On the parameters for electrocaloric effect predicted by indirect method*

Hong-Bo Liu(刘宏波)†

School of Materials Engineering, Shanghai University of Engineering Science, Shanghai 201620, *China*

(Received 29 June 2017; revised manuscript received 5 August 2017; published online 30 September 2017)

The influences of specific heat capacity C_P, temperature step ΔT, electric field step ΔE, and initial electric field E_1 on predicted electrocaloric (EC) temperature ΔT of monodomain $BaTiO_3$ are examined by combining the Maxwell equation and phenomenological theory. Since the procedure is similar to indirect measurement of the EC effect, the results can serve as a reference for experiments. The results suggest that (i) it is reasonable to use zero-field C_P, (ii) optimized ΔT should be 2 K, (iii) it is better to keep $\Delta E < E_C$, and (iv) $E_1 < E_C$. Here, E_C is the coercive field of material.

Keywords: electrocaloric effect, indirect method, $BaTiO_3$

PACS: 77.70.+a **DOI:** 10.1088/1674-1056/26/11/117701

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 to or removed from the material. It has received great attention since finding the 12 K temperature change in $PbZr_{0.95}Ti_{0.05}O_3$[1] and more than 12 K temperature change in P(VDF-TrFE) (55/45 mol%),[2] and potential applications in chip-scale cooling.[3–13]

In the study of the EC effect, the indirect measurement has been used based on the Maxwell relations because of its simple testing setup and good consistency.[14–18] In the method, the adiabatic temperature change ΔT can be evaluated from the following equation:[19]

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

in which ρ and C_P are the density (in kg/m^3) and specific heat capacity (in J/(K·kg)), respectively. By using Eq. (1), one must first choose and use appropriate parameters, i.e., specific heat capacity C_P, boundary conditions E_1 and E_2, and more importantly, appropriate temperature step ΔT and electric field step ΔE for precisely deciding $(\partial P/\partial T)_E$. The E_2 is the maximum electric field applied, which is naturally smaller than the breakdown field of material. However, it is interesting to see that the selection principles for other parameters are generally omitted and different authors may adopt different parameters. Moreover, from the view of an experiment, in $(\boldsymbol{E}, \boldsymbol{T})$ field, it would take lots of time to give a rough answer to the influence of parameter selection on predicted EC ΔT.

Fortunately, the theoretical prediction EC ΔT by phenomenological method is also based on Eq. (1).[20] Thus, if we use a numerical method rather than an analytical method, the influences of parameter selection on the EC effect can be investigated theoretically. More importantly, the results will help those who work on experiments as a reference to select appropriate parameters to evaluate the EC effect by indirect measurement.

2. Results and discussion

In this work, we investigate the EC ΔT of $BaTiO_3$ (BTO), a prototype ferroelectric and also an EC material. For a monodomain BTO single crystal with the domain direction along [001] and electric field $\boldsymbol{E}$ along [001], the Landau–Devonshire potential including terms up to the eighth-power term under unconstrained, stress-free state 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_0 is the Gibbs free energy density without considering the contribution of polarization. In this work, we adopt the Landau coefficients proposed by Wang *et al.* [21] The Landau potential for BTO has been developed by different authors, i.e., Mers,[22] Pertsev *et al.*,[23] Bell *et al.*,[24] and Wang *et al.* The advantage of the potential proposed by Wang *et al.* is its adequate description of cubic-tetragonal phase transition by including either-order term, which exhibits a higher quality in reproducing polar properties. The polarization $\boldsymbol{P}$ under $(\boldsymbol{T}, \boldsymbol{E})$ field can be evaluated by finding the minimum of Gibbs free energy g, and by differentiating $\boldsymbol{P}$ with respect to $\boldsymbol{T}$ we can calculate EC ΔT according to Eq. (1). It is obvious that the method works in the same manner as experimental indirect measurement.

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

†Corresponding author. E-mail: bohongliu@gmail.com

© 2017 Chinese Physical Society and IOP Publishing Ltd

We first discuss the influence of specific heat capacity C_P on ΔT. It is normally believed that C_P is a function of temperature and electric field. However, almost all the work uses the room temperature zero-field specific heat capacity for calculating ΔT, or casually, the value at phase transition under zero-field.[18] Is it right to neglect the influence of electric field on C_P?

In the classic ferroelectric book published by Lines and Glass, the variation of specific heat capacity under electric field is generally expressed as[25]

$$\Delta C_E(T,E) = -T\left(\partial S/\partial T\right)_E. \tag{3}$$

It should be stressed that the entropy S here only counts the contribution of polarization. The contribution of phonons is excluded. For second-order phase transition, ΔC can be evaluated. For first-order phase transition, since there is a jump for entropy, the application for Eq. (2) will produce divergence. Thus, theoretically it is impossible to obtain an accurate value. The phase latent, which can be evaluated and relates to the jump of entropy, is in fact due to the EC effect under electric field. As a result, on the assumption that the entropy relating to phonon contribution is a weak function of electric field, it is reasonable to choose zero-field specific heat capacity. In this work, we choose $C_P = 407$ and $\rho = 6020$ to evaluate ΔT.[19]

For other parameters, almost all experiments choose $E_1 = 0$ and only very recently it is shown that the initial electric field also has an influence on the EC effect.[26,27] The choices of temperature step ΔT and electric field step ΔE are arbitrary. Here in this work, we study the influences of parameter choice of E_1, ΔT and ΔE on EC ΔT by a simple scenario, i.e., only one parameter may be arbitrarily changed but the others are fixed.

