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Many important breakthroughs and significant engineering developments have been achieved during the past two decades in the field of caloric materials. In this review, we address ferroelectrics emerging as ideal materials which permit both giant elastocaloric and/or electrocaloric responses near room temperature. We summarize recent strategies for improving caloric responses using geometrical optimization, maximizing the number of coexisting phases, combining positive and negative caloric responses, introducing extra degree of freedom like mechanical stress/pressure, and multicaloric effect driven by either single stimulus or multiple stimuli. This review highlights the promising perspective of ferroelectrics for developing next-generation solid-state refrigeration. © *2016 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).* [http://dx.doi.org/10.1063/1.4954056]

Solid-state caloric materials, which undergo an adiabatic temperature change or isothermal entropy change when some external stimulus is applied or removed, are highly sought after for new refrigeration solutions to replace current vapor-cycle cooling technologies.[1–3] The most prominent caloric materials are ferroics which often exhibit giant caloric effects near their ferroic transitions;[4,5] we propose to refer them as "ferrocalorics." Ferrocalorics concern a broad family of materials including ferroelectrics, ferromagnetic materials, ferroelastics/martensitic shape-memory alloys, and multiferroics which are subjected to a moderate magnetic field (magnetocaloric effect), electric field (electrocaloric effect), hydrostatic pressure (barocaloric effect), or uniaxial stress (elastocaloric effect), the last two effects being also considered as "mechanocaloric" effects.[5] All these caloric effects appear promising as they may deliver higher energy efficiency with low environmental impact compared to vapor compression refrigeration.[1–3] For instance, higher coefficient of performance (*COP*), defined as the ratio between the extracted heat with respect to the input work, can be achieved with over 50% of Carnot efficiency.[1–3,6] Many important breakthroughs in the wide field of Materials Science have been achieved so far. At the same time, exciting achievements and significant engineering developments aiming at commercial applications have been realized: e.g., about 60 magnetocaloric prototypes have been developed all over the world.[3] While the research in electrocaloric and mechanocaloric effects is at its infancy,[5] it receives more attention and great efforts are currently conducted to select the appropriate materials and design innovative prototypes as efficient, and even better, as magnetocaloric counterparts.[2,3]

The first-order nature of the ferroic phase transition is commonly known to be the most suitable for achieving enhanced caloric response.[5] For instance, a milestone discovery of giant room-temperature magnetocaloric effect[7] was demonstrated through the discontinuous magnetically induced phase transition in $Gd_5Si_2Ge_2$ compound in 1997, which in turn has stimulated an exponential increase of interest especially by looking for magnetic materials with first-order phase

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transition. However, while the first-order transition exhibits stronger caloric responses, it suffers from several drawbacks. Indeed, as the caloric peak near the first-order transition is sharp, it usually results in a narrow working-temperature window compared to the broad caloric peak accompanying a second-order phase transition. Moreover, concomitant hysteresis losses associated with the first-order-like nature are detrimental in most materials for caloric response[8,9] and refrigerant efficiency while there is no hysteresis losses related to second-order transition.

Ferroelectrics that are characterized by the existence of an electric-field switchable polarization whose appearance is accompanied by structural phase transition have attracted increasingly attention for the last 10 years especially in the field of electrocalorics.[2] In addition to the use of first-order transition materials, other strategies to enhance the caloric properties are possible such as geometrical optimization,[10–14] maximizing the number of close-energy phases near a critical point in the temperature-composition phase diagram,[15–17] combining conventional and inverse caloric responses in a single refrigeration cycle,[18,19] introducing extra available degree of freedom like strain via mechanical stress,[20–22] and multicaloric effect driven by either single stimulus or multiple stimuli (applied/removed simultaneously or sequentially).[5] There are several excellent review articles and books treating on the electrocaloric effect through its history, related properties, and potential design for cooling applications.[2,3,23–28] However, because of the fast growing research in the field, some aspects, e.g., the role of mechanical stresses in ferroelectrics resulting in elastocaloric effect or the recent developments on the so-called negative electrocaloric effect were not taken into account. In this brief review, we address some very recent strategies developed for improving caloric responses using polarization-based materials by exploiting the nature of the ferroelectric transition, i.e., first versus second order as well as its ferroelastic character and the various arrangements of the polarization can take in multiphase compositions or antiferroelectrics.

