

# Effect of composition and pressure on dielectric property in the Sn-modified lead zirconate titanate ceramics

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**Abstract** A detailed study of composition and hydrostatic pressure on the  $\text{Pb}_{0.97}\text{La}_{0.02}[(\text{Zr}_{1-x}\text{Sn}_x)\text{Ti}_{0.114}]\text{O}_3$  ( $x=0.13, 0.19, 0.21, 0.25$ ) ceramics has provided a detailed view of the dielectric response and phase transition of the technologically important material. The incommensurateness of  $\text{Sn}^{4+}$  has a great influence of the BOCT ( $\text{BO}_6$  octahedral in perovskite  $\text{ABO}_3$ ) in the complex perovskite structure. The more Sn doped, the more obvious the character of antiferroelectric behaves and the lower the transformation pressure becomes. The electric energy can be released under the pressure from polarized ferroelectric state to antiferroelectric state. With increasing Sn concentration, the phase transition pressure decreases from 300 to 100 MPa. Dielectric properties were measured as a function of hydrostatic for poled samples. Because of the substitution at the A site, there existed the behavior of dielectric frequency dispersion. Dielectric measurement has the same phase transition point as the test result in the hydrostatic depoling.

**Keywords** Hydrostatic pressure · FE-AFE phase transition · Dielectric

## 1 Introduction

Complex mixed perovskite ceramics of lead zirconate titanate stannate and further modified forms have been studied for many potential applications in energy conversion. Berlincourt et al. reported the process due to the

antiferroelectric to ferroelectric phase transition in  $\text{Pb}(\text{Nb}, \text{Zr}, \text{Sn}, \text{Ti})\text{O}_3$  [1–4]. They have extensively studied for their promising application for electroactuation and micropositioning by the conversion of electrical energy into mechanical energy. These materials are also investigated for the pressure-induced polarization discharge. The first systematic study was done at Clecote laboratories in the 1960s to explore the use of phase change compositions in capacitive energy store.

The composition  $\text{Pb}_{0.97}\text{La}_{0.02}[(\text{Zr}_{1-x}\text{Sn}_x)\text{Ti}_{0.114}]\text{O}_3$  was chosen to characterize AFE-FE phase switching behavior. This composition is located near the boundary between the tetragonal AFE ( $\text{AFE}_{\text{tet}}$ ) phase and rhombohedral FE ( $\text{FE}_{\text{Rh}}$ ) phase. The free energy difference between the antiferroelectric and ferroelectric states may be modified compositionally to such an extent that a phase change between the antiferroelectric state and the ferroelectric state can be forced by an electric field or a hydrostatic pressure. The pressure switching has been extensively investigated upon inversion into the antiferroelectric state; a poled ferroelectric ceramic releases all polarization charges and therefore can supply very high instantaneous current. In particular, effect of hydrostatic pressure on dielectric properties is also examined.

## 2 Experimentals

The chemical compositions discussed in this article are listed in Table 1 with their reference number of the selected compositions.

The  $\text{Pb}_{0.97}\text{La}_{0.02}[(\text{Zr}_{1-x}\text{Sn}_x)\text{Ti}_{0.114}]\text{O}_3$  ceramic with  $\text{Zr}^{4+}$  concentration of  $0.61 \leq 1-x \leq 0.75$  was prepared by conventional ceramic fabrication technique. The sintering process was carried out in a lead rich environment in order to minimize lead

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**Table 1** Chemical compositions and the reference numbers.

Sn/Zr	Composition
25/63	$\text{Pb}_{0.97}\text{La}_{0.02}[(\text{Zr}_{0.63}\text{Sn}_{0.256})\text{Ti}_{0.114}]\text{O}_3$
21/67	$\text{Pb}_{0.97}\text{La}_{0.02}[(\text{Zr}_{0.67}\text{Sn}_{0.216})\text{Ti}_{0.114}]\text{O}_3$
19/69	$\text{Pb}_{0.97}\text{La}_{0.02}[(\text{Zr}_{0.69}\text{Sn}_{0.196})\text{Ti}_{0.114}]\text{O}_3$
13/75	$\text{Pb}_{0.97}\text{La}_{0.02}[(\text{Zr}_{0.75}\text{Sn}_{0.136})\text{Ti}_{0.114}]\text{O}_3$

