

Defect Dipole Thermal-stability to the Electro-mechanical Properties of Fe Doped PZT Ceramics

SUN Yuxuan^{1,2}, WANG Zheng¹, SHI Xue¹, SHI Ying^{1,2}, DU Wentong^{1,2}, MAN Zhenyong¹,
ZHENG Liaoying¹, LI Guorong¹

(1. Key Laboratory of Inorganic Functional Materials and Devices, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, China; 2. Center of Materials Science and Optoelectronics Engineering, University of Chinese Academy of Sciences, Beijing 100049, China)

Abstract: The accepted doping ion in Ti^{4+} -site of $\text{PbZr}_y\text{Ti}_{1-y}\text{O}_3$ (PZT)-based piezoelectric ceramics is a well-known method to increase mechanical quality factor (Q_m), since the acceptor coupled by oxygen vacancy becomes defect dipole, which prevents the domain rotation. In this field, a serious problem is that generally, Q_m decreases as the temperature (T) increases, since the oxygen vacancies are decoupled from the defect dipoles. In this work, Q_m of $\text{Pb}_{0.95}\text{Sr}_{0.05}(\text{Zr}_{0.53}\text{Ti}_{0.47})\text{O}_3$ (PSZT) ceramics doped by 0.40% Fe_2O_3 (in mole) abnormally increases as T increases, of which the Q_m and piezoelectric coefficient (d_{33}) at room temperature and Curie temperature (T_C) are 507, 292 pC/N, and 345 °C, respectively. The maximum Q_m of 824 was achieved in the range of 120–160 °C, which is 62.52% higher than that at room temperature, while the dynamic piezoelectric constant (d_{31}) was just slightly decreased by 3.85%. X-ray diffraction (XRD) and piezoresponse force microscopy results show that the interplanar spacing and the fine domains form as temperature increases, and the thermally stimulated depolarization current shows that the defect dipoles are stable even the temperature up to 240 °C. It can be deduced that the aggregation of oxygen vacancies near the fine domains and defect dipole can be stable up to 240 °C, which pins domain rotation, resulting in the enhanced Q_m with the increasing temperature. These results give a potential path to design high Q_m at high temperature.

Key words: defect dipole; temperature characteristic; oxygen vacancy; electro-mechanical property; mechanical quality factor; hardening doping

Perovskite structure piezoelectric ceramic PZT is the most widely used in piezoelectric applications. They show excellent electro-mechanical properties and thermal-stability, thus they are widely used in transducers, drivers, signal amplifiers and other applications^[1]. High Q_m , d_{33} and T_C are important parameters for high power piezoelectric applications. The transducer requires an especially high Q_m , reducing the mechanical loss and heat during long-term mechanical vibration.

Generally, the piezoelectric properties of ceramics are determined by both intrinsic effects (such as lattice distortion) and extrinsic effects (such as reversible and irreversible movement of domain walls under external fields)^[2-3]. For the latter, in most cases, the defect dipoles

should be robust against the rotation under an external electric field, pinning the nearby domain rotation^[4]. After removing the field, the domain is pulled back to its original state by the recovery force of defect dipoles, which is called the “domain pinning effect”^[5].

The oxygen vacancies ($\text{V}_{\text{O}}^{\bullet\bullet}$) in ceramics locate within the bulk volume, along domain wall and grain-boundary. Accordingly, $\text{B-V}_{\text{O}}^{\bullet\bullet}$ can produce three types of domain-pinning forces depending on their locations^[6-7]: namely, the volume effect, the domain wall effect, and the grain boundary effect. The first volume effect is the strongest and most dominant, and the last one is the weakest, since the space charge field is weak.

It is suggested that the addition of acceptor-like Fe

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Biography: SUN Yuxuan (1999–), female, Master candidate. E-mail: sunyuxuan21@mails.ucas.ac.cn

孙雨萱(1999–), 女, 硕士研究生. E-mail: sunyuxuan21@mails.ucas.ac.cn

Corresponding author: LI Guorong, professor. E-mail: grli@mail.sic.ac.cn

李国荣, 研究员. E-mail: grli@mail.sic.ac.cn

ions leads to the formation of $V_O^{\bullet\bullet}$ and hinders the dipole orientation, resulting in polarization difficulties. The acceptor doping as a substitutional state at Ti-site can promote the formation of donor-like $V_O^{\bullet\bullet}$ and lead to formation of the defect dipoles by B- $V_O^{\bullet\bullet}$ pair. Since the rotation of 90° domains generates high mechanical losses (low Q_m), the high Q_m was achieved by the doped PZT-based piezoelectric ceramics. Sangawar *et al.*^[8] observed the enhanced electromechanical properties of $\text{Pb}(\text{Zr}_{0.53}\text{Ti}_{0.47})\text{O}_3 + 1\% \text{Fe}_2\text{O}_3$ (in mass) ceramics and obtained Q_m of 880, d_{33} of 135 pC/N and electromechanical coupling factor (k_p) of 0.535. Chen *et al.*^[9] observed the electro-mechanical properties of $d_{33}=264$ pC/N, $k_p=0.51$, and $Q_m=572$ in Fe_2O_3 doped $(\text{Pb}_{0.92}\text{Sr}_{0.08})(\text{Zr}_{0.555}\text{Ti}_{0.44}\text{Fe}_{0.005})\text{O}_3$ ceramics after polarization.

