High electrocaloric cooling power of relaxor ferroelectric BaZr$_{1-x}$Ti$_x$O$_3$ ceramics within broad temperature range

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Abstract

Electrocaloric effect (ECE) is much promising to realize high efficiency and environment friendly solution in solid cooling devices. Relaxor ferroelectrics are good candidates for the materials with high electrocaloric cooling power. In this paper, relaxor ferroelectric Ba(Zr$_x$Ti$_{1-x}$)$_2$O$_3$ (BZT, $x = 0.2, 0.21, 0.22, 0.23$) ceramics were prepared with their temperature change ($\Delta T$) induced by the ECE and electrocaloric strength ($\Delta T/E$) measured within broad temperature range. It is found that the BZT21 ($x = 0.21$) exhibits the largest $\Delta T$ of $-4.67$ K and a high $\Delta T/E$ value of $-0.46$ km/MV at 9.9 MV/m and 25 °C. BZT21 also exhibits apparent relaxor ferroelectric response, showing a very broad EC peak in the temperature interval between 15 °C and 50 °C. Moreover, the relationship between EC properties and relaxor features was analyzed by piezoresponse force microscopy test. The results reveal that more dispersed phase structures induce additional configurational entropy, which is in favor for the enhanced EC performance. The interplay and compromise between the kinetic and thermodynamic mechanisms of domain switching determines the optimal composition for the EC performances of the BZT ceramics.

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1. Introduction

Under adiabatic condition, an abrupt temperature change ($\Delta T$) can be detected on a dielectric material upon a quick removal of applied electric field ($\Delta E$), which is called the electrocaloric effect (ECE). Cooling devices based on ECE are all-solid-state without any moving parts, environment friendly without using Freon cooling agent and capable of achieving cooling efficiency that could be detected on a dielectric material upon a quick removal of any moving parts, environment friendly without using Freon cooling agent and capable of achieving cooling efficiency that could be deduced using Maxwell relations [4–7]:

$$\Delta S = \int_{E_1}^{E_2} \frac{\partial P}{\partial T} \, dE,$$

$$\Delta T = - \int_{E_1}^{E_2} \frac{E \partial P}{C_p} \, dE,$$

where $E$ is the applied electric field, $P$ is the corresponding electrical polarization induced, $T$ is the environment temperature, $C_p$ is the specific heat capacity of the dielectrics. According to the relations, large ECE may be obtained in materials which have large polarizability. For ferroelectric materials, ferroelectric-paraelectric (FE-PE) phase transition induces dramatic change in dielectric properties near the Curie temperature ($T_c$). The large polarization change between a polar-disordered and a polar-ordered state gives rise to large entropy change leading to substantial temperature change [7–12]. For instance, a temperature change of $\Delta T = 12$ K was calculated using the Maxwell relation near Curie temperature ($T_c = 226$ °C) under 48 MV/m in PZT thin films [13].

However, in normal ferroelectrics, the substantial change of dielectric properties only occurs within a narrow temperature range close to the Curie temperature, resulting in low average ECE level and limiting their practical use within a narrow temperature window. Relaxor ferroelectrics, with their Curie temperature substantially broadened, exhibit high dielectric permittivity and polarizability in a much wider temperature range hence deliver higher average ECE level within larger temperature range (larger EC temperature window). In addition, relaxor ferroelectrics also possess larger polarization which means higher entropy and temperature change under low electric field, thus...
the EC strength ($\Delta T/E$) is larger than normal ferroelectrics. It is even possible to tune the Curie temperature of relaxor ferroelectrics close to room temperature, making them viable for cooling devices such as refrigerator and air conditioner [9]. For instance, in relaxor ferroelectric $Pb_{0.88}La_{0.11}(Zr_{0.7}Ti_{0.3})_{0.9725}O_{3}$ (PLZT), a very high $\Delta T/E$ value of 0.453 km/kV was found [14]. A $\Delta T = 4.5$ K was achieved in Barium zirconate titanate (Ba(Zr$_{1-x}$Ti$_x$)$_2$O$_3$, BZT) bulk ceramics, at 14.5 MV/m, 39 °C, and good stability in $\Delta T$ could be observed [15]. And in Y5V MLCCs that were basically composed of Zr$^{4+}$ ions doped BaTiO$_3$ (BTO), a giant ECE of $\Delta T = 13.94$ K and the wide temperature window were also observed [16]. Thus, BZT has been widely considered as a good lead-free relaxor ferroelectrics with high dielectric permittivity and polarizability [17]. The introduction of Zr element in BTO transforms BTO from ferroelectrics to relaxor ferroelectrics and adjusts the Curie temperature from ~130 °C for BTO to room temperature. When the content of Zr is >15% in BZT, tetragonal ferroelectric, cubic paraelectric, orthorhombic (O) and rhombohedral (R) phases may coexist at a specific temperature called invariant critical point (ICP), contributing to a significant increase of polar state change to induce large ECE [15,18,19].

