Evolution of electromechanical properties in Fe-doped (Pb,Sr)(Zr,Ti)O₃ piezoceramics

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Abstract: Defects in acceptor-doped perovskite piezoelectric materials have a significant impact on their electrical properties. Herein, the defect mediated evolution of piezoelectric and ferroelectric properties of Fe-doped (Pb,Sr)(Zr,Ti)O₃ (PSZT–Fe) piezoceramics with different treatments, including quenching, aging, de-aging, and poling, was investigated systematically. Oxygen vacancies with a cubic symmetry are preserved in the quenched PSZT–Fe ceramics, rendering them robust ferroelectric behaviors. In the aged PSZT–Fe polycrystals, defect dipole between Fe dopant and oxygen vacancy has the same orientation with spontaneous polarization P_s , which enables the reversible domain switching and hence leads to the emergence of pinched polarization hysteresis and recoverable strain effect. And the defect dipoles can be gradually disrupted by bipolar electric field cycling, once again endowing the aged materials with representative ferroelectric properties. For the poled PSZT–Fe polycrystals, the defect dipoles are reoriented to be parallel to the applied poling field, and an internal bias field aligning along the same direction emerges simultaneously, being responsible

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for asymmetric hysteresis loops.

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1 Introduction

Piezoelectric materials with the ability to directly convert mechanical energy into electrical energy, and vice versa, have found themselves applied in enormous pivotal devices, such as robust fuel injectors, ultrasonic medical diagnostic apparatuses, delicate positioning systems, etc. [1–6]. The outstanding comprehensive properties have enabled lead–zirconate–titanate (PZT) to be the dominating player in the commercial market.

To meet the demands of various implements, the tunable electrical properties of PZT-based piezoelectrics over a broad range are of great importance. For example, acceptor dopants such as $\text{Mn}^{2+,3+}$ and Fe^{3+} are generally adopted to produce “hard” PZT-based ceramics, which are featured by high mechanical quality factor, for high-power applications [7–11]. However, a long-standing issue associated with acceptor-modified piezoelectrics is the strong history or time dependence of electrical properties, which is termed as aging effect [7–10]. It is characterized by the polarization hysteresis loops, which are either pinched or displaced depending on the poling state. Several models have been proposed to explain this intriguing feature, such as charge carrier agglomeration at domain walls or internal barriers, and defect dipoles (acceptor dopant–oxygen vacancy complex) [7,11–13]. In the former scenario, the charge carrier agglomeration at domain walls or internal barriers would result in the built-up of an internal bias field; whereas in the latter case, defect dipoles re-orient with respect to the spontaneous polarization and by that imprint a preferred orientation. So far, it is not clear how much these different mechanisms contribute to the overall aging mechanism and which dominate in the different materials. As the aging effect is undesirable in ferroelectrics, it is important to de-age the aged samples. It can be accomplished by two feasible approaches, bipolar electric field cycling or quenching after heating the samples to a temperature well above the Curie temperature [12,14]. Despite the intensive explorations, the underlying mechanisms being responsible for these observations remain debated.

In this study, the evolution of electromechanical properties, including the large signal properties polarization P_3 and strain S_3 as well as the small signal parameters piezoelectric coefficient d_{33} and permittivity ϵ_{33} for Fe-doped $(\text{Pb,Sr})(\text{Zr,Ti})\text{O}_3$ polycrystals with different treatments, namely quenching, poling, aging, and de-aging, are systematically studied. All these features and their origins are discussed in the context of defect dipole formed between Fe dopant and oxygen vacancy.

