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

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An applied stress field σ_3 can reversibly change the temperature of an elastocaloric material under adiabatic conditions, and the temperature change ΔT_{σ_3} is usually maximized near phase transitions. Using a thermodynamic approach, we demonstrate that an elastocaloric strength $\alpha = |\Delta T_{\sigma_3}|/|\sigma_3|$ of 0.016 K/MPa can be achieved benefiting 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 (~ 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 electrocaloric 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.

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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 ΔE of 10 kV/cm [11]. However, the magnitude of electrocaloric temperature change $|\Delta T_E|$ remains modest (~ 1 K [9–11]), which directly limits further practical applications, not to mention the large voltage required in the experiments. Since the transition temperature (~ 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

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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 σ_3 (all tensors appear in Voigt notation) can reversibly change the temperature of an elastocaloric material under adiabatic conditions, and the temperature change ΔT_σ is usually maximized near phase transitions [7,15–21]. Note that σ_3 here is a uniaxial stress applied along the polar axis of ferroelectric and denoted as σ for short in the following parts. In order to obtain ΔT_σ, one may consider using the indirect method via the Maxwell relation $(\frac{\partial S}{\partial \sigma})_{E,T} = (\frac{\partial u_3}{\partial T})_{\sigma,E}$ [4]:

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

where T is the temperature, S is the entropy, u_3 is the strain, E is the electric field, and C_σ 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 ΔT_σ provided that the irreversible contribution is relatively small [15]. Interestingly, first-principles calculations have demonstrated that ΔT_σ calculated based on Eq. (1) fails to reproduce the direct measurement results in bulk ferroelectric PbTiO$_3$ (PTO) [7]. However, ΔT_σ 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]. Additonal experimental evidence signals that the barocaloric effect in PTO is noticeable only near the pressure-free Curie temperature [26].

To allow direct comparison with recent first-principles studies [7,20], we concentrate on the condition of a uniaxial tensile stress $\sigma > 0$ applied along the [001] direction of BTO.

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]

$$G = \alpha_1 P^2 + \alpha_{11} P^4 + \alpha_{111} P^6 + \alpha_{1111} P^8$$
$$- \tfrac{1}{2} S_{11}\sigma^2 - Q_{11}\sigma P^2, \tag{2}$$

where S_{11} is the elastic compliance and Q_{11} is the electrostrictive coefficient. α_1, α_{11}, α_{111}, and α_{1111} are the dielectric stiffness coefficients at constant stress, and only α_1 is temperature dependent. The higher-order electrostrictive coupling between stress and polarization has been included in the stress-dependent Landau potential coefficients α_{11} and α_{111} [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 $S_{\rm dip}$ and the lattice contribution $S_{\rm latt}$ as follows [24]:

$$S = S_{\rm latt} + S_{\rm dip}, \tag{3}$$

where $S_{\rm dip}$ 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. $S_{\rm latt}$ 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 σ, making it applicable to our case. Following the strategy developed by Pirc *et al.* [10,24], we can then obtain a self-consistent equation to derive $\Delta T_\sigma = T_2 - T_1$ such that