It is important to understand the thermal-stability of ceramics for the extensive applications. However, up to now, there are few reports for the thermal stability and evolution of defect dipoles in Fe doped PZT ceramics. It is generally expected that the defect dipole dissociation with increasing temperature can make the electro-mechanical properties worsen. In this work, the diverse relationship between the thermal-stability of defect dipoles and electro-mechanical properties of ceramics, and the temperature dependence mechanism of Q_m were investigated. Interestingly, the thermal evolution of the Fe_2O_3 doped $\text{Pb}_{0.95}\text{Sr}_{0.05}(\text{Zr}_{0.53}\text{Ti}_{0.47})\text{O}_3$ (PSZT-Fe) ceramics can enhance their electrical properties at room temperature.

1 Experimental

The ceramics of $\text{Pb}_{0.95}\text{Sr}_{0.05}(\text{Zr}_{0.53}\text{Ti}_{0.47})\text{O}_3$ doped with $x\%$ (in mole, $x=0.36, 0.38, 0.40, 0.42$) Fe_2O_3 were prepared by the solid state reaction method, and abbreviated as PSZT- $x\text{Fe}$. The oxide powder raw materials PbO (99.0%), TiO_2 (99.0%), ZrO_2 (99.9%), SrCO_3 (99.0%) and Fe_2O_3 (99.9%) were mixed by ball milling for 10 h according to the stoichiometric ratio, and then calcined at 850°C for 2 h. After the mixed powders were dried by ball milling twice, the polyvinyl alcohol aqueous solution was used as the binder, and the powders were pelleted and pressed into a round sheet with a diameter of 10 mm and a thickness of about 1 mm. The homogeneous PSZT ceramics were prepared by sintering at 1240°C for 2 h. Two sides of the disc were coated with silver paste and burned to 720°C for 20 min, and then were thermally polarized in a direct-current electric field of 3.2 kV/mm in a silicone oil bath at 150°C for 30 min.

The phase structure of ceramic samples was characterized by a powder X-ray diffractometer (DX-2700BH) with

$\text{Cu-K}\alpha$ radiation, and refined by GSAS software. The ceramic crystal morphology and grain size were observed by a field emission scanning electron microscope (FE-SEM, Phenom Pure-SED G6). The domain structure was observed by piezo response force microscope (PFM, Seiko SPA400/3800N) at different temperatures. The hysteresis loop ($P-E$) and current-voltage ($I-E$) curves were measured by a ferroelectric comprehensive test system (TF-2000E). d_{33} was measured by a quasi-static d_{33} tester (ZJ-3A). Q_m and k_p were tested by an impedance analyzer (Agilent 4294A). Dielectric constant (ϵ), dielectric loss ($\tan\delta$) and thermally stimulated depolarization current (TSDC) were investigated by a wideband dielectric spectrometer (Novocontrol GmbH) with test frequencies ranging from 10^{-1} to 10^7 Hz and test voltage of 1 V.

2 Results and discussions

2.1 Phase structure and electrical properties of ceramics at room temperature

The XRD patterns of PSZT ceramics doped with $x\%$ (in mole, $x=0.36, 0.38, 0.40, 0.42$) Fe_2O_3 are shown in Fig. S1, indicating that the ceramics are a pure perovskite structure. The rhombohedral (R) phase and tetragonal (T) phase coexist in ceramics, and the main phase is T phase. This means that the internal stress caused by 90° domain in ceramics is greater. Fig. 1(a) and Fig. S2 are the Rietveld refinement results of XRD patterns. The main T phase is 89.79%, 92.58%, 91.85% and 95.54% for 0.36%, 0.38%, 0.40%, and 0.42% (in mole) Fe_2O_3 doped ceramics, respectively. However, the lattice axis ratio (c_T/a_T , where a_T and c_T mean lattice constants of the T phase) firstly increases and then decreases as the x value increases, and the maximum tetragonal distortion ($c_T/a_T=1.0188$) exhibits at $x=0.40$.

Fig. 1(b) is the grain morphology of PSZT-0.40Fe ceramics. Other PZT ceramic systems generally have a minimum average grain size (AGS) of $3\text{--}4\text{ }\mu\text{m}$ ^[10-12]. But in this study, PSZT- $x\text{Fe}$ ceramics have finer AGS ($1.3\text{--}1.5\text{ }\mu\text{m}$) by the line cutting method (Fig. 1(c) and Fig. S3), the formation of fine grains in ceramics is generally attributed to the solid solution impurity drag mechanism^[13-15]. High Fe acceptor ions doping at B-site can form cation vacancy pairs at grain boundaries, which hinders grain boundary migration and slows down grain growth rate^[16-17]. The finer grain leads to a higher grain boundary density^[18]. The relative density of ceramic reaches its maximum (96.3%) at $x=0.40$, as its AGS is the finest ($1.3\pm 0.4\text{ }\mu\text{m}$) and the lattice arrangement is more compact (Fig. 1(c)).