When content of Zr is >25%, apparent relaxor ferroelectric response can be observed in BZT, and the maximum dielectric permittivity would appear near room temperature [20,21]. In this work, BaZr$_{1-x}$Ti$_x$O$_3$ ($x = 0.2, 0.21, 0.22, 0.23$) ceramic samples were prepared with their EC behaviour investigated near room temperature. Large temperature change of $\Delta T = 4.67$ K is achieved at 9.9 MV/m, 25 °C for BZT21 ($x = 0.21$). It also exhibits very broad EC temperature window near room temperature. The ferroelectric domain structure and switching dynamics of the BZT relaxors were investigated by piezoresponse force microscopy (PFM) within a large temperature range. It is revealed that large entropy change is induced by the separated micro-/nano-domains. These micro-/nano-domains could still be observed up to temperatures much higher than Curie temperature. Results of PFM lithograph further reveal that enhanced relaxor response is induced by increasing content of Zr in BZT. It is thus inferred that the change in kinetic and thermodynamic properties of domains will induce a complex influence upon the ECE.

2. Experimental

2.1. Synthesis of BZT ceramics

The BZT20 ($x = 0.20$), BZT21 ($x = 0.21$), BZT22 ($x = 0.22$), and BZT23 ($x = 0.23$) bulk ceramics were prepared by a conventional solid-state reaction method. All the raw chemicals, i.e., barium carbonate (BaCO$_3$, 99.0%), zirconium dioxide (ZrO$_2$, 98.0%), and titanium dioxide (TiO$_2$, 99.0%), were used directly without further purification. The powder of the three chemicals mixed by stoichiometric weights was milled using zirconia balls for 24 h in ethanol. The mixed powder was then calcined at 1,100 °C for 2 h followed by uniaxial pressing. The corresponding pellets were finally sintered at 1,350 °C for 2 h with a heating rate of 10 °C/min. The sintered pellets were polished and thinned to ~150 μm in thickness with both sides of the samples deposited with Au electrode for dielectric measurements. For the measurement of ECE, vanished copper wires were also pasted to the samples on each side, and were connected to the direct current (DC) power supplier. The samples were then solidified with differential scanning calorimeter (DSC) pans by using insulating glue [8]. For PFM experiments, the ceramics were further polished by using polycrystalline diamond pastes with abrasive particles of 5, 3, 1 and 0.5 μm consecutively, in order to make the roughness of the sample surface minimized.

2.2. Characterization of microstructure and electrocaloric performances

The phase composition of the ceramic was characterized by X-ray diffraction (XRD, Rigaku D/max 2500 V) at room temperature. The cross-section morphologies were examined by scanning electron microscopy (SEM, Hitachi S-4500). The temperature dependence of dielectric constants and loss were measured at 1 kHz using a HP 4294A precision impedance analyser with a temperature controller. Polarization ($P$)-electric field ($E$) unipolar loops as a function of electric field and temperature were measured with a Premier II ferroelectric test system (Radiant Technologies, Inc.). For the measurement of the ECE, DC voltages were applied to the samples that were solidified in DSC pans, then the changed signals of heat flow were recorded by the DSC (TA Instruments Q2000), as seen in Fig. S1a (online). By using the TA software, the heat values generated by ECE can be further obtained, as depicted in Fig. S1b (online). These isothermal heat values were used to calculate the $\Delta S$ and $\Delta T$. A function/arbitrary waveform generator (Agilent 33220 A) were coupled with a high voltage amplifier (TReK 20/20C) for the application of electric field during the ECE measurements. PFM measurements were performed using an atomic force microscope (Asylum Research, MFP 3D infinity) with high voltage and high temperature modules equipped.