We first investigate the influence of temperature step ΔT on EC temperature variation ΔT by fixing $E_1 = 0$ and $\Delta E = 10^4$ V/m. We choose $E_2 = 1.2$ MV/m for comparing with the experimental results,[18,28] which is also a typical value for bulk ferroelectric to switch domain without breakdown. The results are plotted in Fig. 1(a). The predicted ΔT at 1.2 MV/m equals 3.1 K, which is larger than two experimental results, i.e., 0.9 K@1.2 MV/m,[18] or 1.6 K@1 MV/m,[29] but smaller than one, i.e., 4.8 K@1 MV/m,[30] suggesting the validation of prediction. By increasing temperature step ΔT, we can see that the strong EC ΔT zone becomes broader and the EC peak profile changes from asymmetric to symmetric when $\Delta T > 3$ K. In fact, the asymmetric profile is supported by high-resolution direct experimental measurement.[29] Thus, our conclusion obtained here is that a temperature step of 2 K is reasonable for evaluating the EC effect by the indirect method.

Then by fixing the temperature step at 2 K with $E_1 = 0$, we investigate the influence of electric field step ΔE on ΔT as shown in Fig. 1(b). We can find that when $\Delta E \leq 10^4$ V/m, which is the coercive field for BTO at 400 K, an almost identical EC effect is observed. After that, the instability appears. Thus, the result suggests that ΔE should be smaller than coercive field E_C.

Finally, we investigate the influence of E_1 of EC ΔT and we find that there is a big change of EC ΔT if $E_1 > E_C$. By increasing the initial electric field, the EC zone becomes narrow and the EC peak intensity decreases. Thus, the result suggests that $E_1 < E_C$ is reasonable and $E_1 > E_C$ can underestimate the peak value of EC ΔT. It is common to choose $E_1 = 0$[31] or $E_1 > E_C$.[20] For saving time and keeping validity, our results suggest that $E_0 = E_C$ is reasonable for evaluating the EC effect.

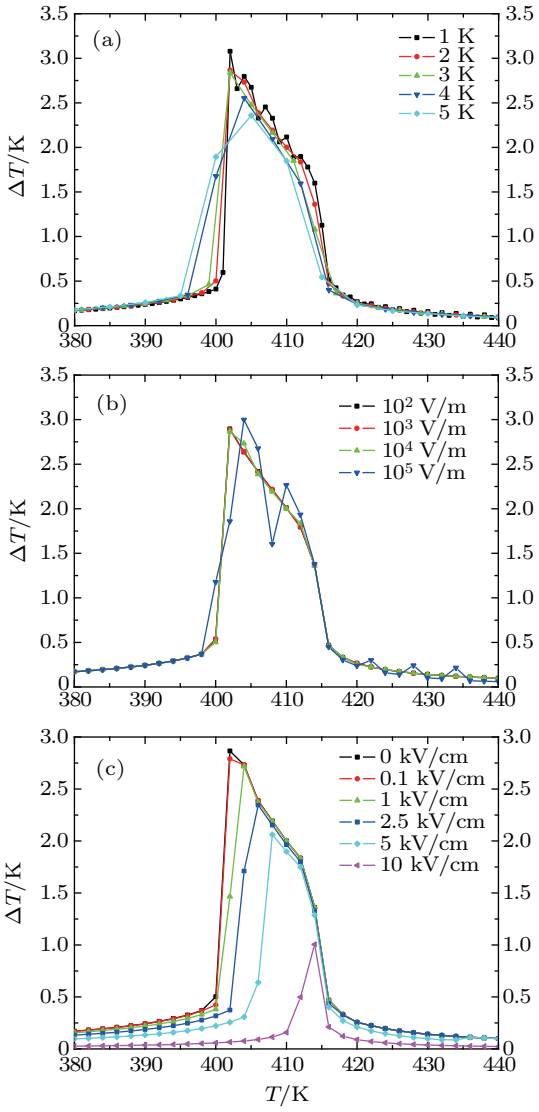


Fig. 1. (color online) Plots of predicted EC temperature change ΔT versus temperature of BTO under different parameter selections: (a) varying ΔT with $\Delta E = 10^4$ V/m and $E_1 = 0$; (b) varying ΔE with $\Delta T = 2$ K and $E_1 = 0$; (c) varying E_1 with $\Delta E = 10^4$ V/m and $\Delta T = 2$ K.

