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Dielectric behaviors of antiferroelectric–ferroelectric transition under electric field

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Abstract

As a nonlinear capacitor, the dielectric behaviors of antiferroelectric–ferroelectric transition under strong electric fields were studied. $(Pb_{0.94}La_{0.04})(Zr_{0.55}Sn_{0.30}Ti_{0.15})O_3$ composition was chosen, which was of a slim double-hysteresis loops at suited electric field. The differential dielectric constant and small signal dielectric constant were measured. Experimental results showed that both the differential and small signal dielectric constants appeared maximal values around the switch electric fields that induced antiferroelectric–ferroelectric transitions. The extremes of differential dielectric constant were always hysteretic electrically to the extremes of small signal dielectric constant whether electric field increasing or decreasing. The phenomena were discussed in light of our current understanding.

Keywords: Dielectric behaviors; Antiferroelectric–ferroelectric transition; Electric field; Lead zirconate stannate titanate ceramics

1. Introduction

For an antiferroelectrics of double-hysteresis loop, the antiferroelectric phase and ferroelectric phase can be switched each other under an alternate electric field. In the transition large electric energy is stored and released. As a nonlinear dielectric material the antiferroelectrics with double-hysteresis loop has been used for charge and discharge capacitor, actuator and microelectromechanical system [1–3].

The relation of dielectric behaviors and electric field is an essential property for nonlinear dielectric material. Dielectric characteristics of ferroelectrics under electric field have been widely studied [4,5]. However, the dielectric characteristics of antiferroelectrics, especially the small signal dielectric behavior under bias electric field has been still known less by now. Besides electric domain orientation there is crystal structure change in the antiferroelectric–ferroelectric transition induced with electric field. These would cause antiferroelectric material some singular behaviors and project a light on understanding the mechanism of antiferroelectric–ferroelectric transition.

In order to study the dielectric behaviors of antiferroelectric–ferroelectric transition, an antiferroelectric lead zirconate stannate titanate ceramics of a slim double-hysteresis loop was selected. The differential and small signal dielectric constants under strong electric field were measured. Phenomena were discussed based on the domain evolvement that happened at antiferroelectric–ferroelectric transitions.

2. Experimental procedure

The composition used in this study is $(Pb_{0.94}La_{0.04})(Zr_{0.55}Sn_{0.30}Ti_{0.15})O_3$, which presents a slim double-hystereresis loop at a suited electric field (Fig. 1). Polycrystalline ceramics were made by normal solid-state reaction. Oxide raw powders, PbO, ZrO_2, SnO_2, TiO_2, La_2O_3, were reagent grade and the chemical purities not less than 99.0%. Weighed raw powders were ground with planet-type ball grinder and calcined at 850 °C for 2.0 h. The dry-pressed pellets were sintered at 1260 °C for 1.5 h in a lead-rich atmosphere to minimize lead volatilization. Fired ceramics were annealed at 860 °C for 6 h in air. Grain sizes of polycrystalline ceramics were about 4–6 μm. Samples were disk sliced off from

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cylinder ceramics, after polished and leaned silver electrodes were printed at the center of sample to prevent edge electric arcing. Test sample was 10 mm in diameter and 0.32 mm in thickness. The diameter of silver electrode was 6.00 mm.

The electric field dependence of polarization was measured with a computer-controlled modified Sawyer-Tower circuit. A Trek 609A high voltage amplifier supplied a sine voltage of 0.4 Hz. Small signal capacitance was measured using a LCR meter (TH2816, Tonghui Electronic Instrument Inc.). dc bias voltage was supplied by a PS350 voltage generator (Stanford Research System Inc.), swept from zero to 1.8 kV and then reversed to zero. Step of dc bias voltage was 10 V at a time. After dc bias voltage stayed 10 s the capacitance of sample was measured. A computer program controlled the measure processing. The dependences of dielectric constants with temperature and frequency were measured using a HP4274A multifrequency meter. The differential and small signal dielectric constants were respectively calculated from following formula:

Differential dielectric constant

$$\varepsilon_{\mathrm{d}} = \frac{1}{\varepsilon_0}\frac{\mathrm{d}P}{\mathrm{d}E}, \tag{1}$$

and small signal dielectric constant

$$\varepsilon_{\mathrm{r}} = \frac{C}{\varepsilon_0}\frac{l}{S} \tag{2}$$

where ε_0 is dielectric constant in vacuum, C is capacitance, l and S are the thickness and area of sample, respectively.