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

where $a_1 \equiv d\alpha_1/dT$ and $C_{\rm latt}$ 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 σ 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 ΔT_σ peaks at $T_c(0)$, which is consistent with the predictions by first-
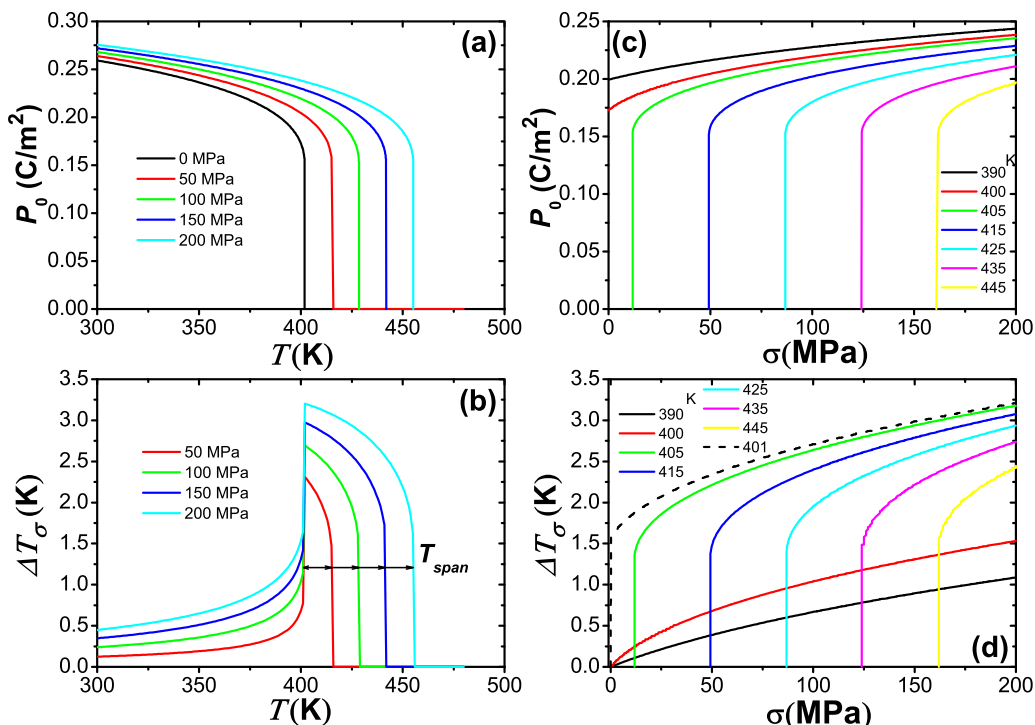
FIG. 1. (Color online) The polarization P_0 and (b) adiabatic temperature change ΔT_σ under different σ as a function of ambient temperature T. The dependence of (c) P_0 and (d) ΔT_σ on σ at different T.

principles calculations [7,20]. Just above $T_c(0)$, ΔT_σ drops sharply due to the dramatic reduction of polarization change $[P(\sigma,T) - P(0,T)]$ as shown in Fig. 1(a). Finally, ΔT_σ 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 ΔT_σ found here is about 3.2 K at 200 MPa, while ΔT_σ can reach 2.3 K at 50 MPa. ΔT_σ at 200 MPa found here (3.2 K) is smaller than that (6 K) in PTO [7] but is larger than that (~ 1 K) in $Ba_{0.5}Sr_{0.5}TiO_3$ (BST) [20] under the same stress condition. In addition, it is shown that as σ increases, the working temperature window T_{span} increases considerably from ~ 15 K at 50 MPa to ~ 50 K at 200 MPa [see Fig 1(b)]. In addition, the elastocaloric strength defined as $\alpha = |\Delta T_\sigma/\sigma|$ 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 ΔS (3.2 J/kg K) and refrigerant capacity $R \simeq |\Delta S \Delta T_\sigma|$ (Ref. [17]) are relatively low (see Table I).

The stress-dependent P_0 and ΔT_σ under different T are shown in Figs. 1(c) and 1(d). It turns out that P_0 increases as σ increases. It can be seen in Fig. 1(c) that above $T_c(0)$ there exists a critical stress field σ_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, σ_c increases significantly from ~ 12 MPa at 405 K to ~ 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 ΔT_σ increases as σ increases irrespective of T. Moreover, Fig. 1(d) clearly indicates that the largest ΔT_σ 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 (~ 1 K [9–11]) depending on the maximum value of mechanical stress applied in the practical situation. This result clearly demonstrates that applied stress may be an effective tool to directly induce the large caloric response for cooling/heating applications especially in ferroelectrics [7,20,21].