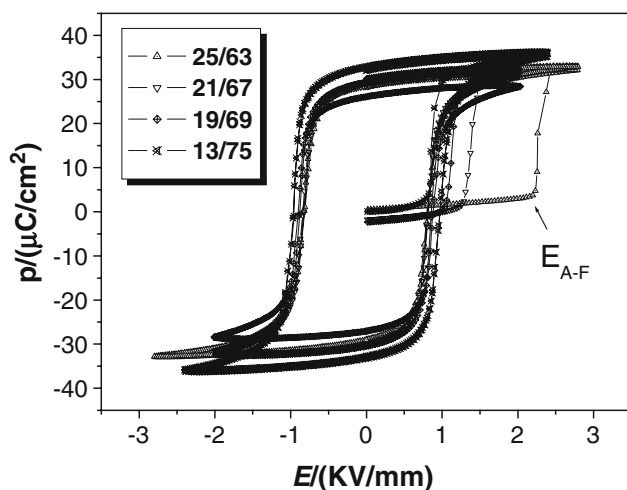
volatilization. The samples were pale yellow after sintering and remained this color throughout processing. The density of the fired disks is in the range of 7.9–8 g/cm<sup>3</sup>. The sintered specimens were cut into thin plates with thickness about 0.5 mm, and silver electrode were coated onto the surfaces for electric tests.

Complex dielectric constant measurements were performed using a Hewlett–Packard 4284A inductance-capacitance-resistance (LCR) meter. The  $P$ – $E$  behavior was characterized using a computer controlled modified Sawyer–Tower circuit. All  $P$ – $E$  curves were measured at a frequency of 1 Hz. The effect of hydrostatic pressure on the phase stability for AFE and FE phases was determined by measuring changes of charge release with pressure. Pressure was measured by a calibrated manganin sensor and increased at a rate of 10 Mpa/s. A 10  $\mu\text{F}$  capacitor was used to collect the charge from the poled ceramic [5].

### 3 Results and discussion

#### 3.1 Composition dependence of field-induced polarization and charge released under stress

The dielectric hysteresis loops for different compositions are sketched in Fig. 1. The loops illustrate that the virgin sample remains antiferroelectric states with  $E_{A-F} > E_C$ . The first loop takes from a virgin sample and a second loop

**Fig. 1** The dielectric hysteresis loops for different compositions

immediately taken after the first. The first  $P$ – $E$  loop starts from the origin and has a small slope ( $dP/dE$ ) of AFE behavior, at  $E_{A-F}$  a step-like transition from AFE state to the field-induced FE state takes place. This induced FE state is metastable.

Figure 1 indicated that the  $E_{A-F}$  increases as Sn/Zr ratio rises, the specimen needs more energy to be poled to the ferroelectric state. The result is similar with the previous reports [6]. The loops became thinner when Sn increased. The saturation polarization remains above 30  $\mu\text{C}/\text{cm}^2$ . The radius of the  $\text{Zr}^{4+}$  and  $\text{Sn}^{4+}$  is about 0.079 and 0.071 nm, so the difference of the radius between the two B-site cations can result in some different results [7, 8]. The incommensurate of  $\text{Sn}^{4+}$  have a great influence of the BOCT in the complex perovskite structure. The more Sn is mixed, the character of the antiferroelectric become more obvious. The stabilization of the AFE phase produced higher switching fields with less hysteresis. The decrease of the coercive field  $E_C$  exhibits some instability of the structure. The attention should be paid to the shape of the  $P$ – $E$  behavior near the composition of 15/73. With  $E_{A-F} < E_C$ , the specimen in which FE is the main phase in Fig. 1 is similar to ording piezo-and ferroelectric ceramics, with  $E_{A-F} > E_C$ , the specimen shows the characteristics of electric field induced AFE-FE phase transition. The behavior of the hysteresis loop shows that when the Sn/Zr ratio is 15/73, the initial phase became ferroelectric. Table 2 shows the transition field as a function of Sn/Zr ratio variation for these compositions. The changes of the composition can induce the samples with high Zr content go into the ferroelectric state, but the other samples exhibits the antiferroelectric state when no electric field is applied.