Based on the Maxwell relationship $(\frac{\partial S}{\partial Y})_T = (\frac{\partial x}{\partial T})_Y$ where S is the entropy, T is the temperature, and x and Y are an extensive variable and its conjugated field, respectively, the reversible caloric change in temperature ΔT_Y of a specific material in response to a change to an external stimulus $\Delta Y = Y_f - Y_i$ $(Y = E, \mu_0 H, \sigma_3, p)$ under adiabatic conditions can be determined by[1–5]

$$\Delta T_Y = -\int_{Y_i}^{Y_f} \frac{T}{C_Y} (\frac{\partial x}{\partial T})_Y dY, \tag{1}$$

where x, the generalized displacements (P, M, ε, V); and C_Y, the heat capacity under constant field $Y(=E, \mu_0 H, \sigma_3, p)$. Note that ΔT_Y is usually maximized near the phase transition (especially for the first-order transition), where thermally driven changes in magnitude of the generalized displacements x$(=P, M, \varepsilon, V)$ are the largest. Usually, one can calculate the caloric effect using temperature dependence of the generalized displacement (isothermal P-T, M-T, ε-T, and V-T curves). This approach based on the Maxwell relationships is the so-called indirect method.

In addition to use adiabatic temperature change ΔT_Y, another quantity called isothermal entropy change ΔS_Y is also equally important to characterize the caloric effect. Isothermal entropy change is directly related to absorbed or ejected isothermal heat $Q = T\Delta S_Y$.[5] In the field of electrocaloric effect and according to the literature, the simple relation between adiabatic temperature change and isothermal entropy change $C_E \Delta T_E = T \Delta S_E$ is often used. Therefore, most studies simply report ΔT_E[25] and estimate ΔS_E through the foregoing relation.[5] This is very useful for rapid selection of electrocaloric materials. In addition, refrigerant capacity defined as $R \approx |\Delta T_E \Delta S_E|$ is used to depict the heat which can be transferred between the cold and hot sinks in one ideal refrigeration cycle. For practical cooling applications this quantity is also a key caloric parameter to evaluate the refrigeration efficiency. Further studies should be carried out measuring independently both adiabatic temperature change and isothermal entropy change in order to inspire confidence for the design of suitable electrocaloric devices.

In order to obtain an electrocaloric effect, one has to apply an electric field, i.e., a voltage with respect to thickness of the ferroelectric capacitor. To be able to apply strong electric field by avoiding to reach the breakdown value requires to make the ferroelectric capacitor as thin as possible. However, by doing so, the amount of matter from which the heat is released becomes smaller and smaller. The compromise is therefore to fabricate multilayer capacitors.[2,10,29–33] Each active
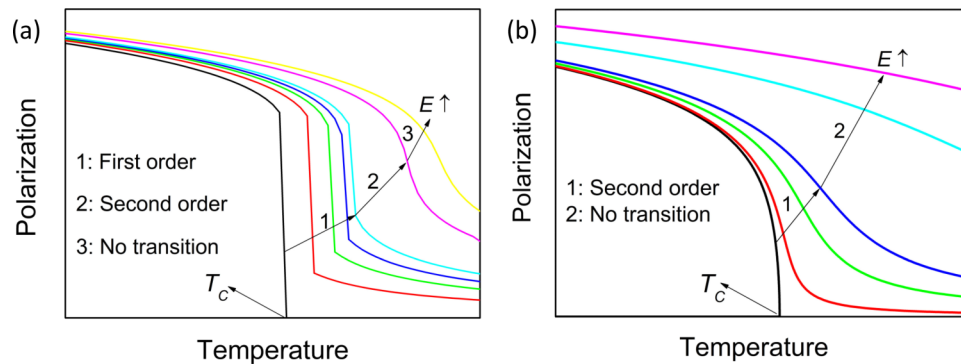
FIG. 1. Schematic of polarization versus temperature curves under various magnitudes of external electric fields: (a) first-order phase transition where polarization changes discontinuously at the phase transition temperature T_c and (b) second-order phase transition where polarization changes continuously with temperature increasing until T_c.

