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Effect of La modifier on the electric hysteresis of lead zirconate stannate titanate compounds

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Abstract

In order to obtain an antiferroelectric material of slim double-hysteresis loop and proper switch electric fields, the effect of lanthanum modifier on the electric hysteresis characteristics of lead zirconate stannate titanate antiferroelectric compounds was studied. The electric hysteresis loops and dielectric constants with temperature variations were measured. The experimental results showed that La addition enhanced the antiferroelectrics of $Pb(Zr,Sn,Ti)O_3$ compounds. The switch electric fields increased and the electric hysteresis width $\Delta E = E_F - E_B$ narrowed with La content increase. Meanwhile, the dielectric constant was dispersed with frequency and the dielectric peak that related to the transition from antiferroelectric to paraelectric phase was broadened. La was an available modifier to tune the electric hysteresis width and switch fields of $Pb(Zr,Sn,Ti)O_3$ antiferroelectrics. Finally, an antiferroelectrics of slim double-hysteresis loop and suited switch electric fields was tailored.
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Keywords: Slim double hystieresis loop; La modifier; Antiferroelectric lead zirconate stannate titanate compounds

1. Introduction

In 1951 C. Kittle proposed the concept of antiferroelectricity and in 1965 D. Berlincour established the ternary phase diagram for lead stannate zirconate titanate antiferroelectrc system [1,2]. From then, the antiferroelectricity and related materials have been widely studied. It has been known that the antiferroelectric phase and ferroelectric phase can be transformed each other with a proper electric field. At antiferroelectric–ferroelectric transition the volume, spontaneous polarization and dielectric constant of material have a tremendous change. The transition performances of antifeeroelectric materials have been applied for the large charge capacitors and actuators [3,4].

The antiferroelectric materials with slim double-hysteresis loop is desired for capacitor and actuator application. Because the broad electric hysteresis will generate more dielectric consume. Pan et al. [5] and Park et al. [6] had investigated the effects of Ba and Sr dopants on the hysteresis characteristics of $Pb(Zr,Sn,Ti)O_3$ compounds. It was shown that the Ba and Sr dopants could reduce the electric hysteresis width $\Delta E = E_F - E_B$, where E_F and E_B are the forward and backward switch electric field, respectively, that induced the antiferroelectric–ferroelectric transitions. The disadvantage of Ba and Sr dopants was that the polarization of ferroelectric phase was also greatly depressed with Ba or Sr addition. This would reduce material's charge capability. Otherwise, Haertling's study had shown that off-valent La^{3+} ion substituted for Pb^{+2} ion in $Pb(Zr,Ti)O_3$ compounds could reduce the coercive electric field and narrow the hysteresis loop of ferroelectrics [7]. In order to explore a material with slim double-hysteresis loop and high polarization, the effect of La modifier on the electric hysteretic and dielectric characteristics of $Pb(Zr,Sn,Ti)O_3$ compounds were studied in the work.

2. Experimental procedure

The compounds studied in this work were formulated as $(Pb_{1-3x/2}La_x)(Zr_{0.55}Sn_{0.30}Ti_{0.15})O_3$, here La^{3+} ion replacing Pb^{2+} ion at A site of perovskite structure. Among of them, $(Pb_{0.97}La_{0.02})(Zr_{0.55}Sn_{0.30}Ti_{0.15})O_3$ composition near the antiferroelectric and ferroelectric morphotropic phase boundary (Fig. 1).

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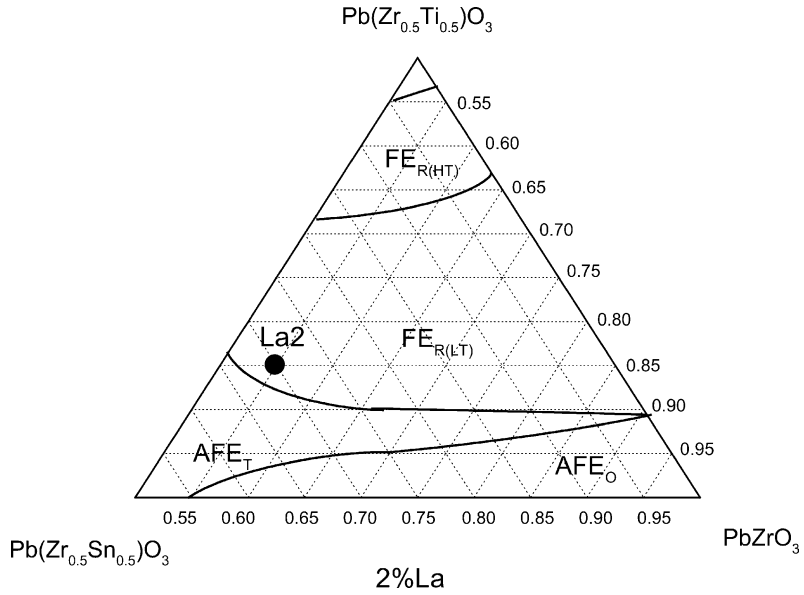

Fig. 1. The ternary phase diagram of lead zirconate stannate titanate system modified 2% La [2], where La2 was $(Pb_{0.97}La_{0.02})(Zr_{0.55}Sn_{0.30}Ti_{0.15})O_3$.