Usually an electric field favors the FE phase and pressure favors the AFE phase. Figure 2 is the charge release curve which is the macroscopic representation of FE-AFE phase transition under hydrostatic pressure. The transformation pressure is defined as the pressure where half of the total charge has been released. The average piezoelectric coefficient of the poled specimen is  $d_{33} = 90 \times 10^{-12} \text{C}/\text{N}$ . The pressure decreases from 290 to 100 MPa with the content of Zr decreasing 16% (Table 2). The phase transition from a metastable ferroelectric state to an antiferroelectric can be triggered by hydrostatic pressure, where the electric charge is collected by the capacitor. The polarization released in the hydrostatic measurement is

**Table 2** Switching data for different compositions.

Sn/Zr	$E_{A-F}$ (KV/mm)	$P_c$ (Mpa)
25/63	2.238	105.5
21/67	1.286	197.6
16/69	1.060	238.6
13/75	0.792	290.7

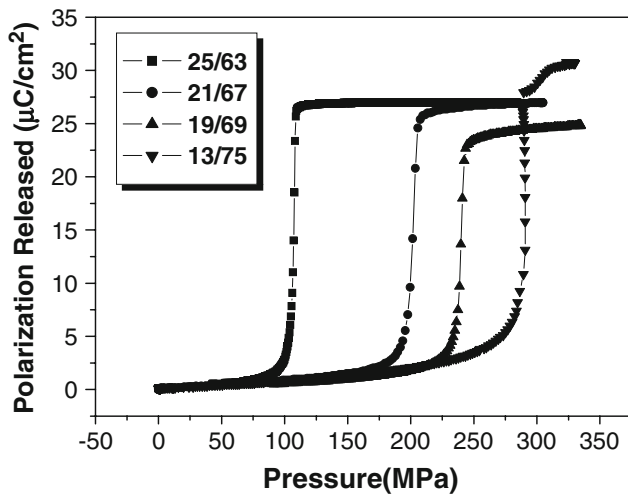


Fig. 2 Hydrostatic depoling characteristics for PLZST ceramics

about 80% of the remanent polarization values. The transformation pressure has a close relationship with the composition. The composition with a high  $E_{A-F}$  would transform from the ferroelectric to antiferroelectric at low hydrostatic pressure. Clearly, it can be assumed that the increase of Sn favors the transformation from ferroelectric to antiferroelectric at this unstable phase region. It is more sensitive to the hydrostatic for Sn-rich composition than Zr-rich composition. This situation reveals that the addition of  $Sn^{4+}$  cause the instability of the structure. When the sample is poled from the antiferroelectric to ferroelectric, the configure of the microdomain changed to the higher energy situation, the unstable structure is sensitive to the external field, the more addition of the Sn, the lower the transformation pressure become. For some compositions [9], switching from the AFE to FE can be easily achieved by a large strain, it is believed that the strain caused by phase switching is mainly due to the change in the primitive perovskite cell [10, 11], phase switching involves multiple steps including both structure transformation and domain

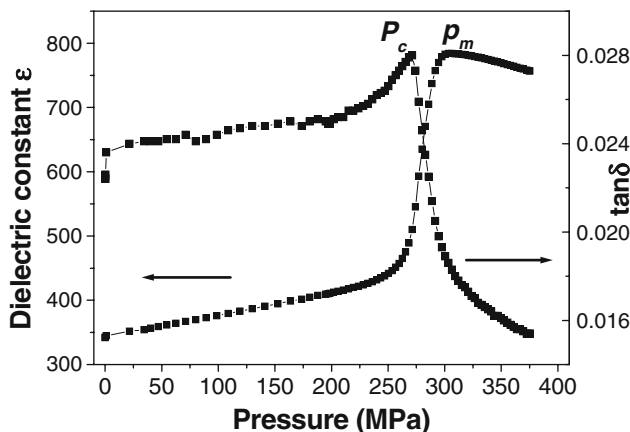


Fig. 3 The dielectric-hydrostatic pressure spectra for samples 13/75

reorientation [11]. When the test is under hydrostatic pressure, the similar situation happens.

