Adjustable giant negative electrocaloric effect in Pb$_{1+x}$ZrO$_3$ thin films

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Abstract

Electrocaloric effect (ECE) driven by electric field is suitable for implementation of built-in cooling in electronic devices. However, most of the known electrocaloric materials show low adiabatic temperature change ($\Delta T$) near room temperature and usually require high electric field. Here, the investigation of ECE in Pb$_{1+x}$ZrO$_3$ ($x=0, 0.1, 0.15$) thin films, which were prepared on Pt/Ti/SiO$_2$/Si substrates by sol-gel method, reveals that both the magnitude and the present temperature range of $\Delta T$ can be controlled by Pb concentration. Through increasing the dosage of PbO, decreased lead vacancies and enhanced interface layer are induced, which postpone the transition from antiferroelectrics to ferroelectrics of PbZrO$_3$ films under a given electric field ($E$), which thus controls the appearance temperature range of negative ECE. As a result, large isothermal entropy change ($\Delta S$) and $\Delta T$ are observed in the temperature range from 260 K to 494 K, depending on the applied electric field and Pb concentration. Giant ECE ($\Delta T \sim -24.9$ K, $\frac{\Delta T}{\Delta E} \sim 0.054$) at room temperature (303 K) is obtained in Pb$_{1.1}$ZrO$_3$ films under 460 kV/cm. This result provides a convenient method for modulating ECE of PbZrO$_3$-based materials and will benefit its applications in cooling devices.

Key words: Negative Electrocaloric Effect; Antiferroelectric; Refrigeration; PbZrO$_3$ thin films.

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Introduction

The electrocaloric effect (ECE) refers to the reversible thermal change of a polar material under applying/removing an external electric field, where the change of polarization by electric field causes adiabatic temperature change ($\Delta T$) and isothermal entropy change ($\Delta S$) [1,2]. The ECE refrigeration has been considered as a promising alternative in modern refrigeration industry. Compared to the traditional vapor compression cooling technology, electrocaloric solid-state cooling has drawn much attention because of its high energy conversion efficiency, environmental-friendly process, low-cost, and small volume [3-5]. The ECE is characterized by $\Delta T$ under external electric fields, where the positive $\Delta T$ is classified as the positive ECE [1, 6] and the reverse belongs to the negative ECE [7, 8]. The coexistence of positive and negative ECEs in one cooling cycle can effectively improve the coefficient of performance and benefit the application in ECE devices.

PbZrO$_3$ (PZO) is a typical antiferroelectric (AFE) material, which possesses positive ECE around the phase transition temperature ($T_c$) from AFE to paraelectric (PE) phase and negative ECE at the transition from AFE to ferroelectric (FE) under the applied electric field [9, 10]. The large positive $\Delta T$ can be achieved around $T_c$ and usually needs high measuring electric field, while the negative ECE, which is considered to originate from the noncollinearity between the applied electric field and ferroelectric dipoles, can be obtained at various temperatures under a moderate field [11, 12]. Therefore, the negative ECE of PZO not only relates to the measured temperature and electric field, but also can be controlled by its structure, chemical constituent, interface, defects, etc. Li et al. pointed that the coexisting of negative and positive ECEs could be optimized by controlling the phase switching of PZO [13]. Wu
et al. reported that both interface and defects show great effect on the ECE of PZO films and remarkably improved the negative ECE by interface engineering [14, 15]. By structural tailoring, Li et al. obtained the large ECE and high coefficient of performance in PZO-based morphotropic phase boundary (MPB) ceramics [16]. Large $\Delta T$ of about -10 K was obtained in 1.0 mol% Yb doped and Nb and Sn co-doped PZO thin films [17, 18]. In addition, cation nonstoichiometry shows a significant effect on the evolution of material properties, especially for the perovskite systems where the polarization and lattice modes are strongly coupled [19, 20]. For PZO, the excess or deficiency of Pb not only affects the defect types but also the amount of antisite defects, where lead ions enter into the site of zirconium ions [21, 22]. As a result, the antiferroelectrics of PZO can be obviously influenced by Pb concentration, which thus controls the temperature-dependent ECE behavior. However, in spite of intense studies about PZO, few works have focused on the impact of Pb nonstoichiometry on ECE. In this paper, Pb$_{1+x}$ZrO$_3$ (x=0, 0.1, 0.15) thin films were fabricated on Pt/Ti/SiO$_2$/Si substrates by sol-gel method. It is found that the temperature ranges of ECE of PZO films can be tuned effectively by Pb concentration. As x varies from 0 to 0.15, the peak temperature of $\Delta T$ changes from 260 K to 309 K under an applied electric field of 460 kV/cm. For Pb$_{1.1}$ZrO$_3$ thin films, large $\Delta T$ of about -24.9 K is obtained under 460 kV/cm at room temperature (303 K), favoring the application of PZO as a room temperature ECE materials.

