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Field-induced ferroelectricity in (doped) hafnia and zirconia has attracted increasing interest in energy-related applications, including energy harvesting and solid-state cooling. It shows a larger isothermal entropy change in a much wider temperature range compared with those of other promising candidates. The field-induced phase transition occurs in an extremely wide temperature range, which contributes to the giant electrocaloric effect. This article examines the possible origins of a large isothermal entropy change, which can be related to the extremely broad phase transitions in fluorite-structured ferroelectrics. While the materials possess a high entropy change associated with the polar–nonpolar phase transition, which can contribute to the high energy performance, the higher breakdown field compared with perovskites practically determines the available temperature range.

As the ferroelectricity in fluorite structured oxides, such as (doped) HfO_2 and ZrO_2, was first reported in 2011,[1] many theoretical and experimental types of research have been performed for identifying the origin of ferroelectricity and pursuing the various electronic applications.[2] Besides the electronic applications, they are also promising as energy related materials for electrocaloric effect (ECE), which originates from a phase transition between the polar orthorhombic phase (o phase, space group: $Pca2_1$) and the nonpolar tetragonal phase (t phase, space group: $P4_2/nmc$). The internal entropy values of t phase and o phase are different, and this entropy difference can be utilized for

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conversion from thermal to electrical energy or vice versa.[3,4] It should be noted that the entropy change multiplied by the temperature gives the reversible heat quantity during the field induced phase transition. From the Si and Al doped HfO_2 and $(Hf,Zr)O_2$ films, the double hysteresis loop resulting from the field induced phase transition could be observed when the Si and Al doping concentration and Zr concentration were slightly higher than that for inducing ferroelectricity.[1–6] Reyes Lillo et al.[7] suggested that double hysteresis originates from the field induced phase transition between t and o phases. Park et al.[4] reported that the Zr rich $Hf_{1-x}Zr_xO_2$ thin films have promising performances for energy related applications, such as pyroelectric energy harvesting (PEH), ECE, and infrared sensing. Similar properties in Si doped HfO_2 and Al doped HfO_2 were confirmed by Hoffmann et al.[3] and Park et al.[6] The giant negative ECE was also reported in $Hf_{1-x}Zr_xO_2$ and Al doped HfO_2 thin films,[5,6] although its mechanism is under debate.

As indicated in previous studies, the phase transition in fluorite structured ferroelectrics is a type of the first order phase transition between the t and o phases. The first order phase transitions have been observed in other ferroelectric materials, including perovskite structured ferroelectrics. The latter is the most intensively studied class of ferroelectric materials. The phase transition in fluorite structured ferroelectrics, however, has critically distinguishable points compared with the perovskite structured ferroelectrics. From experimental observations, the phase transition in fluorite structured ferroelectrics occurred in a temperature range of a few hundreds of K, whereas it is generally a few to a few tens of K for typical bulk and thin films of perovskite ferroelectric materials.[3,4,6]

Nevertheless, the origin of a strong ECE occurring in such an extremely broad temperature range has not been well understood so far. For the case of fluorite structured oxides, even Landau coefficients for the phenomenological interpretation of the free energy function are not known currently, so the theoretical examination on the temperature dependent phase transition is challenging. In this article, therefore, the origin of the strong ECE of fluorite structured ferroelectrics is scrutinized from the available literature. The strong ECE can be attributed to the following two characteristics: 1) the isothermal entropy change ΔS (and the resulting adiabatic temperature change ΔT) value resulting from the phase transition between the t and o phases is high and 2) field induced phase transition

can be observed in an extremely wide temperature range. Thus, these two points are carefully discussed.