Obviously, in real situations, the high stress used in theoretical calculations warrants further consideration. For instance, for compressive stress ($\sigma < 0$), single crystal BTO usually bears an upper bound $|\sigma|$ of less than 30 MPa, while a polycrystalline sample can hold an order of magnitude higher stress (i.e., ~ 300 MPa) [36,37]. As a result, the elastocaloric effect observed by experiment should be significantly smaller than the predicted one produced by the ultrahigh stress [7,20]. In order to achieve large elastocaloric responses, it may be helpful to reconsider the critical elastocaloric behavior near $T_c(0)$. It should be noted that all the elastocaloric data shown in Table I are accomplished by full transition of samples and bounded by $\Delta T_\sigma = \frac{T}{C_\sigma} \Delta S$. In our case, a high stress of 200 MPa can be used for the full transition [see Figs. 1(c) and 1(d)]. At low stresses, the elastocaloric strength $\alpha = |\Delta T_\sigma/\sigma|$ is controlled by the slope in the $\sigma - T$ phase diagram (Clausius-Clapeyron relation) and the sharpness of the transition as shown later. Detailed discussion about this issue in the magnetocaloric effect can be found elsewhere [38]. In addition, only a single domain model is considered in the phenomenological theory here and first-principles calculations

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_{span} (K)	σ (MPa)	$\lvert\Delta T_\sigma\rvert$ (K)	$\Delta T_\sigma/\sigma$ (K/MPa)	$\lvert\Delta S\rvert$ (J/kg K)	$\lvert\Delta S\Delta T_\sigma\rvert$ (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	~ 16	144	[20]
PTO	750	~ 30	1000	20	0.020	~ 9.6	192	[7]
BTO	401	50	200	3.2	0.016	~ 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 σ_c drops remarkably from ~ 30 MPa at 410 K to ~ 0.5 MPa at 402 K. Interestingly, the corresponding elastocaloric temperature change ΔT_{σ_c} 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 in BTO single crystals [9–11]. This finding is of importance since the driving stress can be tuned to be much smaller as long as T is close to $T_c(0)$. Note that here the transition

has just been opened by the critical stress field σ_c and the corresponding temperature change $\lvert\Delta T_{\sigma_c}\rvert$ of about 1.3 K is caused directly by the discontinuous polarization jump near the transition point [see Figs. 1(a) and 1(c)]. In this case, the elastocaloric strength has to be redefined as $\alpha_c = \lvert\Delta T_{\sigma_c}/\sigma_c\rvert$ as we concentrated on elastocaloric response under a low stress. It is shown in Fig. 2(b) that as T decreases towards $T_c(0)$, the elastocaloric strength defined as α_c first increases slowly from 0.043 K/MPa at 410 K to 0.16 K/MPa at 404 K and then experiences a steep jump to 2.32 K/MPa at 402 K. Note that α experiences a sharp drop as T [starting from $T_c(0)$] decreases further (not shown here), which indicates that $\alpha \propto 1/\lvert T - T_c(0)\rvert$ is also maximized at $T_c(0)$. This phenomenon is very similar with the behavior of the electrocaloric strength near $T_c(0)$ [9–11,27]. Note that the giant elastocaloric strength of 2.32 K/MPa found here is two orders of magnitude higher than that (0.016 K/MPa) under full transition induced by a large stress (see Table I). However, just like its electrocaloric counterpart [9–11,27], the giant elastocaloric strength benefits from the sharp first-order phase transition but in turn suffers by the strong temperature dependence of ΔT_σ near $T_c(0)$. As a consequence, the narrow T_{span} (<9 K) limits the potential cooling applications of BTO in elastocaloric and electrocaloric devices. From this regard, martensite shape-memory alloys show better performance.