3. Results and discussion

The curves of polarization with electric field and small signal dielectric constants ε_{r} with temperature variations for $(Pb_{0.94}La_{0.04})(Zr_{0.55}Sn_{0.30}Ti_{0.15})O_3$ composition were shown in Fig. 1. The original phase of $(Pb_{0.94}La_{0.04})(Zr_{0.55}Sn_{0.30}Ti_{0.15})O_3$ was an antiferroelectrics. When electric field increased larger than 40 kV/cm the antiferroelectric phase was transformed into a ferroelectric phase and was polarized. Whereas electric field reduced less than 30 kV/cm the metastable ferroelectric phase returned to antiferroeletric phase and polarization disappeared. The dielectric peak in thermal dielectric curve was related to a transition from antiferroelectric phase to paraelectric phase induced with temperature (Fig. 2). From the temperature dependence of dielectric constants it could be seen that the crystal structure of antiferroelectric phase was relaxed which resulted dielectric constant dispersed with frequency.

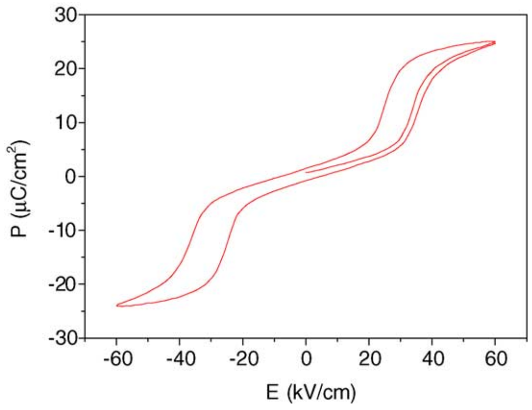

Fig. 1. The electric field dependence of polarization for $(Pb_{0.94}La_{0.04})(Zr_{0.55}Sn_{0.30}Ti_{0.15})O_3$.

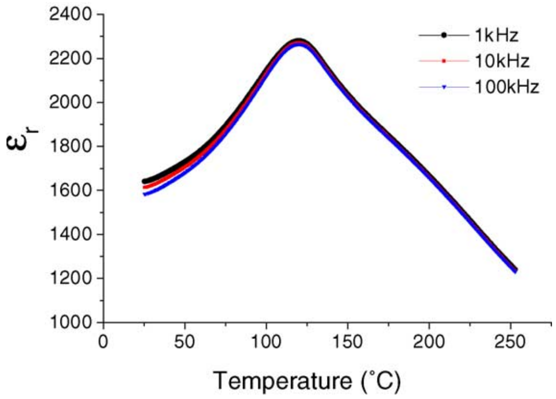

Fig. 2. The temperature dependence of small signal dielectric constant ε_{r} for $(Pb_{0.94}La_{0.04})(Zr_{0.55}Sn_{0.30}Ti_{0.15})O_3$.

According to formula (1) the differential dielectric constant ε_{d} was obtained from the relation of polarization versus electric field, which was shown in Fig. 3. It could be seen that at the inflexions of curve ε_{d} arrived maximums. If define the electric fields that corresponding to the extremes of differential dielectric constant as the switch electric fields, then the forward switch field E_{F} was 34 kV/cm and backward switch field E_{B} was 25 kV/cm, respectively. Here, E_{F} was the least electric field forcing original antiferroelectric phase into ferroelectric phase and E_{B} was the least electric field preventing metastable ferroelectric phase into antiferroelectric phase.

The small signal dielectric constant ε_{r} under dc bias field was shown in Fig. 4. The antiferroelectric phase ε_{r} value at zero electric field was larger than polarized ferroelectric phase ε_{r} value at high electric field. Similarly, ε_{r} also formed maximums around the switch electric fields. Defining $E_{\mathrm{F}}^{\mathrm{S}}$ as the electric field corresponding to the maximum of ε_{r} in increasing bias field and $E_{\mathrm{B}}^{\mathrm{S}}$ as the electric field corresponding the maximum of ε_{r} in reducing bias field, then the $E_{\mathrm{F}}^{\mathrm{S}}$ and $E_{\mathrm{B}}^{\mathrm{S}}$ respectively equaled 32 and 26 kV/cm. Extreme values of ε_{d} were always hysteretic electrically to the extreme values of ε_{r}, whether increasing or decreasing electric field.

