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Multicaloric effect in ferroelectric $PbTiO_3$ from first principles

S. Lisenkov,[*] B. K. Mani, C.-M. Chang, J. Almand, and I. Ponomareva
Department of Physics, University of South Florida, Tampa, Florida 33620, USA

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The critical need in novel or alternative approaches to energy production, conversion, and harvesting, combined with the ongoing pursuit of device miniaturization, have revived interest in the long-known but "doomed" impractical caloric effects in solids. Contrary to the old belief that such effects, while common, are miniscule, a large variety of giant caloric effects has been recently discovered in some ferroic materials. These discoveries have opened the door to the use of these giant effects in an efficient and environmentally friendly solid-state refrigeration technology. Here we report first-principles simulations of multiple caloric effects in a typical ferroelastic ferroelectric $PbTiO_3$ which offer insight into a multicaloric nature of this material. We predict the existence of unusual *multicaloric* effect in such electrically driven ferroelastic (extrinsic multiferroic) which far exceeds either electrocaloric or elastocaloric effect alone. Moreover, given a relative abundance of extrinsic multiferroics among ferroics with multiple order parameters, such prediction may open an unusual route to solid-state refrigeration advancement.

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Recent discoveries of giant caloric effects in some ferroic materials[1–10] have opened the door to the use of solid-state materials as an alternative to gases for conventional and cryogenic refrigeration.[11] The wide class of ferroics includes such diverse materials as ferromagnets and magnetic materials, ferroelectrics, ferroelastics, and multiferroics. As a result, a variety of giant caloric effects has been reported recently with the most notable ones being the giant magnetocaloric,[1,2,9] electrocaloric,[3,4,6,10] barocaloric,[7,8] and elastocaloric[5] effects. In addition, the decrease in size of the high quality samples brings the opportunity to further enhance caloric effects through an application of larger fields. As the potential of ferroics to exhibit giant caloric effects emerges as a universal feature of this important class of materials, the fundamental question about the possibility to combine multiple caloric effects in one ferroic material becomes crucial.

Caloric effect are associated with a reversible change in the temperature under adiabatic application of external fields.[12–14] Alternatively, they can be described as an isothermal change in entropy achieved by the application of the fields. While many naturally occurring materials may exhibit caloric effects, for most of them the effect is extremely small, if measurable. As a result, it was long believed that the effect is miniscule by its very nature[15] and very little effort was directed towards its understanding, or a search of materials with large caloric effects. There has been a drastic change in the situation, however, in the recent years, thanks to the discoveries of giant magnetocaloric effect,[1,2,9] giant electectrocaloric effect,[3,4,6,10] followed by the reports of giant elastocaloric and barocaloric effects.[5,7,8,16] However, except for Refs. 10, 7, 8, and 16, the giant caloric effects were found in very "dissimilar" materials, that are unlikely to "pair" to produce a multiple, or *multi*-, caloric effect. An alternative strategy in the search for multicaloric materials could be to look for large caloric effects in those ferroics which intrinsically combine more than one ferroic property. Such materials are known as multiferroics. Many of them have been widely known for decades,[17] while some of them have been discovered only recently.[18,19] In this paper we predict the existence of an unusual giant multicaloric effect in a well-known (multi)ferroic.

Here we simulate from first-principles multiple caloric effects in a typical ferroelastic ferroelectric (multiferroic) $PbTiO_3$. $PbTiO_3$ is a classic ferroelectric that undergoes reversible structural phase transition at 750 K associated with the onset of spontaneous electric polarization. The spontaneous polarization couples strongly to the strain giving rise to a simultaneous onset of spontaneous strain. As a result, the ferroelastic transition in $PbTiO_3$ is driven by the ferroelectric one, and, therefore, of extrinsic nature. We simulate a bulk sample of $PbTiO_3$ which is subject to slowly varying electric and/or stress fields. Note that such simulations imply that the sample evolves through a succession of nearly equilibrium states. Calculations were done using the direct approach[10,16] which allows us to compute caloric change in temperature ΔT *directly* and without resorting to the use of Maxwell relations. This technique also mimics closely the experimental approach to the direct measurements of caloric effects.[20] To explore the multicaloric nature of $PbTiO_3$ we conducted three sets of simulations. In the first set an electric field E, ranging in magnitude from 0 up to 1000 kV/cm, was slowly applied and subsequently removed from the simulated sample under adiabatic conditions. The temperature was computed for each field. The resulting dependence of the temperature on the applied field quantifies the *electrocaloric* effect in this material. Identical temperature curves were obtained from computations associated with both application (increase) and removal (decrease) of electric field indicating that the process is fully reversible. Note that this check of reversibility is critical when the direct approach to caloric effect investigation is used. To cross-check our results we have also calculated a few temperature curves using the indirect approach which is based on the Maxwell relations.[3] Both approaches yielded very similar data.

