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Citation: Chin. Phys. B . 2018, 27(12): 127701. **doi:** 10.1088/1674-1056/27/12/127701
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Effect of an electric field on the electrocaloric response of ferroelectrics*

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(Received 13 September 2018; revised manuscript received 15 October 2018; published online 10 November 2018)

The electrocaloric effect of the model ferroelectric $BaTiO_3$ was investigated using phenomenological theory. The results indicate that the applied electric field strength is a key factor for the induced electrocaloric response and there are two distinguishing electrocaloric responses. When a moderate electric field is applied, the electrocaloric temperature variation is small but the electrocaloric strength is high. In contrast, the electrocaloric temperature variation is large but electrocaloric strength is low when a very high electric field is applied. These results are consistent with the experimental observations on $BaTiO_3$ based bulk and thin film ferroelectric materials.

Keywords: $BaTiO_3$, ferroelectrics, electrocaloric effect

PACS: 77.70.+a **DOI:** 10.1088/1674-1056/27/12/127701

1. Introduction

The electrocaloric (EC) effect refers to the isothermal entropy change ΔS or adiabatic temperature change ΔT of a dielectric material when an electric field is applied or removed. It has attracted great attention after the findings of 12-K temperature change in $PbZr_{0.95}Ti_{0.05}O_3$[1] and more than 12-K temperature variation in P(VDF-TrFE) (55 mol%/45 mol%).[2] It has been particularly used for applications in cooling.[3–6] Lead-based electrocaloric materials show a large EC effect. However, the toxicity of lead has limited their applications. Therefore, lead-free ferroelectrics have been considered as better candidates for EC refrigeration, such as $Bi_{0.5}Na_{0.5}TiO_3$-based ceramics,[7–9] and $BaTiO_3$-based materials.[10]

The EC ΔT is closely related to the applied electric field. The electrocaloric strength $\Delta T/\Delta E$ is also evaluated in the studies of EC effect. For instance, the large EC effects in $PbZr_{0.95}Ti_{0.05}O_3$ were induced with a field of 77.6 MV/m,[1] which is huge in comparison with the dielectric strengths of common inorganic ferroelectric materials.

To gain an insight into the effect of the applied electric field, we conducted a theoretical study of the EC effect of the model ferroelectric $BaTiO_3$ (BTO). A variety of experimental results has been reported on the EC effect of this material. In single crystal, the reported ΔT varies from 0.9 K@1.2 MV/m,[11] ~1.2 K@1.2 MV/m,[12] to 1.6 K@1 MV/m.[13] In multilayer films, the ΔT varies from 1.8 K@17.6 MV/m,[14] to 7.1 K@80 MV/m.[15] These results indicate that the electric field strength is crucial for the EC response.

2. Theory

Based on the Maxwell equation, the EC adiabatic temperature change ΔT can be evaluated by the following equation[16,17]

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

in which ρ and C_{p} are density and specific heat capacity, respectively, here $\rho = 6020\ \mathrm{kg\cdot m^{-3}}$,[16] and $C_{\mathrm{p}} = 407\ \mathrm{J\cdot kg^{-1}\cdot K^{-1}}$.[11] For a monodomain BTO single crystal with both the polarization $\boldsymbol{P}$ and the applied electric field along [001] axis, the Landau–Devonshire potential including up to eighth-power term can be written as

$$g = g_0 + \alpha_1(T - T_0)P^2 + \alpha_{11}P^4 + \alpha_{111}P^6 + \alpha_{1111}P^8 - EP, \tag{2}$$

where α_1, α_{11}, α_{111}, and α_{1111} are the Landau coefficients, and g is the Gibbs free energy density without considering the contribution of polarization. The polarization in the $(\boldsymbol{T}, \boldsymbol{E})$ field can be obtained by finding the minimum of the potential. By combining Eq. (1) and Eq. (2) the EC ΔT can be calculated. In calculations, t he Landau coefficients were adopted from those published by Wang *et al.*[18] The potential proposed by Wang *et al.* gives the following characteristic temperatures: the phase transition temperature $T_{\mathrm{C}} = 403$ K and the critical point temperature $T_{\mathrm{CP}} = 418$ K at which the phase transition becomes of the second order under electric field.[12] The electric field at the critical point E_{CP} is 1.5 MV/m.

*Project supported by the National Natural Science Foundation of China (Grant No. 11704242) and the Natural Science Foundation of Shanghai, China (Grant No. 17ZR1447200).

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3. Results and discussion

The EC ΔT of BTO at the different electric field strengths are plotted in Fig. 1. For the case of an applied electric field less than E_{CP}, there exists a sharp peak of EC ΔT versus T; as shown in Fig. 1(a).

