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Low hysteresis and enhanced figure-of-merit of pyroelectric energy conversion at compatible phase transformation



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ABSTRACT

The pyroelectricity of polar materials provides great potential for electricity generation from waste heat. The pyroelectric effect of the material can be magnificently enhanced at a first-order phase transformation due to the abrupt jump in spontaneous polarization within a narrow temperature range. Here, we show that the performance of energy conversion by phase transformation is inversely resonant with the hysteresis of thermally driven structural transformations in a $(Ba_{1-x}Sr_x)$ ($Hf_{0.02}Ce_{0.005}Ti_{0.975}$)O₃ system, corresponding to a singular lattice distortion mode satisfying the crystallographic compatibility condition. Among the finely tuned Sr compositions from 0.04 to 0.10, we discovered that Sr0.07 composition is a promising material candidate in this material system for pyroelectric energy conversion. Our work suggests a rational strategy of material development for pyroelectric energy conversion applications.

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About two-thirds of the residential, industrial, and commercial energy consumption is dissipated as waste heat.¹ With the rising usage of electronic devices and computers in data centers, the release of lowgrade waste heat with temperatures below 150 °C has massively increased. To recycle the waste heat and convert it back to electricity not only is a relief of global warming but also plays a profound role in energy economy. Pyroelectric materials that possess a temperaturedependent spontaneous polarization shed light on waste heat harvesting, particularly suitable for electricity generation by small thermal fluctuations.^{2,3} Polar materials, such as relaxor ferroelectrics, are commonly exploited for the pyroelectric energy conversion, characterized by the pyroelectric coefficient dP/dT, where P is the spontaneous polarization at temperature T. Utilizing a first-order phase transformation, the pyroelectric effect of these materials can be magnified by orders of magnitude as shown in Table I for both lead and non-lead ferroelectrics. For most lead based relaxor ferroelectrics, their phase transformation temperatures are relatively high (i.e., around 180 °C), which makes it impractical for low-grade waste heat harvesting. It has been demonstrated in several conversion devices⁴⁻⁶ that the generated pyroelectric current is indeed drastically improved by orders of magnitudes within a small temperature range of 10-15 °C near the first-order phase transformations without any connection to external bias fields.

The performance of a phase-transforming energy conversion device is analyzed by a thermodynamic model⁴ considering a conversion cycle around the temperature in the vicinity of a phase transformation from ferroelectric phase to paraelectric phase and back to ferroelectric phase. The proposed thermodynamic cycle is different from any of Olsen's cycles¹¹ because the external bias electric field is removed throughout the whole energy conversion process. In this case, the work output density (i.e., joule per volume) is analyzed as⁴

$$w = \frac{2\llbracket P \rrbracket \kappa}{\tau} \frac{AR}{d} (T_H - T_L), \tag{1}$$

where $[\![P]\!]$ is the polarization change, $\kappa = |dP/dT|_{\text{max}}$ is the steepest polarization change, T_H and T_L are the upper and lower bounds of temperature between which the thermal cycle is performed, and τ is the time used for such a process. In the second term, A and d are the area and thickness of the planar capacitor made by the transforming material, and R is the load resistor connected in the external electric circuit to pick up the generated electric energy. The first term of Eq. (1) underlies the intrinsic material properties and directly relates to the ferroic-thermal response of the material; we define it as the figure-of-merit (FOM) for the thermodynamic process using phasetransforming ferroelectrics. If the temperature range $[T_H, T_L]$ fully

TABLE I. Pyroelectric coefficients (dP/dT) of lead and non-lead relaxor ferroelectrics
at phase-transition temperature $T_{\rm c}$ and non-transition temperature below $T_{\rm c}$.

	T _c	<i>dP/dT</i> at <i>T</i> _c (μC/cm ² K)	dP/dT at $T < T_c$ $(\mu C/cm^2 K)$
BaTiO ₃ ^{7,8}	120 °C	1.0	0.0016
barium titanate (BT)- barium calcium titanate (BCT) ⁶	110 °C	0.87	0.08
$Pb(Mg_1/3Nb_2/3)O_3$ - $PbTiO_3^9$	180 °C	0.65	0.055
$\operatorname{Ba}(\operatorname{Zr},\operatorname{Ti})O_3^{10}$	125 °C	0.58	< 0.05

covers the phase transformation region, the transformation time τ is proportional to the total heat exchanged between the material and its surroundings. Suppose the temperature oscillations barely cover the transformation, $\tau \propto \ell$, where ℓ is the latent heat of the transforming material. Then, it is reasonable to consider the term

$$FOM = \frac{\llbracket P \rrbracket \kappa}{\ell}, \qquad (2)$$

as the figure-of-merit (FOM) to index the performance of the energy conversion by a first-order phase transforming ferroelectric converter. This FOM yields the SI unit of $C^2 J^{-1} K^{-1} m^{-1}$.

