Prediction of giant elastocaloric strength and stress-mediated electrocaloric effect in BaTiO$_3$ single crystals

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(Received 8 June 2014; revised manuscript received 16 August 2014; published 18 September 2014)

An applied stress field $\sigma_3$ can reversibly change the temperature of an elastocaloric material under adiabatic conditions, and the temperature change $\Delta T_\sigma$ is usually maximized near phase transitions. Using a thermodynamic approach, we demonstrate that an elastocaloric strength $\alpha = |\Delta T_\sigma|/|\sigma_3|$ of 0.016 K/MPa can be achieved benefitting from the full first-order phase transition in BaTiO$_3$ single crystals, which is comparable with typical elastocaloric materials reported in the literature. The elastocaloric temperature change is found to be giant (3.2 K) under a stress of 200 MPa with a temperature span of over 50 K, which can be significantly larger than its electrocaloric counterpart ($\sim$ 1 K). Moreover, it is found that the elastocaloric strength can be remarkably enhanced (2.32 K/MPa) as long as the phase transition is triggered even by a modest stress near the sharp first-order phase transition, which is two orders of magnitude larger than those accomplished by full transition. Therefore, even a low stress ($<30$ MPa) can induce a modest elastocaloric effect (1.3 K) comparable with the electrocaloric counterpart, which is accompanied by a reduction of the working temperature span. In addition, it is found that the elastocaloric peak under tensile stresses moves towards higher temperatures with its magnitude slightly enhanced. Hopefully, our study will stimulate further investigations on elastocaloric and stress-mediated electrocaloric effects in ferroelectrics.

DOI: 10.1103/PhysRevB.90.104107

PACS number(s): 77.80.B—, 77.22.Ej

I. INTRODUCTION

During the last two decades, great efforts have been made to develop solid-state cooling refrigeration mainly due to concern about the environmental impact and energy efficiency limit of the vapor-cycle cooling technologies [1–5]. As a result, there has been rapid progress in research on caloric (including magnetocaloric, electrocaloric, elastocaloric, and barocaloric) effects [1–5]. In recent years, growing attention has also been focused on searching multicaloric materials [6, 7] or designing hybrid caloric structures [8] since enhanced caloric responses, refrigerant efficiency, and capacity can be achieved in these materials [4].

In this context, ferroelectrics can be considered naturally as multicaloric materials since the total entropy may change significantly near the structural phase transition induced by the multistimuli (electric field, stress, pressure, and magnetic field if the magnetoelectric coupling exists). Therefore, there is an increasing amount of experimental and theoretical studies on ferroelectrics in order to investigate the electrocaloric, elastocaloric, and barocaloric effects, which may become in the future of great and significant impact [5]. For instance, intensive studies are focused on BaTiO$_3$ (BTO) single crystals [9–11], which is a classical ferroelectric material. Due to the sharp first-order phase transition, a giant electrocaloric strength defined as $|\Delta T_E|/\Delta E$ has been demonstrated by several groups with its largest value ever reported of 0.48 K cm/kV under a electric field change $\Delta E$ of 10 kV/cm [11]. However, the magnitude of electrocaloric temperature change $|\Delta T_E|$ remains modest ($\sim$ 1 K [9–11]), which directly limits further practical applications, not to mention the large voltage required in the experiments. Since the transition temperature ($\sim$ 400 K) is well above room temperature [9–11], it is also of interest to lower the working temperature and bring it to room temperature. Moreover, barocaloric effect in BTO single crystals was demonstrated recently to be comparable with its electrocaloric response near room temperature [12]. Additionally, it was reported that a hydrostatic pressure can be used to shift the barocaloric peak to room temperature [12]. Note that the study on the elastocaloric effect in BTO single crystals near the sharp first-order phase transition which may show novel and interesting properties is still lacking.

