Large room-temperature electrocaloric effect in lead-free $\text{BaHf}_x\text{Ti}_{1-x}\text{O}_3$
ceramics under low electric field

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ABSTRACT

Ferroelectrics are promising candidate materials for electrocaloric refrigeration. Materials with a large electrocaloric effect (ECE) near room temperature and a broad working temperature range are getting closer to practical applications. However, the enhanced ECE is always achieved under high electric field, which limits their wide cooling applications. In this paper, the phase diagram of lead-free $\text{BaHf}_x\text{Ti}_{1-x}\text{O}_3$ (BHT) ferroelectric ceramics was established. A large ECE under relatively low electric field ($\Delta E=10$ kV/cm) is firstly reported in BHT ferroelectric ceramics. The direct temperature change ($\Delta T=0.35$ °C under 10 kV/cm) in BHT ceramics is comparable with those reported in the literature under high electric fields. Meanwhile, the electrocaloric efficiency ($\Delta T/\Delta E=0.35$ K mm kV⁻¹ under 10 kV/cm) is thirteen percent higher than the best value reported previously under high electric field ($\Delta E=145$ kV/cm). We demonstrate that the ECE can be greatly enhanced by tuning the composition of the lead-free BHT ceramics to its first-order phase transition (FPT), invariant critical point (ICP) or diffuse phase transition (DPT). It is shown that the enhancement in ECE is strongly dependent on the nature of structural phase transition and electric field coupling effect, which has been confirmed by both the indirect and direct ECE measurements. A phenomenological explanation based on Landau model was also proposed to understand this phenomenon. Our findings in this work may provide a better understanding and design methodology for developing more practically useful electrocaloric materials.

Keywords: lead-free ferroelectric ceramics; electrocaloric effect; low electric field; phase transition.

1. Introduction

Electrocaloric effect (ECE) is a phenomenon that the change in adiabatic temperature and/or entropy of a dielectric material is induced by the application and removal of an electric field due to the change in the dipolar state of the material [1, 2]. Being one of the most promising caloric materials for future refrigeration applications, just like magnetocaloric (mC) and mechanocaloric (MC) materials [2], electrocaloric materials have intrigued intense research efforts. In general, the ECE is parameterized by the adiabatic temperature change (ΔT), and the electrocaloric efficiency ($\Delta T/\Delta E$). Therefore, for practical refrigeration, it is necessary for electrocaloric materials to show a giant ΔT and a large $\Delta T/\Delta E$. Simultaneously, large ECE has been predicted and/or discovered in ferroelectric bulk ceramics [3-9], single crystals [10-14], polymers and polymer nanocomposites [15-18], thick and thin films [19-23], and so forth.

The newly developed lead-based electrocaloric materials always show giant ECE [2], such as $(1-x)\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$ - $x\text{PbTiO}_3$ (PMN-PT) [14], $\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$ (PZT) [19], $\text{Pb}_x\text{Ba}_{1-x}\text{ZrO}_3$ (PBZ) [20] and $(\text{Pb}_{0.97}\text{La}_{0.02})(\text{Zr}_{0.95-x}\text{Sn}_x\text{Ti}_{0.05})\text{O}_3$ (PLZST) [21]. However, the toxicity of lead for both human body and the environment has limited their practical applications. Therefore, lead-free ferroelectrics have been considered as better candidate materials for electrocaloric refrigeration, such as BaTiO_3 (BT)-based materials [10, 11], $\text{BaZr}_x\text{Ti}_{1-x}\text{O}_3$ (BZT) [3], $\text{BaSn}_x\text{Ti}_{1-x}\text{O}_3$ [9], $(1-x)\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3$ - $x(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3$ (BZT-BCT) [4, 7], $\text{Na}_{0.5}\text{Ba}_{0.5}\text{TiO}_3$ -based systems [6], $\text{Sr}_x\text{Ba}_{1-x}\text{Nb}_2\text{O}_6$ (SBN) [12, 13], and ferroelectric polymers or polymer nanocomposites [15-18]. For instance, Ye *et al.* [22] reported an ΔT of 7 °C under 195kV/cm in $\text{BaZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$ thick films near room temperature. And Zhang *et al.*