capacitor acts as a basic electrocaloric element with a typical thickness of several micrometers. It is of importance to gain further information once the ferroelectric thickness scales down to the nanoscale. This provides an up-bound limit for the electrocaloric performances, which is useful for optimizing the multilayers going towards on-chip nanorefrigerators allowing heat management in electronic devices. Interest in thin films is obvious,[34] as strong electric field can be achieved avoiding the primary limit of the electric breakdown strength. Moreover, ultrahigh electric fields are usually used in ultrathin ferroelectric films. One may ask whether a large or even giant electrocaloric response can be obtained in ultrathin films under such large external field values unachievable in ferroelectric bulk or relatively thicker films.

As the magnitude of external field increases, the first-order phase transition is smeared out until the critical point is reached where the nature of the transition becomes second-order type (see Fig. 1). With a further increase in field up a critical or threshold value, no phase transition exists above that temperature. While first-principles calculations predicted that the electrocaloric effect could continuously increase with electric field until this critical point,[35] experimental results in BaTiO$_3$ single crystals showed rather a continuous decrease in electrocaloric response, attributed to smooth evolution of the polarization when being close to this critical point.[36] In addition, largest electrocaloric strength, i.e., $\Delta T_E/\Delta E$ is expected near the field value where the first-order type transforms into second-order one.[37] Regarding the second-order transition, it should also disappear as long as the field is high enough. In this case, a continuous decrease in $\Delta T_E/\Delta E$ with the electric field is expected.

Once the mechanical boundary conditions (instead of the electrical ones) are also affected, the first-order nature of the transition can transform into the second order. In case of thin film where the phase transition becomes second-order because of substrate clamping, Landau-type calculations[12] show that the electrocaloric effect above the critical thickness where ferroelectricity disappears is much stronger than that below it and the largest near the critical thickness. Indeed, a giant electrocaloric effect (3.5 K under only 0.24 V) can be achieved in SrRuO$_3$/BaTiO$_3$/SrRuO$_3$ capacitors (BaTiO$_3$ thickness $h = 2.4$ nm) at 300 K (see Fig. 2). Accordingly, the entropy change is about 8 J/kg K.

Usually, electrocaloric properties do not show any direction dependence. However, the existence of built-in field arising from the difference in nature of the top and bottom electrodes in ferroelectric capacitors can lead to asymmetric ferroelectric properties which strongly depend on polarization direction.[13] As shown in Fig. 2, the electrocaloric temperature changes under adiabatic application of an electric field for the two opposite polarization (i.e., ON and OFF states) orientations can be different,[14] just like the tunnel electroresistance effect in ferroelectric tunnel junctions.[38] This difference under 3 V can reach over 1 K.[14]

