0.03$, and a ferroelectric for $x > 0.03$ [26]. The addition of CuO seems to serve two purposes, as a sintering aid it facilitates densification

during sintering, and as an acceptor dopant it leads to the formation of defect dipoles with oxygen vacancies. A direct benefit of CuO modification is that strong electric fields can be repeatedly applied to these ceramic pellets. The electrical treatment established in this work seems to finely adjust the subtle balance between the antiferroelectric and ferroelectric order in the ceramic and to realize reversible antiferroelectric-ferroelectric phase transitions at room temperature for a very long time. Exposure of the ceramic to AC fields of ± 160 kV/cm at 100°C and above apparently shifts the balance toward the ferroelectric order and produces the signature double hysteresis loops at room temperature. The lack of function at 140 kV/cm seems to suggest that the effect is related to defect dipoles. A field of 160 kV/cm may rearrange a sufficient number of defect dipoles in the ceramic at temperatures above 100°C. These rearranged defect dipoles either serve as the seed of the ferroelectric phase, or facilitate the nucleation of the ferroelectric phase during the electric field-induced antiferroelectric to ferroelectric phase transition at room temperature. The inactive diffusional events at room temperature do not disrupt these rearranged defect dipoles, making the double hysteresis loops persist for a long period of time. In such an assisting role, defect dipoles indirectly contribute to the presence of double hysteresis loops in our ceramic.

In summary, an electrical treatment for a NaNbO_3 -based antiferroelectric ceramic is established to produce double hysteresis loops at room temperature. After exposure of the ceramic to a critical field at temperatures of 100°C and above, the defect dipoles are believed to be rearranged and the ferroelectric order is strengthened. As a result, a reversible electric field-induced antiferroelectric-ferroelectric phase transition can be achieved at room temperature. The electrical treatment can be applied to other lead-free antiferroelectric compositions to fine tune the stability of different phases.

Disclosure statement

No potential conflict of interest was reported by the authors.

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References

- [1] Pan W, Zhang Q, Bhalla A, et al. Field-forced antiferroelectric-to-ferroelectric switching in modified lead zirconate titanate stannate ceramics. *J Am Ceram Soc.* **1989**;72:571–578.
- [2] Yang P, Payne DA. Thermal stability of field-forced and field-assisted antiferroelectric-ferroelectric phase transitions in $\text{Pb}(\text{Zr},\text{Sn},\text{Ti})\text{O}_3$. *J Appl Phys.* **1992**;71:1361–1367.
- [3] Viehland D, Forst D, Xu Z, et al. Incommensurately modulated polar structures in antiferroelectric Sn-modified lead zirconate titanate: the modulated structure and its influences on electrically induced polarizations and strains. *J Am Ceram Soc.* **1995**;78:2101–2112.
- [4] Frederick J, Tan X, Jo W. Strains and polarization during antiferroelectric-ferroelectric phase switching in $\text{Pb}_{0.99}\text{Nb}_{0.02}[(\text{Zr}_{0.57}\text{Sn}_{0.43})_{1-y}\text{Ti}_y]_{0.98}\text{O}_3$ ceramics. *J Am Ceram Soc.* **2011**;94:1149–1155.
- [5] Tan X, Ma C, Frederick J, et al. The antiferroelectric $\leftrightarrow$ ferroelectric phase transition in lead-containing and lead-free perovskite ceramics. *J Am Ceram Soc.* **2011**;94:4091–4107.
- [6] Jin L, Li F, Zhang SJ. Decoding the fingerprint of ferroelectric loops: comprehension of the material properties and structures. *J Am Ceram Soc.* **2014**;97:1–27.
- [7] Hao X, Wang Y, Zhang L, et al. Composition-dependent dielectric and energy-storage properties of $(\text{Pb},\text{La})(\text{Zr},\text{Sn},\text{Ti})\text{O}_3$ antiferroelectric thick films. *Appl Phys Lett.* **2013**;102:163903.
- [8] Hu Z, Ma B, Koritala RE, et al. Temperature-dependent energy storage properties of antiferroelectric $\text{Pb}_{0.96}\text{La}_{0.04}\text{Zr}_{0.98}\text{Ti}_{0.02}\text{O}_3$ thin films. *Appl Phys Lett.* **2014**;104:263902.
- [9] Ma B, Hu Z, Koritala RE, et al. PLZT film capacitors for power electronics and energy storage applications. *J Mater Sci Mater Electron.* **2015**;26:9279–9287.
- [10] Peng B, Fan H, Zhang Q. A giant electrocaloric effect in nanoscale antiferroelectric and ferroelectric phases coexisting in a relaxor $\text{Pb}_{0.8}\text{Ba}_{0.2}\text{ZrO}_3$ thin film at room temperature. *Adv Funct Mater.* **2013**;23:2987–2992.
- [11] Shirane G, Newnham R, Pepinsky R. Dielectric properties and phase transitions of NaNbO_3 and $(\text{Na},\text{K})\text{NbO}_3$. *Phys Rev.* **1954**;96:581–588.
- [12] Cross LE, Nicholson BJ. The optical and electrical properties of single crystals of sodium niobate. *Phil Mag.* **1955**;46:453–466.
- [13] Cross LE. Electric double hysteresis in $(\text{K}_x\text{Na}_{1-x})\text{NbO}_3$ single crystals. *Nature.* **1958**;181:178–179.
- [14] Lefkowitz I, Lukaszewicz K, Megaw HD. High temperature phases of sodium niobate and nature of transitions in pseudosymmetric structures. *Acta Cryst.* **1966**;20:670–683.
- [15] Mishra SK, Choudhury N, Chaplot SL, et al. Competing antiferroelectric and ferroelectric interactions in NaNbO_3 : neutron diffraction and theoretical studies. *Phys Rev B.* **2007**;76:024110.
- [16] Fu D, Taniguchi H, Taniyama T, et al. Ferroelectricity and electromechanical coupling in $(1-x)\text{AgNbO}_3$ - $x\text{NaNbO}_3$ solid solutions. *Appl Phys Lett.* **2011**;99:012904.
- [17] Chao L, Hou Y, Zheng M, et al. Macroscopic ferroelectricity and piezoelectricity in nanostructured NaNbO_3 ceramics. *Appl Phys Lett.* **2017**;110:122901.