The second set of simulations was carried out to investigate the *piezocaloric* effect in this material. Note that this effect is also termed the elastocaloric effect.[5] A normal tensile stress field σ, acting on the plane perpendicular to the [001] direction

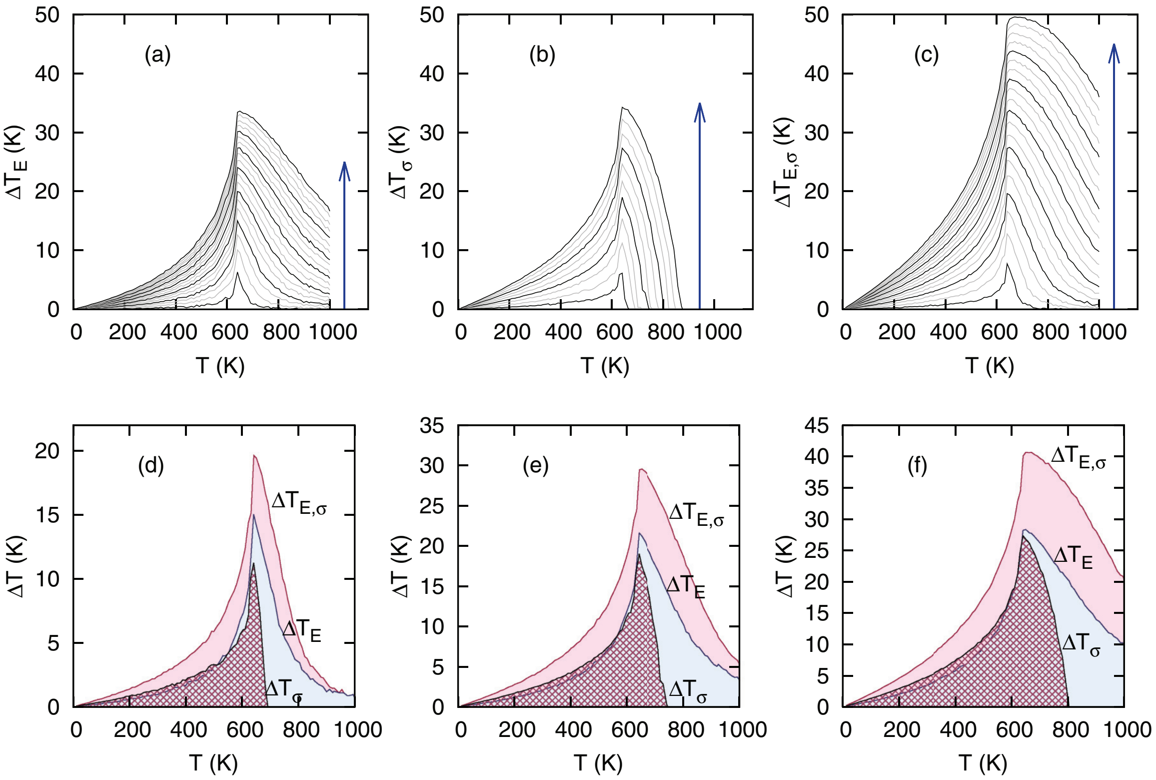

FIG. 1. (Color online) The temperature change as a function of the initial temperature obtained from the electrocaloric (a), piezocaloric (b), and multicaloric (c) effect simulations. Different curves correspond to different fields applied. The strength of the electric (stress) field increases in the direction of the arrow from 45 to 1000 kV/cm (0 to 2 GPa). Panels (d)–(f) give the comparison between ΔT associated with electrocaloric (ΔT_E), piezocaloric (ΔT_σ), and multicaloric ($\Delta T_{E,\sigma}$) effects. The data in (d) correspond to the fields $\Delta E = 195$ kV/cm and $\Delta\sigma = 0.4$ GPa, while panel (e) presents the data for $\Delta E = 395$ kV/cm and $\Delta\sigma = 0.8$ GPa. Panel (f) gives the data for the fields $\Delta E = 695$ kV/cm and $\Delta\sigma = 1.4$ GPa.

(polarization direction in ferroelectric phase) and ranging from 0 up to 2 GPa, was applied to and subsequently removed from the simulated sample using the direct approach as outlined in Ref. 16. The associated change in temperature ΔT_σ due to variation of the stress field quantifies the piezocaloric effect in $PbTiO_3$. In the third set of simulations both the electric and stress fields were applied to (and subsequently removed from) the simulated sample simultaneously. The resulting change in temperature due to the fields' variation was found to be completely reversible and attributed to the *multicaloric* effect. This multicaloric effect in $PbTiO_3$ derives its origin from the coexistence of electrocaloric and piezocaloric effects in this material.