Understanding the stress-mediated electrocaloric effect in BTO single crystals is of particular interest as it may give a hand in tuning the electrocaloric effect. For instance, it was reported that applying compressive stresses on BTO ultrathin films can lead to the enhancement of the electrocaloric response due to the tuning of the depolarizing field [14]. In our work, we used the foregoing model [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 ΔT_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 ΔT_E peak value is about 4.8 K ($E = 10$ kV/cm) [11]. In addition, it is shown that the peak of ΔT_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 ΔT_E peak increases slightly from 0.97 K at 0 MPa to 1.08 K at 200 MPa.
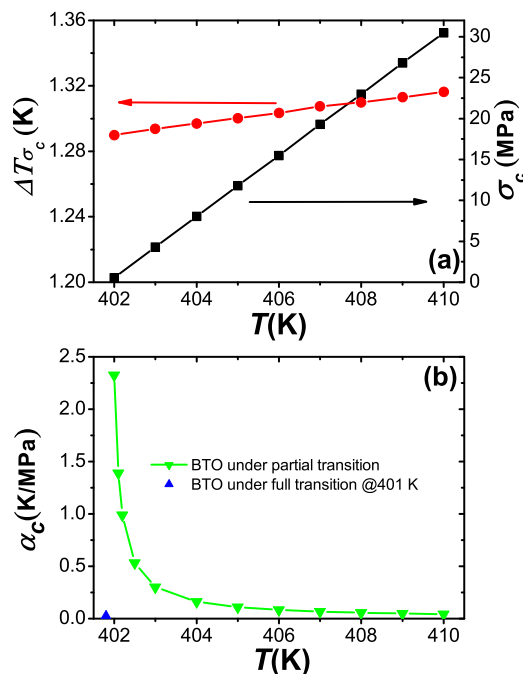
FIG. 2. (Color online) (a) The critical driving stress σ_c and corresponding elastocaloric response ΔT_{σ_c} as a function of T. (b) The critical elastocaloric strength α_c as a function of T (402–410 K). The result obtained in BTO under full transition at 401 K is also added.
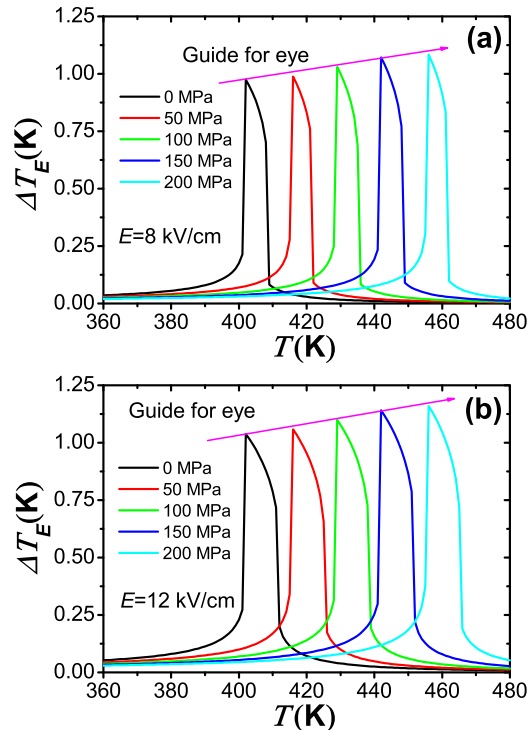
FIG. 3. (Color online) Electrocaloric effect under different mechanical conditions.

The stress-mediated electrocaloric behavior described above can be understood qualitatively as follows. ΔT_E can be estimated using $\Delta T_E \cong -\int_0^E \frac{T}{C_E}(\frac{\partial P_0}{\partial T})_{E,\sigma} dE$, where C_E is the volumetric heat capacity under constant E. In our case, the term $|\frac{\partial P_0}{\partial T}|_{E,\sigma}$, which is the pyroelectric coefficient, is slightly reduced when a tensile stress is applied. Note that a higher $|\frac{\partial P_0}{\partial T}|_{E,\sigma}$ 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 $\frac{T}{C_E}|_{E,\sigma,T}$ is dominant over compensating the reduction stemming from the term $|\frac{\partial P_0}{\partial T}|_{E,\sigma}$. As a result, a slight increase in ΔT_E is observed as σ 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.

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[34] We used the following set of parameters (in SI units): $\alpha_1 = 4.124(T - 388.15) \times 10^5$, $\alpha_{11} = -2.097 \times 10^8$, $\alpha_{111} = 1.294 \times 10^9$, $\alpha_{1111} = 3.863 \times 10^{10}$, $S_{11} = 8.3 \times 10^{-12}$, $Q_{11} = 0.11$, $C_{\mathrm{latt}} = (0.15658 \times 10^3 + 8.50779 \times 10^{-1}T)\rho$, $\rho = 6.768 \times 10^3$. Note that the Landau coefficients, electrostrictive coefficients, and elastic compliances of BTO at room temperature we used are taken from Refs. [34] and [30]. $C_{\mathrm{latt}}(T)$ and mass density ρ 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].

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