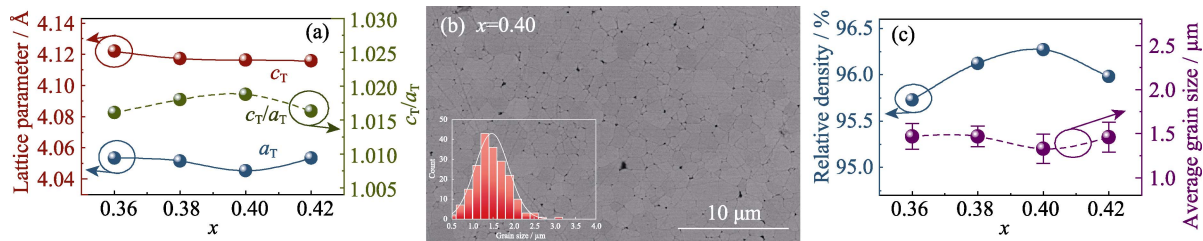


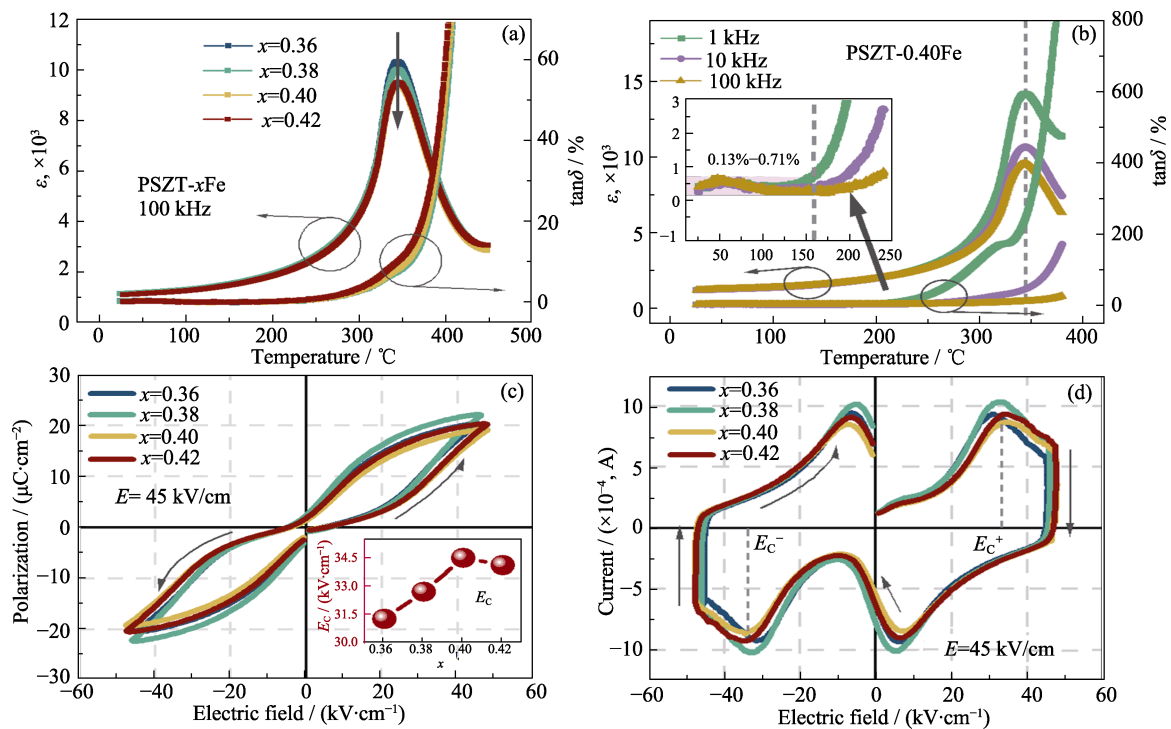
Fig. 1 Lattice, density and SEM image of PSZT-xFe ceramics

(a) Lattice parameters of the T phase; (b) SEM image of PSZT-0.40Fe ceramics with inset showing the grain size distribution; (c) Relative density and average grain size

Fig. 2(a) shows the variations of ε and $\tan\delta$ of PSZT-xFe ceramics with temperature. The curve trends of other ceramic compositions are similar to that of PSZT-0.40Fe. It shows that the maximum dielectric constant ($\varepsilon_{\max}$) decreases as the Fe_2O_3 content increases, indicating an increase in diffuse phase transition, which is caused by the increase of submicron heterogeneous phases in ceramics as the Fe ions doping increases. Fig. 2(b) shows the variations of ε and $\tan\delta$ in the range of 1–100 kHz frequency with temperature. The T_C of ceramics does not vary with increasing frequency, indicating that ceramics are not relaxor ferroelectrics. The low $\tan\delta$ (0.13%–0.71%) at room temperature to 240 °C indicates that the main loss of ceramics is caused by mechanical loss, so the tested Q_m is reliable^[19]. The T_C of ceramics is 343–345 °C (Table 1), which shows that the

ceramic octahedron is stable and positively correlated with the distortion of the perovskite structure. So it is consistent with the variation of tetragonal distortion (c_T/a_T ratio). The ceramics are the displacement type ion crystals, according to the Curie-Weiss coefficient ($C=\varepsilon(T_C-T_\theta)$, where C means the Curie-Weiss coefficient, T_θ means the Curie-Weiss temperature).