2 Experimental

Commercial polycrystals, which have a nominal composition of $(\text{Pb}_{0.92}\text{Sr}_{0.08})(\text{Zr}_{0.555}\text{Ti}_{0.44}\text{Fe}_{0.005})\text{O}_3$ (denoted by PSZT–Fe), were provided by Tongxiang Tsingfeng Technology Company. The phase structure of as-sintered ceramics was examined using X-ray diffraction (XRD). The microstructure and elemental mapping of the ceramics were collected by scanning electron microscope (SEM). The density of the as-sintered ceramics was measured using the Archimedes’ method. The valence of iron ions was determined by X-ray photoelectron spectroscopy (XPS, ESCALab220i-XL). The domain morphologies, including both the in-plane and out-of-plane components, were recorded using a piezoresponse force microscopy (PFM, MPF-3D, Asylum Research, USA). Before conducting measurements of electrical properties, the surfaces of the pellets were polished, followed by painting silver paste onto both sides of the pellets and firing at 550 °C for 30 min. And then the ceramics were poled in silicon oil at 100 °C by applying a DC field of 4 kV/mm for half an hour. The measurements of planar electromechanical coupling factor k_p , mechanical quality factor Q_m , and temperature-dependent permittivity of poled ceramics were performed on an impedance analyzer (HP4194A, USA). The piezoelectric coefficient d_{33} at room temperature was checked using a quasi-static d_{33} meter (ZJ-3A, China).

The quenched ceramics were received by quenching the PSZT–Fe samples in air from high temperature (500 °C, well above the Curie temperature of PSZT–Fe)

to room temperature. The pristine PSZT–Fe ceramics were heated to 500 °C, and then were slowly cooled (1 °C/min) down to ambient temperature to reach an aged state. To de-age the samples, a bipolar electric field (4 kV/mm and 1 Hz) was applied repeatedly. The data of electrical hysteresis, including polarization, strain, piezoelectric coefficient, and permittivity, after different treatments was collected by utilizing a ferroelectric analyzer (aixACCT TF1000, Germany).

3 Results and discussion

Representative PSZT–Fe lead-containing piezoelectric ceramics are the materials of choice. The X-ray diffraction (XRD) pattern of PSZT–Fe sample is shown in Fig. 1(a), indicating that the material has a pure perovskite structure. The observation of split (002) and (200) peaks with a relative intensity I_{002}/I_{200} of 1:2 in the XRD profile confirms that a tetragonal phase dominates in the PSZT–Fe ceramics [15,16]. As presented in Fig. 1(b), the anomaly at the temperature of 321 °C in the permittivity curve corresponds to the phase transition of tetragonal–cubic, which is critical for determining the heat treatment temperature. The XRD analysis can find consistency with temperature-

dependent permittivity measurements. The microstructure of the samples was studied using SEM, as displayed in Fig. 1(c). The polycrystals have a dense microstructure with a high density of approximately 7.52 g/cm³. It is found that the PSZT–Fe ceramics have a uniform grain size distribution of around 2 µm. The EDX mapping results shown in Fig. 1(d) suggest the homogenous distribution of all the elements, excluding the possibility of undesired secondary inclusion and agreeing well the XRD analysis.

For ferroelectric polycrystals, their piezoelectric performance is closely associated with the domain morphology. In the present study, the domain morphology of PSZT–Fe ceramics was recorded using piezoresponse force microscopy (PFM), a powerful instrument to provide a perspicuous schema of domain morphology [17]. Figure 2 presents the lateral piezoresponse force microscopy (LPFM) image and vertical piezoresponse force microscopy (VPFM) image of domain morphology, and the corresponding piezoresponse amplitude of LPFM and VPFM modes of PSZT–Fe ceramics. Submicro-sized domain lamellas were observed in the PSZT–Fe polycrystals with tetragonal phase being dominating. Analogous results have also been reported in ferroelectric ceramics rich in tetragonal phase [18].

Fig. 1 (a) XRD pattern, (b) temperature dependence of dielectric permittivity and dielectric loss, (c) typical SEM image, and (d) EDX elemental maps of PSZT–Fe ceramics.

Fig. 2 (a) Lateral piezoresponse force microscopy (LPFM) image and (b) vertical piezoresponse force microscopy (VPFM) image of domain morphology, and the corresponding piezoresponse amplitude of (c) LPFM and (d) VPFM modes of PSZT-Fe ceramics.