It was reported that the multicaloric effects can be induced either by applications of either single stimulus [6] or several stimuli simultaneously [7]. Due to the strong couplings between different degrees of freedom, i.e., magnetoelectric [6] and ferroelastic couplings [7], the multicaloric effect can exceed any single caloric effect. On the other hand, one may consider combining several stimuli in a “step-by-step” manner according to previous study. For instance, in the case of BTO single crystals the stress applied first (elastocaloric effect) may change the phase transition temperature before the withdrawal of this stimulus, which may act as an effective tool to tune the later caloric (i.e., electrocaloric) effect [13, 14]. It therefore motivates the present study on the elastocaloric
and stress-mediated electrocaloric effects in ferroelectric BTO single crystals. Indeed, although the study on the elastocaloric effect in ferroelectrics has attracted much more attention, it is still at the early stage compared with the shape memory alloys [15–19]. Recently, the remarkable elastocaloric effect in both ferroelectric bulk [7,20] and thin film [21] is predicted using first-principles calculations and the phenomenological approach, respectively, which can even compete with that reported in shape memory alloys [15–19]. It is of specific interest to revisit the elastocaloric response of BTO single crystals using phenomenological calculations since this approach is easy to understand and simple to achieve without using costly large-scale computing. In addition, it can describe the ferroelectric behavior accurately especially near the phase transition.

II. LANDAU THEORY OF ELASTOCALORIC EFFECT

An applied stress field \( \sigma \) (all tensors appear in Voigt notation) can reversibly change the temperature of an elastocaloric material under adiabatic conditions, and the temperature change \( \Delta T_\sigma \) is usually maximized near phase transitions [7,15–21]. Note that \( \sigma \) here is a uniaxial stress applied along the polar axis of ferroelectric and denoted as \( \sigma \) for short in the following parts. In order to obtain \( \Delta T_\sigma \), one may consider using the indirect method via the Maxwell relation (\( \partial S/\partial T \))\(_{\sigma,E} \):

\[
\Delta T_\sigma = -\int_0^\sigma \frac{T}{C_\sigma} \left( \frac{\partial u_3}{\partial T} \right) d\sigma, \tag{1}
\]

where \( T \) is the temperature, \( S \) is the entropy, \( u_3 \) is the strain, \( E \) is the electric field, and \( C_\sigma \) is the volumetric heat capacity under constant stress. The validity of the indirect method is still under debate especially in the field of the electrocaloric effect [9,13,22–25]. Indeed, the Maxwell relations are applicable only for thermodynamically reversible equilibrium and ergodic systems. However, the first-order phase transition is always associated with thermodynamically irreversible hysteretic loss. As a result, Eq. (1) can give only an approximation of \( \Delta T_\sigma \) provided that the irreversible contribution is relatively small [15]. Interestingly, first-principles calculations have demonstrated that \( \Delta T_\sigma \) calculated based on Eq. (1) fails to reproduce the direct measurement results in bulk ferroelectric PbTiO\(_3\) (PTO) [7]. However, \( \Delta T_\sigma \) can be derived through the use of Landau-type theory irrespective of the order nature of phase transition. In this case, we argue that the elastocaloric effect in BTO single crystals may be evaluated in terms of polarization change rather than strain change near the first-order phase transition, as expected in proper ferroelectrics for which the strain variation results from the polarization change [7]. Such treatment is directly supported by first-principles calculations showing that indeed the elastocaloric effect in PTO nearly vanishes to zero in the paraelectric phase due to the disappearance of polarization [7]. Additional experimental evidence signals that the barocaloric effect in PTO is noticeable only near the pressure-free Curie temperature [26].

Moreover, we focus on the transition from the cubic phase to the tetragonal one, which is widely studied in electrocaloric BTO samples in the form of single crystals, thin films, and ceramics [9–12,14,27–32]. Taking into account the foregoing mechanical boundary conditions, the Gibbs free energy can be expressed as [33]

\[
G = a_1 P^2 + a_{11} P^4 + a_{111} P^6 + a_{1111} P^8 - \frac{1}{2} S_{11} \sigma^2 - Q_{11} \sigma P^2, \tag{2}
\]

where \( S_{11} \) is the elastic compliance and \( Q_{11} \) is the electrostrictive coefficient. \( a_1 \), \( a_{11} \), \( a_{111} \), and \( a_{1111} \) are the dielectric stiffness coefficients at constant stress, and only \( a_1 \) is temperature dependent. The higher-order electrostrictive coupling between stress and polarization has been included in the stress-dependent Landau potential coefficients \( a_{111} \) and \( a_{1111} \) [33].