The P - E and I - E loops of PSZT-xFe ceramics at a 45 kV/cm field are shown in Fig. 2(c, d). It shows that the ceramics have the pinched P - E loop, which is formed by the pinning of defect dipoles on domains, making polarization and depolarization processes difficult. The ceramics have double current peaks (Fig. 2(d)). The current peaks at a high electric field are related to the rotation of domains, while the peaks at a low field are related to the depolarization of the domains under the pinning of defect

Fig. 2 Dielectric properties, P - E loops and I - E loops of PSZTs

(a) ε and $\tan\delta$ versus temperatures at 100 kHz of PSZT-xFe ceramics; (b) ε and $\tan\delta$ versus temperatures at frequencies of 1, 10 and 100 kHz for PSZT-0.40Fe ceramic with inset showing $\tan\delta$ versus temperatures in the range of 20–250 °C; (c) P - E loops of PSZT-xFe ceramics; (d) I - E loops of PSZT-xFe ceramics. Colorful figures are available on website

Table 1 Electro-mechanical properties of PSZT-xFe ceramics

x	$T_C/^\circ\text{C}$	$T_\theta/^\circ\text{C}$	$C/(\times 10^4)$	$E_C/(\text{kV}\cdot\text{cm}^{-1})$	$P_r/(\mu\text{C}\cdot\text{cm}^{-2})$	$d_{33}/(\text{pC}\cdot\text{N}^{-1})$	Q_m	k_p	σ	$\varepsilon(1\text{ kHz})$
0.36	343	336	7.0	31.3	1.95	300	409	0.67	0.31	1361
0.38	343	335	8.4	32.8	2.76	295	415	0.66	0.31	1253
0.40	345	333	11.3	34.5	1.65	292	507	0.64	0.32	1098
0.42	343	332	10.6	34.2	2.11	294	499	0.65	0.31	1109

* P_r means the remnant polarization.

dipoles. The definition of coercive field (E_C) is the lowest electric field for domain rotation, so the true E_C field is marked by the dashed line^[20]. The trend of E_C field variation is consistent with the c_T/a_T ratio, reaching the maximum (34.5 kV/cm) at $x=0.40$.

The piezoelectric properties of PSZT ceramics are shown in Table 1. It shows that d_{33} and k_p firstly decrease and then increase with the increase of Fe ions doping. Ceramics have the optimized electro-mechanical properties at $x=0.40$, with $Q_m=507$, $d_{33}=292$ pC/N and $k_p=0.64$. Compared to the other three compositions, the higher c_T/a_T ratio of this composition indicates the domain rotation is subjected to greater internal stress. Finer grain leads to higher grain boundary density. Both of them can pin the domains. Besides, the defect dipoles formed by Fe ions doping can form strong coupling with the spontaneous polarization (P_S) in the main T phase^[21], which can prevent the rotation of domains. The difficulty of domain rotation leads to higher Q_m , and defect dipoles play a dominant role.

2.2 Temperature dependence of electro-mechanical properties of PSZT-0.40Fe ceramic

The thermal effect on the electro-mechanical properties of the acceptor-doped ceramics mainly comes from three aspects. Firstly, it is suggested that the entropy effect should lead to the breaking of defect dipoles, which can result in the loss of ability to pin domain rotation^[22-23]. Secondly, it can change the morphology, domain size and domain orientation^[24-25]. Thirdly, defects are redistributed through domain walls and grain boundaries. Thermal effect can also change the phase transition.

Fig. 3 shows the variations of Q_m and dynamic piezoelectric constant (d_{31}) with temperature. For general lead-based piezoelectric ceramics, the Q_m decreases as the temperature increases up to T_C . But in this study, as the temperature rises to 120–160 $^\circ\text{C}$ ($<T_C$), the maximum of Q_m (824) has abnormally increased by 62.52% compared to the room temperature Q_m (507), and the minimum of d_{31} (125 pC/N) has decreased by 3.85% compared to the room temperature d_{31} (130 pC/N). This phenomenon has been observed in several samples. The growth rate of Q_m is much greater than the decline rate of d_{31} . In addition, the ceramic Poisson's ratio (σ) increases linearly from 0.32 to 0.36, while the k_p decreases linearly

from 0.64 to 0.46.

The abnormally high Q_m is speculated to be due to the aggregation of $V_O^{\bullet\bullet}$ near the fine domain walls under thermal activation, leading to the increase in the domain wall effect and hardness in domain rotation. The contribution of d_{33} mainly comes from P_S and polarization generated by rotatable defect dipoles, and d_{31} is positively correlated with d_{33} . Therefore, as the temperature increases from 120 to 160 $^\circ\text{C}$, the enhancement of domain wall effect prevents the rotation of P_S and weakens its contribution to d_{31} . When the temperature rises, the difficulty in rotating defect dipoles decouples, causing an increase in d_{31} .

Fig. 4 exhibits the temperature dependence of domains, which was investigated by the PFM piezoelectric response force model at a frequency of 7 kHz and a time constant of 2 ms. Fig. 4(b-f) shows that the domains become finer and the domain orientation gradually becomes disordered with increasing temperature. This conforms to the Gibbs free energy formula ($\Delta G=\Delta H-T\Delta S$; ΔG : Gibbs free energy change, ΔH : enthalpy change, T : temperature, ΔS : entropy change). Under isobaric conditions, spontaneous processes in the system always proceed towards decreasing Gibbs free energy (G) until equilibrium is obtained^[26-27]. If the system trends to reduce ΔG under the condition that ΔH remains constant and T increases, ΔS needs to be increased. So as the temperature increases, the energy of thermal activation is greater than that of ceramic ferroelectric activity. The long-range order of spontaneous polarization in crystal structure is disrupted by the disorder of thermal motion, resulting in the refinement of ferroelectric domains.