showed that an electrocaloric temperature change of $\Delta T=12\text{ }^{\circ}\text{C}$ was obtained under 80 to 120 V at 80 $^{\circ}\text{C}$ and 55 $^{\circ}\text{C}$, respectively, in ferroelectric poly(vinylidene fluoride-co-trifluoroethylene) (P(VDF-TrFE)), and poly(vinylidene fluoride-ter-trifluoroethylene-terchlorofluoroethylene) (P(VDF-TrFE-CFE)) thin films [15]. However, materials in the form of thin-films would not provide the necessary cooling volume for refrigeration and would be too expensive to produce on a large scale for practical applications. On the other hand, single crystals, such as BaTiO₃ [10, 11], SBN [12, 13], have been widely studied due to their excellent ECE performance under low electric fields. However, their high cost and difficulty in being scaled up have limited their applications. Thus, from the environmental-friendly, cost/energy more efficient point of view, lead-free ferroelectric bulk ceramics would be better candidate materials for realizing electrocaloric cooling devices. However, the weak intrinsic ECE of ferroelectric bulk ceramics always requires a high electric field to produce a large ΔT [1]. What's more, it was found that the electrocaloric efficiency $\Delta T/\Delta E$ decreases sharply with increasing applied electric field [3]. Thus, the main technical challenge in lead-free ferroelectric bulk materials is how to design and develop materials that are capable of generating a giant electrocaloric temperature change ΔT under a relatively low electric field. In a few recent works, an enhanced ECE in ferroelectric bulk ceramics under a modest electric field have been reported. For example, a ΔT of 0.33 $^{\circ}\text{C}$ and $\Delta T/\Delta E$ of 0.165 K mm kV⁻¹ were induced in BZT-BCT ceramics at 39 $^{\circ}\text{C}$ under an electric field change $\Delta E=20\text{ kV/cm}$ [4]. Similarly, it has been reported that a large value of $\Delta T=1.1\text{ }^{\circ}\text{C}$ ($\Delta T/\Delta E=0.52\text{ K mm kV}^{-1}$) and 4.5 $^{\circ}\text{C}$ ($\Delta T/\Delta E=0.31\text{ K mm kV}^{-1}$) was obtained in glass-modified BZT ceramics at 65 $^{\circ}\text{C}$ under $\Delta E=20\text{ kV/cm}$ and 145 kV/cm, respectively [3]. However, considering the thickness of the ceramics (around 1 mm or 1000 μm) and the normal

electrical voltage for most cooling devices (around 200 V), the modest electric field of 20 kV/cm (equivalent to 200 V applied on a material with the thickness of 100 μm) is still too high for applications. However, it has been demonstrated that ECE can be greatly enhanced in lead-free bulk ceramics by modifying the composition of the ceramics to their invariant critical point (ICP) or tuning them to relaxor ferroelectrics [3, 12, 24]. It is believed that the coexistence of two or more polar phases in ICP and the polar nanoregions (PNRs) in relaxor ferroelectrics can enhance their ECE performance. On the other hand, the contributions of the first-order phase transition (FPT) [25] or diffuse phase transition (DPT) [8] to the ECE of ferroelectrics under low electric fields are still poorly understood, similar to the ECE under relatively low electric fields around the ICP or in relaxors.

In this work, based on previous research results [26-28], the phase diagram of lead-free $\text{BaHf}_x\text{Ti}_{1-x}\text{O}_3$ (BHT) bulk ceramic systems was established. Then, we carried out a detailed ECE study on BHT ceramics with FPT, ICP and DPT, near room temperatures. We have discovered that a large ECE could be achieved in BHT ceramics near room temperature under relatively low applied electric fields (around 10kV/cm). Phase structure transition, electric field and their coupling effect have been considered as the decisive factors for the enhancement of ECE in the BHT systems.

2. Experimental

2.1 Preparation of BHT bulk ceramics

BHT bulk ceramics with different compositions ($x=0, 0.03, 0.06, 0.09, 0.10, 0.11, 0.12, 0.13, 0.15, 0.17, 0.20$) were fabricated via the conventional solid-state

reaction method using barium carbonate (BaCO_3 , 99.8%), titanium dioxide (TiO_2 , 99.8%), and hafnium oxide (HfO_2 , 99.9%) as precursor. BaCO_3 , TiO_2 and HfO_2 were milled for 6 h in absolute ethyl alcohol and zirconia media. The dried mixture was calcined at 1350 °C for 3 h in air. The well-prepared powders added with 7 wt.% PVA binder were compacted into pellets. The green pellets of pure and $x=0.03$, 0.06 were sintered at 1425 °C. Those with $x=0.09$, 0.10, 0.11 were sintered at 1450 °C. And the BHT ceramics with $x=0.12$, 0.13, 0.15 were sintered at 1475 °C, while those with $x=0.17$, 0.20 were sintered at 1495 °C. All the BHT samples were sintered in air for 4 h.

2.2 Characterizations

All the as-prepared pellets were subjected to structural and phase purity characterization by employing powder X-ray diffraction (XRD, Rigaku SmartLab 3) at room temperature. The density of the ceramics was obtained by using an Archimedes' method. The temperature dependence of dielectric permittivity was measured with a LCR meter (HIOKI 3532) equipped with a temperature chamber (Delta 9023). A differential scanning calorimeter (DSC, TA Instruments Q200) was used to characterize the thermal properties of the ceramics. P - E hysteresis loops at different temperatures were measured using a Radiant ferroelectric workstation. Direct ECE measurements were carried out with a modified Differential Scanning Calorimeter (DSC, TA Instruments Q2000).

3. Results and discussion

3.1. Structural characterizations

The XRD patterns of the BHT ceramics with $x=0$, 0.03, 0.11, and 0.17 are shown in Fig. 1(a). A pure pseudocubic phase can be observed for all the BHT ceramics. Evident peak splits and shifts can be noticed in the Hf-substituted BaTiO_3 samples. The change in phase structure of the BHT ceramics can be confirmed from the change of two pseudocubic reflections $\{200\}_C$ and $\{220\}_C$ (see Fig. 1(b) and (c)). As shown in Fig. 1(b) and (c), the pure BaTiO_3 ceramic shows a tetragonal phase, while the BHT ceramics with $x=0.03$ exhibits the coexistence of the orthorhombic and tetragonal phases, which can be seen from its XRD pattern (Fig 1(c), the orthorhombic reflection is labeled by an red arrow). It is believed that the first order nature of the $P4mm\text{-}Amm2$ transition in the BHT system leads to the coexistence of the orthorhombic and tetragonal phases around $x=0.03$ [28]. As x further increases, the BHTs with $x=0.11$ and $x=0.17$ show a rhombohedral phase at room temperature.