The first order phase transition is known to show a giant ECE from the entropy difference between the nonpolar and polar phases, or even between that of two polar phases.[8–10] The theoretical ΔS for fluorite structured ferroelectrics can be calculated from the entropy values of the t and o phases. In this article, the main focus will be on the HfO_2 based materials because more results have been reported in the literature. Based on Materlik et al.'s work using the local density approximation (LDA), ΔS can be calculated as $\approx 171\,mJ\,cm^{-3}\,K^{-1}$ for HfO_2.[11] Based on Huan et al.'s work using the generalized gradient approximation (GGA), on the other hand, the expected ΔS value for HfO_2 is $\approx 342\,mJ\,cm^{-3}\,K^{-1}$.[12] The practical ΔS value may be between 171 and 342 $mJ\,cm^{-3}\,K^{-1}$ due to the different calculation methods used in the two cited works.[11,12] The temperature dependent part of the ΔS value was ignored during the entropy estimation. It is known that $(dS/dT)_P \approx C_p/T$, where C_p is the heat capacity under a constant pressure condition. For the same compounds with a different crystalline structure, a large difference in the C_p value is not reasonable. Also, the molar C_v (the heat capacity under constant volume) of solid crystals is generally limited to 3R (R is the gas constant) when the temperature is sufficiently higher than the Debye temperature, which is the well known Dulong Petit law.[13,14] It should also be noted that for solids, the difference between C_v and C_p is negligible due to the very small PV term. Therefore, the hypothesis of $d\Delta S/dT \approx 0$ is reasonable.

The LDA method in Materlik et al.'s work is known to underestimate the free energy and entropy values, whereas the GGA method in Huan et al.'s work tends to overestimate them.[11,12] These values need to be compared with those of other electrocaloric materials to compare the internal electrocaloric effect of fluorite structured ferroelectrics to the other candidates. Lu and Zhang estimated the theoretical ΔS values of bulk $BaTiO_3$, $Pb(Zr,Ti)O_3$, and P(VDF TrFE), and they were ≈ 23, ≈ 14, and $\approx 112\,mJ\,cm^{-3}\,K^{-1}$, respectively.[10] These values can be calculated from the Landau coefficients and through the spontaneous polarization of bulk materials. However, these values were calculated by an oversimplified method where the temperature dependence of polarization was ignored. ΔS values can be more accurately calculated by considering temperature dependence of polarization based on the Landau Devonshire theory. In this method, the effect of the electric field can also be considered, and ΔS value is identified to be linearly proportional to the applied electric field. The theoretical and experimental ΔS values of various electrocaloric materials in the literature are summarized in **Table 1**. The theoretical ΔS of $Hf_{0.5}Zr_{0.5}O_2$ and HfO_2 (171 342 $mJ\,cm^{-3}\,K^{-1}$) is expected to be much higher than those of other electrocaloric materials, such as $BaTiO_3$ (23 135 $mJ\,cm^{-3}\,K^{-1}$),[10,15,16] $Pb(Zr,Ti)O_3$ (14 170 $mJ\,cm^{-3}\,K^{-1}$),[10,17] $SrBi_2Ta_2O_9$ (59 $mJ\,cm^{-3}\,K^{-1}$),[18] and P(VDF TrFE) (42 112 $mJ\,cm^{-3}\,K^{-1}$).[10,19] The experimentally achieved ΔS values are in reasonable agreements with the theoretical ΔS values as shown in the same table.[3,4,6,8,9,20,21] The theoretical ΔS value of $Pb(Zr,Ti)O_3$ in Wu et al.'s work[17] (170 $mJ\,cm^{-3}\,K^{-1}$) is comparable to that of $Hf_{0.5}Zr_{0.5}O_2$, but the assumed magnitude of the applied electric field was 1000 $kV\,cm^{-1}$, which was higher than the typical experimental breakdown strength of $Pb(Zr,Ti)O_3$ ($\approx 500\,kV\,cm^{-1}$). When the applied electric field is limited to 480 $kV\,cm^{-1}$, which was used in Mischenko et al.'s experimental work,[8] the intrinsic ΔS value decreased to be $\approx 85\,mJ\,cm^{-3}\,K^{-1}$.

From Table 1, it can be noted that the experimentally observed ΔS values of several materials are even larger than the theoretically expected ΔS values. For the calculation of the theoretical ΔS values, the extrinsic factors such as stress were not considered. However, the effects of the extrinsic factors are important especially for the case of thin films. In general, a giant electrocaloric effect can be observed in thin films, whereas rather low ΔS and ΔT values are observed in bulk materials.[3,4,6,8,20,21]

Currently, however, the experimentally achieved ΔS values in preliminary studies on ferroelectric (doped) HfO_2 are rather lower compared with the best values from perovskite ferroelectrics or polymer ferroelectrics. However, higher intrinsic (theoretical) ΔS value suggests that the maximum ΔS and ΔT values of (doped) HfO_2 can be further improved by the material and process optimization.

