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Towards multicaloric effect with ferroelectrics

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Utilizing thermal changes in solid-state materials strategically offers caloric-based alternatives to replace current vapor-compression technology. To make full use of multiple forms of the entropy and achieve higher efficiency for designs of cooling devices, the multicaloric effect appears as a cutting-edge concept encouraging researchers to search for multicaloric materials with outstanding caloric properties. Here we report the multicaloric effect in $BaTiO_3$ single crystals driven simultaneously by mechanical and electric fields and described via a thermodynamic phenomenological model. It is found that the multicaloric behavior is mainly dominated by the mechanical field rather than the electric field, since the paraelectric-to-ferroelectric transition is more sensitive to mechanical field than to electric field. The use of uniaxial stress competes favorably with pressure due to its much higher caloric strength and negligible elastic thermal change. It is revealed that multicaloric response can be significantly larger than just the sum of mechanocaloric and electrocaloric effects in temperature regions far above the Curie temperature but cannot exceed this limit near the Curie temperature. Our results also show the advantage of the multicaloric effect over the mechanically mediated electrocaloric effect or electrically mediated mechanocaloric effect. Our findings therefore highlight the importance of ferroelectric materials to develop multicaloric cooling.

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I. INTRODUCTION

The term caloric effect refers to the reversible thermal changes (adiabatic change in the temperature or isothermal change in the entropy) in solids driven by external stimuli, which is usually largest near their phase transitions [1]. Solid-state refrigeration based on the caloric effect offers environmentally friendly and energy-efficient solutions to displace current cooling technology mainly based on vapor compression [2]. It is known that the caloric effect mainly involves magnetocaloric, electrocaloric, and mechanocaloric (elastocaloric and barocaloric) types, corresponding respectively to magnetic, electric, and mechanical field (uniaxial stress and hydrostatic pressure) [1,2]. Recently the multicaloric effect appears to be a promising concept to take advantage of the multiple forms of the entropy and higher energy efficiency [3]. Driven either by a single stimulus [3–5] or by multiple stimuli acting in concerted sequence [1,6], the multicaloric effect may yield larger caloric response compared to the caloric effect induced by a single stimulus. This leads to an enthusiastic search for multicaloric materials and encourages fast-growing research activities in this field [1,7]. For instance, recent experimental work demonstrates that a dual-stimulus magnetic-electric multicaloric cycle can not only overcome the irreversibility existing in the pure magnetocaloric cycle but also creates greater caloric response in multiferroic $FeRh/BaTiO_3$ heterostructures [6].

Among the ferroic materials ferroelectrics can be good potential candidates for developing multicaloric effect, due to the fact that the phase transition in ferroelectrics can be triggered by electric field, uniaxial stress, and hydrostatic pressure [7]. According to the literature, individual caloric effects such as electrocaloric [8–20], elastocaloric [21–28], and barocaloric [28–33] scenarios have all been reported in ferroelectric materials. In this context only a few theoretical studies have been published to understand the multicaloric effect in ferroelectric bulk and thin films driven by simultaneous application of electric and mechanical fields [22,34]. In order to inspire confidence for future experiments, theoretical investigations allowing deeper insights into this effect are highly desired, since the advantage of multicaloric effect over individual caloric responses is not quite clear so far. This requires detailed comparison about the sensitivity of multicaloric effects with respect to different stimuli (electric field, uniaxial stress, and pressure) that is basically unknown.

In this work we present a thermodynamic study of multicaloric effects specifically in single crystals of $BaTiO_3$ (which is a prototype of ferroelectrics) under simultaneous electric and mechanical fields (uniaxial stress or hydrostatic pressure). Taking into account recent experimental evidences and theoretical developments, we provide critical insights into the use of ferroelectric materials for potential multicaloric cooling. Our findings address the dominant role of mechanical field in manipulating the multicaloric behavior in ferroelectrics and reveal the upper bound for multicaloric response near the Curie temperature. Our results show that uniaxial stress rather than hydrostatic pressure is the optimum mechanical stimulus to drive the multicaloric effect. In addition, we make comparison between the multicaloric effect and mechanically (electrically) mediated electrocaloric (mechanocaloric) effect.

