Large electrocaloric effect obtained in $\text{Ba}(\text{Sn}_x\text{Ti}_{1-x})\text{O}_3$ lead-free ceramics using direct and indirect measurements

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The electrocaloric effect (ECE) in lead-free $\text{BaSn}_x\text{Ti}_{1-x}\text{O}_3$ (BSnT, $x = 0.05, 0.10$ and 0.15) ceramics were investigated using a direct ECE measurement. Results indicate that the maximum ECE occurs near the Curie temperature and it slightly shifts towards high temperatures. The directly measured ECE is larger than that calculated using the Maxwell relation and P-E loops. A maximum electrocaloric efficiency $\Delta T/\Delta E = 0.49 \times 10^{-6} \text{ K mV}^{-1}$ was procured for the composition with $x = 0.15$ at $T = 299.2 \text{ K}$. And it also shows a broad peak in the temperature range of $250\text{--}320 \text{ K}$.

Keywords: BaSnTiO_3 ceramic; direct measurement; electrocaloric effect.

1. Introduction

Recently, large electrocaloric effects (ECEs) have been reported in various organic and inorganic ferroelectric materials,^{1–6} since these materials hold the advantages of high energy conversion efficiency, simple structure and environmental friendliness, and are considered as potential candidates for making cooling devices. Up to now, however, most reported inorganic ferroelectric materials with a giant ECE contain lead element which is not environment benign. To achieve a high ECE with lead-free materials, barium titanate (BaTiO_3 (BTO)) is a good candidate due to its first-order phase transition, large thermal conductivity compared with the ferroelectric polymer counterpart, and ease of doping chemical elements to adjust its phase transition temperature and the randomness of the electric domains within the ceramics. A disadvantage for BTO, however, is the phase transition temperature ($\sim 120^\circ\text{C}$) which is far above the room temperature.⁷ Since usually the ECE occurs at the Curie temperature, a challenge is to shift the ferroelectric–paraelectric (FE–PE) phase transition temperature towards room temperature. In this work, the Sn^{4+} ions were chosen to be doped in BTO, since the Sn^{4+} ions can move the phase transition towards low temperatures linearly, as well as broaden the transition regime at the same time, which are favorable for the ECE devices to be used at room temperature and to have a wide working temperature range.^{8–10} The permittivity as a function of temperature and frequency, the

polarization as a function of electric field and temperature and the ECE were directly measured.

2. Experimental Procedure

The doped BSnT ceramics were prepared using a solid state reaction. The raw materials include: BaCO_3 (99%, Aladdin), SnO_2 (99.5%, Aladdin), and TiO_2 (99%, Aladdin). After weighing, the batch materials were ball milled, dried, ground, sieved and calcined at 1235°C for 2 h. Then, the powder was ground with an organic binder (PVA) in an agate mortar, pellets (12 mm in diameter and 1 mm in thickness) were pressed using a tablet press machine under the pressure of 2 MPa. These pellets were then sintered at 1355°C for 3 h with a heating rate of $5^\circ\text{C}/\text{min}$. Finally, gold electrodes were sputtered on both surfaces of the ceramics.

The density was measured using the Archimedes' principle. X-ray diffraction (XRD) measurement (Rigaku Ultima-IV) were pursued at room temperature with a scanning speed of 8 degree/min. The scanning electron microscope (SEM) (Hitachi S-3400N) was used to characterize the morphologies. The temperature dependences of permittivity and loss tangent were procured (Agilent 4284) at $f = 0.1, 1$ and 10 kHz . Polarization–electric field (P–E) hysteresis loops were obtained using a Sawyer–Tower circuit (Radiant Multiferroic Test System). The ECE was directly measured using a homemade ECE measurement setup.