Good piezoelectric properties were obtained for the poled PSZT-Fe ceramics at room temperature. The piezoelectric coefficient d_{33} and planar electro-mechanical coupling factor k_p of PSZT-Fe ceramics are 264 pC/N and 0.51, respectively, being comparable to the corresponding values of representative hard piezoceramics PZT-4 (Table 1) [19]. Hard piezoceramics usually have a conspicuous feature of large mechanical quality factor Q_m [20,21]. The Q_m of PSZT-Fe reaches 572, demonstrating the hard nature of this material, which originates from the stabilized domain and domain wall by defect dipole formed between the acceptor dopants and oxygen vacancies.

Bipolar polarization, strain, piezoelectric coefficient, and permittivity hysteresis loops were recorded for the PSZT-Fe ceramics in the aged, poled, and quenched states, as displayed in Fig. 3. For quenched PSZT-Fe ceramics, representative hysteresis loops of ferroelectric materials are observed, i.e., fully opened P_3-E_3 and $d_{33}-E_3$ hysteresis loops as well as butterfly-shaped

$S_{33}-E_3$ and $\epsilon_{33}-E_3$ curves, accompanied by a moderate polarization, strain, piezoelectric coefficient, and permittivity. In the case of aged state, a distinct scenario emerges. The polarization hysteresis P_3-E_3 shows a typical pinched shape, with relatively low remanent and maximum polarizations of 6.54 and 19.60 $\mu\text{C}/\text{cm}^2$, respectively. Sprout-shaped strain hysteresis $S_{33}-E_3$ with negligible remanent and negative strain is observed, and the maximum strain merely reaches about 0.15%. The shape of piezoelectric coefficient curve $d_{33}-E_3$ is in analogy to that of P_3-E_3 , because of the positive correlation between piezoelectric coefficient and polarization [22,23]. The remanent piezoresponse in the $d_{33}-E_3$ hysteresis is approximately 160 pm/V. A broad plateau presents in the permittivity $\epsilon_{33}-E_3$ hysteresis loop when $-2 \text{ kV}/\text{mm} < E_3 < 2 \text{ kV}/\text{mm}$, and the permittivity values at zero and maximum fields are about 1158 and 754, respectively.

In comparison to the hysteresis loops of quenched and aged states, all the curves of poled PSZT-Fe samples undergo drastic changes. It is noted that P_3-E_3 hysteresis loop shifts along the negative direction of electric field (namely, internal bias field arises), while $S_{33}-E_3$ and $\epsilon_{33}-E_3$ curves develop an asymmetric shape. The electrical properties of polarization, strain, and piezoelectric coefficient are significantly enhanced

Table 1 Electrical properties of PSZT-Fe ceramics and compared to those of PZT-4

Material	d_{33} (pC/N)	k_p	Q_m	ϵ_{33}	$\tan\delta$
PSZT-Fe	264	0.51	572	797	0.005
PZT-4	289	0.58	500	1300	0.004

after poling treatment. For instance, the remanent polarization reaches $30 \mu\text{C}/\text{cm}^2$, nearly one-fold growth in the value compared to the one of quenched samples, as shown in Fig. 3(a). Simultaneously, the piezoelectric coefficient goes up along with polarization. The remanent piezoresponse in the d_{33} – E_3 hysteresis loop is 285 pm/V, being comparable to the value measured by commercial d_{33} meters (Fig. 3(c) and Table 1). Large

remanent and maximum strain of 0.28% and 0.40%, respectively, are obtained in the poled ceramics.

Bipolar electric field cycling was applied to de-age the PSZT–Fe samples in the aged state. Figure 4 depicts the conspicuous evolution in these hysteresis loops when the aged samples being subjected to bipolar electric field cycles. The pinched P_3 – E_3 and d_{33} – E_3 loops gradually become open with increasing

Fig. 3 (a) P_3 – E_3 , (b) S_{33} – E_3 , (c) d_{33} – E_3 , and (d) ϵ_{33} – E_3 hysteresis loops of quenched, aged, and poled PSZT–Fe ceramics.