Fig. 2(a) shows the temperature dependence of dielectric permittivity of the BHT bulk ceramics with different compositions ($x=0.03$, 0.10, 0.11, 0.17). Fig. 2(b) shows the phase diagram of the BHT ceramic systems, which is established by using the temperature-dependent dielectric permittivity data of the BHT ceramics with $x=0$, 0.03, 0.06, 0.09, 0.10, 0.11, 0.12, 0.13, 0.15, 0.17, 0.20. From Fig 2(b), one sees that for pure BaTiO_3 ceramics the ferroelectric phase transition from tetragonal (T) to paraelectric cubic (C) occurs at 120 °C (T_C), and the ferroelectric phase transition from tetragonal (T) to ferroelectric orthorhombic (O) takes place at -5 °C (T_{T-O}), and

the ferroelectric phase transition from orthorhombic (*O*) to ferroelectric rhombohedra (*R*) happens at -90 °C (T_{O-R}), which is consistent with the results in the literature on pure BaTiO₃ ceramics [28]. As the hafnium doping level x increases, the T_C of the BHT ceramics decreases, while T_{T-O} and T_{O-R} increases. The three peaks marked with the pink arrows in the permittivity curve for the $x=0.10$ composition demonstrate the transitions from cubic to tetragonal to orthorhombic to rhombohedral. In contrast, only a single sharp permittivity peak is shown for the $x=0.11$ (ICP) composition, which displays the phase transition from cubic to rhombohedral. Also, the heat flow curves shown in the inset of Fig. 2(a) further confirm the dielectric results. Therefore, element doping is indeed an efficient way to adjust the phase transition of BHT. For the $x=0.11$ composition, the invariant critical point, there is only one single permittivity peak at 72 °C. The permittivity of the $x=0.11$ composition is almost twice higher than that of the other compositions, which is in agreement with the improved dielectric and piezoelectric properties at the ICP point reported previously [29]. In contrast, the BHT with $x=0.17$ displays a diffusive phase transition from the *C* phase to *R* phase at 32 °C. The specific heat capacity data of the BHT ceramics obtained from DSC measurements during the cooling process are illustrated in Fig. 2(c). It is found that the DSC data are in good agreement with the dielectric results (Fig. 2(a)) for the BHT ceramics with $x=0.03$. Three exothermic peaks appear at around -37 °C, 28 °C, and 110 °C, respectively, indicating the *C-T-O-R* phase transitions sequence, while only a single peak can be identified for both the ICP composition ($x=0.11$) and the DPT composition ($x=0.17$) from the DSC curves. In addition, with increasing the

Hafnium doping concentration, the exothermic peak is suppressed considerably and the phase transition becomes gradually diffused. This temperature diffuseness may also be revealed on the dielectric data (Fig. 2(a)) when one compares the dielectric peaks of the BHT ceramics with $x=0.11$ and $x=0.17$.

3.2. ECE study

Indirect ECE measurements [30]

Using the well-known Maxwell relation $(\partial P/\partial T)_E = (\partial S/\partial E)_T$, the adiabatic temperature change (ΔT) of an electrocaloric materials upon the application of an electric field from E_1 ($E_1=0$) to E_2 can be determined as [19]

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

where c_p is the specific heat capacity, ρ is the density of the BHT ceramics. Both c_p and ρ were measured under zero electric field. The values of $(\partial P/\partial T)_E$ for the BHT ceramics with different compositions were obtained from the fourth-order polynomial fits to the polarization versus temperature data.

Direct ECE measurements [2]

To evaluate the specific heat exchange values (ΔQ), the area under the exothermic and endothermic peaks was integrated. Then, the isothermal electrocaloric temperature change (ΔT), was estimated for a given temperature according to the following equation [4]

$$\Delta T = \frac{\Delta Q}{c_p} K \quad (2)$$

where c_p is the specific heat capacity and K is the thermal loss factor. Normally, K is greater than 1 [4]. Here, we defined $K=1$ (that is, thermal loss is neglected during the measurements). A contribution related to Joule heating can be neglected since the DSC signal returns to the baseline after the field was switched on or off.

3.2.1 ECE around the FPT

Fig. 3 shows both the indirect and direct ECE performances around FPT. In order to estimate the ECE of the BHT ceramics, the temperature-dependent P - E hysteresis loops were collected under different electric fields every 5 °C during the cooling process, as shown in Fig. 3(a). Fig. 3(b) displays the evolution of the P_{max} - T curves at different electric fields ranging from 0 to 20 kV/cm. By increasing the strength of the electric field, the P_{max} - T curves become smoother but the observed inflection is not shifted toward higher temperatures. Fig. 3(c) shows the temperature dependences of the ECE, ΔT is indirectly calculated according to Eq. (1). For ΔT , a sharp increase around 27 °C and a sharp decrease around 40 °C in the ECE are observed for all the electric fields applied. At the lower field (e.g., 10 kV/cm), the ΔT reaches the maximum (i.e., $\Delta T=0.22$ °C) with the $\Delta T/\Delta E=0.22$ K mm kV⁻¹ at 27 °C, which is in agreement with the transition temperature estimated from the dielectric measurements. With increasing the electric field (20 kV/cm), the ΔT is elevated to 0.4 °C, and $\Delta T/\Delta E$ still remains above 0.2 K mm kV⁻¹. Meanwhile, the ΔT maximum shifts to higher temperatures and becomes broader. Fig. 3(d) displays typical direct ECE measurement results of our BHT ceramics ($x=0.03$) with a modified DSC under