The FOM underlies a material development strategy for phasetransforming ferroelectrics, but it does not account the thermal hysteresis between the transition temperatures during heating and cooling branches. In general, due to lattice incompatibility between crystal structures in low/high temperature phases, the transition temperatures usually differ by about 5 to 20 K.^{12–14} To harvest thermal fluctuations, especially within small temperature differences, it is essential to minimize such thermal hysteresis for the reversible phase transformations. In this paper, we demonstrate a material development method to achieve the simultaneous optimization for both FOM and thermal hysteresis by tuning the lattice compatibility between the low/high temperature phases.

A non-lead ferroelectric Hf, Ce doped Ba_{1-x}Sr_xTiO₃ system is selected as the developing candidates, since barium titanate-based ferroelectrics usually exhibit first-order phase transformations at 100 to 130 °C.^{3,10,15,16} Without lead toxicity, it is a sustainable material system for low-grade waste heat harvesting. The dopants Hf and Ce are chosen based on the literature and our previous studies in similar phase-transforming ferroelectric systems. Experimental evidence¹⁷ shows that the element Hf can improve the electrocaloric effect in the barium titanate system and can lower the transformation temperature of its first-order phase transformation. Since the pyroelectric effect is a reverse of electrocaloric effect and both are related to the thermalelectric response of a ferroelectric material, we conjecture that the addition of element Hf could amplify the polarization sensitivity in response to the thermal variation, especially near the first-order phase transformation. The dopant Ce reduces the leakage current in the barium titanate system, as seen in Refs. 6 and 18. Our previous experimental study shows that only subtle addition of Ce lowers the electric leakage current density by a factor of 6, compared to that of the pure barium titanate. Therefore, we fixed the composition of Hf and Ce at 2 and 0.5 at. % based on the literature so that the basic transport properties of this material family meet our goal to convert low-grade waste heat below 100 °C to electricity without prominent electric degradation during the conversion cycles due to the intrinsic leakage. Sr additions can further lower the transition temperature,¹⁹ more importantly, the Sr composition is used as a tuning parameter to change the lattice parameters, so that the crystallographic compatibility between the tetragonal and cubic structures can be optimized. As a material development procedure, lattice parameters are tuned by systematically changing the compositional variable $x \in [0.04, 0.10]$. Raw powders of SrCO₃ (Alfa Aesar, 99.99%), CeO₂ (Alfa Aesar, 99.9%), HfO₂ (ZNXC, 99.99%), BaCO₃(Alfa Aesar, 99.8%), and TiO₂ (Alfa Aesar, 99.8%) were weighed according to the stoichiometric formula $(Ba_{1-x}Sr_x)$ $(Hf_{0.02}Ce_{0.005}Ti_{0.975})O_3$, simply denoted as Sr_x for x = 0.04, 0.05, 0.06, 0.07, 0.08, and 0.10. The mixed powders were dissolved in ethanol and ball-milled by zirconia balls in a planetary ball miller at 630 rpm for 24 h. The ball-milled solution was dried and calcined at 1000 °C for 10 h to obtain the ferroelectric oxides through solid-state reactions.²⁰ The calcined oxide is cold-pressed into a rod-shaped green body of 6 mm diameter and 10 mm length under 30 MPa hydrostatic pressure for 30 min. The green body was cut into thin slices of 1-2 mm and sintered in a tube furnace (Thermoconcept ROHT 75/300/18) at 1500 °C for 6 h. The microstructure of the sintered specimens for Sr0.07 and Sr0.08 is shown in Figs. 2(a) and 2(b). After surface polishing and chemical etching using 37% hydrochloride acid for 10 min, the grain morphology is revealed under the differential interference contrast microscope. The grains are mostly equiaxed, and the grain size is about 10 μ m for both compositions. Other compositions show similar grain sizes as observed under the same microscope. In addition, the textures seen as the phase contrast of grains in Fig. 1 are rather randomly distributed. There is no preferred orientations existing in all sintered specimens. The energy-dispersive x-ray spectroscopy analysis under SEM (JOEL 6390) is conducted along a 2 mm straight line on the surface of Sr0.07 and Sr0.08 specimens, showing sufficient chemical homogeneity of the doping elements.