Note that although the ultrahigh electric field (>1.5 GV/m) is expected to enlarge the electrocaloric effect, previous works[12,14] quantitatively demonstrate that its contribution to the enhancement of ΔT_E is not so significant. Indeed, ΔT_E in Pt/BaTiO$_3$/SrRuO$_3$ junctions is at least twice
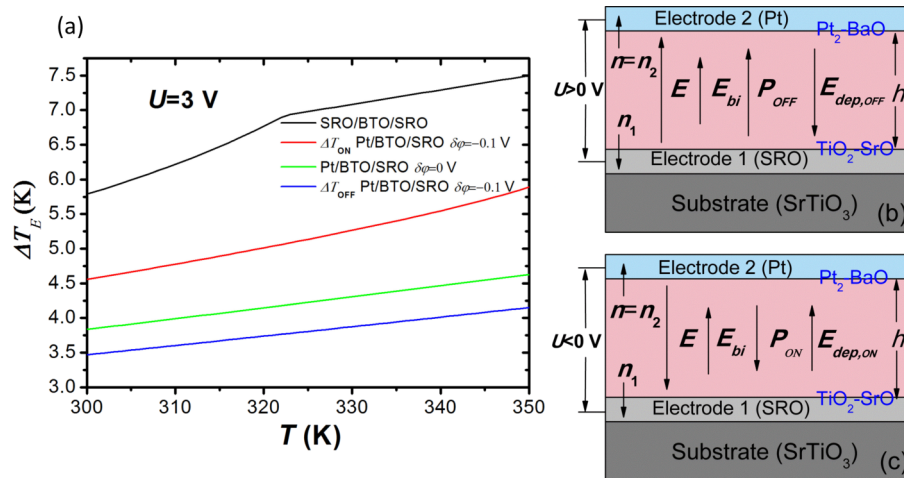
FIG. 2. (a) The temperature-dependent adiabatic electrocaloric temperature change in (001)-oriented Pt/BaTiO$_3$/SrRuO$_3$ and SrRuO$_3$/BaTiO$_3$/SrRuO$_3$ ferroelectric tunnel junctions ($h = 2.4$ nm, voltage $U = 3$ V) with/without considering the effect of the built-in fifield ($\delta\varphi$ is defined as the difference in the work function steps at two ferroelectric/electrode interfaces); Sketch of (b) OFF and (c) ON states in (001)-oriented Pt/BaTiO$_3$/SrRuO$_3$ ferroelectric tunnel junctions under adiabatic application of an electric field along the polarization direction, E_{bi} and E_{dep} are the built-in field and depolarizing field, respectively; Theoretical results reproduced with permission from Liu *et al.*, Appl. Phys. Lett. **104**, 082901 (2014). Copyright 2014 AIP Publishing LLC.

weaker than in PbZr$_{0.95}$Ti$_{0.05}$O$_3$ films[34] and PVDF-based polymer films.[39,40] Given that $\Delta T_E/\Delta E$ in ferroelectric thin films is usually smaller than in bulk. Here, $\Delta T_E/\Delta E$ decreases even further as the film thickness decreases to only a few nanometers (see Table I in Ref. 14). Note that the second-order nature of the phase transition in Pt/BaTiO$_3$/SrRuO$_3$ junctions may also reduce $\Delta T_E/\Delta E$.

Using ultrahigh external stimulus, a giant electrocaloric effect (1.53 K/V) with ΔT_E being over 4.5 K can be achieved at 300 K. Compared with superconductor tunnel junctions which can be employed as low-temperature electronic on-chip coolers with a sub-kelvin temperature change,[41] asymmetric ferroelectric tunnel junctions with ΔT_E of several Kelvin (>4.5 K) and low operational voltage (<5 V) appear as very serious alternative candidates for room temperature on-chip nanorefrigerators.

Imposed by upper bounds in bulk polar solids,[42] the intrinsic electrocaloric properties are expected to be significantly improved near the critical point[15] where in somehow the shape of potential energy is changed by introducing some anharmonicity. Similarly, a giant piezoelectricity was reported near a kind of quasi-critical point[43,44] composition where phases with different symmetries coexist allowing the polarization to easily rotate because of a rather flat energy landscape and thus small energy barriers to overcome (see Fig. 3). In the point (as denoted as QP, i.e., quadruple point in the inset of Fig. 3), the energy barriers vanish indicating that the polarization is ready to rotate and extend when subject to any, even weak, external field.[22] Therefore, it results in a significant change in the polar state and strong elecrocaloric responses with great entropy change are expected. For medium- or large-scale cooling facilities and household applications, engineering the materials by bringing such critical point near room temperature is therefore very desired.