The bulk sample of $PbTiO_3$ was simulated by a $16 \times 16 \times 16$ (20 480 atoms) supercell with periodic boundary conditions applied along all three directions. The total energy of this supercell is given by the effective Hamiltonian[21,22] with the parameters derived from first principles.[23] This Hamiltonian correctly predicts a variety of structural and thermodynamical properties of $PbTiO_3$ which include the polarization, Curie point, teragonality, and some others. The total energy given by the Hamiltonian was used in the framework of the isoenthalpic Monte Carlo simulations as proposed in Refs. 10 and 16 and which extends the classical Monte Carlo technique to the simulations of adiabatic conditions. Technically, the electric field was applied at an extremely slow rate of 0.1 kV/m per one Monte Carlo sweep to ensure reversibility. Similarly, the elastic field was applied at a slow rate of 1 kPa per Monte Carlo sweep. The temperature was averaged over 10 000 Monte Carlo sweeps. These settings were found to provide fully convergent results.

Figure 1(a) shows the electrocaloric temperature change ΔT_E as a function of the initial temperature T. Different curves represent simulation data for different electric fields, ΔE. This figure demonstrates that even for the smallest field shown (45 kV/cm) the electrocaloric change in temperature near the Curie point already reaches a large value of 6 K in agreement with experimental findings of Ref. 3. Further increase in ΔE leads to a significant increase in ΔT_E which, however, shows a tendency for saturation for the highest fields. We observe that for all fields investigated, ΔT_E peaks near the zero-field Curie point of $PbTiO_3$. Note that the first-principles Hamiltonian predicts the zero-field Curie point at 630 K. Our computational data for electrocaloric effect are in excellent agreement with a recent experimental study where a thermodynamical approach was used to estimate the electrocaloric effect in $PbTiO_3$.[24] For example, the largest ΔT_E reported in Ref. 24 for $E = 1.5$ kV/cm is 1.9 K which is in quantitative agreement with our computed value of 1.3 K obtained for the same field.

Figure 1(b) gives the piezocaloric temperature change as a function of the initial temperature for different stress fields,

$\Delta\sigma$, applied. It reveals that, in addition to giant electrocaloric effect, the material also exhibits a giant piezocaloric effect. Indeed, even for the smallest stress shown (0.2 GPa) ΔT_σ is about 6 K which is very similar to the electrocaloric ΔT_E for the lowest fields. Furthermore, for the range of electric and stress fields investigated the piezocaloric and electrocaloric ΔT exhibit rather comparable values in a very large temperature range. There exists, however, one unusual feature, which critically differentiates the piezocaloric effect in $PbTiO_3$ from the electrocaloric one. We find that for the temperatures of 890 K and above the piezocaloric effect in $PbTiO_3$ nearly vanishes. This is in contrast to the electrocaloric effect, which persists for all temperatures investigated.

These first-principles results could be explained by a simple thermodynamic argument. According to the Maxwell relation the piezocaloric change in temperature is given by $\Delta T_\sigma = -\int \frac{T}{C_\sigma}(\frac{\partial \varepsilon}{\partial T})_\sigma d\sigma$. Here ε is the strain, while C_σ is the heat capacity under constant stress. The equation suggests that an appreciable piezocaloric effect can be observed in materials for which the strain depends strongly on the temperature. This is typically the case in ferroelastics. However, $PbTiO_3$ is an extrinsic ferroelastic in which ferroelastic behavior only occurs in the ferroelectric phase. Consequently, the piezocaloric effect will be appreciable in the ferroelectric phase of the material as well.[25]

To confirm that, we traced the dependence of the temperature, polarization, and relative strain on the stress field applied. Figure 2 shows our data obtained for an initial temperature of 700 K. This figure clearly demonstrates that the large piezocaloric effect occurs in the ferroelectric phase associated with nonzero spontaneous polarization and strain. In the paraelectric phase the piezocaloric effect is extremely small. Above 890 K the simulated sample remains in the paraelectric phase for all stress fields considered, which explains why we do not observe an appreciable piezocaloric effect in this temperature range.