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3. Results and Discussion

3.1. Microstructural analysis

As shown in Fig. 1, the XRD patterns indicate a pure pseudo-cubic perovskite structure, and the diffraction peaks shift towards lower angles with the increasing Sn^{4+} content. This is due to the substitution of Ti^{4+} ions (radius 0.0605 nm) by larger Sn^{4+} ions (radius 0.069 nm) at the central positions of the oxygen octahedra. For $x = 0.05$, the (200) and (002) peaks are clearly distinguished. But for $x = 0.10$ and 0.15, it is hard to distinguish them, which means a pseudo-cubic structure is formed.

Figure 2 shows the morphologies of BSnT ceramics with $x = 0.05$, 0.10 and 0.15. One can see that the three ceramics are dense, and free of pores. The average grain sizes are almost the same for all the three ceramic samples.

3.2. Dielectric properties

Figure 3 shows the permittivity and loss tangent as a function of temperature and frequency measured in the heating run ($f = 0.1$, 1 and 10 kHz). With the increase of Sn^{4+} ionic

Fig. 1. (a) XRD patterns for $x = 0.05$, 0.10 and 0.15; (b) XRD patterns for 2θ ranging from 44.6 to 45.6.

Fig. 2. SEM images of BSnT ceramic samples sintered at 1355°C for 3 h with compositions: (a) $x = 0.05$, (b) $x = 0.10$ and (c) $x = 0.15$.

content, the permittivity maximum shifts towards low temperatures, i.e., from 350 to 320 and 280 K, respectively. The permittivity peak value, however, decreases firstly from 14,000 to 10,500, then increases to 13,000. For $x = 0.05$, there is a peak associated with the phase transition from orthorhombic to tetragonal phases observed at 210 K. This is in consistence with the results reported by Shvartsman *et al.*¹¹ The larger permittivity measured is probably originated from the phase transition from NF to RF for $x = 0.15$ in BSnT ceramics, since a quasi-quadruple point at Sn^{4+} concentration $x = 0.11$ ¹² or $x = 0.105$ ¹³ has been observed for BSnT ceramics, where four phases C, T, O and R coexist, which leads to the larger permittivity.^{12,13}

3.3. Directly and indirectly measured electrocaloric effect

The P-E hysteresis loops as a function of electric field and temperature were collected with the increase of every 8 K of temperature during the heating run, as shown in Figs. 4(a)–4(c). With the increasing temperature, the loop becomes slimmer because the BSnT ceramics have FE–PE phase transitions taken place near the Curie temperatures. The differences are not significant, but the loop for $x = 0.05$

(a)

(b)

(c)

Fig. 3. Permittivity and loss tangent as a function of temperature for BSNT ceramics measured in a heating run, with a voltage of 1 V and frequency of 0.1, 1 and 10 kHz. The arrows in Fig. 3(a) show the phase transition of orthorhombic to tetragonal at 316 K and of tetragonal to cubic at 357 K.

is fatter than other two. In the insets of Figs. 4(a)–4(c), the polarizations as a function of temperature are shown for ceramics applied at three electric fields ($E = 1, 3$ and 5 MV/m). The polarization versus temperature curves are extracted from the upper branches of P-E hysteresis loops.

The continuous relationship of polarization versus temperature can be approximately applied by the Maxwell relation,¹⁴ i.e., $(\partial P/\partial T)_E = (\partial S/\partial E)_T$. Using the Maxwell relation, the ΔS and ΔT can be calculated. The C_E of 0.4 J/gK

(a)

(b)

(c)

Fig. 4. P-E hysteresis loops at some representative temperatures for BSNT ceramics ($x = 0.05, 0.10$ and 0.15 , respectively). The insets show the polarization as a function of temperature at 1, 3 and 5 MV/m.

was used.¹⁵ The $(\partial P/\partial T)_E$ values were procured from the fitting to P-T curves. The density $\rho_1 = 6.0632$, $\rho_2 = 6.1302$ and $\rho_3 = 6.1399$ g/cm³ for $x = 0.05, 0.10$ and 0.15 respectively. Figures 5(a) and 5(b) show the calculated ΔT and ΔS versus temperature for BSNT ceramics at $E = 1, 3$ and 5 MV/m. A small shift of the ECE peak towards high temperatures occurs as the electric field increases from 1 to 5 MV/m, which are consistent with the electric field induced as shift in the phase transition temperature.¹⁶

Fig. 5. Indirect calculation of adiabatic temperature change (ΔT , (a)) and isothermal entropy change (ΔS , (b)) for BSnT ceramics at 1, 3 and 5 MV/m for each composition.