The temperature-dependent ferroelectric properties are characterized by an aix ACCT ferroelectric analyzer 2000E system, as shown in Figs. 2(a) and 2(b). The Sr0.07 specimen shows the highest spontaneous polarization, 7.45 μ C/cm² at 40 °C, corresponding to the polarization jump of 4.32 μ C/cm² and $\kappa = 0.19 \mu$ C/cm² K in a temperature



FIG. 1. Grain morphology of sintered ferroelectric oxides for (a) $(Ba_{0.93}Sr_{0.07})$ $(Hf_{0.02}Ce_{0.005}Ti_{0.975})O_3$ and (b) $(Ba_{0.92}Sr_{0.08})(Hf_{0.02}Ce_{0.005}Ti_{0.975})O_3$.



FIG. 2. Pyroelectric properties and thermal property of Hf, Ce doped barium strontium titanate (BST) specimens with Sr compositions varying from 0.04 to 0.10. (a) Polarization vs temperature, (b) pyroelectric coefficient vs temperature, (c) thermal flows during heating/cooling through first-order phase transformations.

interval [80, 120]° C. In contrast, with just subtle change in composition and similar microstructure (Fig. 1), the Sr0.08 exhibits much lower spontaneous polarization $3.32 \ \mu\text{C/cm}^2$ at room temperature corresponding to the $[\![P]\!] = 1.52 \ \mu\text{C/cm}^2$ and $\kappa = 0.05 \ \mu\text{C/cm}^2\text{K}$ within the same temperature interval. The differential scanning calorimetry (DSC) measurements were performed by TA instrument DSC 250, to characterize the thermal properties of the series of materials upon heating and cooling through phase transformations in a temperature range of 40–125 °C, as shown in Fig. 2(c). All six specimens show the heat absorption/emission peaks during both heating and cooling processes, which indicate that phase transformations reversibly occur, featured as martensitic transformation.²¹ From the transport properties (i.e., temperature dependent polarization and its derivatives) shown in Figs. 2(a) and 2(b), the nature of phase transformation becomes inconspicuous in Sr0.08 and Sr0.10 specimens compared to other compositions. A trend of decreasing in transition temperatures is observed as the increase in Sr composition, and this trend is consistently suggested by both ferroelectric and thermal characterizations shown in Figs. 2(a) and 2(c). The transition temperatures of Sr0.07, Sr0.08 and Sr0.10 are below 100 °C, allowing the pyroelectric energy conversion from abundant low-grade waste heat energies.

The hysteresis of the phase transformation is characterized as $\Delta T = \frac{1}{2}(A_s + A_f - M_s - M_f)$, where A_s , A_f , M_s , M_f denote the start/finish temperatures during heating and cooling, which is consistent with the thermal hysteresis definition of martensitic materials.²¹ It has been theorized that the height of thermal energy barrier for a reversible martensitic transformation depends on the condition of compatibility^{13,14,22} that is governed by the middle eigenvalue λ_2 of the transformation stretch tensor U.²³ As the compatibility index λ_2 approaching to unity, the thermal hysteresis of a reversible phase transformation gets minimized. For the tetragonal (ferroelectric) to cubic (paraelectric) transformation in the series of $(Ba_{1-x}Sr_x)(Hf_{0.02}Ce_{0.005}Ti_{0.975})O_3$, the transformation stretch tensor U is determined as

$$\mathbf{U} = \begin{bmatrix} \frac{a}{a_0} & 0 & 0\\ 0 & \frac{a}{a_0} & 0\\ 0 & 0 & \frac{c}{a_0} \end{bmatrix},$$
(3)

where *a* and *c* are the lattice parameters of ferroelectric tetragonal phase below transition temperature and a_0 is the lattice parameter of paraelectric cubic phase above transition temperature. The middle eigenvalue of the transformation stretch tensor in Eq. (3) is calculated as

$$\lambda_2 = \frac{a}{a_0}.\tag{4}$$

We conducted x-ray powder diffraction (Panalytical X'pert pro diffractometer) for all compositions, and it is verified in all compositions that the ferroelectric phase is tetragonal (space group P4mm) and the paraelectric phase is cubic (space group $Pm\bar{3}m$). Their lattice parameters a_0 for cubic symmetry and a, c for tetragonal symmetry were refined from the diffraction patterns characterized as the temperature varying from 20 to 120 °C. The temperature-dependent tetragonality, defined as c/a, is shown in Fig. 3(a). Below the transition temperature, c/a > 1suggests that the [001] (c-axis) is the polar axis of the ferroelectric phase. Within a narrow temperature interval (i.e., <10 °C), the tetragonality suddenly drops to unity, indicating a structural transformation from tetragonal to cubic. We chose the lattice parameters $a(T^+)$ and $a(T^{-})$ at temperatures right before and after the transition temperature to calculate the compatibility index λ_2 by Eq. (4). We also calculated the measurable errors of λ_2 arising from the temperature varying XRD experiments. Figure 3(b) correlates the distance of λ_2 to 1 with the thermal hysteresis, which agrees with the prediction by the aforementioned compatibility theory^{13,22} up to experimental errors. In this material system, the thermal hysteresis is minimized at the composition Sr0.07 corresponding to λ_2 closest to 1. It suggests that the phase interfaces are elastically compatible during a large structural transformation between cubic and tetragonal symmetries. Interestingly, the figure-of-merit (FOM) is also correlated with the value of λ_2 . The maximum FOM appears at the same composition

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FIG. 3. (a) The temperature dependent tetragonality (c/a ratio) of the lattices for all developed compositions, which reveal the correlations between (b) thermal hysteresis and lattice compatibility and (c) figure-of-merit and lattice compatibility among all developed compositions.