For lead-free BaTiO$_3$-based ceramic materials, lots of efforts were made towards room-temperature applications. One typical electrocaloric which benefits from the existing invariant critical point (four phases coexistence) near room temperature is Ba(Zr$_{0.2}$Ti$_{0.8}$)O$_3$ bulk ceramic.[16] As a result, a giant electrocaloric effect of 4.5 K is achieved under large electrical stimulus of 140 kV/cm. Another example is BaTi$_{0.895}$Sn$_{0.105}$O$_3$ (see Fig. 3).[17] Such electrocaloric effect can be further enhanced in thick film form.[45] The phase transition temperature where the maximum electrocaloric response occurs can be tailored by varying the doping level[16,17] without destroying the multiphase coexistence[45] or through solid solutions.[46] Such approach is therefore efficient for tuning the working temperature and improving electrocaloric responses of materials.[47]
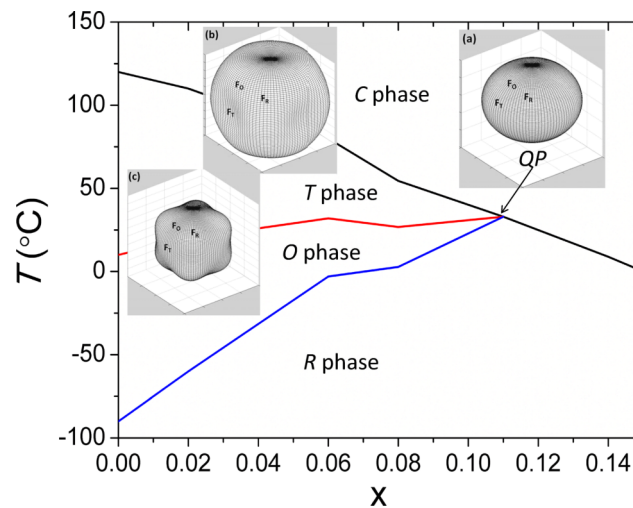
FIG. 3. Experimental results on temperature-composition phase diagram of BaTi$_{1-x}$Sn$_x$O$_3$. The insets show the schematic diagram of the free-energy profile for a ferroelectric system for different situations: (a) *Cubic-Tetragonal-Orthorhombic-Rhombohedral* quadruple point, (b) *cubic-tetragonal* phase boundary, and (c) *tetragonal-orthorhombic* phase boundary. Reproduced with permission from Luo *et al.*, Appl. Phys. Lett. **105**, 102904 (2014). Copyright 2014 AIP Publishing LLC.

A negative or inverse caloric effect refers to the case where materials cool when an electric field is applied, whereas they warm when the field is withdrawn.[5] This effect may enhance the cooling efficiency in combination with conventional (positive) caloric effect. In conventional electrocalorics, the electric field effect results in the ordering of electrical dipoles and therefore should always be accompanied by materials heating in adiabatic conditions.[2] This physical picture was changed since negative electrocaloric effect was found in relaxor ferroelectrics[48,49] and anti-ferroelectrics.[50–52] Moreover, the mechanism underlying the negative electrocaloric effect is still elusive, and recent findings in the literature appear controversial. A negative electrocaloric effect of −1 K was first revealed in antiferroelectric PbZrO$_3$ ceramics under 100 kV/cm at 37 °C via direct measurements.[52] Single crystals of relaxor PbMg$_{1/3}$Nb$_{2/3}$O$_3$-0.30PbTiO$_3$ were also found to display a negative electrocaloric effect;[48,49] however, ceramics of the same composition do not.[53]