II. THERMODYNAMIC MODEL

On the basis of previous phenomenological efforts [11,12,24,31] we can deduce the caloric behavior in normal

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ferroelectric simply in terms of its order parameter, i.e., polarization. The principle idea is to "transform" the lattice entropy change due to structural transition into polar contributions. This treatment can provide reasonable estimations of caloric behaviors: mechanocaloric entropy change exists only if structural changes are induced by uniaxial stress or hydrostatic pressure, which is always accompanied by a change of a polar degree of freedom, since the ferroelectric phase transition is of a structural nature. Therefore, the key assumption used here is that the total entropy can be divided into a lattice part, which is field independent, and a polar part which depends strongly on external stimulus [11]. The polarization of course arises from polar optical phonons of long wavelength ($q = 0$), which include both propagating and overdamped modes. By "lattice contribution" we refer to the other nonpolar modes and to phonons at nonzero wave vector, away from the Brillouin-zone center. These contribute to the specific heat but not to the macroscopic polarization. As a result, based on a Landau-type free-energy model, the caloric response can be calculated without employing the Maxwell relations, which may be questionable for first-order phase transitions [11,31]. By carrying out these kinds of calculations we could at least obtain qualitative information about the multicaloric effect, which acts as an important guide to future experimental studies. Moreover, previous results [11,12,24,31] based on this model appear to be compatible with the recent developments from both first-principles predictions and experimental data [21,22,26,30].

Considering simultaneous application of electric field E and uniaxial stress σ_3 (denoted as σ in the following) along polarization z direction or hydrostatic pressure p adiabatically on $BaTiO_3$ single crystals, the multicaloric temperature change $\Delta T = T_2 – T_1$ can be obtained through the following relation [11]:

$$T_2 = T_1 \exp\left(\frac{1}{2C_{\text{latt}}(T)}[a_1(T_2)P^2(p \text{ or } \sigma, E, T_2) - a_1(T_1)P^2(0,0,T_1)]\right), \tag{1}$$

where P is the polarization and $C_{\text{latt}}(T)$ is the lattice contribution to the total heat capacity, which is field independent [11]. Moreover, $a_1 = d\alpha_1/2dT$, with α_1 being a temperature-dependent Landau free-energy expansion coefficient. Here we are particularly interested in the transition from cubic phase ($P_1 = P_2 = P_3 = 0$) to tetragonal phase ($P_1 = P_2 = 0$, $P = P_3 \neq 0$). The temperature dependence of polarization under different electric and mechanical fields $P(p,E,T)$ or $P(\sigma,E,T)$ can be deduced by solving for the Gibbs free energy under the condition of thermodynamic and mechanical equilibrium $\partial G/\partial P = 0$. Specifically, Gibbs free energy under hydrostatic pressure and electric field can be expressed as [35]

$$G_{\text{p}} = \alpha_1 P^2 + \alpha_{11} P^4 + \alpha_{111} P^6 + \alpha_{1111} P^8 - \left(\tfrac{2}{3}S_{11} + 3S_{12}\right)p^2 + p(Q_{11} + 2Q_{12})P^2 - EP, \tag{2}$$

where S_{mn} are the elastic compliances and Q_{mn} are the electrostrictive coefficients.

For the mechanical boundary conditions under uniaxial stress, G can be written as [35]

$$G_{\sigma} = \alpha_1 P^2 + \alpha_{11} P^4 + \alpha_{111} P^6 + \alpha_{1111} P^8 - \tfrac{1}{2}S_{11}\sigma^2 - Q_{11}\sigma P^2 - EP. \tag{3}$$

The Landau coefficients, electrostrictive coefficients, and elastic compliances of $BaTiO_3$ at room temperature we used are the same as in previous works [24,31]. $C_{\text{latt}}(T)$ can be obtained by fitting the experimental results to the linear relationship $C_{\text{latt}}(T) = (0.157 \times 10^3 + 0.85T)\rho$ where ρ is the mass density [12].

III. RESULT AND DISCUSSION

A. Tuning of the Curie temperature

The tuning of the Curie temperature under different stimuli is shown in Fig. 1. In normal ferroelectrics such as $BaTiO_3$ the long-range-ordered ferroelectric phase can be stabilized by external electric field even in the paraelectric phase above the Curie temperature, which is accompanied by the ordering of electrical dipoles. This leads to the reduction of entropy under isothermal conditions or heating of ferroelectrics under adiabatic conditions, which is known as the positive (conventional) electrocaloric effect, indicated by a positive ΔT peak near the Curie temperature [7,36]. Similarly, the mechanocaloric effect (elastocaloric and barocaloric) under tensile uniaxial stress or negative (tensile) hydrostatic pressure belongs to the conventional caloric type. On the contrary, the ferroelectric instability can be induced by moderate positive (compressive) hydrostatic pressure [31,35,37]. As a result, the ferroelectric to paraelectric transition temperature is shifted to lower values with the compressive pressure, decreasing at a rate of −50 K/GPa (which agrees well with the previously reported data of about −50 K/GPa in Ref. [37]). This dependence is in contrast to the trend under electric field (0.75 K cm/kV, which agrees with the experimental value [12]