Another very important property of electrocaloric materials is the temperature range within which the field induced phase

Table 1. Theoretical and experimentally observed ΔS values and applied electric field of electrocaloric materials.

Material	Theoretical ΔS [mJ cm^{-3} K]	Electric field [kV cm^{-1}]	Reference	Exp. ΔS [mJ cm^{-3} K]	Electric field [kV cm^{-1}]	Reference
$BaTiO_3$	23	N/A	[10]	61	700	[20]
	135	N/A	[15]			
	35	150	[16]			
$Pb(Zr,Ti)O_3$	14	N/A	[10]	66	480	[8]
	170	1000	[17]			
$SrBi_2Ta_2O_9$	59	600	[18]	25	600	[21]
P(VDF-TrFE)	112	N/A	[10]	230	3070	[9]
	42	1000	[19]			
$(Hf,Zr)O_2$	171	N/A	[11]	96	3260	[4]
HfO_2	342	N/A	[12]			
$Si:HfO_2$				85	3330	[3]
$Al:HfO_2$				61	3900	[6]

transition can occur with the large ΔS values. This can be easily deduced from Equation (1), which is the general equation for ΔS estimation based on Maxwell's relation.

$$\Delta S = \frac{1}{\rho} \int_{E_1}^{E_2} \left(\frac{\partial P}{\partial T} \right)_E \mathrm{d}E \tag{1}$$

where ρ and P are the density and polarization of the electro caloric material, respectively, and E is the electric field. For first order phase transition materials, large $(\partial P/\partial T)_E$ values are expected at the electric field for the field induced phase tran sition. Thus, a giant ΔS value is expected within a temperature range where the characteristic double hysteresis with the field induced phase transition can be observed.

Equation (2) is an equation for the free energy of the first order phase transition materials based on the well known Landau Devonshire theory,[22,23] when the sixth order polynomial form was assumed for the sake of convenience.

$$G = \frac{1}{2}\alpha_0(T - T_0)P^2 + \frac{1}{4}\beta P^4 + \frac{1}{6}\gamma P^6 - P \times E_{ext} \tag{2}$$

Here, α_0, β, and γ are Landau coefficients. β is negative whereas α_0 and γ are generally positive. T_0 is the Curie Weiss temperature, and it is one of the four characteristic transition temperatures of the ferroelectric materials. The three other char acteristic transition temperatures are Curie temperature T_c, the limit temperature of ferroelectric properties T_1, and the limit temperature of field induced ferroelectric properties T_2. The free energy (G) polarization (P) curves are shown in **Figure 1**a e and the intrinsic polarization (P) electric field (E) curves are shown in Figure 1f j in various temperature ranges: $T < T_0$ (Figure 1a, f), $T_0 < T < T_c$ (Figure 1b, g), $T_c < T < T_1$ (Figure 1c, h), $T_1 < T < T_2$ (Figure 1d, i), and $T_2 < T$ (Figure 1e, j). P E curves could be derived by differentiating G with respect to P and transpose the two axes. From

Equation (2), T_c, T_1, and T_2 can be formulated as Equation (3), (4), and (5), respectively.[24]

$$T_c = T_0 + \frac{3}{16}\frac{\beta^2}{\alpha_0\gamma} \tag{3}$$

$$T_1 = T_0 + \frac{1}{4}\frac{\beta^2}{\alpha_0\gamma} \tag{4}$$

$$T_2 = T_0 + \frac{9}{20}\frac{\beta^2}{\alpha_0\gamma} \tag{5}$$

From Equations (3) (5), the term $\beta^2/\alpha_0\gamma$ determines the broadness of phase transition. Thus, for the ferroelectrics with the known Landau coefficients, the broadness of phase transition can be estimated. The temperature difference between T_1 and T_2 is a critical temperature range for the observation of double hysteresis, which is strongly related to the giant ECE. **Table 2** summarizes the Landau coefficients, resulting in the $\beta^2/\alpha_0\gamma$ term, and four characteristic temperatures for the $BaTiO_3$, $PbTiO_3$, and P(VDF TrFE).[25–27] Lu et al. reported that the critical temperature estimated from Landau coefficients well matched with the experimental values for the $BaTiO_3$.[25]