Experiments

Pb$_{1+x}$ZrO$_3$ (x=0, 0.1, 0.15) thin films were fabricated by sol-gel method. Pb(OAc)$_2$·3H$_2$O and C$_{12}$H$_{28}$O$_4$Zr were used as the precursors of Pb and Zr, which were
dissolved in 2-methoxyethanol, respectively. After adding acetylacetone, the two solutions were mixed at 40 °C for 2 hours. The concentration of final solution was adjusted to 0.2 mol/L by 2-methoxyethanol. After aging for 24 h, the precursor solution was deposited on Pt/Ti/SiO2/Si substrates by spin-coating. Then, the films were dried at 200 °C for 5 min in air on a heating stage and annealed at 700 °C for 8 min in O2 by rapid thermal annealing. The above processes were repeated several times to get the desired film thickness. Finally, the coated films were crystallized at 700 °C for 15 min in O2. To measure the electrical properties of the films, Pt dot electrodes were deposited by sputtering through a shadow mask. X-ray diffraction (XRD, Bruker D8) with Cu Kα radiation was used for the phase analysis. Surface morphology and thickness were studied by Atomic Force Microscope (AFM, Icon) and scanning electron microscopy (SEM, Nova NanoSEM230). The antiferroelectric and dielectric properties were measured by TF2000 standard ferroelectric test unit and HP4194A impedance analyzer coupled with a heating/cooling stage (TMS94). The combination states of Pb 4f and O 1s electrons were examined by X-ray photoelectron spectroscopy (XPS, PHI5000 VersaProbe).

Results and discussion

Figure 1(a) shows the X-ray diffraction patterns of Pb1+xZrO3 (x=0, 0.1, 0.15) thin films. It is observed that all the films possess polycrystalline perovskite structure and no impurity phase is detected within the apparatus resolution, implying that the Pb nonstoichiometry does not change the crystal structure of PZO. Figure 1(b)-(d) show the topography of Pb1+xZrO3 thin films, and spherical nanograin (~20 nm) are observed for the films with x=0. While the grain size increases with the increase of x, large grains (~150 nm) are obtained in the films with x=0.15, implying that the addition of excess PbO benefits the nucleation and growth of PZO. Meanwhile, the surface root mean
square (RMS) roughness increases from 3.20 nm to 4.16 nm as $x$ changes from 0 to 0.15. Such results indicate that though the addition of excess PbO can increase the crystalline perfection through compensation for the possible lead loss during the high-temperature annealing process, the surface RMS roughness is enhanced due to the variation of the nucleation and growth environment.

Figure 2 shows the cross-section images of $\text{Pb}_{1+x}\text{ZrO}_3$ films on Pt/Ti/SiO$_2$/Si substrate, which help us directly observe the thickness and interface layer of the films. It is seen that all the films possess similar thickness of about 220 nm, while different interfaces are observed with the increase of $x$. As shown in Fig. 2, compared with PbZrO$_3$, the inter-diffusion between Pt bottom electrodes and films is more obvious in $\text{Pb}_{1.10}\text{ZrO}_3$ and $\text{Pb}_{1.15}\text{ZrO}_3$ films. Such diffusion can increase the interface thickness and thus affect the electric properties of films since the charge defects prefer to accumulate at the interface.