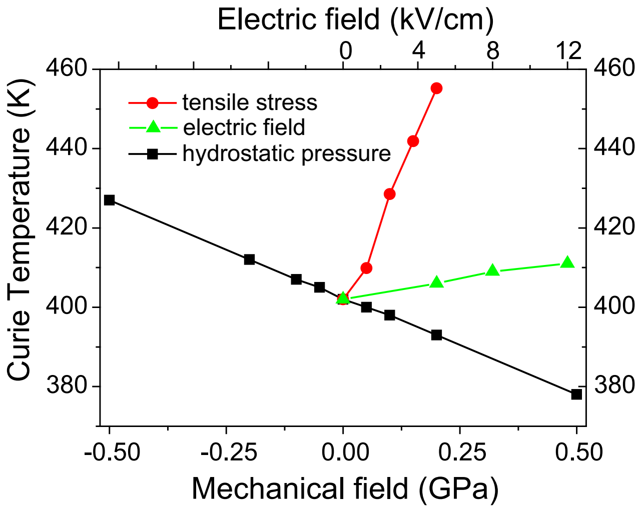

FIG. 1. The Curie temperature of $BaTiO_3$ single crystals under different external stimuli (electric field, mechanical stress, and pressure). Theoretical data points are shown via symbols while the solid lines are guides for the eyes.

of $\sim$0.78 Kcm/kV) and tensile stress (266 K/GPa). Therefore, the sign of the barocaloric effect under positive (compressive) hydrostatic pressure is negative [31], which is consistent with experimental results [33]. In addition, 0.05 GPa pressure or stress can fully drive the narrow first-order phase transition ($\sim$2.5 K, as reported in Ref. [14]).

Figure 1 indicates that the phase transition from cubic to tetragonal in $BaTiO_3$ is most sensitive to tensile stress compared to hydrostatic pressure and electric field for realistic values of stress, pressure, and electric field. This highlights the promising potential to develop the mechanocaloric effect, especially the elastocaloric effect, in ferroelectric materials, compared with the electrocaloric effect. As it will be shown later, it is indeed found that the optimized multicaloric behavior is mostly dominated by the mechanical stimuli, whereas the electric field has relatively weak influences on the total caloric response.

B. Multicaloric effect under mechanical and electric fields

Let us first concentrate on the multicaloric effect under compressive hydrostatic pressure and electric field (Figs. S1a–S1d in the Supplemental Material [38]). Due to the opposite sign in tuning of phase transition temperature by electric field and pressure (see Fig. 1), the multicaloric caloric response is accompanied by the change in its sign depending on the magnitude of electric field and pressure. In most cases it is found that the magnitude of multicaloric response is reduced compared to either electrocaloric or barocaloric response, which is accompanied by the shrinking of the operational temperature window. According to Eq. (1), there exists a critical crossover in the sign change of caloric response where the effects of electric and pressure fields on the phase transition compensate each other (Fig. S2b, Supplemental Material [38]). In addition, our theoretical result predicts that under high compressive pressure the working temperature window is mainly expanded asymmetrically towards lower temperature (Figs. S1a–S1d, Supplemental Material [38]), which is consistent with experimental data [33].

These results may yield a negative indication about the use of multicaloric effect, in addition to the fact that the existence of elastic heating due to elastic deformation makes the total thermal behavior more complex [39,40]. In our model the lattice heat capacity $C_{\mathrm{latt}}(T)$ is assumed to be field independent, whereas the elastic heating [39,40] (that is usually linearly dependent on the pressure or stress) is not taken into account. The elastic heating at 0.2 GPa uniaxial stress results in heating of only 0.03 K estimated from the Maxwell relation, which contributes about 1% of the elastocaloric temperature change. This implies that Eq. (1) is reasonable in describing the multicaloric effect using uniaxial stress. However, in the case of hydrostatic pressure, recent calorimetry measurements on $BaTiO_3$ ceramics reported a reduction of barocaloric response with increasing pressure p [33] due to elastic heating [32]. The elastic heating, acting as a competing effect with barocaloric cooling, as we predict, limits its performances, especially at high pressure.

In the spirit of the recent experimental demonstration of negative pressure in ferroelectrics [41,42], we exploit the multicaloric effect under negative pressure and electric field. Negative hydrostatic pressure in real experiments is generally provided by chemical substitution of slightly larger ions; a good example is replacement of Ca in $Ca_3Co_2O_6$ by Y [41]. In addition, recent experimental results demonstrated that negative pressure as low as -4 GPa can be realized by the transformation between a lower-density crystal structure and the perovskite phase in freestanding $PbTiO_3$ nanowires [42]. Although the elastic heating would probably exist even under negative pressure, its contribution is expected to be reduced in single crystals under lower pressure [39,40]. However, it is found that application of a low negative pressure can only result in a considerable enhancement of the multicaloric effect with a broadening of the working temperature (a temperature range with $\Delta T \geqslant \Delta T_{\mathrm{m}}/2$, where ΔT_{m} is the largest temperature change). Specifically, compared to the pure electrocaloric effect ($E = 12\,\mathrm{kV/cm}$), applying a negative pressure of -0.2 GPa in addition to this specific electric field can increase the maximum ΔT from 2.08 K to 2.42 K by a factor of nearly 16%, as shown in Fig. 2(a); this is unlikely to overcome the elastic cooling which tends to reduce the total temperature change by roughly the same amount as implied from the experiments [33].