For ferroelectric HfO_2, however, the Landau coefficients are not available. Therefore, the broadness of the phase transition needs to be estimated using another method as follows. T_0 is the temperature at which the metastable nonpolar phase starts to occur; this means that G of the nonpolar phase is equivalent to the barrier height between the two polarization states of the polar phase. At above T_0, G of the nonpolar phase compared with that of the polar phase decreases with increasing temperature. Finally, the G values of the polar and nonpolar phases become identical at T_c. Because S is $-(\partial G/\partial T)_P$, the ΔS value can be cal culated from $-(\partial \Delta G/\partial T)_P$. When it is assumed that ΔG is line arly proportional to T, the temperature difference between T_c and T_0 ($T_c - T_0$) can be calculated as $-[(\Delta G(T_c) - \Delta G(T_0))/\Delta S]_P$.
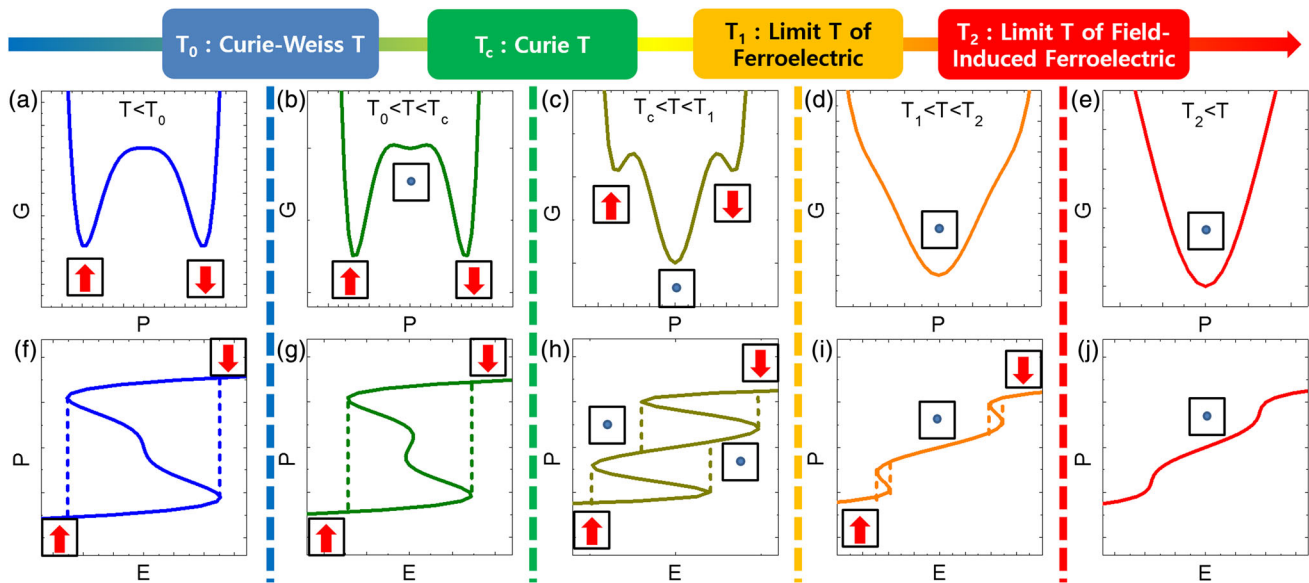

Figure 1. a e) Free energy polarization curves and f j) intrinsic polarization electric field curves derived by differentiating Equation (2) by P at various temperature ranges from $T < T_0$ (a and f), $T_0 < T < T_c$ (b and g), $T_c < T < T_1$ (c and h), $T_1 < T < T_2$ (d and i), and $T_2 < T$ (e and j).