- [18] Xu YH, Hong W, Feng YJ, et al. Antiferroelectricity induced by electric field in NaNbO_3 -based lead-free ceramics. *Appl Phys Lett*. **2014**;104:052903.
- [19] Shimizu H, Guo H, Reyes-Lillo SE, et al. Lead-free antiferroelectric: $x\text{CaZrO}_3$ -($1-x$) NaNbO_3 system ($0 \leq x \leq 0.10$). *Dalton Trans*. **2015**;44:10763–10772.
- [20] Guo H, Shimizu H, Mizuno Y, et al. Strategy for stabilization of the antiferroelectric phase (Pbma) over the metastable ferroelectric phase ($\text{P2}_1\text{ma}$) to establish double loop hysteresis in lead-free ($1-x$) NaNbO_3 - $x\text{SrZrO}_3$ solid solution. *J Appl Phys*. **2015**;117:214103.
- [21] Gao L, Guo H, Zhang S, et al. A perovskite lead-free antiferroelectric $x\text{CaHfO}_3$ -($1-x$) NaNbO_3 with induced double hysteresis loops at room temperature. *J Appl Phys*. **2016**;120:204102.
- [22] Chen K, Zhou J, Zhang F, et al. Screening sintering aids for $(\text{K}_{0.5}\text{Na}_{0.5})\text{NbO}_3$ ceramics. *J Am Ceram Soc*. **2015**;98:1698–1701.
- [23] Lin D, Kwok KW, Chan HLW. Double hysteresis loop in Cu-doped $\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$ lead-free piezoelectric ceramics. *Appl Phys Lett*. **2007**;90:232903.
- [24] Lee JH, Kim DH, Seo IT, et al. Large strain in CuO-added $\text{Na}_{0.2}\text{K}_{0.8}\text{NbO}_3$ ceramic for use in piezoelectric multilayer actuators. *J Am Ceram Soc*. **2016**;99:938–945.
- [25] Jimenez R, Sanjuan ML, Jimenez B. Stabilization of the ferroelectric phase and relaxor-like behavior in low Li content sodium niobates. *J Phys Condens Matter*. **2004**;16:7493–7510.
- [26] Yuzyuk YI, Gagarina E, Simon P, et al. Synchrotron x-ray diffraction and Raman scattering investigations of $(\text{Li}_x\text{Na}_{1-x})\text{NbO}_3$ solid solutions: evidence of the rhombohedral phase. *Phys Rev B*. **2004**;69:144105.
- [27] Zhang LX, Ren XB. Aging behavior in single-domain Mn-doped BaTiO_3 crystals: implication for a unified microscopic explanation of ferroelectric aging. *Phys Rev B*. **2006**;73:094121.