In addition, lead-antisite defects, which have smaller formation energy than that of zirconium vacancies under oxygen-rich growth conditions, can be formed even there is only a small amount of lead excess [19]. In order to explore the evolution of antisite defects with the variation of $x$, $\text{Pb}_{1+x}\text{ZrO}_3$ films were investigated by XPS technique. Figure 3(a)-(c) shows the Pb 4f XPS spectra of $\text{Pb}_{1+x}\text{ZrO}_3$ thin films. Two typical peaks are observed at about 138.0 eV and 142.9 eV for the Pb 4f 7/2 and 4f 5/2 electrons, respectively. It is reported that the valence of antisite Pb$_Z$ can possess 4+ under oxidizing conditions to maintain electrical neutrality [22-24]. While as seen from Fig. 3(a)-(c), both peaks show symmetrical patterns, and no obvious shoulder or satellite peaks are observed, implying that the valence of Pb ions is dominated by 2+ probably
due to the relatively low oxygen pressure (the flowing oxygen is used in the experiments). That is to say, a small amount of antisite defects PbZr\(^{2+}\) may be present in the films with larger x, which can increase the oxygen vacancies (\(V_o^-\)) due to the charge imbalance requirement. The concentration of \(V_o^-\) can also be estimated by XPS. As shown in Fig. 3(d)-(f), two associated peaks are observed in O1s XPS spectra of Pb\(_{1+x}\)ZrO\(_3\) films, which can be fitted into two peaks. The fitted peak with lower binding energy of about 529.4 eV, denoted by O[1], represents the oxygen in the lattice, while the other one at about 531.2 eV, denoted by O[2], is assigned to absorbed oxygen species, relating to the presence of \(V_o^-\). The relative amount of oxygen vacancies can be estimated by \(I_{O[2]}/I_{O[1]}\) (\(I_o\) represents the integral intensity of the corresponding peak) [25]. As shown in the inset of Fig. 3(f), \(I_{O[2]}/I_{O[1]}\) increases as x increases, indicating that more \(V_o^-\) are involved in the samples with the increase of x and implying the formation of the antisite defects of PbZr\(^{2+}\) since \(V_o^-\) induced by V\(_{Pb}\) should be decreased by the addition of PbO. Taken together, by adding excess PbO, lead vacancies (V\(_{Pb}\)) gradually decrease while the antisite defects gradually increase, which will affect the polarization switching and thus the ECE of PZO.

Figure 4 shows the hysteresis loops and switching currents of Pb\(_{1+x}\)ZrO\(_3\) thin films at room temperature. Typical AFE loops are observed for Pb\(_{1+x}\)ZrO\(_3\) films with different x. While with the increase of x, the forward electric field (\(E_f\)) from AFE to FE increases from 415 kV/cm to 481 kV/cm under the applied electric field of about 550 kV/cm. At around \(E_f\), the polarization increases quickly with the increase of electric field, contributing to negative ECE. Therefore, the variation of \(E_f\) can directly affects the
appearing temperature range of ECE. As aforementioned, the adding of excess PbO can compensate for the lead loss during the high-temperature annealing process and decrease the concentration of \( V_{Pb} \). Such a decrease can postpone the transition from antiferroelectric to ferroelectric and contribute to the increase of \( E_f \) since \( V_{Pb} \) benefits the movement of domain walls and thus promotes the polarization reorientation [26].

Moreover, compared with PZO, the interface layer between films and Pt bottom electrodes is more obvious in \( \text{Pb}_{1.10}\text{ZrO}_3 \) and \( \text{Pb}_{1.15}\text{ZrO}_3 \) films (Fig. 2). When an electric field is applied, it firstly concentrates on such interface layer due to its lower dielectric constant and then switches the \( \text{Pb}_{1+x}\text{ZrO}_3 \) films to ferroelectrics, also contributing to the enhanced \( E_f \) with increasing \( x \). In addition, it is reported that the antisite defects in PZO can increase its saturation polarization \( (P_s) \) while the residual of PbO shows the opposite effect [19, 21]. For our \( \text{Pb}_{1+x}\text{ZrO}_3 \) films, both the antisite defects and the possible residual of PbO increase with the increase of PbO concentration. The competition effect of these two factors causes a nonmonotonic variation of \( P_s \) and as the result, the largest \( P_s \) of about 69 \( \mu \text{C/cm}^2 \) is observed in \( \text{Pb}_{1.10}\text{ZrO}_3 \) under the applied electric field of about 550 kV/cm, which benefits the enhancement of \( \Delta T \).