Fig. 4 (a) P_3 – E_3 , (b) S_{33} – E_3 , (c) d_{33} – E_3 , and (d) ϵ_{33} – E_3 hysteresis of PSZT–Fe in the aged state and after different bipolar cycles.

the cycles, and the shapes of S_{33} – E_3 and ε_{33} – E_3 curves evolve from sprout to butterfly. At the end stage of electric field cycling or after 100 bipolar cycles, the electromechanical properties are comparable to those of quenched samples, suggesting that all the aged ceramics have been successfully de-aged. To quantify the de-aging process, characteristic parameters were extracted from Fig. 4 and summarized in Fig. 5.

The de-aging cycle number dependence of characteristic parameters, including the switchable polarization $2P_r$, maximum polarization $P_{\max}$, remanent strain S_{rem} , maximum strain $S_{\max}$, and remanent piezoelectric coefficient d_{33} are shown in Fig. 5. All the electromechanical properties have an increasing trend within the electric field cycle range. The remanent strain S_{rem} and switchable polarization $2P_r$ have the strongest increment, reaching about 1540% and 298%, respectively, after 100 cycles. An increase of approximately 150% was observed for maximum polarization $P_{\max}$, maximum strain $S_{\max}$, and piezoelectric coefficient d_{33} .

The underlying mechanism accounting for the

Fig. 5 Normalized (a) polarization P_x , (b) strain S_x , and (d) piezoelectric coefficient d_{33} of PSZT–Fe ceramics as functions of de-aging cycle.

dramatic evolution of electromechanical properties of defect engineered piezoceramics after various treatments is proposed here. As Fe is an element with multiple valences, it is crucial to precisely determine the valence of Fe for better understanding the potential mechanism. To this end, X-ray photoelectron spectroscopy (XPS) experiment was conducted. The XPS spectra of Fe 2p for PSZT–Fe ceramics reveal that the dominant valence of Fe ions is 3+ (Fig. S1 in the Electronic Supplementary Material). In this work, Fe ions occupy the Zr/Ti sites because of the nearly equivalent ionic radius, acting as an acceptor dopant. Meanwhile, oxygen vacancies are necessarily introduced at O sites in order to maintain charge neutrality. Fe dopants and oxygen vacancies are the point defects and their statistical distribution in the host PSZT polycrystals plays an important role. Usually, the distribution of these point defects is considered to be random. However, for a given point defect, the local environment or the statistical distribution of surrounding defects could present certain symmetry, termed as defect symmetry [11,24,25].

For the Fe-doped PSZT polycrystals, the short-range distribution of oxygen vacancies centre on a Fe ion is the defect symmetry of interest in this study. The Fe-doped PSZT polycrystals have different crystal symmetries in various temperature regions. Above the Curie temperature T_C (321 °C, refer to the temperature-dependent permittivity in Fig. 1(b)), the PSZT–Fe polycrystals are paraelectrics and show a cubic crystal symmetry (Fig. 6(a)). Given the equivalent of the six oxygen ion sites around a Fe dopant, the probability for oxygen vacancy occupying one of the six oxygen ion sites should be identical, suggesting that the symmetry of point defects is cubic at equilibrium state, conforming to the one of crystal structure.

When PSZT–Fe polycrystals are quenched in air from high temperature (500 °C, well above T_C) to room temperature, tetragonal crystal symmetry develops in the samples, accompanied by the presence of spontaneous polarization P_S along the $\langle 001 \rangle$ directions (Fig. 6(b)). However, defect symmetry remains cubic as sketched in Fig. 6(b), because the migration of oxygen vacancies requires some time to accomplish (the exchange of ions is diffusive) and it cannot be attained in such short time during the quenching process [25]. The un-aged state is preserved, and hence representative hysteresis loops, such as fully opened P_3 – E_3 and d_{33} – E_3 as well as butterfly-shaped S_{33} – E_3 and ε_{33} – E_3 curves, of ferroelectric materials are obtained in the quenched PSZT–Fe samples.