Polycrystalline ceramics were prepared by conventional solid-state reaction. The chemical purities of raw oxides powders were not less than 99.0%. Powders were mixed by ball mill and calcined at 850 °C for 2 h. Dry-pressed pellets were sintered at 1260 °C for 1.5 h in a lead-rich atmosphere to minimize lead volatilization. Fired ceramics were then annealed at 860 °C for 6 h in air. Disk Samples sliced from cylinder ceramics were 11 mm in diameter and 0.32 mm in thickness. After samples polished and leaned the silver electrodes of 6.0 mm diameter were printed at the center of samples to prevent edge electric arcing.

The electric hysteresis loops were measured with a computer-controlled modified Sawyer–Tower circuit. A Trek 609A high voltage amplifier supplied sine voltage of 0.4 Hz. Heating sample used a self-made heat chamber, temperature was monitored with a platinum resistance thermometer. During measuring the sample was submerged in insulating oil.

The temperature and frequency dependences of dielectric constants were measured with a HP4274A multifrequency meter. Samples were put in a heat chamber, temperature varied from room temperature to 200 °C with a fix rise rate of 3 °C/min.

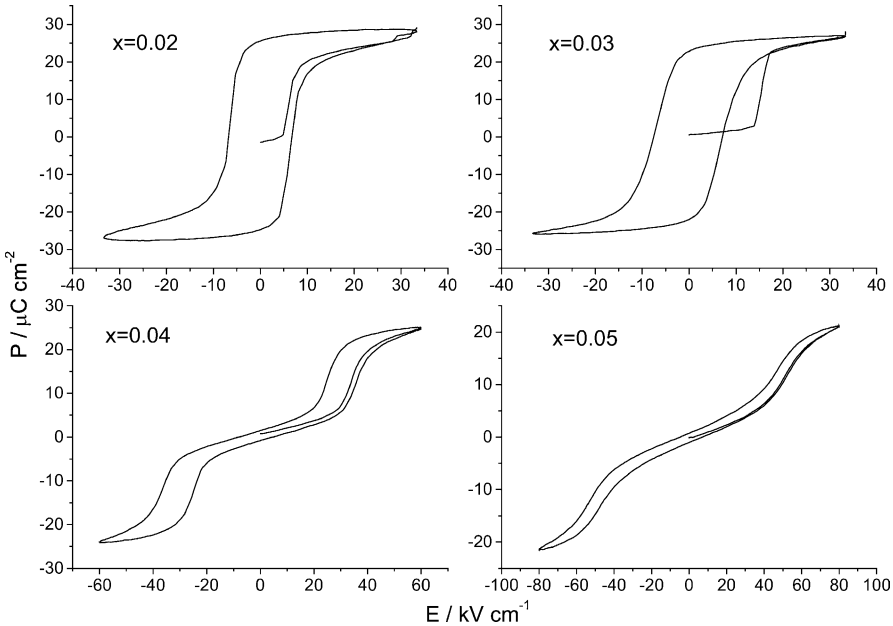

Fig. 2. Electric hysteresis loops of $(Pb_{1-3x/2}La_x)(Zr_{0.55}Sn_{0.30}Ti_{0.15})O_3$ compounds in first cycle at room temperature.

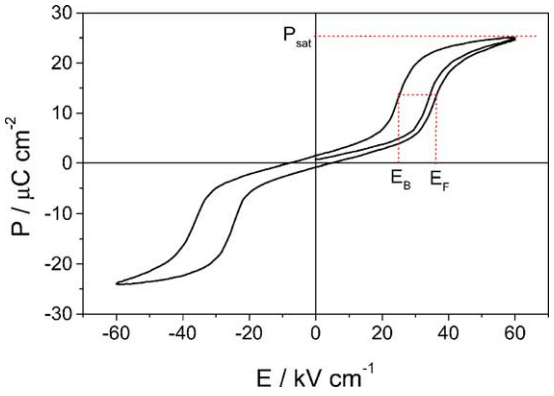

Fig. 3. Chart of switch electric fields of antiferroelectric–ferroelectric transition (E_F is the electric field forced antiferroelectric phase to ferroelectric phase and E_B is the electric field prevented ferroelectric phase to antiferroelectric phase).