Table 2. Landau coefficients and characteristic temperatures of $BaTiO_3$, $PbTiO_3$, and P(VDF TrFE). The coefficients are taken from previous studies.[25 27]

Material	$\alpha_0 \times 10^5$ [m^2N C ^{2}]	$\beta \times 10^7$ [m^6N C ^{4}]	$\gamma \times 10^8$ [m^{10}N C ^{6}]	$\beta^2/\alpha_0\gamma$ [K]	T_0 [K]	T_c [K]	T_1 [K]	T_2 [K]	T_2 T_1 [K]
$BaTiO_3$	6.60	54.8	166	27.5	368	374	375	381	6
$PbTiO_3$	7.60	29.20	15.6	71.9	752	765	770	784	14
P(VDF-TrFE)	7.50×10^2	1.90×10^5	1.90×10^6	253	306	354	370	421	51

The kinetic energy barrier between the two polarization states in HfO_2 has been reported by several research groups.[12,28–30] Clima et al. reported that the energy barrier between the two polarization states of HfO_2 is about 100 meV f.u.$^{-1}$ [28] However, the possible occurrence of an intermediate metastable phase was not considered in their work. Huan et al. examined the kinetic barrier height, and the calculated value was $\approx$108 meV f.u.$^{-1}$ [12] They also reported that even at 0 K, there existed a local minimum state near $P \approx 0$, which refers to the t phase. This result suggests that T_0 is even lower than 0 K.[12] In Barabash et al.'s work, the kinetic energy barrier was $\approx$94 meV f.u.$^{-1}$,[29] and as in Huan et al.'s work, T_0 could not be reached even at 0 K. The energy difference between the highest energy transition state and the metastable tetragonal phase was only $\approx$4 meV f.u.$^{-1}$, i.e., local energy minimum was quite shallow. The recent result obtained by Maeda et al.[30] showed similar local minimum energy at P $\approx$ 0, but the kinetic energy barrier was slightly lower ($\approx$84 meV f.u.$^{-1}$).

These works revealed that, even at 0 K, the G P curve of bulk HfO_2 has three local minimum states, suggesting that it might not have a practical T_0. However, T_c can be estimated from the free energy values of the t and o phases. Among the previously mentioned three works, the temperature dependence was considered only in Huan et al.'s work.[12] Thus, in this article, the broadness of the phase transition is discussed based on their reports.[12] It is also estimated that increasing doping concentration and decreasing film thickness are expected to decrease T_0 further.[12] Therefore, $(T_c \ T_0)$ should be larger than $(T_c \ 0)$ K, although T_0 is unphysical because it cannot be reached even at 0 K. The entropy difference between the t and o phases is $\approx$0.072 meV f.u.$^{-1}$ K^{-1} ($\approx$342 mJ cm^{-3} K^{-1}) in their work, and T_c can be calculated from the differences in free energy at 0 K and entropy values of the t and o phases. From this, T_c of bulk HfO_2 is higher than 1500 K. Thus, the temperature difference between T_c and T_0 was estimated to be even larger than 1500 K. This value is much larger compared with those of perovskite structured ferroelectrics, as shown in Table 2. From Equations (3) (5), the temperature difference between T_1 and T_2 is expected to be larger than 1600 K for bulk HfO_2. From Equations (3) (5) $(T_c \ T_0)$ and $(T_2 \ T_1)$ are $\frac{3\beta^2}{16\alpha_0\gamma}$ and $\frac{\beta^2}{5\alpha_0\gamma}$, respectively. This value is estimated by the calculated $\frac{\beta^2}{\alpha_0\gamma}$ from the calculated T_c (Equation (3)). In principle, therefore, field induced phase transition with a double hysteresis loop in thin ferroelectric HfO_2 films can be observed in a temperature range wider than 1600 K if a sufficient electric field can be stably applied for achieving the double hysteresis without the breakdown.

A potentially limiting factor for the observation of the field induced phase transition is, however, the highest applicable electric field, which can be determined by the breakdown strength.

From Equation (2), the free energy difference between the non polar and polar phases can be overcome by applying an external electric field of E_{ext}, if the difference is smaller than $\Delta P_s \times E_{ext}$. Here, ΔP_s is the difference between the spontaneous polarization of the polar and nonpolar phases. The temperature dependent changes in the electric field required for field induced phase transition (E_t) can be estimated using Equation (6) based on the Clausius Clapeyron equation.

$$\left(\frac{\partial E_t}{\partial T}\right)_{eq} = \frac{\Delta S}{\Delta P_s} \tag{6}$$

From the ΔS (0.072 meV f.u.$^{-1}$ K$^{-1} \approx$342 mJ cm^{-3} K^{-1}) and ΔP_s (52 μC cm^{-2}) values for HfO_2, the $(\partial E_t/\partial T)$ value of 6.6 kV cm^{-1} K^{-1} was calculated. As P_s of the o phase is larger than that of the t phase, the ΔP_s and $(\partial E_t/\partial T)_{eq}$ values are negative and positive, respectively.