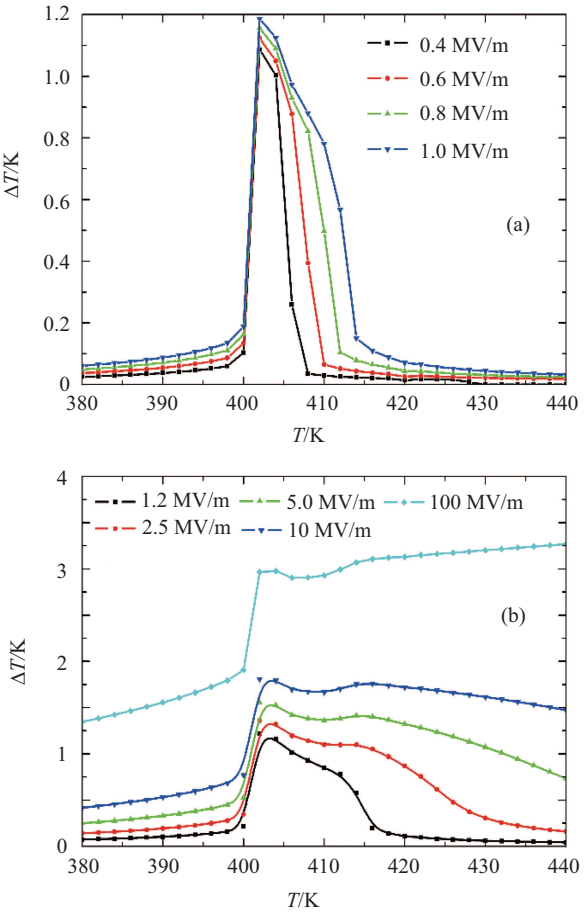


Fig. 1. (color online) Calculated EC ΔT of BTO at different electric field strengths by the phenomenological method.

This profile of ΔT–T is consistent with the experimental observations.[11–13] Both the intensity and the width of the peak increase slightly with the increase of the applied electric field strength. The starting temperature of the ΔT peak is T_C, and the stopping temperature is T_{CP}. The predicted ΔT at 1 MV/m is 1.2 K, and the EC strength $\Delta T/\Delta E$ is 1.2×10^{-6} K·m·V^{-1}. These values agree with the experimental observations in the crystals of BTO as listed in Table 1.

In contrast, the EC ΔT–T profiles become broad and flat at the electric field strengths approaching and higher than E_{CP}; as shown in Fig. 1(b). These profiles are similar to the experimental results in the thin films of BTO,[15] $PbZr_{0.95}Ti_{0.05}O_3$,[1] and P(VDF-TrFE) (55mol%/45 mol%).[2] At 100 MV/m, ΔT is 3 K and $\Delta T/\Delta E$ is 0.03×10^{-6} K·m·V^{-1}, which are comparable with those obtained with BTO multilayer film (see Table 1).

To disclose these two types of EC responses, we calculated $\boldsymbol{P}$–$\boldsymbol{E}$ loops at selected temperatures and $\boldsymbol{P}$ at selected electric field strengths. The typical $\boldsymbol{P}$–$\boldsymbol{E}$ loops are shown in Fig. 2(a). These temperatures satisfy the following relations: 400 K$< T_C$, $T_C <$ 41 K $< T_{CP}$, and $T_{CP} <$ 420 K. Thus, the BTO shows ferroelectric $\boldsymbol{P}$–$\boldsymbol{E}$ loop at $T < T_C$. However, the coercive field E_C decreases with the increasing temperature. It becomes zero at T_C. The double loop presents at $T_C < T < T_{CP}$. Finally, linear $\boldsymbol{P}$–$\boldsymbol{E}$ relation is observed at $T_{CP} < T$. Since a small electric field can induce a large variation of polarization at $T_C < T < T_{CP}$, a sharp EC ΔT peak with large $\Delta T/\Delta E$ is observed; as shown in Fig. 2(a).

The electric field effect on the evolution of polarization is depicted in Fig. 2(b) at selected electric field strengths. Note that the critical point E_{CP} is 1.5 MV/m for BTO. The discontinuity of polarization versus temperature becomes faint after 1.2 MV/m. When the electric field strength is higher than 10 MV/m, the polarization is a weak function of temperature and the polarization variation decreases with the increasing electric field. Thus, a giant electric field can induce large ΔT but the $\Delta T/\Delta E$ is small, and a flat ΔT–T profile is observed; as shown in Fig. 2(b).