Fig. 6 Schematic illustration of the perovskite structure for (a) an ideal ABO_3 and (b) quenched, (c) aged, and (d) poled Fe-doped PZT-based ceramics.

When slowly cooled from the paraelectric (500 °C) to ferroelectric (room temperature) state, the PSZT–Fe polycrystals undergo the same transition of crystal symmetry from cubic to tetragonal with the quenched samples as aforementioned. Simultaneously, the oxygen vacancies have enough time to migrate to reach a more stable state. Oxygen vacancies would have large probability to occupy site 4, which is closer to the Fe dopant, resulting from the Coulomb attractive force between the effectively positive oxygen vacancies and effectively negative Fe dopant [25]. Therefore, the point defects have a tetragonal symmetry, consistent with the crystal symmetry (Fig. 6(c)). And the charge defects, namely Fe dopant and oxygen vacancy, would form defect dipole D along the direction of spontaneous polarization P_s . When the aged PSZT–Fe polycrystals are subjected to external electric field, the orientation of spontaneous polarization P_s could be switched instantly, whereas the defect dipole along with the defect symmetry cannot afford an abrupt change. Thus, the unchanged defect dipole D would drive domain to switch back to its pristine state, after removing external electric field.

As a result, macroscopic pinched polarization and piezoelectric coefficient hysteresis and a recoverable strain effect (Fig. 3) can be expected.

The above experiments have demonstrated that bipolar electric field cycling can effectively de-age the PSZT–Fe polycrystals, which can be attributed to the randomly redistributed oxygen vacancies induced by bipolar electric field cycling. Cubic defect symmetry is restored in PSZT–Fe samples after consecutive bipolar cycling. In consequence, the electromechanical properties of typical ferroelectrics gradually develop for PSZT–Fe, resembling to the case of quenched state.

For the poled PSZT–Fe polycrystals, both the spontaneous polarization P_s and defect dipole D are driven to be parallel to external poling electric field. Ideally, P_s and D are unidirectional in the poled samples. These immobile unidirectional defect dipoles create an internal bias field, which also aligns along the same direction. When the applied electric field is parallel to internal bias field, extended spontaneous polarization and defect dipole benefit the enhancement of maximum polarization and strain output. However, when an electric field opposite to the internal bias field

is applied, both defect dipole and internal bias field hold their original orientation during this diffusionless process and provide intrinsic restoring forces to impede the switching of spontaneous polarization. As a result, only small fraction of polarization could be switched toward the direction of applied field, and hence strain output would be restrained. Therefore, the internal bias field accounts for the offset of P_3 – E_3 loop, asymmetry in S_{33} – E_3 and ε_{33} – E_3 curves, and large remanent strain (Fig. 3).

4 Conclusions

In summary, the defect mediated evolution of electro-mechanical properties of Fe-doped (Pb,Sr)(Zr,Ti)O₃ (PSZT–Fe) with different treatments, namely quenching, poling, aging, and de-aging, is studied systematically. And a universal mechanism based on defect dipole is proposed to explicate the corresponding changes. The quenched PSZT–Fe ceramics have robust ferroelectric behaviors because of the preserved oxygen vacancies with a cubic symmetry. The defect dipoles between Fe dopant and oxygen vacancy aligning along the direction of spontaneous polarization P_s provide a restoring force for reversible domain switching in the aged PSZT–Fe polycrystals, which are featured with pinched polarization hysteresis and recoverable strain effect. But bipolar electric field cycling could progressively disrupt the defect dipoles and robust ferroelectric properties can be reestablished in the de-aged samples. The asymmetric hysteresis loops of poled PSZT–Fe polycrystals are mainly attributed to the emergence of internal bias field, which aligns along the direction of external poling field.

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Electronic Supplementary Material

Supplementary material is available in the online version of this article at <https://doi.org/10.1007/s40145-021-0460-7>.

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