Fig. 5 shows the XRD patterns of PSZT-0.40Fe ceramics in the range of 20–240 $^\circ\text{C}$. As the temperature increases, the intensity of the tetragonal (200)_T diffraction peak increases and the peak position shifts to the left. The R phase slowly transitions to the main phase (T phase) with increasing temperature. In addition, the distance between crystal planes slightly increases and the c_T/a_T ratio decreases, according to Bragg's equation. The internal stress generated by the transition from R to T phase can provide a driving force for the refinement of domains.

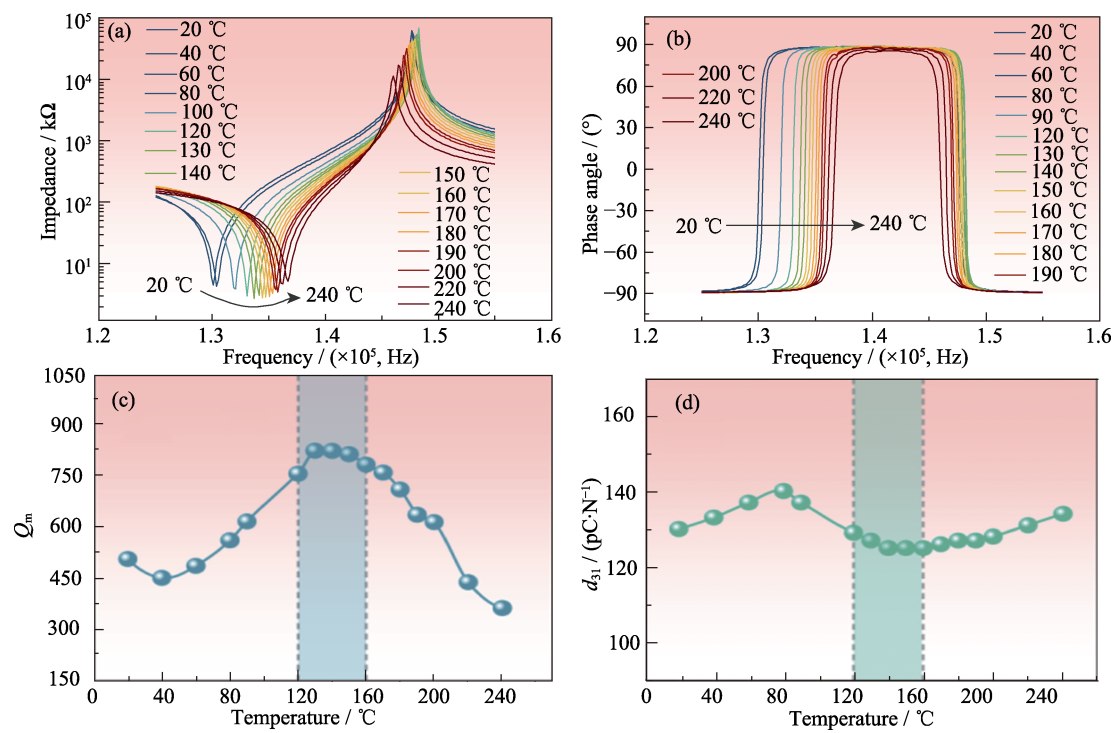


Fig. 3 Electro-mechanical properties of PSZT-0.40Fe ceramic in the range of 20–240 °C

(a) Impedance of 120–160 kHz; (b) Phase angle of 120–160 kHz; (c) Calculated Q_m ; (d) Calculated d_{31} . Colorful figures are available on website