### 3.2 Effect of hydrostatic pressure on dielectric properties

The dielectric constant and dissipation were measured under hydrostatic pressure at room temperature. The poled specimen was in rhombohedral ferroelectric state. From Fig. 3 we can see that the dielectric and dissipation increased with the increasing pressure at first, and then a maximum  $\epsilon_{max}$  appeared at a certain pressure, marked as  $p_m$ , and then a maximum  $\tan\delta$  at a transition pressure, marked as  $p_c$ , whereas, the transition pressure  $p_c$  was lower than the peak pressure  $p_m$ . the difference  $\Delta P$  between  $p_m$  and  $p_c$  was about 10 Mpa. For this sample, the falling curve of the dielectric constant was a sharp one. It is a first order phase transition. It also suggested that the transition from ferroelectric to antiferroelectric occurred at a pressure point~290 MPa. This result has the same value as we do in the pressure depoling above. Figure 4 give some details about frequency dissipation and dielectric relaxation in the whole pressure range, and especially, there exists strong frequency dispersion near the phase transition pressure.

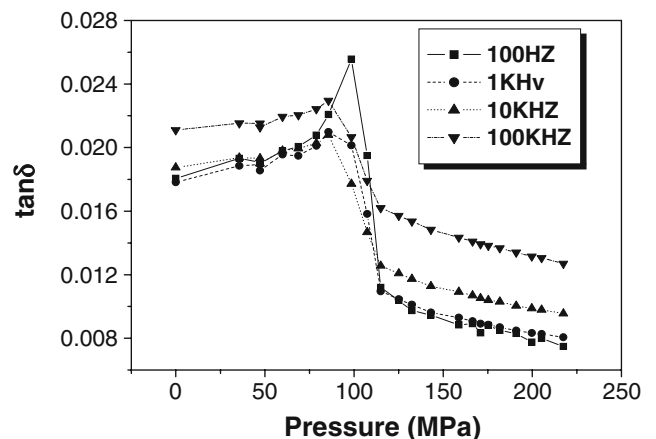
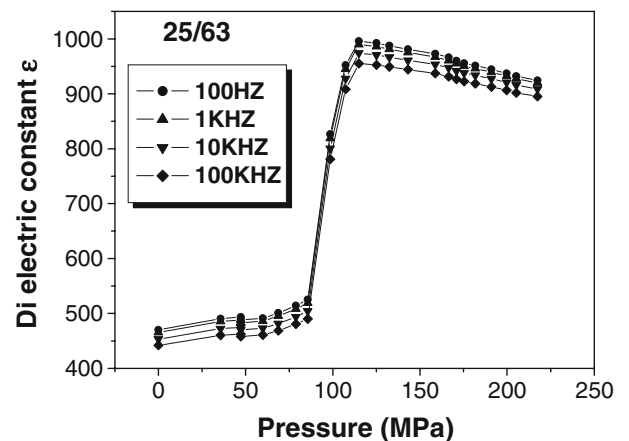


Fig. 4 The dielectric-hydrostatic pressure spectra for samples 25/63 at room temperature

This indicates that dielectric property was sensitive to both pressure and frequency. The partial substitution of La for Pb located in site A resulted in the formation of local polar nano microdomains. The poled sample has the ferroelectric phase at first. Under the action of hydrostatic pressure, the long-range order was destroyed, the existence of nano-domains in ferroelectric phase resulted in the appearance of frequency dispersion and relaxor behavior [12]. When the pressure is increased, the nanodomains coupling is enhanced, this process favors the antiferroelectric and is sufficient to induce frequency dispersion.

#### 4 Conclusion

This work has presented some useful evidence into the physics and phase transition of PLZST. The stabilities of FE and AFE phase were influenced by compositions in the PLZST system. The result also shows characteristic of other compositions near the morphotropic phase boundary of this material system. We have observed that Sn<sup>4+</sup> on B-site have great influence on the dielectric character of the disordered ABO<sub>3</sub> perovskites, and it appears that the more Sn mixed, the character of the antiferroelectric become more obvious. The polarization and transition fields are the function of Sn/Zr ratio. We found that as Sn/Zr ratio decreases, while the transition field  $E_{A-F}$  decreases, the transformation pressure increased. Although Sn and Zr are all the antiferroelectric phase stabilizer, but the change of the Sn/Zr ratio creates

very different results. On the other hand, the nanodomains polar fluctuation resulted in frequency dispersion with increasing pressure. It reveals more obvious physical details of the phase transition. However, more study is required to explore the phenomenon.

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