Electrocaloric effect in bulk and low-dimensional ferroelectrics from first principles

S. Prosandeev,[1,2] I. Ponomareva,[1] and L. Bellaiche[1]

[1]*Physics Department, University of Arkansas, Fayetteville, Arkansas 72701, USA*
[2]*Physics Department and Research Institute of Physics, Southern Federal University, 344090 Rostov on Don, Russia*

First-principles-based effective Hamiltonians are combined with nonequilibrium molecular dynamics to determine the electric-field-induced change in temperature in ferroelectrics. As a result, (i) the applied field can be ac in nature with a wide frequency range, (ii) bulks *and* nanostructures (with homogeneous or highly inhomogeneous dipolar configurations) can be investigated, and (iii) the influence of various phenomena on the electrocaloric effect can be revealed. This scheme yields an electrocaloric coefficient in excellent agreement with measurement and that strongly depends on the field-induced variation of volume in $Pb(Zr_{1-x}Ti_x)O_3$ bulks. An unusual phenomenon is also reported in dots under ac fields.

Ferroelectrics constitute an important class of materials that found its way in many applications—such as nonvolatile memories, communication devices, and microactuators[1]—exploiting the ability to switch or alter their polarization and/or change of shape when subject to an electric field. Another interesting property of ferroelectrics is the electrocaloric effect, that is, the change in temperature induced by a change in electric field.[2–7] As a result, ferroelectrics can be, e.g., put in use in fridges as cooling systems, in principle. However, the electrocaloric coefficient, to be denoted by α and that directly relates the change in temperature with the change in electric field, is typically too small in bulk ferroelectrics for a practical device to be efficient[2,3,5,7] (note, however, that one can get a relatively large change of temperature in *thin films* even if α is small because their relatively small thickness implies that the application of a reasonable voltage results in an electric field of relatively large amplitude in such films[6,7]). Moreover, many important issues related to the electrocaloric effect are currently unknown. For instance, one may wonder how does the temperature change when the applied electric field is ac in nature rather than dc. In particular, can it follow the frequency of this ac field and become a periodic time-dependent quantity (even in the gigahertz to terahertz regime)? Similarly, it is worthwhile to know if *low-dimensional* ferroelectrics, such as dots and that exhibit striking dipole patterns including highly inhomogeneous ones (see Ref. 8 and references therein), also change their temperature under an electric field; if they do, can the electrocaloric coefficient be tuned by varying some of their characteristics, such as their boundary conditions? One reason for this paucity of knowledge is that theoretical works on the electrocaloric effect are not only very scarce[7] but also use the "Nye's formula"[5]—that is, $\Delta T = -T \int_{E_i}^{E_f} \frac{p(E)}{c_E \rho} dE$, where ΔT is the change in temperature around T, c_E is the specific heat capacity at a fixed electric field, ρ is the mass density, $p(E)$ is the pyroelectric coefficient at constant E field, and E_i and E_f are the magnitudes of the initial and final electric fields, respectively.[5] As a matter of fact, such formula—which has been shown to be very accurate in some compounds under dc fields[7]—is technically valid for quasistatic (thermodynamics) conditions in polarized materials, while additional effects (e.g., nonequilibrium) effects may also arise for materials under ac fields and/or with highly inhomogeneous configurations.

Ideally, one would like a general and accurate scheme able to directly compute the field-induced change in temperature not only for a wide range of frequency but also for bulk and low-dimensional ferroelectrics under different boundary conditions, as well as for homogeneous and inhomogeneous dipolar configurations. The purpose of this Brief Report is to demonstrate that such scheme can be developed and to apply it to $Pb(Zr_{1-x}Ti_x)O_3$ bulks and dots. As we will see, it provides the answer to all the questions aforementioned.

Here, we first consider a *bulk* made of disordered $Pb(Zr_{0.4}Ti_{0.6})O_3$ (PZT) solid solutions (that is known to exhibit a tetragonal ground-state with a polarization lying along a $\langle 100 \rangle$ pseudocubic direction[9]), as mimicked by a $14 \times 14 \times 14$ supercell that is periodic along any direction under an applied electric field $\mathbf{E}$. Its total energy is given by the sum of the first-principles-based effective Hamiltonian energy provided in Ref. 9 and an additional term mimicking the effect of the field on the physical properties of the system—which consists of minus the dot product between the electric dipole moments and $\mathbf{E}$.[10]