3. Conclusion

In conclusion, combining Maxwell equation and phenomenological theory we study the EC ΔT of monodomain

$BaTiO_3$ by emphasizing the influences of parameter selection to serve as a reference for experiments. Our results suggest that the parameters do have significant influence on predicted EC ΔT: the optimized temperature step ΔT is 2 K; the electric field ΔE should be smaller than E_C; and the maximum initial electric field is E_C. In addition, it is reasonable to use zero-field specific heat capacity for predicting the EC effect.

The author thanks professor Z Y Cheng at Auburn University for our meaningful discussion.

References

[1] Mischenko A, Zhang Q, Scott J, Whatmore R and Mathur N 2006 *Science* **311** 1270
[2] Neese B, Chu B, Lu S G, Wang Y, Furman E and Zhang Q 2008 *Science* **321** 821
[3] Kar-Narayan S and Mathur N D 2009 *Appl. Phys. Lett.* **95** 242903
[4] Epstein R I and Malloy K J 2009 *J. Appl. Phys.* **106** 064509
[5] Jia Y and Sungtaek Ju Y 2012 *Appl. Phys. Lett.* **100** 242901
[6] Gu H, Qian X, Li X, Craven B, Zhu W, Cheng A, Yao S C and Zhang Q M 2013 *Appl. Phys. Lett.* **102** 122904
[7] Plaznik U, Kitanovski A, Rožič B, Malič B, Uršič H, Drnovšek S, Cilenšek J, Vrabelj M, Poredoš A and Kutnjak Z 2015 *Appl. Phys. Lett.* **106** 043903
[8] Wang Y D, Smullin S J, Sheridan M J, Wang Q, Eldershaw C and Schwartz D E 2015 *Appl. Phys. Lett.* **107** 134103
[9] Blumenthal P, Molin C, Gebhardt S and Raatz A 2016 *Ferroelectrics* **497** 1
[10] Sette D, Asseman A, Gérard M, Strozyk H, Faye R and Defay E 2016 *APL Mater.* **4** 091101
[11] Liu Y, Scott J F and Dkhil B 2016 *APL Mater.* **4** 064109
[12] Liu Y, Scott J F and Dkhil B 2016 *Appl. Phys. Rev.* **3** 031102
[13] Wang X Y, Chu R J, Wei S N, Dong Z C, Zhong C G, Cao H X, Sciences S O and University N 2015 *Acta Phys. Sin.* **64** 117701 (in Chinese)
[14] Pelaiz-Barranco A, Wang J and Yang T 2016 *Ceram. Int.* **42** 229
[15] Le Goupil F, Berenov A, Axelsson A K, Valant M and Alford N M 2012 *J. Appl. Phys.* **111** 124109
[16] Kar-Narayan S and Mathur N 2010 *J. Phys. Appl. Phys.* **43** 032002
[17] Kaddoussi H, Lahmar A, Gagou Y, Asbani B, Dellis J L, Cordoyiannis G, Allouche B, Khemakhem H, Kutnjak Z and El Marssi M 2016 *J. Alloy. Compd.* **667** 198
[18] Moya X, Stern-Taulats E, Crossley S, González-Alonso D, Kar-Narayan S, Planes A, Mañosa L and Mathur N D 2013 *Adv. Mater.* **25** 1360
[19] Liu H and Yang X 2015 *AIP Adv.* **5** 117134
[20] Akcay G, Alpay S P, Mantese J V and Rossetti G A 2007 *Appl. Phys. Lett.* **90** 2909
[21] Wang Y L, Tagantsev A K, Damjanovic D, Setter N, Yarmarkin V K, Sokolov A I and Lukyanchuk I A 2007 *J. Appl. Phys.* **101** 104115
[22] Merz W J 1953 *Phys. Rev.* **91** 513
[23] Pertsev N, Zembilgotov A and Tagantsev A 1998 *Phys. Rev. Lett.* **80** 1988
[24] Bell A and Cross L 1984 *Ferroelectrics* **59** 197
[25] Lines M E and Glass A M 1977 (Oxford: Oxford University Press) p. 67
[26] Ma Y B, Novak N, Koruza J, Yang T, Albe K and Xu B X 2016 *Phys. Rev. B* **94** 100104
[27] Ma Y B, Novak N, Albe K and Xu B X 2016 *Appl. Phys. Lett.* **109** 242903
[28] Novak N, Kutnjak Z and Pirc R 2013 *Europhys. Lett.* **103** 47001
[29] Bai Y, Ding K, Zheng G P, Shi S Q and Qiao L 2012 *Phys. Status Solidi A* **209** 941
[30] Bai Y, Han X, Zheng X C and Qiao L 2013 *Sci. Rep.* **3** 2895
[31] Qian X S, Ye H J, Zhang Y T, Gu H, Li X, Randall C and Zhang Q 2014 *Adv. Funct. Mater.* **24** 1300