The dielectric measuring results can also confirm the variation of defects. Figure 5(a)-(c) shows the temperature dependent dielectric constant at various frequencies. Compared with pure PZO, the \( T_c \) of \( \text{Pb}_{1.10}\text{ZrO}_3 \) and \( \text{Pb}_{1.15}\text{ZrO}_3 \) films slightly increases probably due to the improvement of crystalline perfection by compensating for the lead loss. Meanwhile, a small dielectric anomaly at around 380 K is observed in \( \text{Pb}_{1.10}\text{ZrO}_3 \) and becomes more predominant in \( \text{Pb}_{1.15}\text{ZrO}_3 \), which possibly stems from the antisite
defects. Though more antisite defects are possibly involved in Pb$_{1.15}$ZrO$_3$ films, the excessive residual of PbO decreases its dielectric constant and $P_s$ (Fig. 4(c)).

On the basis of the above results, fascinating ECE is expected in Pb$_{1+x}$ZrO$_3$ thin films. In order to evaluate the ECE, P-E loops of the Pb$_{1+x}$ZrO$_3$ thin films were measured under different electric fields and temperatures. As shown in Fig. 5(d)-(f), at a given electric field, the Pb$_{1+x}$ZrO$_3$ films gradually translate from AFE to FE with the increase of temperature, resulting in a rapid increase of polarization. Figure 6 (a)-(c) shows the temperature dependence of maximum polarization ($P$-$T$ curves), which were extracted from the P-E loops measured at various electric fields and temperatures. The maximum polarization ($P_{\text{max}}$) of all the Pb$_{1+x}$ZrO$_3$ thin films increases rapidly with the increase of temperature at around $E_f$ for a given electric field, where $E_f$ changes with the variation of temperature, electric field, and Pb concentration. When the transition from AFE to FE finishes, $P_{\text{max}}$ tends to saturation and then decreases quickly at around $T_c$. The rapid increase and decrease of polarization respectively correspond to the negative and positive ECEs.

Now we discuss the ECE of Pb$_{1+x}$ZrO$_3$ thin films. According to the Maxwell relation $\left( \frac{\partial P}{\partial T} \right)_E = \left( \frac{\partial S}{\partial E} \right)_T$, $\Delta S$ and $\Delta T$ can be given by the following equations:

$$
\Delta S = -\frac{1}{\rho} \int_{E_1}^{E_2} \left( \frac{\partial P}{\partial T} \right)_E dE
$$

$$
\Delta T = -\frac{T}{\rho C_p} \int_{E_1}^{E_2} \left( \frac{\partial P}{\partial T} \right)_E dE
$$

Where $\rho$ is the density, $C_p$ is the heat capacity, $P$ is the polarization, and $E$ is the electric field (here, $E_1 = 0$ is chosen as the initial electric field and $E_2$ is the applied electric field. $\rho = 8.22$ g/cm$^3$ and $C_p = 330$ J/(K * kg) are used in the
calculation [27]. The values of \( \left( \frac{\partial P}{\partial T} \right)_E \) are obtained by fitting the \( P-T \) curves using a ninth-order polynomial. It should be noted that a constant value of \( C_p \) is used for simplicity though it usually changes with the variation of temperature [28]. As is shown in Fig. 6(d)-(i), interesting variations with the increase of temperature are observed for both \( \Delta S \) and \( \Delta T \). There are four features worth mentioning. First, large negative \( \Delta S \) and \( \Delta T \), which dependent on the applied electric field and Pb concentration, are observed in the temperature from 260 K to 494 K. Second, for a given electric field, the peak temperature of \( \Delta T \) \( (T_{\Delta T_{max}}) \) increases with the increase of \( x \), corresponding to the increased \( E_f \) in Fig. 4. As given in Table I, \( T_{\Delta T_{max}} \) increases from 260 to 309 K under 460 kV/cm as \( x \) increases from 0 to 0.15, changing almost 50 K and favoring the application of PZO as a cooling device around room temperature. Third, \( T_{\Delta T_{max}} \) decreases with the increase of applied electric field for a fixed Pb concentration. For PbZrO\(_3\) and Pb\(_{1.1}\)ZrO\(_3\) thin films, \( T_{\Delta T_{max}} \) decreases from 453 to 260 K and from 490 to 303 K respectively as the applied electric field varies from 230 to 460 kV/cm (Table I). That is to say, the negative ECE can be effectively controlled by applied electric field and Pb concentration. Finally, larger polarization is one of the key factors to the improvement of \( \Delta T \) since it shows great effect on the value of \( \left( \frac{\partial P}{\partial T} \right)_E \). Therefore, compared with PbZrO\(_3\) and Pb\(_{1.15}\)ZrO\(_3\), Pb\(_{1.1}\)ZrO\(_3\) films possess larger \( \Delta T \) at the same electric field because of its larger polarization. It is seen from Table I that \( \Delta T \) of Pb\(_{1.1}\)ZrO\(_3\) films reaches -24.9 K at room temperature (303 K) under 460 kV/cm. Compared with other reported values of PZO-based materials, such \( \Delta T \) and its corresponding \( \frac{\Delta T}{\Delta E} \) are all larger (Table II). Taken together, superior negative ECE can
be obtained around room temperature by controlling the Pb concentration in Pb\textsubscript{1+x}ZrO\textsubscript{3} thin films. Moreover, as shown in Fig. 6(d)-(f), positive ECE is also observed in Pb\textsubscript{1+x}ZrO\textsubscript{3} films around \( T_c \) corresponding to the transition from AFE to PE phase. The combination of positive and negative ECEs in one cooling cycle can effectively improve the refrigeration efficiency.