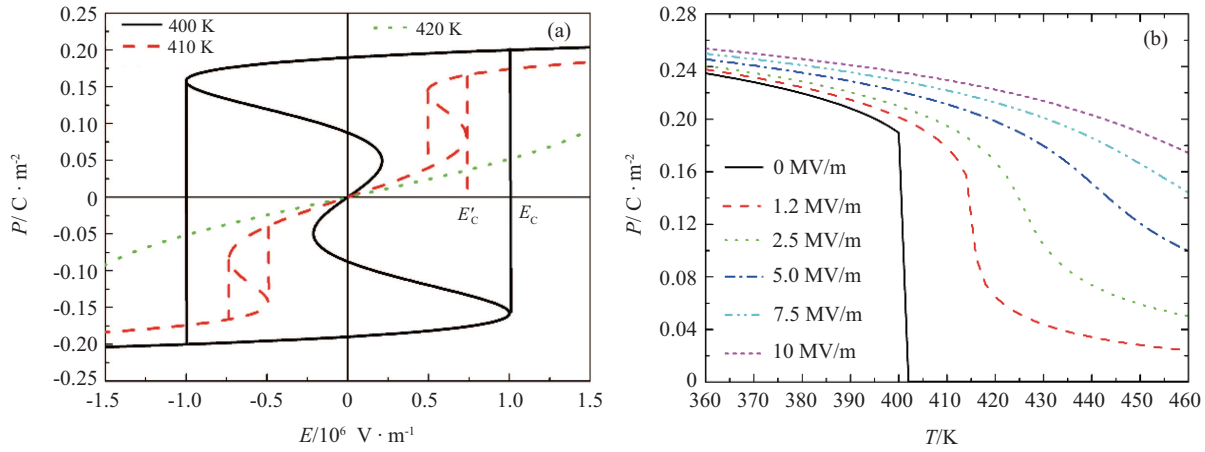


Fig. 2. (color online) The $\boldsymbol{P}$–$\boldsymbol{E}$ loops at selected temperatures (a) and the polarization as a function of temperature at selected electric field strengths (b).

Finally, we suggest that the finding in BTO is universal for ferroelectrics with first-order phase transition. At an electric field

approaching E_{CP}, ferroelectric materials have small ΔT about 1 K but high EC strength, and a sharp EC ΔT–T peak. Under a strong electric field, they produce giant ΔT but low EC strength, and a flat ΔT–T profile is observed. Since ferroelectric ceramics in bulk have low dielectric strengths around E_{CP}, a sharp ΔT–T peak and tiny ΔT are normally observed. Because the dielectric strength is significantly enhanced in the thin films of ferroelectrics, a broad ΔT–T profile and large ΔT are observed. Table 1 lists some recent experimental observations on EC effect of BTO-based materials, which agree quantitatively with the theoretical prediction.

Table 1. Data of EC properties of BTO and doped BTO in the literature.

Materials	Form	ΔE/(MV/m)	ΔT/K	$\Delta T/\Delta E/10^{-6}$ K·m·V^{-1}	Ref.
$BaTiO_3$	single crystal	1	1.6	1.6	[13]
$BaTiO_3$	single crystal	1.2	0.9	0.75	[11]
$BaTiO_3$	single crystal	1.2	~ 1.2	1	[12]
$BaZr_{0.5}Ti_{0.95}O_3$	ceramic	3	2.4	0.8	[19]
$BaHf_{0.5}Ti_{0.95}O_3$	ceramic	5	1.64	0.33	[20]
$BaZr_{0.21}Ti_{0.79}O_3$	ceramic	9.9	4.7	0.46	[21]
$BaZr_{0.20}Ti_{0.80}O_3$	ceramic	14.5	4.5	0.31	[10]
$BaTiO_3$	multilayer film	80	7.1	0.09	[15]

4. Conclusion and perspectives

In conclusion, the present study indicates that there are two distinguishing EC responses for ferroelectrics with first-order phase transition, which are mainly decided by the applied electric field. When the applied electric field strength is comparable with E_{CP}, there exists a sharp ΔT–T peak with large $\Delta T/\Delta E$ between $[T_C, T_{CP}]$. When the applied electric field strength is much higher than E_{CP}, because of the vanishing of the first-order phase transition, the polarization is a weak function of temperature. The large EC ΔT can be induced by a large electric field but the EC $\Delta T/\Delta E$ is quite small. A flat EC ΔT–T profile is observed commonly. This result explains the experimental observations on BTO-based materials from bulks to thin films. It also inspires researchers to find alternative ways to achieve both large EC ΔT and $\Delta T/\Delta E$ simultaneously.

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