3. Results and discussion

3.1. Microstructure and phase compositions

Fig. 1a shows the cross-section image of BZT21. As seen, BZT ceramics are of high densities, which are over 98.1% measured by Archimedes’ principle. From Figs. 1a and S2 (online), it can be seen that the average grain size is roughly uniform with mean value of 2–3 μm. XRD patterns of BZT20-23 ceramics at room temperature are shown in Fig. 1b. Pure perovskite phases are observed for all...
of the samples. No apparent shift in peak position can be found within all cases.

3.2. Dielectric properties

In Fig. 2a, the electric polarization loops (@10 Hz) of the BZT21 ceramic are presented. The polarization \( P \) of BZT21 can reach 18.1 \( \mu \text{C/cm}^2 \) at 8.4 MV/m, showing high polarizability. Also observed in Fig. 2a are the slim \( P-E \) loops and the low remnant polarization, which confirm that BZT21 is relaxor in nature. Similar feature in \( P-E \) loops can also be observed in other compositions (Fig. S3 online). The temperature dependences of polarizations \( (P) \) of BZT20-23 samples are shown in Fig. 2b. As seen, for all the samples, \( P \) decreases continuously with the increase of temperature from 25 °C to over 50 °C, which also indicates that BZT has good relaxor feature [22]. Furthermore, at the same temperature, BZT21 exhibits the largest \( P \) than other samples, which is about 6% larger than that of BZT20. Fig. 3a shows the dielectric constant of BZT20-23 ceramics as function of temperature measured at 1 kHz. As observed, for each sample, the dielectric constant evolution displays a broad peak. Moreover, the temperature where the peak value of permittivity appears decreases steadily with increasing content of Zr, e.g., from 29 °C for BZT20 to 12 °C for BZT21. All samples exhibit very low loss (Fig. S4 online), which is important to practical EC devices. In Figs. 3b and S5 (online), the dielectric constant versus temperature curves in different frequencies are presented. As seen, for all samples, the permittivity peaks move toward high temperatures with higher frequencies, indicating the relaxor nature of the BZT. In addition, the movements of peak temperatures are 3.5, 4.6, 6.3 and 8.2 K for BZT20, BZT21, BZT22 and BZT23, respectively. It can be inferred that more content of Zr can lead to more apparent relaxor nature. From the dielectric properties, it can be confirmed that all BZT samples exhibit apparent relaxor feature, which is in favour for the large EC temperature window.

3.3. Electrocaloric behaviors

Fig. 4 shows the temperature change (\( \Delta T \)) induced by ECE of BZT21-23 at 25 °C. The \( \Delta T \) were deduced from \( Q = \frac{\Delta T}{\Delta S} = \int \frac{d T}{C_p} d T \) [11,12], where \( C_p \) is the specific heat of the ceramic sample, \( T \) is the environmental temperature. As shown in Fig. S6 (online), the specific heat of the BZT ceramic does not change significantly with temperature. Also, no apparent difference in specific heat can be seen for samples with different compositions. BZT20 exhibits \( \Delta T = 4.43 \text{ K} \) and ECE strength of \( \Delta T/E \sim 0.35 \text{ km/MV} \) at 12.5 MV/m, which is consistent with previous report [20]. Increase in the content of Zr to \( x = 0.21 \) gives rise to much
enhanced ECE performance, e.g., $\Delta T = 4.67$ K, $\Delta S/T = 0.46$ km/MV at 9.9 MV/m. This is attributed to the large temperature and entropy change in the BZT21 ceramics (Fig. S7 online), which are almost unchanged in the temperature range of 25 °C to 45 °C. We note that higher content of Zr induces the coexistence of different phases, which then contributes to more different polar states and lower coercive electric field for domain switching [15,22]. In addition, with the apparent relaxor feature, BZT20–23 shows stable ECE in a large temperature interval (Figs. S7–S10 online), which is essential to EC devices.