More recently, a giant negative electrocaloric effect with a significantly enhanced ΔT_E of about −5 K was revealed in antiferroelectric La-doped Pb(Zr$_{0.95}$Ti$_{0.05}$)O$_3$ thin films near room temperature.[19] A simple mechanism is proposed to understand such negative effect in which the antiferroelectric ordered state is destabilized under electric field towards a less ordered one on the way going towards the ferroelectric ordered state.[19] Note that similar observations have been earlier reported in Pb(Zr$_{0.95}$Ti$_{0.05}$)O$_3$ films in Young's thesis.[54] This result is complementary to the pioneering 2006's work[34] in which the antiferroelectric-to-ferroelectric phase transition is deliberately avoided by applying a high electric field. Both conventional and negative electrocaloric effect contribute to the caloric response near room temperature and there exists a crossover temperature, at which $(\partial P/\partial T)_E = 0$ is satisfied, above which the nature of electrocaloric effect transforms from negative to positive type.[19] This finding is in qualitative agreement with the prediction based on the Kittel model[52] but requires further investigations to fully reveal the underlined mechanism. For instance, the strong competition between negative and positive effects, found in thin films[19,54] and not observed in PbZrO$_3$ ceramics,[52] when the field is close to the antiferroelectric-to-ferroelectric switching field has to be elucidated.

More theoretical insights using *ab initio* calculations could help to understand the origin of the negative effect in antiferroelectrics and relaxors in which antiferroelectric-like interactions are believed to be a needed ingredient.[55] For instance, the existence of a scaling law for ΔT_E was recently revealed in antiferroelectrics[56] using *ab initio* calculations. In addition, the magnitude of the negative effect is relatively smaller than its positive counterpart underlining the need to pursue more effort into the understanding of the negative electrocaloric effect. Nevertheless, antiferroelectrics appear as serious candidates in the field of solid-state coolers.

Multicaloric effects[5] driven by either single stimulus or multiple stimuli (applied/removed simultaneously or sequentially) can exploit multiple sources of entropy in multiferroic materials.[57] This definition not only has enlarged the initial Vopson's definition[58] but also has taken into account recent state-of-the-art findings especially during the past 3 years.[18,59] Due to couplings between different ferroic orders, the multicaloric effect may be larger than either single caloric effect. Multicaloric effect may also lead to search for hitherto unobserved caloric effect in ferroics[5] (e.g., elastocaloric effects in ferroelectrics[18,20,60]) or tuning and optimizing of one single caloric effect in multiferroic materials by using a non-conjugated field (e.g., electrocaloric effect with stress[21]).

Elastocaloric properties in bulk[20,60] and thin films[18,61] ferroelectrics were predicted to be remarkable and comparable with those of martensites,[62,63] expanding the elastocaloric family. Interestingly, the mechanism of elastocaloric effect in thin films purely stems from the continuous changes of the strain, which differs from that in shape-memory alloys[3] and ferroelectric bulk.[20,60]

The giant elastocaloric effect predicted in ferroelectric materials including bulk and thin films may open an alternate direction to search suitable elastocaloric materials for desired device applications. Similar exploration of barocaloric effect in ferroelectrics is also ambitious through their strong pressure dependence, for instance, of their transition temperature.[64] Ferroelectric barocalorics[21,65] may widen the barocalorics family as barocaloric effect is more often related to a property of some magnetic materials. Interestingly, experimental demonstrations of elastocaloric effect in ferroelectrics,[66] relaxors[67] as well as giant effect in ferrielectric ammonium sulphate[68] have been reported very recently. Recent theoretical works in $BaTiO_3$ single crystals[65] have predicted enhanced barocaloric effect achievable near room temperature with an adiabatic temperature change of more than 3 K and a temperature span of about 50 K (see Fig. 4). Research in barocaloric effect is actually at its very early stage and more efforts need to be made.