The existence of negative pressure has been shown to stabilize ferroelectric order [42], which is also found in Fig. 2(b), consistent with previous prediction by first-principles calculations [43]. This requires higher pressure (magnitude) to reach larger caloric response which, however, is parasitically compensated by the elastic cooling associated with the elastic deformation. In this regard the multicaloric effect (denoted as Multi2) under tensile uniaxial stress and electric field in Fig. 2(c) is more desirable than the case (denoted as Multi1) under negative pressure and electric field in Fig. 2(a). This is not only due to the negligible elastic thermal contributions under uniaxial stress in Multi2 but also attributed to its significantly larger caloric strength and wider operational window compared to Multi1. To be specific, the caloric strength (defined as $|\Delta T/\Delta E \Delta p|$ or $|\Delta T/\Delta E \Delta \sigma|$) obtained from Multi2 is about 1.37 K cm/kV GPa, which is much larger than that (1.01 K cm/kV GPa) from Multi1 at the same magnitude of the external stimuli ($E = 12\,\mathrm{kV/cm}$, $p = -0.2\,\mathrm{GPa}$ and $\sigma = 0.2\,\mathrm{GPa}$). Although the uniaxial stress and hydrostatic pressure have nominally the same magnitude, it is even more notable that a uniaxial stress of 0.2 GPa has larger effects than a pressure of -0.2 GPa. The working temperature window for Multi2 is $\sim$70 K ($E = 12\,\mathrm{kV/cm}$ and $\sigma = 0.2\,\mathrm{GPa}$), which is much wider than the counterpart ($\sim$25 K) for Multi1 ($E = 12\,\mathrm{kV/cm}$ and $p = -0.2\,\mathrm{GPa}$). The significantly enhanced caloric properties in Multi2 are attributed to the fact that the transition is more sensitive to uniaxial stress than to pressure (Fig. 1). To be more specific, the ferroelectric transition to a tetragonal phase implies that c/a is larger than 1 where c and a are the lattice constants along the z direction and x (and y) direction. Applying a stress along the z direction can lead to a much larger increase in the tetragonality c/a compared to that under a negative pressure [43]. As a result, Fig. 2(d) presents a much larger polarization change in a wider temperature range in Multi2 compared to Multi1.

The multicaloric effect (Multi2) was also studied in $PbTiO_3$ bulk by first-principles-based calculations using significantly

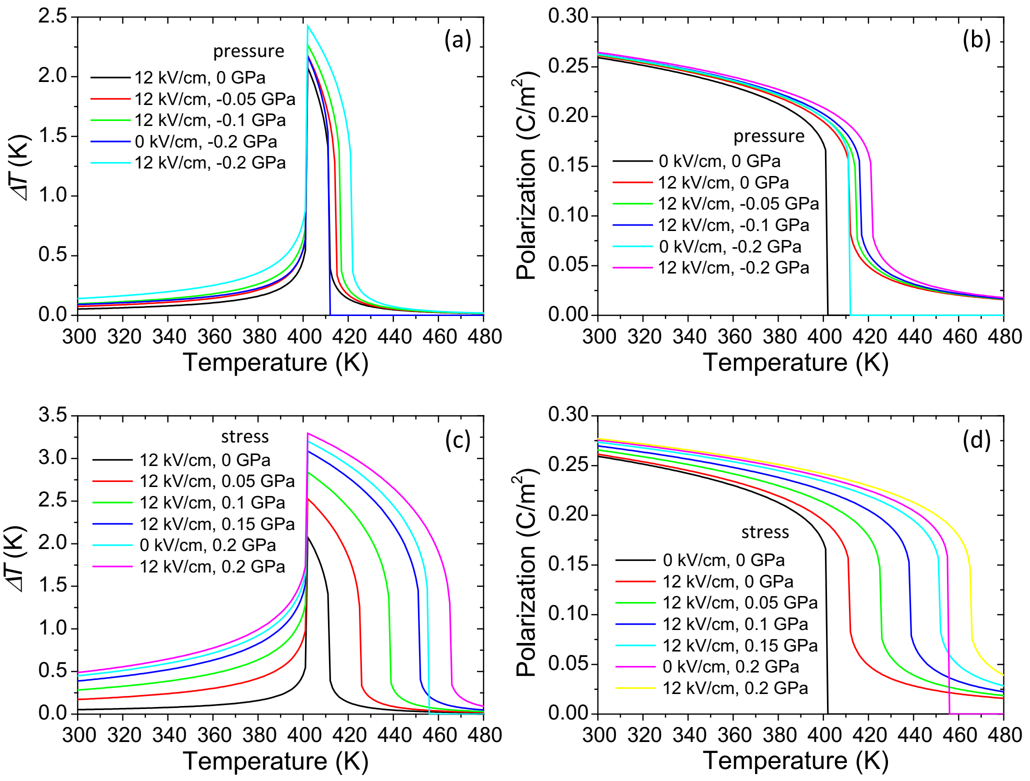

FIG. 2. Multicaloric temperature change ΔT induced by simultaneous application of electric field (from 0 kV/cm to 12 kV/cm) and (a) tensile hydrostatic pressure or (c) tensile uniaxial stress. Accordingly, panels (b) and (d) correspond to the polarization-temperature curves under different electric fields and pressures (decreasing from 0 to −0.2 GPa) or stresses (increasing from 0 to 0.2 GPa).