Sr0.07 corresponding to λ_2 closest to 1 as well. Compared to its nearby compositions (Sr0.08 and Sr0.10), the FOM rapidly reduces by a factor of 8. The trend of FOM is inversely resonant with the variation of hysteresis. Such a strong correlation between the crystallographic compatibility and the pyroelectric property suggests a rational material development strategy for polar materials to achieve optimal energy conversion performance.

We setup a current pickup circuit as shown in Fig. 4(a) to verify the relationship between the FOM and the pyroelectric current generated by the first-order phase transformations among all developed compositions. The circuit in Fig. 4(a) corresponds to the yellow shadowed thermodynamic cycle depicted on the P–E curves of Sr0.07 sample in ferroelectric and paraelectric phases, shown in Fig. 4(b). This is consistent with the bias-free thermodynamic cycle proposed in Eq. (1). In contrast, the blue shadowed thermodynamic cycle illustrates the electric Ericsson cycle, i.e., one of the popular Olsen cycles proposed for single phase pyroelectric energy conversion. As the surrounding temperature gradually increases from 60 to 120 °C, we captured the pyroelectric current in the pickup circuit for all compositions around their transformation temperatures during heating and cooling. Figures 4(c) and 4(d) show their pyrocurrent densities (i.e., current per area) corresponding to the applied temperature oscillation. All compositions show two peaks of current density associated with the forward and backward phase transformation, among which the composition Sr0.07 exhibits the highest current density of 203 nA/cm^2 .

For each of the compositions, we conducted three measurements for the pyroelectric current and correlated their mean values with the FOM in Fig. 5 with the standard deviations as error bars. Their relationship is nearly linear, indicating that the FOM is an effective performance factor when considering the energy conversion from heat to electricity via small temperature fluctuations near a phase transformation. For the optimized composition Sr0.07, the thermodynamic efficiency is calculated as

$$\eta = \frac{\omega}{\ell} = 7.51 \times 10^{-6}\%,\tag{5}$$

where the electric work density $\omega = 2.75 \times 10^{-7}$ J/cm³ and the latent heat $\ell = 0.3661$ J/cm³ for the piece of Sr0.07 specimen used in the demonstration. The Carnot efficiency is estimated as $1 - T_L/T_H$ = 3%, where $T_{L,H}$ are the minimum and maximum temperatures, at



FIG. 4. (a) Electric circuit to pick up pyroelectric current without the application of bias field, corresponding to (b) the thermodynamic cycle. (c) The heating and cooling temperature profiles covering the transformation temperature of the developed ferroelectric material system. (d) Generated pyroelectric current density corresponding to the heating and cooling profiles in (c).

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which the energy converter runs. The relative efficiency of our device with respect to the Carnot cycle is about 2.5×10^{-4} %. Admittedly, the conversion efficiency is quite small, which, indeed, can be seen from the bias-free cycle in Fig. 4(b). Compared to the area of Ericsson cycle, the bias-free cycle is much smaller. However, we believe that introducing the phase transformation and removing the external bias field are significant advance in this field. Economically, the energy source is waste heat while the output is electricity. A standalone thermodynamic device to output electric energy purely from surrounding thermal fluctuations is still very valuable. Based on our thermodynamic analysis in Eq. (1), the performance and the efficiency of the device can be improved by increasing the rate of transformation and reducing the thickness of the planar capacitor. For example, if the planar capacitor's thickness reduces from submillimeter scale to nanometer scale, the electric work density will increase by four to five orders of magnitude. By (5), the thermodynamic efficiency becomes competitive to the Carnot efficiency.

In summary, we demonstrate a rational material development strategy in Hf, Ce doped $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ system with $x \in [0.04, 0.10]$. With the finely tuned Sr composition, the crystal structures of ferroelectric (tetragonal) and paraelectric (cubic) phases at Sr0.07 are crystallographically compatible upon the reversible solid–solid phase transformation. As a result, we achieved the lowest hysteresis and highest FOM in this material system, providing a promising material candidate for electricity generation from waste heat stored as small temperature fluctuations in nature.

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DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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