a low electric field. Application of a low electric field results in an exothermic peak, corresponding to heat release to the environment. By switching off the electric field, the DSC signal shows an endothermic peak corresponding to the heat absorption from the environment. Both the exothermic and the endothermic peaks are of a similar magnitude, which verifies the reversibility of the ECE effect. However, when the environment temperature is 35 °C, a large exothermic peak appears immediately after applying an electric field for the first time, while the followed endothermic and exothermic peaks decrease dramatically, and a large $\Delta T=0.33$ °C is achieved under 10 kV/cm at 35 °C. As Bai *et al.* [25] mentioned before, the *T* or *O* phases can remain in a metastable state in the cooling or heating process in the absence of an applied field. Here, considering the coexistence of the *O* and *T* phase, it is believed that the appearance of the large exothermic or endothermic peak after the first application or removal of electric field is attributed to the lattice energy contribution from the electric-field-induced structural phase transition. Fig. 3(e) presents both the direct and indirect ECE around FPT under a low electric field (i.e., 10 kV/cm), a large $\Delta T=0.33$ °C at 35 °C is achieved during the first cycle after the application of an electric field. After that, ΔT decreases sharply. A large $\Delta T=0.19$ °C is achieved under 10 kV/cm at 45 °C, which is twice higher than the indirect ECE. However, the thermal stability of ECE around FPT is not very well, which is attributed to the low temperature range of FPT. All the results above show that ECE around FPT is extremely sensitive to the phase structure and the electric field applied, which was also confirmed by our direct ECE measurements.

3.2.2 ECE around the ICP

Fig. 4 displays both the indirect and direct ECE performances around ICP. The representative temperature-dependent P - E hysteresis loops around ICP are shown in Fig. 4(a). The hysteresis loops become slimmer and slimmer with increasing temperatures, which demonstrates the phase transition from the ferroelectric to the paraelectric phase. Fig. 4(b) shows the evolution of the P_{max} - T curves at different electric fields ranging from 0 to 50 kV/cm. By increasing the strength of the electric field, the P_{max} - T curves become smoother but the observed inflection is not shifted toward higher temperatures. Fig. 4(c) shows the temperature dependences of the ECE, in which ΔT was indirectly calculated from Eq. (1). At the low electric field (i.e., 10 kV/cm), both a large $\Delta T=0.42$ °C and a large electrocaloric efficiency $\Delta T/\Delta E=0.42$ K mm kV⁻¹ are obtained at 65 °C. As the electric field further increases, ΔT still increases and reaches 1.35 °C at 50 kV/cm, while $\Delta T/\Delta E$ decreases to 0.27 K mm kV⁻¹. All the above results indicate that ECE under a low electric field shows a large electrocaloric efficiency than that under a high electric field. Meanwhile, the ECE peaks at 65 °C, and the temperature range of ECE around ICP is broad. Fig. 4(d) displays the direct ECE measurements of the BHT ($x=0.11$) ceramic under a low electric field (10 kV/cm) at 70 °C. Both the exothermic and endothermic peaks are of the similar magnitude, which verifies the reversibility of the effect. Fig. 4(e) presents the direct and indirect ECE around ICP under a low electric field (i.e., 10 kV/cm). The direct data in this figure are lower than the indirect data, which is attributed to the

slightly thermal loss during the direct measurements. Generally, both the direct and indirect data show the same tendency around the ICP. Meanwhile, the direct ECE reaches the maximum ($\Delta T=0.35$ °C) and a large $\Delta T/\Delta E$ (0.35 K mm kV^{-1}) at 70 °C, which is in good agreement with the transition temperature estimated from the dielectric measurements.

As suggested by Liu et al.[24], the ECE performance around ICP can be explained by using the following equation

$$S_{dip} = \sum_i \frac{k}{v_i} c_i \ln \left(\frac{c_i}{\Omega_i} \right) \quad (3)$$

where k is the Boltzmann constant, c_i is the volume fraction of i th phase, Ω_i is the number of the polar-states in the i th phase, and v_i is the average volume associated with each dipolar unit in the i th phase (the smallest unit of v_i is given by the volume per molecular unit). It can be seen from Eq. (3) that the entropy of an EC material depends on the total number of the polar states in a specific phase. With the coexistence of the R ($\Omega=8$), O ($\Omega=12$), and T ($\Omega=6$) phases near an ICP, there is a significant increase in the entropy of the non-polar phases, leading to a giant ΔT . Moreover, the near zero energy barriers near ICP also imply that a low field could readily induce switching between these different states and hence a giant ECE can be obtained under low electric fields [3, 9].