larger tensile uniaxial stress and electric fields [22]. The caloric strength is about 0.25 K cm/kV GPa at 630 K ($E = 195\,\mathrm{kV/cm}$ and $\sigma = 0.4\,\mathrm{GPa}$), which is much smaller than that (1.37 K cm/kV GPa) in BaTiO$_3$ at 402 K. This unexpected smaller caloric strength in PbTiO$_3$ may be understood by the much stronger strain sensitivity of BaTiO$_3$ compared to PbTiO$_3$ [44]. The profiles of multicaloric behavior were found to be qualitatively similar to our findings in lead-free BaTiO$_3$, while the dominant role of mechanical field as analyzed later is not revealed in the previous work of Ref. [22]. In electrocalorics, including mechanically mediated electrocalorics, all the interaction between stress and polarization is via strain, i.e., piezoelectricity (which is usually large and well studied) and electrostriction. Both works address the important role of piezoelectricity in achieving enhanced multicaloric effect in ferroelectric electrocalorics [22,24]. The analogous situation does not arise in magnetocalorics, which often does not distinguish piezomagnetism [45,46] and magnetostriction.

C. Insights into the multicaloric effect in normal ferroelectrics

In order to gain deeper insights, we make further analysis about the multicaloric behavior by comparing its largest temperature change ΔT_{m} with that in pure electrocaloric or mechanocaloric effects as shown in Figs. 3(a)–3(d). Figures 3(a) and 3(b) show that electric field can lead to only a slight enhancement in the total temperature change while mechanical field (especially tensile stress) can result in a significantly larger variation in ΔT_{m}. This can be seen more clearly in Figs. 3(c) and 3(d) where the electric and mechanical fields increase simultaneously. Therefore, the multicaloric effect here is actually dominated by the mechanical field due to its high sensitivity in tuning the phase transition (Fig. 1), which is further confirmed in Fig. 3(d). Figure 3(d) shows that the difference in the largest temperature change between multicaloric effect $|\Delta T_{E\sigma,\mathrm{m}}|$ (or $|\Delta T_{Ep,\mathrm{m}}|$) and electrocaloric effect $|\Delta T_{E,\mathrm{m}}|$ increases much more significantly compared to the difference between multicaloric effect and mechanocaloric effect. Specifically, the contribution from the electric field to the total temperature change remains nearly constant for Multi1 while it decreases considerably for Multi2. In addition, the operational temperature window for Multi2 is expanded by about 10 K towards higher temperatures compared to the pure elastocaloric effect [Fig. 2(c)]. As a result, the advantage of using multicaloric effects is to enhance significantly the electrocaloric effect, although it seems to compete with the mechanocaloric effect, except for a relatively narrow high-temperature range. For instance, in the temperature above ∼455 K, the multicaloric response is superior—significantly larger than either electrocaloric or elastocaloric effects [Fig. 2(c)].

Our results also demonstrate that the multicaloric response ($|\Delta T_{E\sigma,\mathrm{m}}|$ or $|\Delta T_{Ep,\mathrm{m}}|$) near the Curie temperature cannot be larger than the sum of individual caloric response $|\Delta T_{E,\mathrm{m}}| + |\Delta T_{\sigma,\mathrm{m}}|$ (or $|\Delta T_{E,\mathrm{m}}| + |\Delta T_{p,\mathrm{m}}|$). This finding further imposes an upper bound for the multicaloric effect in normal ferroelectrics which can be understood as follows. As long as the phase transition can be triggered either by