In the following part, we use a phenomenological Landau-type model which was initially proposed to describe the electrocaloric effect in relaxor ferroelectric and BTO single crystals [10,24]. The theoretical predictions of this model were found to agree well with the experimental results [10,24]. In addition, this model was recently developed to describe the barocaloric effect in BTO single crystals [12]. It assumes that the total entropy \( S \) can be divided into two parts, namely, the dipolar contribution \( S_{\text{dip}} \) and the lattice contribution \( S_{\text{latt}} \) as follows [24]:

\[
S = S_{\text{latt}} + S_{\text{dip}}, \tag{3}
\]

where \( S_{\text{dip}} \) is due to the entropy contribution of the dipolar degrees of freedom and is thus a function of the dielectric polarization \( P(E,T) \), which depends on \( E \) at a given \( T \). \( S_{\text{latt}} \) is an electric field independent lattice contribution. Another assumption is that the dipolar free energy can be written in the standard Landau form [24]. For the elastocaloric effect here, both assumptions can be satisfied. To be more specific, this model may be developed by replacing the electric stimulus by stress \( \sigma \), making it applicable to our case. Following the strategy developed by Pierc et al. [10,24], we can then obtain a self-consistent equation to derive \( \Delta T_\sigma \) = \( T_2 - T_1 \) such that

\[
T_2 = T_1 \exp \left\{ \frac{a_1}{2C_{\text{latt}}^0} \left( P_0^2(\sigma,T) - P_0^2(0,T) \right) \right\}, \tag{4}
\]

where \( a_1 \equiv d\alpha_1/dT \) and \( C_{\text{latt}}^0 \) is the lattice contribution to the total heat capacity. \( P_0 \) is the equilibrium polarization obtained from the equilibrium condition \( \partial G/\partial P = 0 \). All the coefficients we used are listed in Ref. [34].

III. RESULTS AND DISCUSSION

Figure 1(a) summarizes the equilibrium polarization \( P_0 \) under different \( \sigma \) as a function of \( T \). It is shown that the Curie temperature \( T_c(\sigma) \) increases with increasing stress. Specifically, \( T_c(\sigma) \) increases from 401 K at 0 MPa to 455 K at 200 MPa. As a result, \( P_0 \) is consistently enhanced especially at temperatures above the stress-free Curie temperature \( T_c(0) \approx 401 \) K.

The elastocaloric behavior of BTO single crystals is revealed in Fig. 1(b). It can be seen that \( \Delta T_\sigma \) peaks at \( T_c(0) \), which is consistent with the predictions by first-
principles calculations [7,20]. Just above $T_c(0)$, $\Delta T_e$ drops sharply due to the dramatic reduction of polarization change [$P(\sigma,T) \sim P(0,T)$] as shown in Fig. 1(a). Finally, $\Delta T_e$ vanishes due to the disappearance of polarization, which again agrees with the results obtained by first-principles calculations [7]. Our finding is also in line with the barocaloric effect reported in PTO in which the maximum barocaloric response was observed at the pressure-free Curie temperature of PTO [26]. The largest $\Delta T_e$ found here is about 3.2 K at 200 MPa, while $\Delta T_e$ can reach 2.3 K at 50 MPa. $\Delta T_e$ at 200 MPa found here (3.2 K) is smaller than that (6 K) in PTO [7] but is larger than that ($\sim 1$ K) in Ba$_5$Sr$_5$Ti$_6$O$_{17}$ (BST) [20] under the same stress condition. In addition, it is shown that as $\sigma$ increases, the working temperature window $T_{\text{span}}$ increases considerably from $\sim 15$ K at 50 MPa to $\sim 50$ K at 200 MPa [see Fig 1(b)]. In addition, the elastocaloric strength defined as $\sigma = |\Delta T_e/\sigma|$ in BTO (0.016 K/MPa) is already in the range of the previous results obtained from CuZnAl shape memory alloys and other ferroelectric bulk materials though the entropy change $\Delta S$ ($3.2$ J/kg K) and refrigerant capacity $R \approx |\Delta S|/\Delta T_e|_{T_c}$ (Ref. [17]) are relatively low (see Table I).

The stress-dependent $P_0$ and $\Delta T_e$ under different $T$ are shown in Figs. 1(c) and 1(d). It turns out that $P_0$ increases as $\sigma$ increases. It can be seen in Fig. 1(c) that above $T_c(0)$ there exists a critical stress field $\sigma_c$ at which $P_0$ jumps to roughly $0.15$ C/m$^2$ due to the stress-induced first-order phase transition. As $T$ increases, larger stresses are needed to induce the discontinuous transition. Consequently, $\sigma_c$ increases significantly from $\sim 12$ MPa at 405 K to $\sim 161$ MPa at 445 K. Below $T_c(0)$, the polarization jump does not occur as BTO is already in its ferroelectric phase. In addition, it is found that the closer to $T_c(0)$, the larger the change of polarization will be. Accordingly, the elastocaloric response in Fig. 1(d) shows that $\Delta T_e$ increases as $\sigma$ increases irrespective of $T$. Moreover, Fig. 1(d) clearly indicates that the largest $\Delta T_e$ occurs at $T_c(0)$, which is consistent with the findings in Fig. 1(b). In addition, the elastocaloric effect predicted here has the potential to compete with the measured electrocaloric counterpart ($\sim 1$ K [9–11]) depending on the maximum value of mechani-