3.2.3 ECE around the DPT

Fig. 5 presents both the indirect and direct ECE performances around the DPT. The representative temperature-dependent P - E hysteresis loops around the DPT are

shown in Fig. 5(a). The hysteresis loops become slimmer and slimmer as temperature increases from 32 °C to 62 °C, in comparison with the hysteresis loops around FPT or ICP. This behavior demonstrates a diffuse phase transition taking place in this temperature range. Fig. 5(b) shows the evolution of the P_{max} - T curves at different electric fields ranging from 0 to 50 kV/cm. By increasing the strength of the electric field, the P_{max} - T curves become smoother and the observed inflection is shifted toward higher temperatures. Fig. 5(c) shows the ECE as function of temperature under different applied electric fields, in which ΔT was indirectly calculated according to Eq. (1). It can be seen that a sharp increase in the ECE is observed around 32 °C for all the electric fields applied. This behavior is in good agreement with the temperature-dependent dielectric permittivity data (T_m). At the low field (i.e., 10kV/cm), the ECE reaches the maximum ($\Delta T=0.3$ °C) and a large $\Delta T/\Delta E$ (0.3K mm kV⁻¹) could be obtained around 40 °C, which is a few centidegrees above the transition temperature estimated from the dielectric measurements. However, when higher electric fields are applied to this DPT system, the ΔT continues to increase and the maximum ΔT is shifted to higher temperatures. The increase in ΔT at high temperatures becomes more significant under strong applied electric fields. For an applied field of 50 kV cm⁻¹, the maximum ΔT is 1 °C, which was observed 20 °C above T_m . Fig. 5(d) displays the direct ECE measurements of the BHT ($x=0.17$) ceramic under a low electric field (i.e., 10 kV/cm) at 50 °C. Both the exothermic and endothermic peaks are of the similar magnitude, which verifies the reversibility of the effect. Fig. 5(e) presents both the direct and indirect ECE around the DPT under low

electric field (i.e., 10 kV/cm). It is found that although the thermal loss during measurements has been neglected, the direct data in this figure is still higher than the indirect data. Meanwhile, the direct ECE reaches the maximum ($\Delta T=0.32$ °C) and a large electrocaloric efficiency $\Delta T/\Delta E=0.32$ K mm kV⁻¹ is obtained at 40 °C, which agrees with the ECE estimated from the indirect ECE measurements.

In order to understand the ECE behavior in Fig. 5(e), a possible mechanism around DPT is given as follows. It is known that the dielectric permittivity of a normal ferroelectric above the Curie temperature (T_C) follows the Curie-Weiss law. Diffuse phase transition (DPT) is generally characterized by the broadening of the dielectric constant maximum at the phase transition temperature, a large separation between the maxima of dielectric constant and a deviation from the Curie-Weiss law in the vicinity of T_C [31, 32].

The parameter ΔT_m , which describes the degree of the deviation from the Curie-Weiss law, is defined as follows [31]

$$\Delta T_m = T_{CW} - T_m \quad (4)$$

where T_{CW} denotes the temperature from which the permittivity starts to deviate from the Curie-Weiss law and T_m represents the temperature of the dielectric maximum. Fig. 6(a) presents the inverse of dielectric constant as a function of temperature at 100Hz. The solid lines are plotted for the BHT ($x=0.17$) ceramics using the Curie-Weiss law. It can be found that the dielectric behavior does not completely follow the Curie-Weiss law at temperatures above $T_m=32$ °C. A deviation from the Curie-Weiss law starts at $T_{CW}=70$ °C, and the ΔT_m of BHT($x=0.17$) ceramics is 38 °C, which

further provides the evidence of a composition-induced diffuse phase transition behavior in our sample.

A modified Curie-Weiss law also has been proposed to describe the diffuseness of a phase transition [31, 32]

$$\frac{1}{\varepsilon} - \frac{1}{\varepsilon_m} = \frac{(T-T_m)^\gamma}{C'} \quad (5)$$

where γ and C' are assumed to be constant. The parameter γ gives information on the character of the phase transition: for $\gamma=1$, a normal Curie-Weiss law is obtained, $\gamma=2$ describe a complete diffuse phase transition.

The plot of $\ln(1/\varepsilon - 1/\varepsilon_m)$ as a function of $\ln(T-T_m)$ for the BHT ($x=0.17$) sample is shown in Fig. 6(b). A linear relationship is observed for the sample. The slope of the fitting curve (using Eq. (5)) is used to determine the γ value. The determined value of γ is 1.575, clearly implying the BHT($x=0.17$) ceramic exhibit a stronger diffuse phase transition.

As described above, we believe that BHT ceramic with the hafnium composition $x=0.17$ shows a stronger diffuse phase transition from T_m (32 °C) to T_{CW} (70 °C). In order to gain an underlying mechanism of the ECE around DPT, we also adopt a modified schematic Landau free-energy landscape initially proposed in Refs.[33-36], which phenomenologically describes the state of a system in terms of both the configuration coordinate and the average order parameter. Consequently, the locally ordered polarization in the microstates can be taken into consideration. The free energy F of the system can be written in terms of polarization (P) [37]