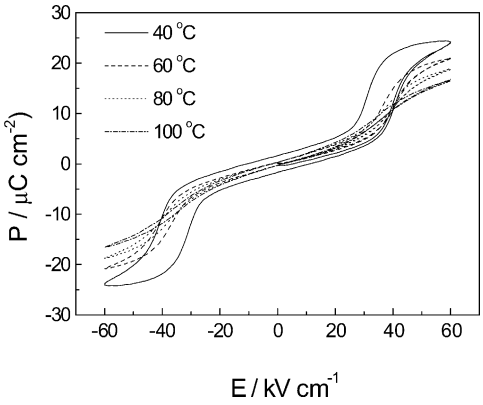

Fig. 4. Hysteresis loops of $(Pb_{0.94}La_{0.04})(Zr_{0.55}Sn_{0.30}Ti_{0.15})O_3$ at various temperature.

3. Results and discussion

The measured results of electric hysteresis loops in first cycle at room temperature were shown in Fig. 2. $(Pb_{0.97}La_{0.02})(Zr_{0.55}Sn_{0.30}Ti_{0.15})O_3$ composition was normal ferroelectrics. The original phase of $(Pb_{0.955}La_{0.03})(Zr_{0.55}Sn_{0.30}Ti_{0.15})O_3$ was an antiferroelectrics with a signal-hysteresis loop and $(Pb_{0.94}La_{0.04})(Zr_{0.55}Sn_{0.30}Ti_{0.15})O_3$ was an antiferroelectrics with a double-hysteresis loop. Increasing the substitution of La for Pb at A site of perovskite structure the forward switch field E_F and backward switch field E_B were all enhanced. Meanwhile, the electric hysteresis loop width $\Delta E = E_F - E_B$ was also narrowed. For example, the hysteresis loop width ΔE of $(Pb_{0.94}La_{0.04})(Zr_{0.55}Sn_{0.30}Ti_{0.15})O_3$ composition was equal to 11 kV/cm and $(Pb_{0.925}La_{0.05})(Zr_{0.55}Sn_{0.30}Ti_{0.15})O_3$ composition was narrowed to 7 kV/cm. The forward switch electric field E_F is the electric field which forces antiferroelectric phase to ferroelectric phase and the backward switch electric field E_B is the electric field which prevents ferroelectric phase to antiferroelectric phase. For simplifying in the measurement E_F was the electric field that increasing the polarization up to the half of saturation polarization P_{sat} and E_B was the electric field that preventing the polarization down to the half of P_{sat} (Fig. 3). A disadvantage, as Ba and Sr dopants, La addition also made the hysteresis loop slanted and saturation polarization P_{sat} depressed. The hysteresis characteristics of $(Pb_{1-3x/2}La_x)(Zr_{0.55}Sn_{0.30}Ti_{0.15})O_3$ compounds were summarized in Table 1.

Table 1
Hysteretic and dielectric properties of $(Pb_{1-3x/2}La_x)(Zr_{0.55}Sn_{0.30}Ti_{0.15})O_3$ compounds

x (%)	E_F (kV/cm)	E_B (kV/cm)	ΔE (kV/cm)	P_{sat} (μC/cm^2)	T_m (°C)
2	–	–	–	32	150
3	16	–	–	31	136
4	35	24	11	24	119
5	50	43	7	21	91

The temperature dependence of hysteresis loop was also studied. For typical $(Pb_{0.94}La_{0.04})(Zr_{0.55}Sn_{0.30}Ti_{0.15})O_3$ composition the backward switch field E_B became larger but forward switch field E_F almost fixed on heating (Fig. 4). This made hysteresis width gradually narrowed and finally developed into a gradient line with temperature increase.

From above experiments it was seen that La replacing Pb in (Pb,La)(Zr,Sn,Ti)O_3 compounds obviously changed the phase and hysteresis characteristics. The antiferroelectricity and switch electric were enhanced with La adding. Meanwhile, the electric hysteresis width $\Delta E = E_F - E_B$ was narrowed because of E_F accretion being slower than E_B accretion. With temperature increasing the backward switch field E_B went on but the forward switch field E_F stayed still. This specialty was useful for capacitor service at wide temperature range.