![FIG. 1. (Color online) The polarization $P_0$ and (b) adiabatic temperature change $\Delta T_e$ under different $\sigma$ as a function of ambient temperature $T$. The dependence of (c) $P_0$ and (d) $\Delta T_e$ on $\sigma$ at different $T$.](image-url)
TABLE I. Comparison of elastocaloric properties of BTO single crystals developed in this work with those in the literature.

| Material  | $T_c(0)$ (K) | $T_{\text{span}}$ (K) | $\sigma_c$ (MPa) | $|\Delta T_{\alpha}|$ (K) | $|\Delta T_E/\sigma_c|$ (K/MPa) | $|\Delta S|$ (J/kg K) | $|\Delta S|/\Delta T_{\alpha}$ (J/kg) | Reference |
|-----------|--------------|------------------------|------------------|--------------------------|-------------------------------|-----------------|---------------------------------|-----------|
| NiTi      | 242          | —                      | 600              | 17                       | 0.023                         | —               | —                               | [16]      |
| FePd      | 230          | 50                     | 100              | 2                        | 0.020                         | —               | —                               | [18]      |
| TiNiCu    | 318          | —                      | 330              | 6                        | 0.018                         | —               | —                               | [17]      |
| CuZnAl    | 234          | 130                    | 275              | 6                        | 0.022                         | 17.9            | 107                             | [19]      |
| BST       | 250          | 50                     | 1000             | 9                        | 0.009                         | $\sim$16        | 144                             | [20]      |
| PTO       | 750          | $\sim$30               | 1000             | 20                       | 0.020                         | $\sim$9.6       | 192                             | [7]       |
| BTO       | 401          | 50                     | 200              | 3.2                      | 0.016                         | $\sim$3.2       | 10.2                            | This work |

[7,20], which just gives the static or quasistatic solutions. In the practical conditions, it will be of interest to include other domain structures, i.e., 90° domain switching [36] in future studies. In this regard, stress relaxation taking place in the region of deformation related to twin boundary motions [39,40] should also be taken into account.

The elastocaloric properties especially at the temperatures approaching $T_c(0)$ are depicted in Figs. 2(a) and 2(b). It can be seen that the critical driving stress $\sigma_c$ drops remarkably from $\sim$30 MPa at 410 K to $\sim$0.5 MPa at 402 K. Interestingly, the corresponding elastocaloric temperature change $\Delta T_\alpha$ remains nearly unchanged from 1.32 K at 30 MPa to 1.29 K at 0.5 MPa, which is still comparable with its electrocaloric counterpart [9–11,27]. The giant elastocaloric strength $\Delta T_E/\sigma_c$ [10,24] to study the effect of tensile stress on the electrocaloric effect in BTO single crystals, which is shown in Fig. 3. It can be seen that the largest electrocaloric temperature changes $\Delta T_E$ induced by two typical electric fields of 8 and 12 kV/cm at 0 MPa are 0.97 and 1.03 K, respectively. These results are consistent with the direct measurement data, i.e., 0.80 and 0.90 K (Ref. [21]) or 1.10 and 1.20 K (Ref. [23]), respectively. On the contrary, the calculated values here differ from those obtained by an indirect approach where the $\Delta T_E$ peak value is about 4.8 K ($E = 10$ kV/cm) [11]. In addition, it is shown that the peak of $\Delta T_E$ moves remarkably towards higher temperatures, which is essentially attributed to the shift of $T_c(\sigma)$ [Fig. 1(a)]. Moreover, the magnitude of the $\Delta T_E$ peak increases slightly from 0.97 K at 0 MPa to 1.08 K at 200 MPa.