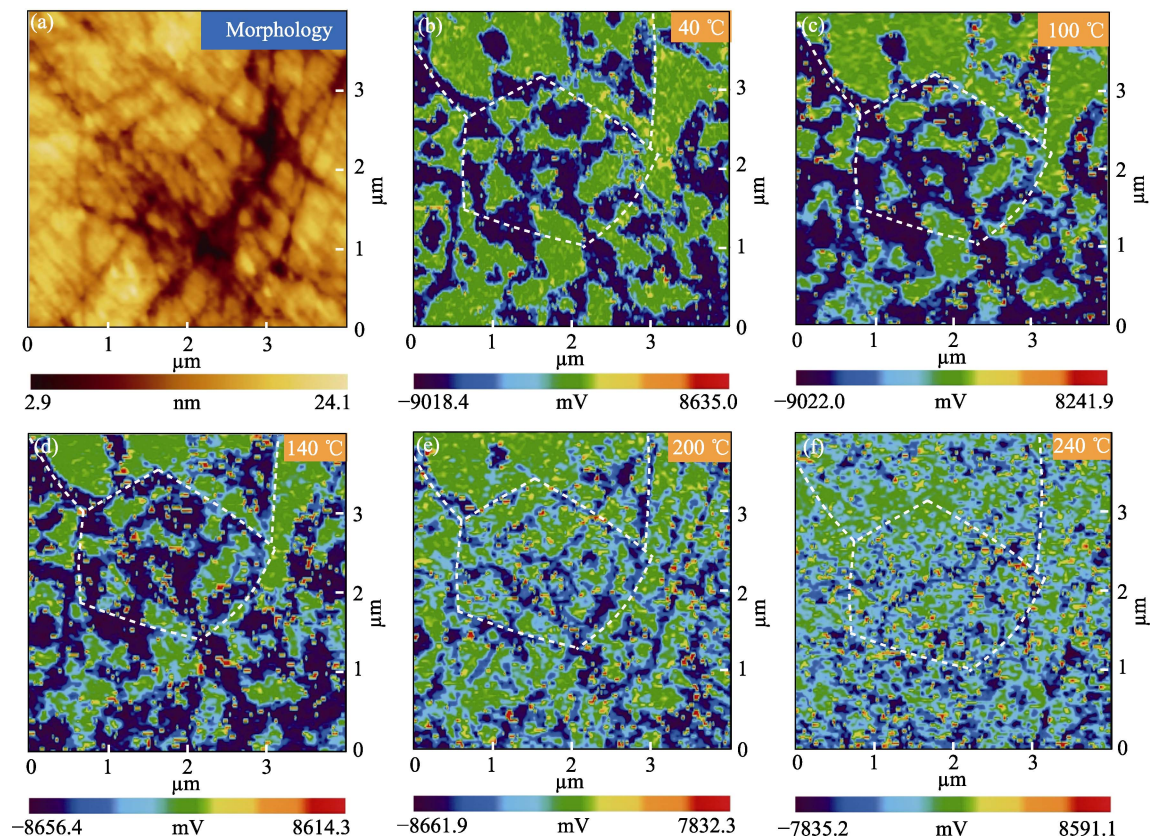


Fig. 4 Morphology and longitudinal piezoelectric response images of PSZT-0.40Fe ceramics in the same region

(a) Morphology at room temperature; (b-f) Longitudinal piezoelectric response image in the range of 40–240 °C. Colorful figures are available on website

Fig. 6 shows the TSDC current of the poled ceramic under room temperature to 300 °C. A widened current peak appears in the range of 120–160 °C and the current

value remains basically unchanged. Combined with the abnormally increased Q_m , it indicates that the internal stress induced domain refinement caused by the

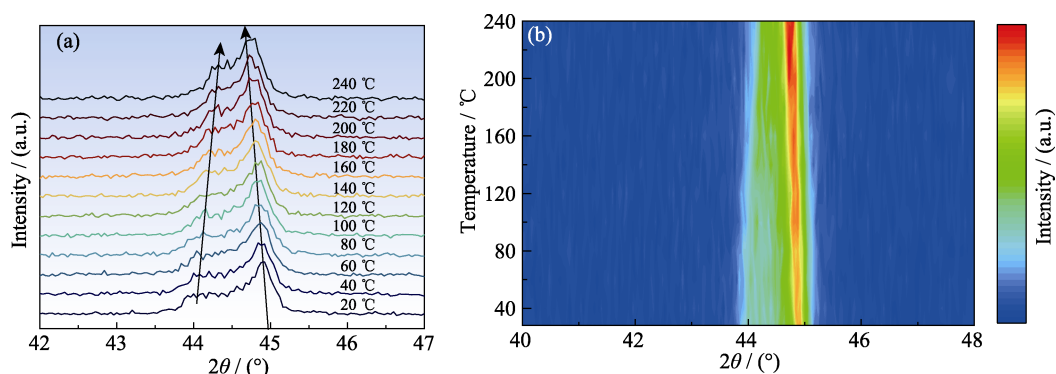


Fig. 5 XRD patterns of PSZT-0.40Fe ceramics in the range of 20–240 °C

(a) XRD patterns; (b) Color map. Colorful figures are available on website

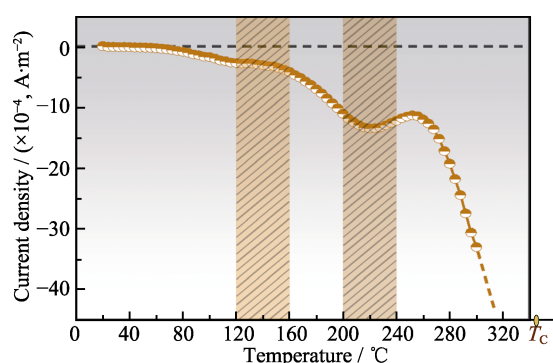


Fig. 6 TSDC curve of poled PSZT-0.40Fe ceramic

transformation from R to T phase under thermal activation, leading to the aggregation of $V_{O}^{\bullet\bullet}$ near the fine domains. Producing more difficulty in rotate defect dipoles, increasing the domain wall effect and hindering domain rotation. In addition, the current peak near 200–240 °C is more pronounced, which is related to the rotation or decoupling of defect dipoles, causing charge release and generating thermally stimulated current.

3 Conclusions

(1) In comparison to the other Fe_2O_3 dopant content, the highest Q_m of the doping 0.40% Fe_2O_3 (in mole) in PSZT ceramics at room temperature is owing to lots of dipole defects caused by Fe ions and $V_{O}^{\bullet\bullet}$, which can prevent domain walls rotation, the other attributions are higher c_T/a_T ratio and smaller grain size. That is because higher c_T/a_T indicates greater internal stress and difficulty in domain rotating. This finer grain leads to higher grain boundary density, and excessive grain boundary density hinders domain rotation.