The temperature variations of dielectric constants for $(Pb_{1-3x/2}La_x)(Zr_{0.55}Sn_{0.30}Ti_{0.15})O_3$ compounds were shown in Fig. 5. Combining the electric hysteresis measurements, it confirmed that the elevated step at 115 °C in dielectric curve of $(Pb_{0.97}La_{0.02})(Zr_{0.55}Sn_{0.30}Ti_{0.15})O_3$ was caused by a transition from ferroelectric to antiferroelectric phase and the dielectric peak at 150 °C caused by the transition from antiferroelectric to parelectric phase. In thermal dielectric curve of $(Pb_{0.955}La_{0.03})(Zr_{0.55}Sn_{0.30}Ti_{0.15})O_3$ the elevated step at 56 °C was caused by a transition from antiferroelectric orthogonal AFE_O to tetragonal AFE_T phase. With La content increasing the temperature T_m that related to the dielectric peak gradually decreased. At the same time the dielectric constant was dispersed with frequency at the low temperature side of dielectric peak. Above phenomena implied that La modifier made crystal structure distorted

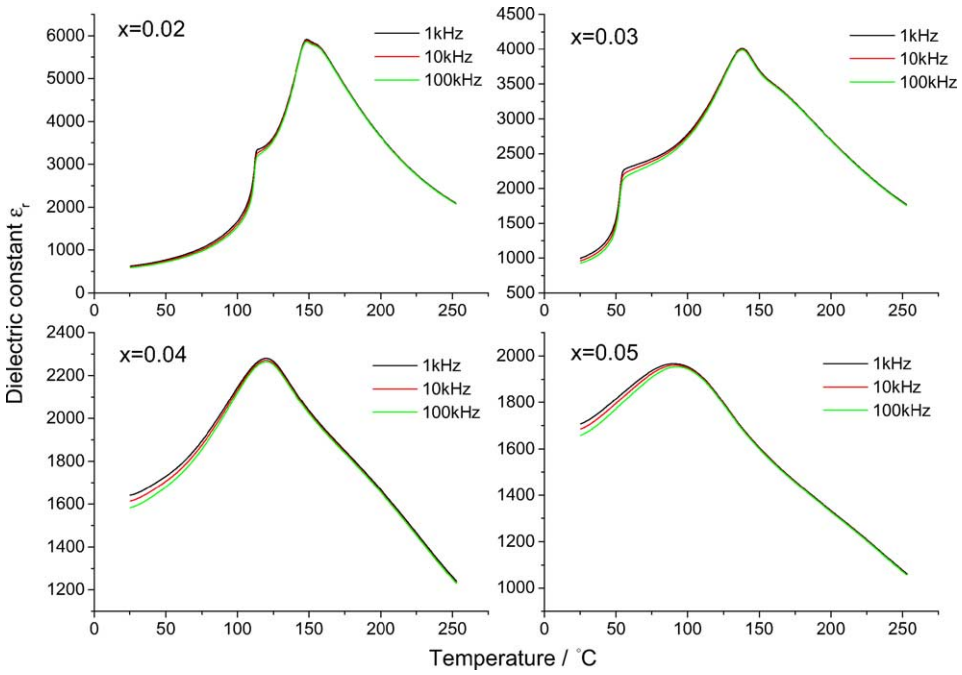

Fig. 5. Temperature dependence of dielectric constant for $(Pb_{1-3x/2}La_x)(Zr_{0.55}Sn_{0.30}Ti_{0.15})O_3$ compounds.

and brought a normal antiferroelectrics to a relaxed antiferroelectrics.

4. Conclusions

La modifier was an antiferroelctric intensifier for Pb(Zr,Sn,Ti)O_3 compounds. Substituting La for Pb could convert a ferroelctric phase into an antiferroelectric phase. The forward and backward switch electric fields were increased, meanwhile the double-hysteresis loop width $\Delta E = E_F - E_B$ was narrowed with La adding. $(Pb_{0.94}La_{0.04})(Zr_{0.55}Sn_{0.30}Ti_{0.15})O_3$ composition was proper antiferroelectrics of double loop. The forward switch field E_F that induced antiferroelectric phase to ferroelectric phase hardly changed with temperature variation for $(Pb_{0.94}La_{0.04})(Zr_{0.55}Sn_{0.30}Ti_{0.15})O_3$ composition. This specialty was useful for capacitors service at broad temperature range. La was an available modifier to tune the electric hysteresis width and the switch fields of Pb(Zr,Sn,Ti)O_3 compounds.

The dielectric constant dispersed with frequency for higher La content of (Pb,La)(Zr,Sn,Ti)O_3 compounds. The dielectric peak that related to the transition from antiferroelectric to ferroelectric phase was broadened and the temperature T_m that related to dielectric peak was decreased with La increasing. La addition made normal antiferroelectrics to relaxed antiferroelectrics.

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