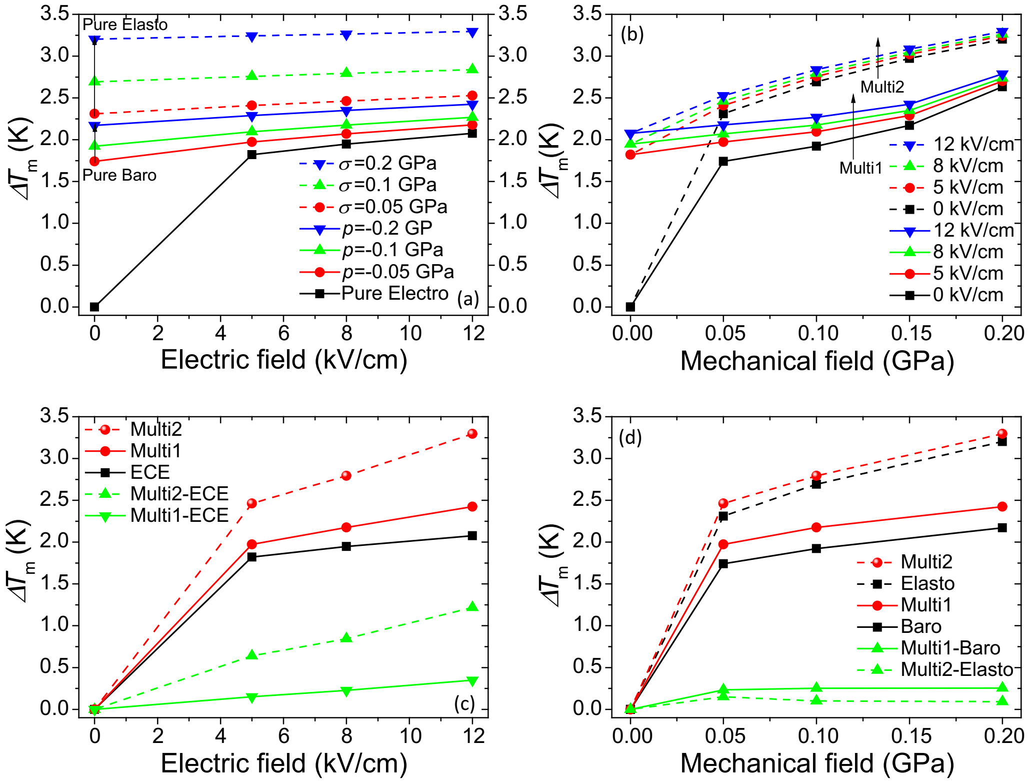

FIG. 3. The largest caloric responses ΔT_m at the Curie temperature (402 K) with a specially fixed electric field (a) or a mechanical field (b); comparison in ΔT_m between multicaloric effect and (c) electrocaloric effect (ECE) or (d) mechanocaloric effect. Baro and Elasto refer to barocaloric and elastocaloric effect. The label "Multi-ECE (Baro or Elasto)" indicates the difference between multicaloric effect and individual caloric response. Panels (c) and (d) employ the combination of electrical and mechanical stimuli (magnitude) from 0 kV/cm, 0 GPa, to 5 kV/cm, 0.05 GPa, 8 kV/cm, 0.1 GPa, and finally 12 kV/cm, 0.2 GPa. Theoretical data points are shown via symbols while the solid lines are guides for the eyes.

multiple stimuli or by a single stimulus, the largest polarization difference between $P(p,E,T)$ [or $P(\sigma,E,T)$] and $P(0,0,T)$ remains at almost the same level, i.e., around $0.2\,\mathrm{C/m^2}$ in $BaTiO_3$ [see Figs. 2(b) and 2(d)]. The polarization will saturate under large enough stimulus, and there is thus very limited space for further inducing a significant variation in the magnitude of polarization. For instance, reaching this upper limit requires at least three times enhancement in the induced polarization (about $0.8\,\mathrm{C/m^2}$), according to Eq. (1), which is unrealistic for $BaTiO_3$. This may result from that mechanical and electric fields are correlated in ferroelectrics due to the coupling between the strain and polarization. We also note that the limit imposed on bulk ferroelectrics here is in contrast to recent theoretical results in ferroelectric thin films, which can overcome this limit due to the so-called piezoelectrocaloric effect [34]. This may be due to the change in the mechanical boundary conditions leading to secondary contributions [47].

The multicaloric effect does not significantly exceed the elastocaloric effect near (and below) the Curie temperature, which further implies that elastocaloric effect alone may be strong enough to develop elastocaloric-based devices. However, this does not necessarily mean that multicaloric effect is not useful in ferroelectrics, since Fig. 2(c) shows that in the high-temperature range (above 455 K), the multicaloric response exceeds both electrocaloric and elastocaloric effect by several orders of magnitude.