(2) The abnormal enhancement of Q_m at high temperature, especially in the temperature range of 120–160 °C, is due to the finer domain size and higher density of domain walls per unit volume formed under thermal activation, where R phase transfers to T phase, the

lattice expansion. Thus, $V_{O}^{\bullet\bullet}$ located in grain boundary, domain wall or defect dipole migrates to finer domain wall, leading to a significant enhancement of domain wall effect on the domain rotation. As the temperature further increases, the defect dipoles are uncoupled and lose the ability to pin the domain walls, and the degree of domain wall motion is enhanced, Q_m tends to decrease.

Supporting Materials

Supporting materials related to this article can be found at <https://doi.org/10.15541/jim20240244>.

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缺陷偶极子热稳定性对 Fe 掺杂 PZT 陶瓷机电性能影响研究

孙雨萱^{1,2}, 王政¹, 时雪¹, 史颖^{1,2}, 杜文通^{1,2},
满振勇¹, 郑嘹赢¹, 李国荣¹

(1. 中国科学院 上海硅酸盐研究所, 中国科学院无机功能材料与器件重点实验室, 上海 200050; 2. 中国科学院大学 材料科学与光电子工程中心, 北京 100049)

摘要: 在 $\text{PbZr}_y\text{Ti}_{1-y}\text{O}_3$ (PZT) 基压电陶瓷的 Ti^{4+} 位点掺杂受主离子是一种众所周知的增加机械品质因数(Q_m)的方法, 受主离子与氧空位结合形成缺陷偶极子, 阻碍畴在外电场下的转动。但通常而言, 氧空位随温度升高而迁移, 缺陷偶极子因此而解耦, Q_m 降低。本研究发现掺杂 0.40% (摩尔百分数) Fe_2O_3 的 $\text{Pb}_{0.95}\text{Sr}_{0.05}(\text{Zr}_{0.53}\text{Ti}_{0.47})\text{O}_3$ (PSZT) 陶瓷的 Q_m 随着温度升高而异常增大 (在室温下陶瓷的 Q_m 、压电系数(d_{33})和居里温度(T_C)分别为 507、292 pC/N 和 345 °C), 最大 Q_m 在 120~160 °C 可达 824, 比在室温下高 62.52%, 而动态压电常数(d_{31})仅降低了 3.85%。X 射线衍射(XRD)和压电力显微镜结果表明, 随着温度升高, 陶瓷内部晶面间距增加, 电畴细化。热激励去极化电流结果表明, 缺陷偶极子在 240 °C 以下保持稳定, 细畴附近的氧空位逐渐聚集, 并与温度稳定性良好的缺陷偶极子结合, 增加了对畴的钉扎作用, 导致 Q_m 增加。本研究为压电陶瓷高温下高 Q_m 的应用提供了一种可能性。

关键词: 缺陷偶极子; 温度特性; 氧空位; 机电性能; 机械品质因数; 硬化掺杂

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Supporting materials:

Defect Dipole Thermal-stability to the Electro-mechanical Properties of Fe Doped PZT Piezoelectric Ceramics

SUN Yuxuan^{1,2}, WANG Zheng¹, SHI Xue¹, SHI Ying^{1,2}, DU Wentong^{1,2}, MAN Zhenyong¹,
ZHENG Liaoying¹, LI Guorong¹

(1. Key Laboratory of Inorganic Functional Materials and Devices, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, China; 2. Center of Materials Science and Optoelectronics Engineering, University of Chinese Academy of Sciences, Beijing 100049, China)

Based on the ionic radius of the doped Fe ion (64 pm is Fe^{3+} , 76 pm is Fe^{2+}), Fe ion prefer to occupy the B-site of Ti^{4+} (68 pm) or Zr^{4+} ions (80 pm) of PSZT ceramic, while Sr^{2+} ions (113 pm) replace the A-site of Pb^{2+} ions (120 pm). The tolerance factor t of PSZT ceramics without Fe ions doping is 0.86 which is between 0.77–1.0, showing that this perovskite structure is stable. Fig. S1(b) is the overlapping triple peaks of the $(200)_\text{T}$, $(200)_\text{R}$ and $(002)_\text{T}$ planes in the range of $2\theta=44^\circ\text{--}45^\circ$ fitted by the Gauss profile function.

Due to Fe dope ions enter the B-site of the oxygen octahedron, the orbitals participating in $\text{Fe}_\text{B}\text{--O}$ bonding split, which causes the “Pseudo Jahn-Teller distortion” of the BO_6 octahedron. It can be speculated that the contraction of the two planar Fe–O bonds along the c -axis direction and the elongation of the four axial bonds in the a or b -axis direction result in an increase in c_T/a_T ratio, and conversely, c_T/a_T ratio decreases.