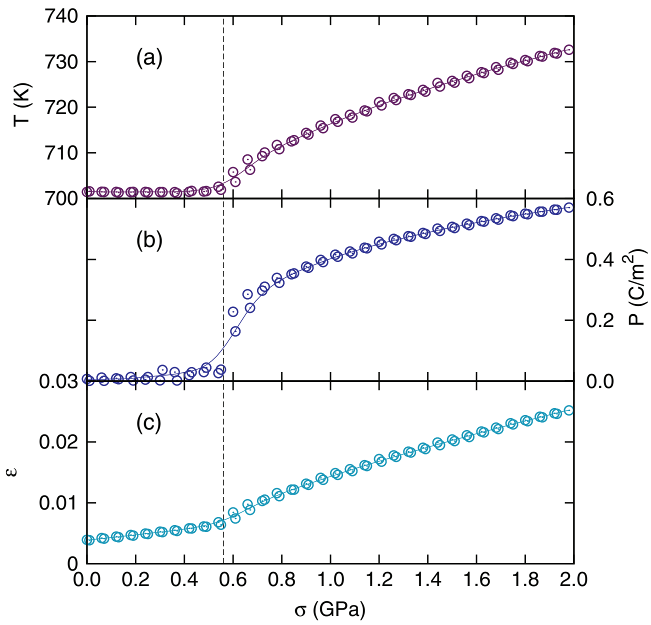

FIG. 2. (Color online) The dependence of the temperature (a), polarization (b), and relative strain (c) on the applied stress. The circles indicate data from simulations, while the solid lines are guides to the eye. Vertical dashed line indicates the point of stress-induced ferroelectric structural phase transition.

While we are not aware of any experimental studies of piezocaloric effect in $PbTiO_3$, our computational findings can be qualitatively compared to the experimental data on barocaloric effect in the same material. For example, a recent study[24] reports a barocaloric change in the temperature of −0.8 K under the application of 0.01 GPa pressure which compares well with our computed value of 0.4 K under stress with the same magnitude. Note that the difference in sign of ΔT_σ is due to the fact that we simulate tensile stress, while the hydrostatic pressure applied in Ref. 24 produces compressive stress.

Figure 1(c) shows the computational data for multicaloric temperature change $\Delta T_{E,\sigma}$ which were obtained in simulations with stress and electric fields applied simultaneously. This figure demonstrates the existence of giant multicaloric effect in this multiferroic material. Moreover, the numerical value of multicaloric $\Delta T_{E,\sigma}$ far exceeds the values associated with either piezocaloric or electrocaloric effects in the same material. To gain further insight we compare data obtained for the same fields in Figs. 1(d)–1(f). From this comparison it becomes obvious that the multicaloric $\Delta T_{E,\sigma}$ significantly exceeds both ΔT_E and ΔT_σ in the whole temperature range considered. The observed enhancement leads to a considerable broadening of the $\Delta T_{E,\sigma}$ as compared to either ΔT_E or ΔT_σ. Such broad response curves are extremely desirable for practical applications of caloric effects in solid-state refrigeration. In fact, the inability of many solid-state refrigerants to produce relatively broad response curves is among the most critical obstacles for the advancement of solid-state refrigeration technology. The multicaloric effect is very robust and can even lead to a significant enhancement of $\Delta T_{E,\sigma}$ in the region where the piezocaloric effect is negligible [for example, for the temperatures above 800 K in Fig. 1(f)]. To explain such an unusual finding we recall that the region where the piezocaloric effect dies off is associated with a nonpolar state of the material. Application of the electric field, however, polarizes the material and shifts the Curie temperature up. Once polarized, the material develops a relatively large strain, thanks to the strong piezoelectric coupling, which gives rise to an appreciable piezocaloric effect.

We believe that our findings could potentially open ways for practical advances in solid-state refrigeration. For example, we found that all three caloric effects (electrocaloric, piezocaloric, and multicaloric) are maximized near the Curie point. Given that for some ferroelectrics [$(Ba_{0.75}Sr_{0.25})TiO_3$ being one good example] the Curie point is near the room temperature, these findings become attractive for near room-temperature refrigeration. Moreover, our finding of strong enhancement of multicaloric effect in the paraelectric phase is potentially promising as many ferroelectrics have a Curie point below the room temperature. In addition, the predicted broadening of $\Delta T_{E,\sigma}(T)$ with respect to the electrocaloric and piezocaloric ΔT may even make high-T_C ferroelectrics, such as $PbTiO_3$, attractive for practical applications. The best promise of $PbTiO_3$ as potential solid-state refrigerant is, however, in the area of high-temperatures refrigeration.

In summary, our first-principles computations predict the existence of an unusual multicaloric effect in extrinsic ferroelastic ferroelectric $\mathrm{PbTiO_3}$. This effect was found to far exceed either piezocaloric or electrocaloric effect in the same material. Moreover, the strong coupling between the two ferroic order parameters, which is typical for many extrinsic (multi)ferroics, appears to play a critical role in the dramatic enhancement of the caloric effect when multiple fields are applied. We believe that our results unravel one more exotic feature of the multiferroics, as well as ferroics in general, and provide an unusual approach to caloric effects engineering. We hope that they will stimulate further work on the fundamental understanding of the ferroics and their exotic properties as well as future advances in the solid-state refrigeration.

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[*] slisenk@usf.edu

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