FIG. 2. (Color online) (a) The critical driving stress $\sigma_c$ and corresponding elastocaloric response $\Delta T_\alpha$ as a function of $T$. (b) The critical elastocaloric strength $\alpha_c$ as a function of $T$ (402–410 K). The result obtained in BTO under full transition at 401 K is also added.
The stress-mediated electrocaloric behavior described above can be understood qualitatively as follows. $\Delta T_E$ can be estimated using $\Delta T_E \approx -\int_0^E \left( \frac{\partial P}{\partial T} \right)_{E,\sigma} dE$, where $C_E$ is the volumetric heat capacity under constant $E$. In our case, the term $\left| \frac{\partial P}{\partial T} \right|_{E,\sigma}$, which is the pyroelectric coefficient, is slightly reduced when a tensile stress is applied. Note that a higher $\left| \frac{\partial P}{\partial T} \right|_{E,\sigma}$ does not necessarily guarantee a larger magnitude of the electrocaloric effect [25,28], because the ambient temperature, heat capacity, and electric field change also contribute to the above integration. In BTO single crystals, it is found that the enhancement in the term of $\frac{\partial T}{\partial E} |_{E,T}$ is dominant over compensating the reduction stemming from the term $\left| \frac{\partial P}{\partial T} \right|_{E,\sigma}$. As a result, a slight increase in $\Delta T_E$ is observed as $\sigma$ increases.

IV. CONCLUSIONS

In summary, using a thermodynamic model, we demonstrate that a giant elastocaloric strength of 2.32 K/MPa can be achieved near zero-field Curie temperature in BTO single crystals. The giant elastocaloric strength found here benefits from the sharp first-order phase transition but in counterpart the elastocaloric response suffers from the strong temperature dependence. It is found that the tensile stress can shift the electrocaloric peak to higher temperatures and simultaneously increase the magnitude of the electrocaloric peak slightly. Our findings clearly show that the elastocaloric effect in BTO single crystals has great potential to compete with its electrocaloric counterpart depending on the stress applied in practice. Hopefully, our study will stimulate further experimental and theoretical investigations on the elastocaloric effect and stress-mediated electrocaloric effects especially in ferroelectrics. In particular, the elastocaloric effect under compressive stresses taking into account ferroelastic domain switching [36] is highly desirable.

ACKNOWLEDGMENTS

The authors thank R. Pirc, N. Novak, and Z. Kutnjak for fruitful discussions and the anonymous reviewers for their suggestions to improve the manuscript. Y.L., P.-E.J., I.C.I., and B.D. acknowledge the Agence Nationale pour la Recherche for financial support through the NOMIOPS project (Grant No. ANR-11-BS10-016-02). Y.L. and J.W. wish to acknowledge the China Scholarship Council (CSC). X.J.L., J.W., Y.L., and B.D. acknowledge support from the National Science Foundation of China (Grants No. 51272204 and No. 51372195), the Ministry of Science and Technology through a 973-project (No. 2012CB619401), the Fundamental Research Funds for the Central Universities (Grant No. 2013JDGZ03), National Key Laboratory of Shock Wave and Detonation Physics through a fund (Grant No. LSD201201003), and the “One Thousand Youth Talents” program. J.K. acknowledges support from the National Research Fund, Luxembourg (FNR/P12/4853155).

[34] We used the following set of parameters (in SI units): 
\[ \alpha_1 = 4.124(T - 388.15) \times 10^5, \quad \alpha_11 = -2.097 \times 10^8, \]
\[ \alpha_{111} = 1.294 \times 10^9, \quad \alpha_{1111} = 3.863 \times 10^{10}, \quad S_{11} = 8.3 \times 10^{-12}, \]
\[ Q_{11} = 0.11, \quad C_{\text{lat}} = (0.15658 \times 10^3 + 8.50779 \times 10^{-1}T) \rho, \]
\[ \rho = 6.768 \times 10^3. \]
Note that the Landau coefficients, electrostrictive coefficients, and elastic compliances of BTO at room temperature we used are taken from Refs. [34] and [30]. 
\[ C_{\text{lat}}(T) \] and mass density \( \rho \) are taken from the experimental data reported in Ref. [10]. When solving the particular transition from paraelectric phase to ferroelectric tetragonal phase, the respective results calculated by pressure/stress-dependent [33] and -independent Landau coefficients [35] are exactly the same and are both in good agreement with experimental data as long as the magnitude of pressure/stress is below 6.5 GPa [33]. As a result, the Landau potential coefficients used here are obtained at zero pressure/stress. Further studies should take into account the pressure/stress-dependent Landau coefficients and quantum saturation of the order parameter (especially at low temperatures) [33].