It has been known that the small signal dielectric constant describes the reversible part of polarization. Reversible polarization includes the electron and ion polarizations and also the electric domain wall flicker, which can recover after excitation signal being removed [4,5]. Besides the reversible polarization the differential dielectric constant includes irre-

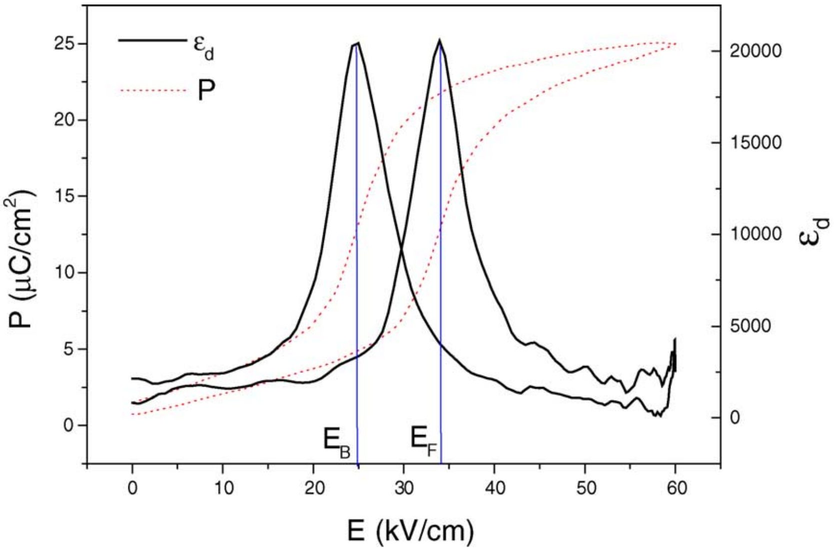

Fig. 3. The differential dielectric constant ε_d under electric field.

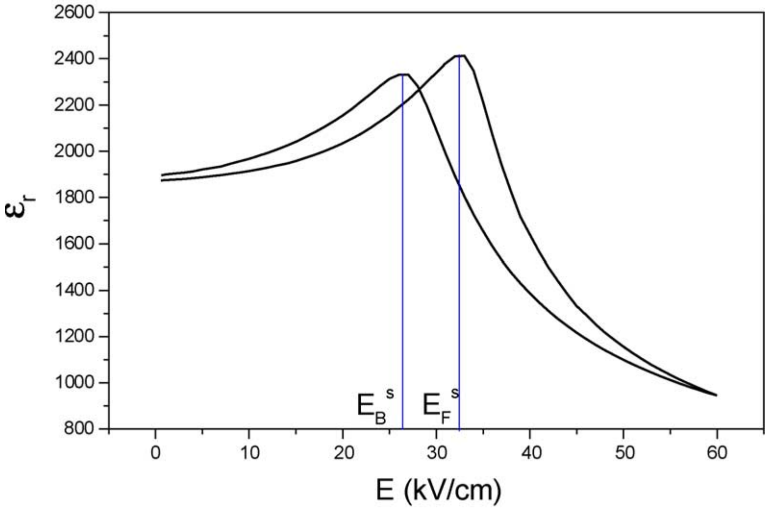

Fig. 4. The small signal dielectric constant ε_r under dc bias field.

versible contribution, such as domain's motion and orientation under electric field.

It is reasonable that there are some polar micro-regions (or micro-domain) in antiferroelectric body [6–8]. The polar micro-regions are sensitive to weak electric field and contributed to the small signal dielectric constant. In electric field increasing a mass of micro-domains are yielded to increase the small signal dielectric constant. During antiferroelectric phase is transformed to ferroelectric phase numerous micro-domains are aggregated to incorporate into the macro-domain. In this processing the small signal dielectric constant begins to decrease because of reversible contribution reducing, but the differential dielectric constant continually increases because of spontaneous polarization increasing. As a result, the small signal dielectric constant first arrives to maximum then is the differential dielectric constant with increasing bias electric field. In the case of polarized ferroelectric phase is reverted to antiferroelectric phase the macro-domains are first divided into numerous micro-domains to release internal stress. Therefore, the small signal dielectric constant increases and first arrives to maximum in electric field reducing.

4. Conclusions

The differential dielectric constant and small signal dielectric constant had an apparent change at the antiferroelectric–ferroelectric transition induced with electric field. Both the differential and small signal dielectric constants formed maximum around the switch electric fields. However, the extremes of differential dielectric constant were always hysteretic electrically to the extremes of small signal dielectric constant. The small signal dielectric constant is contributed from the reversible polarization and the differential dielectric constant includes reversible and irreversible contribution. Since the reversible polarization is more sensitive than the irreversible polarization, the small signal dielectric constant is prior to apperceive the microstructure changes occurred at antiferroelectric–ferroelectric transition and arrives maximum.

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