**Conclusions**

In summary, we have investigated the ECE of Pb\textsubscript{1+x}ZrO\textsubscript{3} \((x=0, 0.1, 0.15)\) thin films on Pt/Ti/SiO\textsubscript{2}/Si substrates by sol-gel method. Excess PbO can result in the decrease of Pb vacancies and the increase of interface thickness, which can postpone the transition from AFE to FE of PZO under a given electric field and thus controls the appearance temperature range of negative ECE. The \( \Delta T \) peak can be tuned effectively from 260 to 309 K by changing \( x \) from 0 to 0.15. While the superfluous PbO can decrease the polarization and thus \( \Delta T \). Based on these competition effects, larger ECE \((\Delta T\sim −24.9 \text{ K, } \frac{\Delta T}{\Delta E}\sim 0.054)\) is obtained at room temperature \((303 \text{ K})\) in Pb\textsubscript{1.1}ZrO\textsubscript{3} films under 460 kV/cm. The present work provides a feasible alternative method for modulating ECE of PZO-based materials and will favor its applications in solid-state refrigeration.

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References

1. F.P. Zhuo, Q. Li, J.H. Gao, Y.J. Wang, Q.F. Yan, Y.L. Zhang, X.Q. Xi, X.C. Chu, W.W. Cao, Appl. Phys. Lett. 108, 082904 (2016)
2. B. Lu, P.L. Li, Z.H. Tang, Y.B. Yao, X.S. Gao, W.G. Kleemann, S.G. Lu, Sci. Rep. 7, 45335 (2017)
3. M. Valant, Prog. Mater. Sci. 57, 980 (2012)
4. R.J. Ma, Z.Y. Zhang, K. Tong, D. Huber, R. Kornbluh, Y.S. Ju, Q.B. Pei, Science 357, 1130 (2017)
5. A. Kitanovski, U. Plaznik, U. Tomc, A. Poredoš, Int. J. Refrig. 57, 288 (2015)
6. T.D. Zhang, W.L. Li, W.P. Cao, Y.F. Hou, Y. Yu, W.D. Fei, Appl. Phys. Lett. 108, 162902 (2016)
7. B. Allouche, H.J. Hwang, T.J. Yoo, B.H. Lee, Nanoscale 12, 3894 (2020)
8. Y. Bai, G.P. Zheng, S.Q. Shi, Mater. Res. Bull. 46, 1866 (2011)
9. J. Parui, S. B. Krupanidhi, Phys. Status. Solidi. Rapid. Res. Lett. 2, 230 (2008)
10. M.Y. Guo, M. Wu, W.W. Gao, B.W. Sun, X.J. Lou, J. Mater. Chem. C 7, 617 (2019)
11. Xihong Hao, Jiwei Zhai, Ling Bing Kong, and Zhengkui Xu, Prog. Mater. Sci. 63, 1 (2014)
12. I. Ponomareva, S. Lisenkov, Phys. Rev. Lett. 108, 167604 (2012)
13. Y. Li, H.C. Gao, Y.Y. Liu, L.W. Zhang, X.H. Hao, J. Mater. Sci: Mater. Electron. 29, 14528 (2018)