It should be noted that E_t in Equation (6) is the electric field at which the free energies of the t and o phases become equivalent, i.e., $\Delta P_s \times E_t = \Delta G$. In practical field induced phase transitions, however, an activation energy between the nonpolar and polar phases exists when the field induced phase transition was attempted. Therefore, an additional field is necessary to effectively overcome the barrier, and thus, the experimental field to induce the field induced switching must be higher than E_t in Equation (6). The width of the double hysteresis loop (W), thus, coincides with twice the additionally required electric field.

Figure 2b shows the schematic diagram for the temperature window for the field induced phase transition due to the limitation imposed by the breakdown field, E_{bd}. E_{bd} of a fluorite structured ferroelectric thin film is generally $\approx$4 5 MV cm^{-1}.[1–6] Although W may be affected by various factors, including the
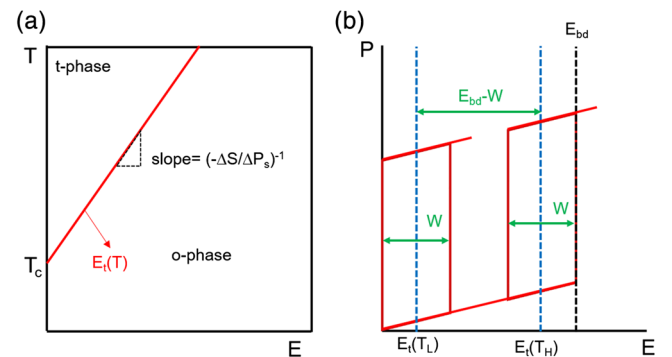

Figure 2. a) Schematic phase diagram for the nonpolar tetragonal and polar orthorhombic phases in the temperature (T) electric field (E) plane. b) Schematic diagram for the temperature limit for field induced phase transition by breakdown strength.

dopant species, doping concentrations, film thickness, and strain, the W value for $Hf_{1-x}Zr_xO_2$ was assumed to be $2\,MV\,cm^{-1}$ based on the previous results obtained by the authors.[4] As such, the available temperature range can be calculated using Equation (7).

$$T_H \quad T_L = \frac{E_{bd} \quad W}{(\partial E_t / \partial T)_{eq}} = \frac{E_{bd} \quad W}{(\Delta S / \Delta P_s)} \tag{7}$$

Substituting the above deduced values into Equation (7) results in a $T_H \quad T_L$ window of $\approx 300 \quad 450\,K$ when E_{bd} is $4 \quad 5\,MV\,cm^{-1}$. It should be noted that this calculation was conducted, assuming the fully c oriented o phase. Thus, the actual temperature window will be narrower for the HfO_2 thin films with different crystallographic orientations because $P_s \times E_{ext}$ is proportional to the polarization axis component of E_{ext}. Thus, ΔP_s changes to $\Delta P_s \cos\theta$ when the angle between E_{ext} and P_s is θ.

Up to this point, the two potential limiting factors that can determine the temperature window for the observation of the field induced phase transition were compared. It can be concluded that the temperature range for double hysteresis is limited by E_{bd}, not by the intrinsic material parameter, such as ΔS. E_{bd} is usually determined not by the intrinsic material parameters, such as bandgap, but by extrinsic factors, such as local defects and roughness, which degrades the E_{bd} performance. For example, it is well known that the intrinsic E_{bd} of amorphous SiO_2 film is as high as $\approx 15\,MV\,cm^{-1}$, but the practically available values in semiconductor devices are only $\approx 5\,MV\,cm^{-1}$.[31]

From Table 1, it can be noted that the electric field utilized for the doped HfO_2 or $(Hf,Zr)O_2$ thin films is higher than that utilized for the perovskite materials. The application of higher applied electric field is probably due to the higher E_{bd} of doped HfO_2 or $(Hf,Zr)O_2$ thin films compared with those of the perovskite oxides. However, it should also be noted that the temperature range for the field induced phase transition resulting in the high ΔS of perovskite materials is limited by intrinsic factors determined by different Landau coefficients. Thus, such a wider temperature range for the field induced phase transition is not expected even when E_{bd} of perovskite oxide is enhanced. For the case of doped HfO_2 or $(Hf,Zr)O_2$ thin films, on the other hand, an even wider temperature range for the field induced phase transition would be achieved when E_{bd} of the films is further improved by a better material processing.