Fig. 6. ECE as a function of time during the removal of electric field for direct measurement for $x = 0.05$ (a, b), $x = 0.10$ (c, d), and $x = 0.15$ (e, f).

Fig. 7. Directly measured ECE results for $x = 0.05, 0.10$ and 0.15 . $E = 1, 2$ and 3 MV/m.

Table 1. Comparison of ECE in this work and other results reported.

Material	T (°C)	ΔT (K)	ΔE (MVm ⁻¹)	$\Delta T/\Delta E$ (10 ⁻⁶ KmV ⁻¹)	Ref.
Doped Pb(Sc _{0.5} Ta _{0.5})O ₃	-38–11	1.5	2.5	0.6	19
PMN-PT 85/15	18	1.71	1.6	1.07	20
Ba _{0.65} Sr _{0.35} TiO ₃	23	0.42	2	0.21	21
Irradiated P(VDF-TrFE)	33	35	180	0.13	22
BZT	39	4.5	14.5	0.31	11
Pb(Zr _{0.455} Sn _{0.455} Ti _{0.09})O ₃	44	0.6	3	0.20	23
PLZT thin film	45	40	120	0.33	24
0.7 BZT–0.3BCT	60	0.3	2	0.15	25
PMN-PT 87/13	70	0.55	2.4	0.23	26
BTO thick film	80	0.5	3	0.17	7
Ba _{0.98} Ca _{0.02} Zr _{0.085} Ti _{0.915} O ₃	85	0.6	4	0.15	27
Pb(Sc _{0.5} Nb _{0.5})O ₃	97	0.9	2	0.45	28
BaTi _{0.95} Sn _{0.05} O ₃	95	1.45	3	0.48	This work
BaTi _{0.90} Sn _{0.10} O ₃	65	1.24	3	0.41	This work
BaTi _{0.85} Sn _{0.15} O ₃	26	1.49	3	0.49	This work

The direct ECE measurements were carried out at $E = 1, 2$ and 3 MV/m, respectively. Figure 6 shows the results of ΔT at 3 MV/m. It is obvious that the ECE peaks occur near the FE–PE phase transition, a maximum value of $\Delta T = 1.49$ K was obtained at $T = 299.2$ K, which is probably due to the occurrence of RF that increases the random orientations of the polar domains, thus the larger ECE entropy change.¹⁷ All the directly measured results are summarized in Fig. 7. One can see that the ECE results are similar to but larger than the indirectly measured results.¹⁸

The electrocaloric efficiency, defined as $\eta = \Delta T/\Delta E$, which can be used to evaluate the cooling ability of the ECE materials. Various η data are listed in Table 1. In our study, a maximum of $\Delta T/\Delta E = 0.49 \times 10^{-6}$ KmV⁻¹ was obtained for the composition $x = 0.15$ at $T = 299.2$ K. The large efficiency value indicates that a composition close to RF might be helpful for the enhancement of ECE.

4. Conclusion

The ECEs of BaSn_xTi_{1-x}O₃ ceramics have been investigated using direct and indirect measurement approaches. Both results show that the maximum ECE occurs near the Curie temperature and it slightly shifts towards high temperatures with the increasing electric field. The directly measured ECE is larger than that calculated using the Maxwell relation. A maximum of $\Delta T/\Delta E = 0.49 \times 10^{-6}$ KmV⁻¹ was obtained for the composition with $x = 0.15$ at $T = 299.2$ K. It also presents a broad peak in the temperature range of 250 K–320 K.

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