14. M. Wu, D.S. Song, M.Y. Guo, J.H. Bian, J.N. Li, Y.D. Yang, H.T. Huang, S.J. Pennycook, X.J. Lou, ACS Appl. Mater. Interfaces 11, 36863 (2019)
15. M. Wu, D.S. Song, G. Vats, S.C. Ning, M.Y. Guo, D.W. Zhang, D.Q. Xue, S.J. Pennycook, X.J. Lou, J. Mater. Chem. C 6, 10332 (2018)
16. J. Li, J. Li, H.H. Wu, S. Qin, X. Su, Y. Wang, X. Lou, D. Guo, Y. Su, L. Qiao, Y. Bai, ACS Appl. Mater. Interfaces 12, 45005 (2020)
17. W.H. Wang, X.Q. Chen, Q. Sun, T.Z. Xin, M. Ye, J. Alloy. Compd. 830, 154581 (2020)
18. Q.L. Zhao, T.Y. Sheng, L. Pang, G.P. He, J.J. Di, L. Zhao, Z.L. Hou, M.S. Cao, RSC Adv. 9, 34114 (2019)
19. D.A. Tenne, A.K. Farrar, C.M. Brooks, T. Heeg, J. Schubert, H.W. Jang, C.W. Bark, C.M. Folkman, C.B. Eom, D.G. Schlom, Appl. Phys. Lett. 97, 142901 (2010)
20. S. Lee, Z.K. Liu, M.H. Kim, C.A. Randall, J. Appl. Phys. 101, 054119 (2007)
21. R. Kagimura, D.J. Singh, Phys. Rev. B 78, 174105 (2008)
22. G. Suchanek, A. Deyneka, L. Jastrabik, M. Savinov, G. Gerlach, Ferroelectrics 318, 3 (2005)
23. R.W. Whatmore, Z. Huang, M. Todd, J. Appl. Phys. 82, 5686 (1997)
24. M. Chotsawat, K. Sarasamak, P. Thanomngam, J.T. Thienprasert, Integr. Ferroelectr. 156, 86 (2014)
25. C.M. Pradier, C. Hinnen, K. Jansson, L. Dahl, M. Nygren, A. Flodström, J. Mater. Sci. 33, 3187 (1998)
26. X.J. Qiao, W.P. Geng, X. Chen, L. Zhang, D.W. Zheng, L.Y. Zhang, J. He, X.J. Hou, Y. Yang, M. Cui, K.Y. Zeng, X.J. Chou, Sci. China. Mater. 63, 2325 (2020)
27. W. Geng, Y. Liu, X. Meng, L. Bellaiche, J.F. Scott, B. Dkhil, A. Jiang, Adv. Mater. 27, 3165 (2015)
28. E. Sawaguchi, G. Shirane, Y. Takagi, J. Phys. Soc. Jpn. 6, 333 (1951)
29. M. Ye, T. Li, Q. Sun, Z.K. Liu, B.L. Peng, C.W. Huang, P. Lin, S.M. Ke, X.R. Zeng, X. Peng, L. Chen, H.T. Huang, J. Mater. Chem. C 4, 3375 (2016)
30. S.P. Bag, X. Hou, J.T. Zhang, S.H. Wu, J. Wang, IEEE. Trans. Electron. Devices. 67, 1769 (2020)
31. Z.H. Niu, Y.P. Jiang, X.G. Tang, Q.X. Liu, W.H. Li, X.W. Lin, S.G. Lu, Mater. Res. Lett. 6, 384 (2018)
32. Y.C. Zhao, Q.X. Liu, X.G. Tang, Y.P. Jiang, B. Li, W.H. Li, L. Luo, X.B. Guo, ACS Omega 4, 14650 (2019)
Fig. 1 (a) XRD patterns of Pb$_{1+x}$ZrO$_3$ thin films. AFM surface morphology of (b) PbZrO$_3$, (c) Pb$_{1.10}$ZrO$_3$, (d) Pb$_{1.15}$ZrO$_3$ thin films.