3.4. Room-temperature PFM images

Fig. 5 shows the piezoresponse amplitude and phase degree images of the polished BZT samples measured by vertical PFM, where the piezoresponse amplitude and phase can provide information on the electromechanical coefficient (proportional to the local polarization) and on the direction of the local polarization, respectively [23]. For each sample, the piezoresponse amplitude and phase degree are basically consistent with each other. Hence the room temperature domain structures of the BZT ceramics can be clearly observed in Fig. 5c, f, i, l. From the images of phase degree, complex domain patterns consisting of antiparallel domains are observed. Both micro- and nano-sized domains are observed. Within the samples, with the increase of Zr content, the minimum size of the nano-domains decreases, and ferroelectric domains become more dispersive. For instance, as seen in Fig. 5 and Table S1 (online), the minimum domain size of BZT20 is ~350 nm, whereas the value of BZT22 decreases to ~150 nm. The nanosized domain is also an indication of a relaxor ferroelectric. As mentioned before, the complexity of the domain patterns is induced by the co-existing phase structures near ICP. The coexistence of different phases can lead to the formation of polar nano-regions (PNRs) with very low energy barriers [24]. As seen in Fig. 5, large amounts of nano-domains are composed of PNRs. Owing to the PNRs, when the temperature deviates from the Curie temperature, high polarizability can still be remained in BZT, which ensures that BZT exhibits relaxor ferroelectric response within a large

![Fig. 5](https://engine.scichina.com/doi/10.1016/j.scib.2018.02.016)
temperature range. Moreover, the near zero energy barriers imply a low electric field for switching the micro- and nano-domains, hence a giant ECE may be induced under low electric fields. With increasing Zr content, more PNRs form within domain structures, inducing larger ECE. However, further increase in the content of Zr to x = 0.22 or 0.23 results in lower polarizability for BZT ceramics (Fig. 2b), which could compromise the entropy change hence is less desirable to the electrocaloric effect. The average intensity of ferroelectric domain structures is calculated from the brightness and area in Fig. 5, and is 110.01, 110.92, 104.71, 102.75 for BZT20, BZT21, BZT22, BZT23, respectively. If the samples have higher intensity, when the domain structures are changed to an ordered state under a modified electric field, total change of entropy will be larger for generating the ECE. A domain intensity of ~110 is observed for BZT20, BZT21 ceramics and decreases to ~102 for BZT ceramics with higher content of Zr (x = 0.22, 0.23). This trend is consistent with the polarizability shown in Fig. 2b. It is also worth noting that, P of BZT21 is only 6% larger than that of BZT20 at the same temperature, as seen in Fig. 2b. From the thermodynamic perspective, the temperature change (ΔT) can be described as ΔT = βTD^2/2c, where c is the specific heat capacity, β is a coefficient [25]. It can be estimated that the 6% larger P only lead to 12.4% increase in ΔT with the assumption of same β coefficient for all BZT ceramics. The substantial enhancement in ΔT (25%) in BZT21 ceramics thus could not be solely attributed to entropy change induced by the change in electrical polarization. According to Kutnjak et al. [26], the entropy change can be described as

\[ S_{\text{up}} = S_0 + S_1(P), \]

where \( S_0 \) is the configurational entropy of the dipolar entities, and \( S_1(P) \) is entropy induced by polarization change. This equation demonstrates that the extra entropy change is induced by the configurational energy. In BZT21, domain structures with a higher complexity are observed, which may contribute to larger configurational entropy (\( S_0 \)).