$$F(\vec{P}) = F_0 + aP^2 + bP^4 + cP^6 + dP \quad (6)$$

where d represents the average field caused by an external electric field and a , b and c represent the coefficients for different order terms. F_0 is the free energy of the paraelectric phase. In Fig. 7 we draw a Landau free energy profile in which $k_B T$ represents the thermal activation energy. Dotted lines describe the local barriers which influence the local structures and can be caused by inhomogeneity (composition or local field). It is considered that the local barriers (dotted lines) increase with decreasing temperature and $k_B T$ is higher than the local barriers at $T > T_{CW}$, but lower than the local barriers at $T < T_m$ [34]. When $T > T_{CW}$, despite that the activation energy is higher than the local barriers (i.e., $k_B T > \text{the local barrier}$), the nonpolar phase shows the minimum energy valley and at the same time is thermodynamically stable, as shown in Fig. 7(a). When $T < T_m$, $k_B T < \text{the local barrier}$ and the polar phase is in the stable state, as shown in Fig. 7(c). The orange part in Fig. 6(c) shows the ECE measured in the polar state. It can be seen that a sharp increase in the ECE could be observed and the maximum ECE is achieved at T_m (32 °C). This sharp rise in the ECE corresponds to the strong entropic contribution from the formation and alignment of the polar phase around T_C , in the vicinity of which the maximum ECE is observed for classical ferroelectrics [14, 38].

However, it can be seen in the magenta part that the ECE measured in the DPT is also growing above T_m with the increase of electric field. In particular, when electric field is E_0 (i.e., 5 kV/cm), the ECE reaches the maximum around 10 °C, which is a few centidegrees above the T_m . However, when stronger electric fields (i.e. $2E_0$, $6E_0$ or $10E_0$) were applied, the maximum ECE is shifted to higher temperatures

and meanwhile a wider ECE temperature range is obtained. It was assumed that this phenomenon originates from the composition fluctuations in DPT, which leads to the appearance of the mixed phase of small sized polar phase in nonpolar phase matrix (and the average structure is still nonpolar phase) in a large temperature range, as shown in Fig. 7(b). The appearance of mixed phase can be attributed to the local barrier, which is higher than $k_B T$.

At $T=T_1$ ($T_m \leq T_3 < T_2 < T_1 \leq T_{CW}$), the nonpolar phase is more stable than the polar phase (Fig. 7(d₁)), meaning that at this critical temperature only a small number of the small sized polar phase are embedded in the nonpolar matrix. When the system is applied with a low electric field (E_0 and E_1), the free energy of the polar phase becomes lower than that of the nonpolar phase (Fig. 7(d₂), (d₃)), the field-induced polar phase will still be able to return to the stable nonpolar phase due to the low local barrier ($k_B T > \text{the local barrier}$) after the removal of the electric field. Therefore, the BHT ceramic will show an enhanced ECE behavior at T_1 .

At $T=T_2$ ($T_m \leq T_3 < T_2 < T_1 \leq T_{CW}$), the free energy of the polar phase becomes equal to that of the nonpolar phase. However, the spontaneous phase transition cannot occur due to the kinetic limitation (as $k_B T < \text{the local barrier}$) (Fig. 7(e₁)). When a relatively low electric field E_0 is applied to the system, the field-induced polar phase becomes more stable than the nonpolar phase (Fig. 7(e₂)), the field-induced polar phase will still be able to go back to the stable nonpolar phase due to the low local barrier ($k_B T > \text{the local barrier}$) after the removal of the electric field. When a low electric field E_1 is applied to the system, the field-induced polar phase becomes more

stable (Fig. 7(e₃)). Therefore, the BHT ceramic at T_1 under E_1 will show a similar behavior like the sharp increase of ECE in the orange part.

At $T=T_3$ ($T_m \leq T_3 < T_2 < T_l \leq T_{CW}$), the polar phase is more stable than the nonpolar phase, however, the spontaneous phase transition still cannot occur due to the kinetic limitation ($k_B T < \text{the local barrier}$) (Fig. 7(f₁)). When the system is under an applied electric field (E_0 and E_1), the polar phase becomes more stable than the nonpolar phase, but is still dynamically stable after the removal of an electric field (Fig. 7(f₂), (f₃)), which is due to the high local barrier ($k_B T < \text{the local barrier}$). Like the ECE behavior in the orange part, there is also a sharp increase in the ECE, which could be observed when higher electric fields (e.g., $2E_0$, $6E_0$, $10E_0$) is applied to the BHT ceramic. The same phenomena have been observed in the ferroelectrics with DPT previously [39, 40]. It is shown that a polar phase can be induced by applying an electric field within the nonpolar phase and vice versa, depending on whether the temperature is above or below T_C . From the above discussion, we conclude that the enhanced ECE behavior around DPT is strongly dependent on the nature of the local barriers, structural phase transition and the electric field coupling effect. All the aforementioned results prove that the ECE under low electric fields can be enhanced by tuning the diffuseness of phase transition.

Table 1 presents the ECE properties of typical lead-free electrocaloric materials, such as ferroelectric bulk ceramics, single crystals and polymers that have potential for practical cooling applications. Although high ECE values are obtained in these ferroelectric bulk ceramics, such as $0.82(\text{Na}_{0.5}\text{Bi}_{0.5})\text{TiO}_3$ - $0.18(\text{K}_{0.5}\text{Bi}_{0.5})\text{TiO}_3$

(NBT-KBT) [6], these values can only be maintained at high temperatures ($> 100\text{ }^{\circ}\text{C}$), which would be difficult for commercial applications. Similarly, these ceramics with giant temperature change ΔT were normally achieved under high electric fields, which is not be economical and practical. As can be seen, lead-free bulk ceramics such as BST or BZT-BCT [4, 7, 8], always display a weak ECE at their working temperature range under low electric fields. However, the BHT ceramics developed in this work show both a high temperature change ΔT ($> 0.3\text{ }^{\circ}\text{C}$) and a large electrocaloric efficiency $\Delta T/\Delta E$ ($> 0.3\text{ K mm kV}^{-1}$) under relatively low electric fields (10 kV/cm) near room temperature. Concurrently, the ECE values reported in this work in the BHT ceramics are comparable to that of single crystals such as SBN75 or Cerium doped SBN61 [12, 13]. The combination of these super performances indicates the potential of using the BHT ceramics for the ECE-based solid state cooling devices.