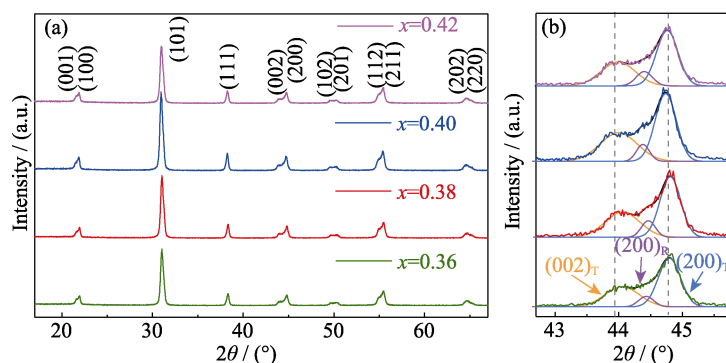


Fig. S1 XRD patterns of PSZT- x Fe ceramics
(a) $2\theta=17.5^\circ\text{--}67.5^\circ$; (b) $2\theta=42.7^\circ\text{--}45.8^\circ$

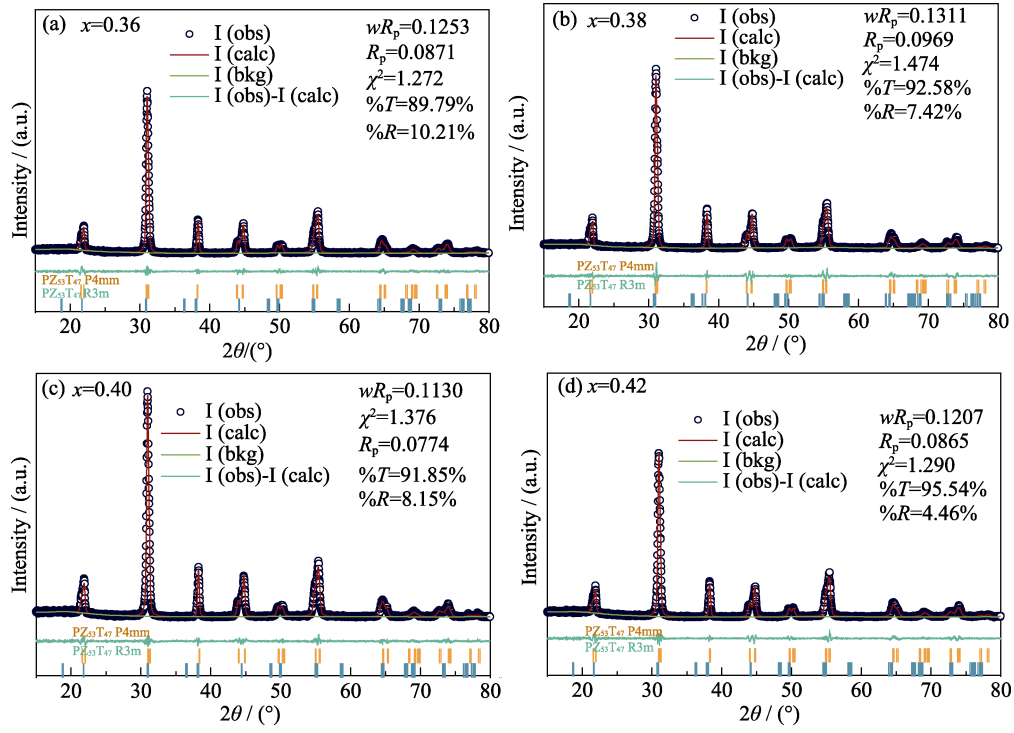


Fig. S2 Rietveld refinement results of PSZT-xFe ceramics XRD patterns
(a) $x=0.36$; (b) $x=0.38$; (c) $x=0.40$; (d) $x=0.42$

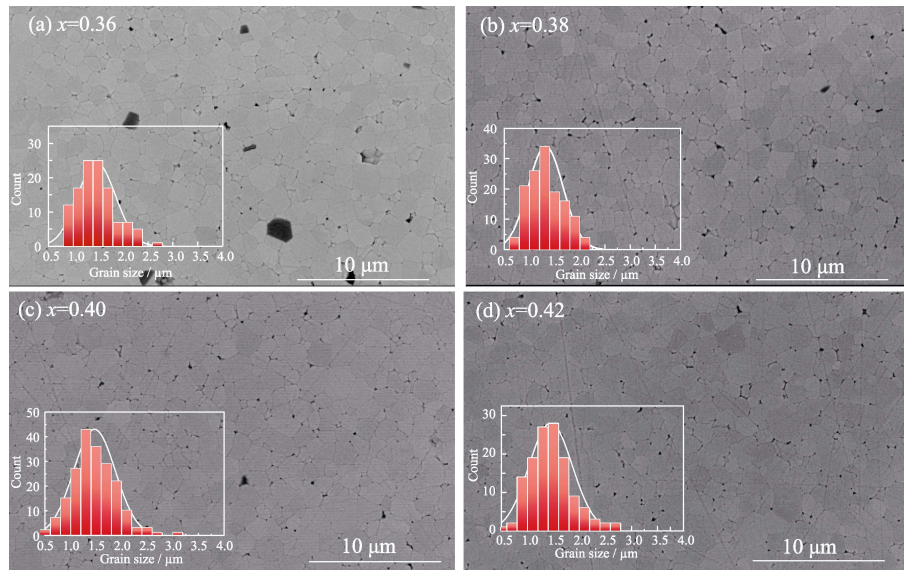


Fig. S3 SEM images of PSZT-xFe ceramics with insets showing corresponding grain size distribution
(a) $x=0.36$; (b) $x=0.38$; (c) $x=0.40$; (d) $x=0.42$