Finally, we focus on the comparison between multicaloric effect and mechanically mediated electrocaloric effect or electrically mediated elastocaloric effect. The stimulus-mediated caloric effects refer to the caloric properties tuned by another external stimulus. For instance, the mechanically mediated electrocaloric effect can be obtained by fixing the samples

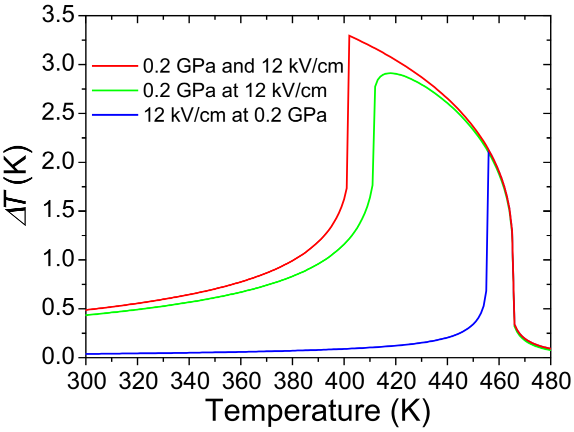

FIG. 4. Comparison of adiabatical temperature between multicaloric effect (red line) and mechanically (electrically) mediated electrocaloric (elastocaloric) effect [blue (green) line].

strained already by a mechanical field and then applying an electric field to trigger only the electrocaloric response of interest. The stimulus-mediated caloric effect has attracted much more attention since the additional stimulus applied on the samples may help to optimize the caloric properties such as the tuning of phase transition temperature (thus the working temperature) and to modify the largest caloric response [24–27,31]. A typical result is shown in Fig. 4. Our findings show that multicaloric effect especially making use of mechanical entropy can exhibit a much larger temperature change with its working temperature expanded significantly towards room temperature as compared to the stress-mediated electrocaloric effect. In this regard, the working temperature window is widened by a factor of 6 from 10 to 70 K, which is desired for cooling applications.

IV. CONCLUSION

In summary, we have studied the multicaloric effect in ferroelectrics by systematic comparisons between multicaloric effect and individual or stimulus-mediated caloric effect. For the selection of mechanical stimulus, our results suggest that uniaxial stress is particularly favored due to higher caloric strength and nearly no elastic thermal changes compared to pressure. We also reveal the existence of an upper limit imposed on multicaloric response near the Curie temperature. Our findings demonstrate exciting perspectives of multicaloric effect and offer opportunities for developing multicaloric concept using ferroelectric perovskites for future cooling applications.

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[1] X. Moya, S. Kar-Narayan, and N. D. Mathur, Nat. Mater. **13**, 439 (2014).

[2] A. Kitanovski, J. Tušek, U. Tomc, U. Plaznik, M. Ozbolt, and A. Poredoš, *Magnetocaloric Energy Conversion: From Theory to Applications* (Springer, Switzerland, 2015).

[3] M. M. Vopson, Solid State Commun. **152**, 2067 (2012); J. Phys. D: Appl. Phys. **46**, 345304 (2013); M. M. Vopson, D. Zhou, and G. Caruntu, Appl. Phys. Lett. **107**, 182905 (2015).

[4] Ch. Binek and V. Burobina, Appl. Phys. Lett. **102**, 031915 (2013).

[5] A. Planes, T. Castán, and A. Saxena, Philos. Mag. **94**, 1893 (2014).

[6] Y. Liu, L. C. Phillips, R. Mattana, M. Bibes, A. Barthélémy, and B. Dkhil, Nat. Commun. **7**, 11614 (2016).

[7] Y. Liu, J. F. Scott, and B. Dkhil, APL Mater. **4**, 064109 (2016).

[8] A. S. Mischenko, Q. Zhang, J. F. Scott, R. W. Whatmore, and N. D. Mathur, Science **311**, 1270 (2006).

[9] B. Neese, B. Chu, S. G. Lu, Y. Wang, E. Furman, and Q. M. Zhang, Science **321**, 821 (2008).

[10] S. Prosandeev, I. Ponomareva, and L. Bellaiche, Phys. Rev. B **78**, 052103 (2008).

[11] R. Pirc, Z. Kutnjak, R. Blinc, and Q. M. Zhang, J. Appl. Phys. **110**, 074113 (2011).

[12] N. Novak, R. Pirc, and Z. Kutnjak, Europhys. Lett. **103**, 47001 (2013).

[13] Y. Bai, X. Han, X.-C. Zheng, and L. J. Qiao, Sci. Rep. **3**, 2895 (2013).

[14] X. Moya, E. Stern-Taulats, S. Crossley, D. González-Alonso, S. Kar-Narayan, A. Planes, L. Mañosa, and N. D. Mathur, Adv. Mater. **25**, 1360 (2013).

[15] W. Geng, Y. Liu, X. Meng, L. Bellaiche, J. F. Scott, B. Dkhil, and A. Jiang, Adv. Mater. **27**, 3165 (2015).

[16] G. Zhang, Q. Li, H. Gu, S. Jiang, K. Han, M. R. Gadinski, M. A. Haque, Q. M. Zhang, and Q. Wang, Adv. Mater. **27**, 1450 (2015).

[17] X. S. Qian, H. J. Ye, T. Yang, W. Z. Shao, L. Zhen, E. Furman, L. Q. Chen, and Q. M. Zhang, Adv. Func. Mater. **25**, 5134 (2016).

[18] G. Zhang, X. Zhang, H. Huang, J. Wang, Q. Li, L. Q. Chen, and Q. Wang, Adv. Mater. **28**, 4811 (2016).