4. Conclusions

In summary, we have demonstrate that both a large adiabatic temperature change (ΔT) and a large electrocaloric efficiency ($\Delta T/\Delta E$) could be achieved in the lead-free BHT bulk ceramics under relatively low electric field (i.e., 10 kV/cm) by tuning the composition to its FPT, ICP or DPT. We have also shown that the enhancement in ECE is strongly dependent on the structure transition and the electric field coupling effect. The BHT bulk ceramic with FPT shows a large ECE under low electric fields, which is attributed to the electric-field-induced phase transition of a

metastable phase in FPT. However, this large ECE only appears during the first cycle after the application or removal of the electric field, and is therefore practically difficult for electrocaloric cooling. Nevertheless, understanding the ECE behaviors in FPT may shed new light on the mechanisms of achieving a large ECE under low electric fields. For the BHT bulk ceramic near ICP, the coexistence of multi-phases provides more randomness in the systems, leading to more available polarization states and the low energy barriers near ICP in the system, which implies that a low field could induce switching between these different states and hence a large ECE can be obtained under low electric fields. The BHT bulk ceramic near DPT shows a large ECE around room temperature and a wide temperature range under low electric fields, which is promising for practical electrocaloric cooling devices. The BHT ceramic near DPT shows composition fluctuations, which provides more polar or nonpolar metastable states and hence the system is more sensitive to electric field. Thus, phase structure and the electric field coupling effect are considered to be the main contributions for the enhancement of ECE near FPT, ICP or DPT. Our work therefore underlines a few important ways to achieve high ECE performances under low electric fields, though more deep studies are needed to deepen our understanding on the ECE in ferroelectric or other polar materials.

Acknowledgments

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Table 1. Comparison of the ECE properties of the BHT ceramics studied in this work with those in the literature

		T	ΔT	ΔE	$\Delta T/\Delta E$		
Material	Form	(°C)	(°C)	(kV cm ⁻¹)	(K mm kV ⁻¹)	Method	Reference
BST	Ceramic	16	0.23	10	0.23	DSC ^d	7
BZT-7BCT	Ceramic	28	0.16	40	0.04	Thermometer ^e	6
BZT-35BCT	Ceramic	65	0.33	20	0.165	DSC	3
BZT	Glass + Ceramic	38	1.1	21	0.52	Direct ^f	2
NBT-KBT	Ceramic	160	0.73	22	0.33	DSC	5
KNN-STO	Ceramic	23	1.2	159	0.075	DSC	4
P(VDF-TrFE) ^a	Polymer	33	20	1600	0.125	Direct	13
Polymer/BST ^b	Polymer composite	26	32	1500	0.213	Direct	16
BT	Single crystal	129	0.7	12	0.58	Direct	8
BT	Single crystal	140	1.6	10	1.6	DSC	9
SBN75	Single crystal	85	0.4	10	0.4	DSC	10
Doped SBN	Single crystal	61	0.85	28	0.3	DSC	11
BHT (x=0.03)	Ceramic	35	0.33 ^c	10	0.33	DSC	This work
BHT (x=0.03)	Ceramic	45	0.19	10	0.19	DSC	This work
BHT (x=0.11)	Ceramic	70	0.35	10	0.35	DSC	This work
BHT (x=0.17)	Ceramic	40	0.32	10	0.32	DSC	This work

^aP(VDF-TrFE) refers to irradiated poly(vinylidene fluoride-co-trifluoroethylene)

^bPolymer/BST refers to poly(vinylidene fluoride-ter-trifluoroethylene-terchlorofluoroethylene) (P(VDF-TrFE-CFE)) with

$\text{Ba}_{0.67}\text{Sr}_{0.33}\text{TiO}_3$ (BST) nanofiller

^cECE after first applying or removing electric field

^dDirect ECE measurement using modified differential scanning calorimetry (DSC)

^eDirect ECE measurement using a thermometer

^fDirect ECE measurement using adiabatic method

Captions for Figures:

Fig. 1. XRD patterns of the BHT ceramics. (a) the powder XRD results of the BHT ceramics with $x=0, 0.03, 0.11$ and 0.17 , respectively. (b)-(c) Pseudocubic $\{200\}_C$ and $\{220\}_C$ reflections of the BHT ceramics. The arrow indicates the reflections from the respective phase (O=orthorhombic reflection).

Fig. 2. Dielectric permittivity, phase diagram and the specific heat data of the BHT ceramics. (a) Temperature dependence of dielectric permittivity of the BHT ceramics with $x=0.03, 0.10, 0.11$ and 0.17 , respectively, measured at 100Hz . The inset shows the DSC curves of the BHT ceramics with $x=0.10$ and 0.11 , respectively, measured during the cooling process. The cooling rate is $5\text{ }^\circ\text{C}/\text{min}$. (b) the phase diagram of the BHT ceramics constructed by using the dielectric permittivity versus temperature results shown in (a). (c) The specific heat data of the BHT ceramics with $x=0.03, 0.11$ and 0.17 , respectively, measured during the cooling process. The cooling rate is $5\text{ }^\circ\text{C}/\text{min}$.