Nonetheless, the finally calculated phase transition broadness of $300 \quad 450\,K$ is surprisingly wide, although it was based on the assumption of the electric field being applied along the polarization axis. Thus, a giant ΔS of $342\,mJ\,cm^{-3}\,K^{-1}$ is expected within the $300 \quad 450\,K$ temperature width. From these values, the theoretically expected refrigerant capacity (RC) (or the harvestable energy density [HED]) can also be calculated using Equation (8).

$$RC = \int_{T_L}^{T_H} \Delta S dT \tag{8}$$

When a temperature window of $300\,K$ is conservatively assumed, Equation (8) gives $\approx 102\,J\,cm^{-3}$ cycle of an RC. This is several times larger than the previously reported values for polycrystalline $Hf_{0.2}Zr_{0.8}O_2$, Si doped HfO_2, and Al doped HfO_2 thin films. From the theoretical ΔS in Table 1 and the $(T_2 \quad T_1)$ temperature range in Table 2, the RC values of $BaTiO_3$, $Pb(Zr,Ti)O_3$, and $P(VDF\ TrFE)$ are 0.092, 0.154, and $5.6\,J\,cm^{-3}$ cycle. It should also be noted that unlike HfO_2, the temperature window for the field induced phase transition of $BaTiO_3$, $Pb(Zr,Ti)O_3$, and $P(VDF\ TrFE)$ is limited by $T_2 \quad T_1$, which is determined by the temperature dependent changes in the free energy polarization curves. The theoretical RC value of HfO_2 ($102\,J\,cm^{-3}$ $9530\,J\,kg^{-1}$) is even one order higher than those of the most promising magnetocaloric materials, such as Eu_4PdMg ($1346\,J\,kg^{-1}$),[32] $Gd_2Ni_{0.5}Cu_{1.5}Mg$ ($688\,J\,kg^{-1}$),[33] $Gd_5Si_2Ge_2$ ($535\,J\,kg^{-1}$),[34] $Pr_{0.63}Sr_{0.37}MnO_3$ ($511\,J\,kg^{-1}$),[35] and $La_{0.7}Sr_{0.3}Mn_{0.98}Ni_{0.02}O_3$ ($459\,J\,kg^{-1}$).[36] The RC values of the magnetocaloric materials were calculated within the temperature range, which refers to the full width half maximum near phase transition.[37]

To date, the direct measurement of ΔT or ΔS of doped HfO_2 or $(Hf,Zr)O_2$ thin films has not been reported. This might be due to the rather small thickness (generally $\approx 10\,nm$) of the frequently used fluorite structured oxide thin films. However, it does not necessarily imply that direct measurement is impossible. With the chemical solution deposition, fluorite structured ferroelectric oxide films with thickness up to $390\,nm$ were fabricated.[38] Therefore, direct measurement of ΔT or ΔS of doped HfO_2 or $(Hf,Zr)O_2$ thin films should be possible in the near future.

In conclusion, the theoretical origin of the strong electrocaloric effect (ECE) in fluorite structured ferroelectrics was examined based on previous works. It could be noticed that the phase transition in HfO_2 is significantly different from those in other ferroelectrics. Although very broad phase transitions in ferroelectric (doped) HfO_2 were reported in several studies, the origin is rigorously discussed in this article based on the values available from the literature. It can be concluded that the fluorite structured ferroelectrics are intrinsically promising for the pyroelectric energy harvesting (PEH) and electrocaloric cooling applications with a larger ΔS value and a ≈ 1 to 2 order wider temperature range available for practical thermodynamic cycles compared with perovskite structured ferroelectrics or ferroelectric polymers. Due to the two factors mentioned earlier, the theoretically expected RC values were even larger than those of the most promising magnetocaloric materials. In conclusion, this material system could result in a significant breakthrough for electrocaloric or pyroelectric applications.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

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