When a ferroelectric is subject to simultaneous application of electric field and mechanical stress, a multicaloric effect with magnitude larger than either caloric effect is induced, accompanied by a broader working temperature window.[59] In addition, combining both electrocaloric and elastocaloric effects in a proper sequence can be designed in refrigeration cycle[18] to enhance the temperature change. In that case, the basic principle is to use compressive stress to make the polarization disappear (ferroelectric-to-paraelectric phase transition) while using the electric field to recover the polarization by re-triggering the transition from paraelectric to ferroelectric phase.[18] In this regard, even a modest electric field can induce a giant electrocaloric effect (see details in Ref. 18).

We note that ferroelectric switching retains good potential for electrocaloric and elastocaloric devices. However, ferroelastic switching is quite subtle and qualitatively different from that in
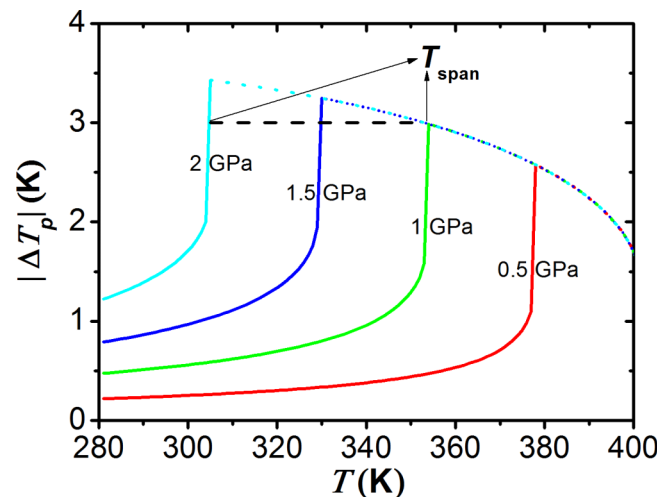

FIG. 4. Dependence of barocaloric effect on the initial temperature T of $BaTiO_3$ single crystals, where the temperature range T_{span} is also plotted; theoretical predictions reproduced with permission from Liu *et al.*, Appl. Phys. Lett. **104**, 162904 (2014). Copyright 2014 AIP Publishing LLC.

pure ferroelectrics (such as KTiOPO$_4$). To be ferroelastic,[69] the crystal class must change at the transition (treating hexagonal and rhombohedral as a "superclass" and Laue type I and Laue type II tetragonals as different). The important thing is that the high- and low-temperature phases must have different non-zero piezoelectric tensor elements, e.g., C_{16} in the case of Laue types I and II. In addition, ferroelastic switching from $+\sigma_3$ to $-\sigma_3$ (where σ_3 is stress) is glassy, with extremely complex transient domain structures. This causes violation of the Kittel relationship between thickness, domain width, and curved walls. Such "domain glasses" can possess large entropies and hence should be explored further.

Finally, electrocaloric effect can be tuned by mechanical stress or pressure. A remarkable enhancement and broadening of the electrocaloric response can be achieved in BaTiO$_3$ thin films under compressively loaded conditions compared with the unloaded case.[21] In addition, the electrocaloric peak moves towards higher temperatures with its magnitude slightly enhanced under tensile stresses.[20] While under pressure, it shifts towards room temperature[22] with only a slight reduction of the magnitude in contrast to relaxor ferroelectrics[70] and LiNbO$_3$.[35]

Ferroelectrics as ferrocalorics is an emerging field. Based on current research stage in the field of electrocaloric effect, it is difficult to make a conclusion on which material is the better especially between inorganic ceramics and organic polymers.[71] In this regard, the compromise through composite materials by combining these two compounds together may be promising. For instance, a "colossal" electrocaloric effect was reported in nanocomposites from Penn State University.[72–74] More efforts are desired to optimize the electrocaloric properties of nanocomposites for the design of cooling devices. In addition to room-temperature applications, cryogenic devices deserve further considerations. It is known that first cryogenic electrocaloric concept was proposed in SrTiO$_3$ ceramics in 1956[75] while first measurement on cryogenic electrocaloric effect was carried out in SrTiO$_3$ and CdTiO$_3$ ceramics in 1961.[76] However, the magnitude of cryogenic electrocaloric effect is small for applications. Interesting, ferroelectric junction structure might be employed as low-temperature coolers as its transition temperature can be tuned in quite a wide range by film thickness.[12]