Fig. 3. The ECE properties of the BHT ceramics with $x=0.03$, a composition being around FPT. (a)-(c) The indirect ECE measurement results of the BHT ceramics. The P - E loops were measured under $20\text{ kV}/\text{cm}$ @ 100Hz . (d) The direct ECE results of the BHT ceramics with $x=0.03$ measured under $10\text{ kV}/\text{cm}$. (e) shows the comparison of the direct and indirect ECE data of the BHT ceramics with $x=0.03$ measured under $10\text{ kV}/\text{cm}$ at $25\text{ }^\circ\text{C}$, $35\text{ }^\circ\text{C}$ and $45\text{ }^\circ\text{C}$, respectively

Fig. 4. The ECE properties of the BHT ceramics with $x=0.11$, a composition being around ICP. (a)-(c) The indirect ECE measurement results of the BHT ceramics. The P - E loops were measured under 20 kV/cm @ 100Hz. (d) The direct ECE results of the BHT ceramics with $x=0.11$ measured under 10 kV/cm. (e) shows the comparison of the direct and indirect ECE data of the BHT ceramics with $x=0.11$ measured under 10 kV/cm at 50 °C, 60 °C, 70 °C and 80 °C, respectively

Fig. 5. The ECE properties of the BHT ceramics with $x=0.17$, a composition being around DPT. (a)-(c) The indirect ECE measurement results of the BHT ceramics. The P - E loops were measured under 20 kV/cm @ 100Hz. (d) The direct ECE data of the BHT ceramics with $x=0.17$ measured under 10 kV/cm. (e) shows the comparison of the direct and indirect ECE data of the BHT ceramics with $x=0.17$ measured under 10 kV/cm at 30 °C, 40 °C and 50 °C, respectively

Fig. 6. The diffuse phase transition behavior of the BHT ceramic with $x=0.17$. (a) The inverse dielectric permittivity ($1/\epsilon'$) measured at 100Hz as a function of temperature. (The red symbols: the experimental data; the blue solid line: the fitting curve using the Curie–Weiss law.) (b) the plot of $\ln(1/\epsilon' - 1/\epsilon'_m)$ as a function of $\ln(T - T_m)$. (The blue symbols: the experimental data; the red solid line: the fitting curve using Eq. (4).) (c) The ECE properties of the BHT ceramic with $x=0.17$ versus temperature for different electric fields E_0 (5 kV/cm), $2E_0$, $6E_0$ and $10E_0$, respectively. The insets show the P - E

loops measured under $2E_0$ at 22 °C, 52 °C and 72 °C, respectively.

Fig. 7. (a), (b) and (c) show the schematic Landau free-energy curves at zero electric field for different temperature regions: (a) $T > T_{CW}$ (nonpolar region), (b) $T_m < T < T_{CW}$ (DPT region), (c) $T < T_m$ (polar region). (d₁), (d₂) and (d₃) show the free-energy curve of DPT at $T = T_1$ ($T_m < T_3 < T_2 < T_1 < T_{CW}$) for $E = 0$, $E = E_0$ and $E = E_1$ ($E_0 < E_1$), respectively. (e₁), (e₂) and (e₃) show the free-energy curve of DPT at $T = T_2$ ($T_m < T_3 < T_2 < T_1 < T_{CW}$) for $E = 0$, $E = E_0$ and $E = E_1$ ($E_0 < E_1$), respectively. (f₁), (f₂) and (f₃) show the free-energy curve of DPT at $T = T_3$ ($T_m < T_3 < T_2 < T_1 < T_{CW}$) for $E = 0$, $E = E_0$ and $E = E_1$ ($E_0 < E_1$), respectively.

Figure(1)

Figure(2)

Figure(3)

Figure(4)

Figure(5)

Figure(6)

Figure(7)

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^cECE after first applying or removing electric field

^dDirect ECE measurement using modified differential scanning calorimetry (DSC)

^eDirect ECE measurement using a thermometer

^fDirect ECE measurement using adiabatic method

Fig. 1(a) displays the direct ECE measurements of the BHT ($x=0.17$) ceramic under a low electric field (i.e., 10 kV/cm) at 50 °C. Both the exothermic and endothermic peaks are of the similar magnitude, which verifies the reversibility of the electrocaloric effect. Fig. 1(b) presents both the direct and indirect ECE around the DPT under low electric field (i.e., 10 kV/cm). It is found that although the thermal loss during measurements has been neglected, the direct data in this figure is still higher than the indirect data. Meanwhile, the direct ECE reaches the maximum ($\Delta T=0.32$ °C) and a giant electrocaloric efficiency $\Delta T/\Delta E=0.32$ K mm kV⁻¹ is obtained at 40 °C, which agrees with the ECE estimated from the indirect ECE measurements. The BHT ceramic near DPT shows composition fluctuations, which provides more polar or nonpolar metastable states and hence the system is more sensitive to electric field. Thus, phase structure and the electric field coupling effect are considered to be the main contributions for the enhancement of ECE near DPT.