3.5. Domain switching kinetics probed by PFM lithograph

To further explore the relaxation behavior of the BZT ceramics, PFM lithograph is performed. For each of the BZT ceramics, an area of 1 μm × 1 μm is poled by applying a poling voltage of 20 V at the tip. The written pattern is then read continuously at a lower tip voltage of ~0.8 V in the following 15 min. As seen in the piezo-response phase images (Fig. 6a), owing to their relaxor characteristics, all the BZT ceramics can be poled easily under low electric fields, as indicated by the large contrast between the poled and unpoled area in the phase images. With time elapsing, the dipoles gradually relax back to the equilibrium random configuration at zero field as evidenced by fading of the written patterns. Owing to the near-zero energy barriers of PNRs, the coercive field of relaxor ferroelectrics become much smaller. Hence, the phases of domains can switch to zero field state in a greatly shorter period of time compared with normal ferroelectrics. The relaxation rates of the ferroelectric domain in the BZT ceramics are then determined from the variation of average domain intensity with time (Fig. 6b). It could be readily distinguished that the relaxation rate decreases substantially with increasing amount of Zr. For comparison, same PFM lithograph is also performed on ferroelectric BTO ceramics. In stark contrast to the substantial relaxation of domains in BZT ceramics over time, very minor relaxation of ferroelectric domains is observed for the BTO ceramics (Fig. S11 online). Less than 10% of the domain area relaxed even after 60 min for the BTO ceramics (Fig. S11b online), compared to ~80% for BZT23 ceramics after only 15 min.

The increased relaxation rate indicates that higher concentration of Zr induce more dispersive phases and lower energy barriers in PNRs. The dipoles become “soft” hence are easier to switch at lower electric fields. These favourable features give rise to much improved EC strength (ΔT/E) and faster response speed in practical cooling devices. From the perspective of switching kinetics, higher content of Zr in BZT is desirable for large ECE.

3.6. Thermal stability of domains at elevated temperatures

We now turn to the thermal stability of domains in BZT ceramics. The BZT ceramics are subjected to heat treatments from 30 to 110 °C with their PFM images collected with increasing temperature. As shown in Fig. 7a, higher temperature induces depolarization of the BZT ceramics as indicated by the decrease in domain intensity. Two features could be readily observed from the PFM images at elevated temperatures. First, apparent domain patterns can still be seen up to 70 °C, which indicates that BZT samples indeed exhibit strong relaxor response within broad temperature range. Second, larger domains fade first while the smaller domains are more stable. At 110 °C, almost all of the domains vanish, and only a few residual nano-domains still can be found.

The variations of normalized domain intensity with temperature are shown in Fig. 7b. As seen, the domain intensity of BZT ceramics decreases mildly up to 70 °C, beyond which a much faster decrease in the domain intensity is observed. In ferroelectric BTO ceramics, the intensity of domains drops dramatically when the temperature is over its Curie temperature (~130 °C), as shown in Fig. S12b (online). This apparent difference between BTO and BZT
also implies relaxor ferroelectric response in BZT. Also observed in Fig. 7b is that BZT23 exhibit the lowest rate of domain relaxation with increasing temperature. We are thus led to the conclusion that domains in BZT ceramics with higher content of Zr are thermodynamically more stable at elevated temperatures. The implication of such higher thermal stability is that the same change in temperature (ΔT) induces smaller change in polarization (ΔP), hence smaller entropy change (ΔS) in BZT ceramics with higher content of Zr. From the perspective of thermodynamics, higher content of Zr in BZT ceramics is less desirable for large ECE.

By doping of Zr element, both kinetic and thermodynamic properties of the BZT ceramics are changed. And the two factors have competitive influence on the EC effect. From the micro domain structures and the macro dielectric properties, it can be inferred that 21% of Zr is the optimal point for the two factors. In BZT21, apparent relaxor feature can be obtained, which is beneficial to higher EC strength and broader temperature window. And higher compositions of Zr element induce decrease in polarizability hence compromise ECE performance.

4. Conclusions

In summary, BaZr$_x$Ti$_{1-x}$O$_3$ ($x$ = 0.2, 0.21, 0.22, 0.23) ceramics are prepared with their electrocaloric performances investigated within a broad temperature range. The result shows that BZT21 exhibits the best EC performance, which is $ΔT = 4.67$ K at 9.9 MV/m, 25 °C. And BZT21 also shows a very broad applicable temperature range from 15 to 50 °C. The obtained large ECE near room temperature will promote the practical application of lead-free solid cooling devices in the future. Moreover, the domain structures are observed by PFM test, showing that domain structures are affected by both of the kinetic and thermodynamic factors. PFM test can provide an effective method to investigate the relationship between relaxor features and electrocaloric effect.