There is still a very basic problem in commercializing these devices: In very thin films one has large ΔT_E cooling but very small volume, so heat extracted is very small. Niche markets are not obvious. In this regard, multilayer capacitors can be considered to enhance the active electrocaloric volume without compromising the large electric breakdown field in each capacitor. Commercially available BaTiO$_3$-based multilayer capacitors were intensively studied with only a modest ΔT_E of about 0.5 K. While challenging because of economic factors and engineering difficulties, alternative materials are desired. Considering the cyclic refrigeration, in magnetocalorics one can use magnetic switches to turn on or off the connection to the sample in a fast, optimal way. The turning on and off for an electrocaloric device is not quite so trivial. In addition to the improvement in ΔT_E, the thermal conductivity in multilayer capacitors needs optimization especially for the electrocaloric active ceramic/polymer layers.

Ferroelastics are materials that exhibit hysteretic stress-strain relationships and most ferroelectrics are also ferroelastic.[77] The important criteria for a stress-driven caloric device are paradoxically both hysteresis and the lack of it: the material should lack thermal hysteresis (that is, its phase transition should be second-order) to minimize any latent heat. In that way the cooling cycle is optimized by running through the phase-transition temperature. However, ideally there should be strong stress–strain hysteresis to optimize the Carnot-like cooling cycle. One of the best pure ferroelastics for possible cooling devices near room temperature is probably LaP$_5$O$_{14}$,[76] because (1) miniscule stresses are required for its orthorhombic-monoclinic transition; (2) this material is cheap and non-toxic; and (3) no cracking will occur during cycles and the transition is of second order. Note that the transition of LaP$_5$O$_{14}$ is displacive and not order-disorder, which however entails a smaller entropy change.[78]

In addition to uniaxial stress for elastocaloric effects, it is worth mentioning that rotational stress might also be useful. Similarly, toroidocaloric effect in ferrotoroidic materials was reported recently by a Landau free energy framework.[79] From a practical point of view it is not trivial to apply a torque to a thin film but might be feasible for other geometries such as nanorods and nanotubes. One might consider applying torques to nanotubes to cool a uid inside it. Applied torques

are especially interesting for incommensurate ferroelectrics/ferroelastics, because most incommensurate ferroelectrics have screw axes.[80] There is also a special interest in tetragonal structures such as Scheelites (AMO_4, with A = Ba, Ca, Sr and M = Mo or W). These structures have Laue type-II tetragonal symmetry, which means that they have nonzero (unusual) d_{16} piezoelectricity.[81] Application of some stresses can retain the tetragonal symmetry (e.g., C_{4h} to C_4 point group) but eliminate d_{16}, causing large hysteresis. In addition, hoop stress plays an unexpected role in the free energy for small devices such as nanotubes, etc.,[82] which may be considered in further analysis of the elastocaloric effect in ferroelectrics.

And as postscripts—"things to worry about"—the recent emphasis on electrocaloric relaxor ferroelectrics is interesting, but readers must be reminded that relaxors are definitely not in equilibrium, and the Maxwell relations often used to model electrocalorics require equilibrium.[82,83]

The review here provides a timely summary of recent strategies used to improve caloric response in ferroelectrics. It clearly demonstrates promising perspectives for ferroelectrics in solid-state refrigeration. Indeed, ferroelectrics are natural multicaloric materials in which both mechano- and electro-caloric (conventional and negative) responses can be achieved and combined near room temperature. The search of optimized new polar/elastic materials and architectures with multicaloric effects[5,57,84] can open the routes to significantly enhanced caloric response and smartly designed devices.

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