[19] F. Weyland, M. Acosta, J. Koruza, P. Breckner, J. Rödel, and N. Novak, Adv. Func. Mater. **26**, 7326 (2016).

[20] Y. Liu, B. Dkhil, and E. Defay, ACS Energy Lett. **1**, 521 (2016); Y. Liu, H. Strozyk, B. Dkhil, and E. Defay, Appl. Phys. Lett. **109**, 212902 (2016).

[21] S. Lisenkov and I. Ponomareva, Phys. Rev. B **86**, 104103 (2012).

[22] S. Lisenkov, B. K. Mani, C.-M. Chang, J. Almand, and I. Ponomareva, Phys. Rev. B **87**, 224101 (2013).

[23] Y. Liu, I. C. Infante, X. J. Lou, L. Bellaiche, J. F. Scott, and B. Dkhil, Adv. Mater. **26**, 6132 (2014).

[24] Y. Liu, J. Wei, P.-E. Janolin, I. C. Infante, J. Kreisel, X. J. Lou, and B. Dkhil, Phys. Rev. B **90**, 104107 (2014).

[25] Y. Liu, J. Wei, X. J. Lou, L. Bellaiche, J. F. Scott, and B. Dkhil, Appl. Phys. Lett. **106**, 032901 (2015).

[26] A. Chauhan, S. Patel, and R. Vaish, Appl. Phys. Lett. **106**, 172901 (2015).

[27] A. Chauhan, S. Patel, and R. Vaish, Acta Mater. **89**, 384 (2015).

[28] S. Patel, A. Chauhan, R. Vaish, and P. Thomas, Appl. Phys. Lett. **108**, 072903 (2016).

[29] E. Mikhaleva, I. Flerov, V. S. Bondarev, M. V. Gorev, A. D. Vasilliev, and T. N. Davydova, Phys. Solid State **53**, 510 (2011).

[30] E. Mikhaleva, I. Flerov, M. Gorev, M. Molokeev, A. Cherepakhin, A. Kartashev, N. Mikhashenok, and K. Sablina, Phys. Solid State **54**, 1832 (2012).

[31] Y. Liu, J. Wei, P.-E. Janolin, I. C. Infante, X. J. Lou, and B. Dkhil, Appl. Phys. Lett. **104**, 162904 (2014).

[32] P. Lloveras, E. Stern-Taulats, M. Barrio, J.-Ll. Tamarit, S. Crossley, W. Li, V. Pomjakushin, A. Planes, Ll. Mañosa, N. D. Mathur, and X. Moya, Nat. Commun. **6**, 8801 (2015).

[33] E. Stern-Taulats, P. Lloveras, M. Barrio, A. Planes, E. Defay, M. Egilmez, J.-L. Tamarit, L. Mañosa, N. D. Mathur, and X. Moya, APL Materials **4**, 091102 (2016).
[34] I. A. Starkov and A. S. Starkov, Int. J. Solids Struct. **100**, 187 (2016).
[35] J. J. Wang, P. P. Wu, X. Q. Ma, and L. Q. Chen, J. Appl. Phys. **108**, 114105 (2010).
[36] Y. Liu, J. F. Scott, and B. Dkhil, Appl. Phys. Rev. **3**, 031102 (2016).
[37] G. A. Samara, Ferroelectrics **2**, 277 (1971).
[38] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevB.94.214113 for multicaloric effect under compressive hydrostatic pressure and electric field.
[39] K. Alex Müller, F. Fauth, S. Fischer, M. Koch, A. Furrer, and P. Lacorre, Appl. Phys. Lett. **73**, 1056 (1998).
[40] T. Strässle, A. Furrer, Z. Hossain, and Ch. Geibel, Phys. Rev. B **67**, 054407 (2003).
[41] S. Rayaprol and E. V. Sampathkumaran, Pramana-J. Phys. **65**, 491 (2005).
[42] J. Wang, B. Wylie-van Eerd, T. Sluka, C. Sandu, M. Cantoni, X.-K. Wei, A. Kvasov, L. J. McGilly, P. Gemeiner, B. Dkhil, A. Tagantsev, J. Trodahl, and N. Setter, Nat. Mater. **14**, 985 (2010).
[43] S. Tinte, K. M. Rabe, and D. Vanderbilt, Phys. Rev. B **68**, 144105 (2003).
[44] N. A. Pertsev and B. Dkhil, Appl. Phys. Lett. **93**, 122903 (2008).
[45] I. E. Dzialoshinskii, Sov. Phys. JETP **6**, 621 (1958).
[46] A. S. Borovik-Romanov, Sov. Phys. JETP **11**, 786 (1960).
[47] T. Tong, J. Karthik, R. V. K. Mangalam, L. W. Martin, and D. G. Cahill, Phys. Rev. B **90**, 094116 (2014).