Fig. 2 SEM cross-sectional images of (a) PbZrO$_3$, (b) Pb$_{1.10}$ZrO$_3$, (c) Pb$_{1.15}$ZrO$_3$ thin films.
Fig. 3  (a)-(c) Pb 4f and (d)-(f) O 1s XPS spectra and their dividing results of Pb_{1+x}ZrO_3 thin films. The inset in (f) represents the x dependent I_{O[2]}/I_{O[1]}.

Fig. 4 Room-temperature antiferroelectric hysteresis loops (P-E loops) and switching currents of (a) PbZrO_3, (b) Pb_{1.10}ZrO_3, (c) Pb_{1.15}ZrO_3 thin films under 550 kV/cm.
Fig. 5 Temperature dependent dielectric constant $\varepsilon_r$ of (a) PbZrO$_3$, (b) Pb$_{1.10}$ZrO$_3$, (c) Pb$_{1.15}$ZrO$_3$ thin films at various frequencies of $10^2$ Hz, $10^{2.5}$ Hz, $10^3$ Hz, $10^{3.5}$ Hz, $10^4$ Hz, $10^{4.5}$ Hz, $10^5$ Hz, $10^{5.5}$ Hz, $10^6$ Hz. $P$-$E$ loops of (d) PbZrO$_3$, (e) Pb$_{1.10}$ZrO$_3$, (f) Pb$_{1.15}$ZrO$_3$ thin films measured under 460 kV/cm and different temperatures.

Fig. 6 Temperature dependent (a)-(c) polarization ($P$-$T$ curves), (d)-(f) $\Delta T$ and (g)-(i) $\Delta S$ of Pb$_{1+x}$ZrO$_3$ thin films measured under various electric fields.
**Table I.** The ECE parameters of Pb$_{1+x}$ZrO$_3$ thin films.

| Sample         | $T_{\Delta T_{\text{max}}}$ (K) | $\Delta T_{\text{max}}$ (K) | 230 kV/cm | 276 kV/cm | 322 kV/cm | 368 kV/cm | 414 kV/cm | 460 kV/cm |
|----------------|---------------------------------|-----------------------------|-----------|-----------|-----------|-----------|-----------|-----------|
| PbZrO$_3$      | 453                             | -9.1                        | 426       | 389       | 343       | 305       | 260       |
| Pb$_{1.2}$ZrO$_3$ | 490                            | -7.9                        | 451       | 424       | 384       | 342       | 303       |
| Pb$_{1.12}$ZrO$_2$ | 494                           | -5.9                        | 464       | 437       | 399       | 359       | 309       |

**Table II.** The negative ECE values and their corresponding conditions for various PZO-based materials.

| Sample                        | Morphology  | Temperature (°C) | $\Delta T$ (K) | $\Delta E$ (kV/cm) | $-\Delta T/\Delta E$ (K/cm/kV) |
|-------------------------------|-------------|------------------|----------------|--------------------|-------------------------------|
| Eu-PZO [29]                   | 550 nm thin film | 30              | -6.62         | 709                | 0.009                          |
| Yb-PZO [17]                   | 400 nm thin film | 70              | -12.5         | 800                | 0.016                          |
| Pb(Zr$_{0.52}$Ti$_{0.48}$)O$_3$ [30] | 650 nm thin film | 135             | -1.81         | 374                | 0.005                          |
| (Pb$_{0.95}$La$_{0.05}$)[$Zr$_{0.35}$Ti$_{0.65}$]O$_3$ [31] | Bulk ceramics | 190             | -12.45        | 50                 | 0.249                          |
| (Pb$_{0.95}$La$_{0.05}$)[$Zr$_{0.2}$Sn$_{0.3}$Ti$_{0.9}$]O$_3$ [32] | Bulk ceramics | 30              | -11.5         | 110                | 0.105                          |
| Pb$_{1.96}$Nb$_{0.04}$[$Zr$_{0.66}$Sn$_{0.13}$]Ti$_{0.11}$O$_3$ [18] | 1 µm film | 50              | -9.8          | 200                | 0.049                          |
| PZO before [14]               | 400 nm film | 93              | -18.5         | 700                | 0.026                          |
| Pb$_{1.7}$ZrO$_3$ (This work) | 217 nm film | 30              | -24.9         | 460                | 0.054                          |