We also investigate a cubic nanodot made of $Pb(Zr_{0.4}Ti_{0.6})O_3$ with a lateral size of 48 Å and having {001} Pb-O terminated surfaces. It is represented by a $12 \times 12 \times 12$ supercell that is finite in any direction with its total energy being

$$E_{\text{tot}} = E_{\text{mat}}(\{\mathbf{u}_i\}, \{\mathbf{w}_i\}, \hat{\eta}, \{\sigma_i\}) + \frac{\beta}{2} \sum_i \langle \mathbf{E}_{\text{dep}} \rangle \cdot Z^* \mathbf{u}_i$$

$$+ E_{\text{surf}}(\{\mathbf{u}_i\}, \{\mathbf{w}_i\}) - \sum_i \mathbf{E} \cdot Z^* \mathbf{u}_i, \quad (1)$$

where $\mathbf{u}_i$ is the local soft mode at the site i of the supercell (the product of $\mathbf{u}_i$ with the Born effective charge, Z^*, yields the electrical dipole moment at site i) and $\mathbf{w}_i$ is a dimensionless vector related to the inhomogeneous strain around this site, while $\hat{\eta}$ is the homogeneous strain tensor. $\{\sigma_i\}$ characterizes the alloy configuration[9] that is presently randomly chosen. The expression and first-principles-derived parameters of E_{mat}, the intrinsic alloy effective Hamiltonian energy,

are those given in Ref. 9 for PZT *bulk*, except for the dipole-dipole interactions for which we use the analytical expressions derived in Refs. 8 and 11 for our supercells under *ideal open-circuit* (OC) *conditions*. Such electrical boundary conditions naturally lead to the existence of a maximum depolarizing field (denoted by $\langle \mathbf{E}_{dep} \rangle$ and determined from the atomistic approach of Ref. 8) inside the system for a nonvanishing polarization. The second term of Eq. (1) mimics a screening of $\langle \mathbf{E}_{dep} \rangle$ via the β parameter. More precisely, $\beta = 0$ corresponds to ideal OC conditions, while an increase in β lowers the magnitude of the resulting depolarizing field, and $\beta = 1$ corresponds to ideal short-circuit (SC) conditions for which the depolarizing field has vanished. The third term of Eq. (1), E_{surf}, mimics how the existence of free surfaces affects the dipoles and strains near them.[12] Its analytical expression is indicated in Ref. 12 with its parameters having been determined from a first-principles computation on a PZT slab surrounded by vacuum. The last term of Eq. (1) represents the effect of the applied electric field on the properties of the investigated system.[10] Note that the effective Hamiltonian approaches have been shown to be rather accurate by, e.g., confirming the existence of a monoclinic phase in the phase diagram of bulk PZT and of novel dipole configurations—such as periodic nanostripe domains—in low-dimensional ferroelectrics (see Refs. 8, 9, and 13, and references therein).

The total energy of both the studied ferroelectric bulk and nanosystem is used in molecular dynamics (MD) with Newton's equations of motion being solved for all the degrees of freedom of the effective Hamiltonian approach.[14] The determination of the electrocaloric effect is accomplished via two steps. First, MD computations corresponding to an electric field applied along the x axis (chosen to lie along the [100] pseudocubic direction) and of constant value, to be denoted by C, are conducted for 40 000 steps with each step lasting 0.5 fs. An Evans-Hoover thermostat[15–17] is used in these simulations in order to equilibrate the system at a fixed temperature and under this constant external field. Then, the thermostat is turned *off* as soon as we apply an ac electric field $E(t) = [A - B \cos(2\pi\nu t)]$ along the x direction—where A and B are constant such as $A - B = C$ and ν and t are the frequency and time, respectively—during subsequent MD simulations. These latter simulations typically last 100 000 steps and technically correspond to *nonequilibrium* MD situations since the Hamiltonian explicitly depends on time through the fourth term of Eq. (1) that involves the ac electric field. The temperature $T(t)$ is obtained at any time t during these nonequilibrium MD simulations via the equipartition theorem, that is: $T(t) = \frac{1}{3Nk_B} \Sigma_i M(\mathbf{v}_i(t) - \langle \mathbf{v}_i(t) \rangle)^2$,[18] where N is the number of sites in the supercell, k_B is the Boltzmann constant, M is the mass associated with the local soft modes,[19] $\mathbf{v}_i(t)$ is the time derivative of the local mode $\mathbf{u}_i(t)$ at time t, and $\langle \, \rangle$ denotes the average over all the supercell sites.

Our proposed method thus allows the direct computation of the electrocaloric effect at an *ab initio* level in ferroelectric systems of *any* dimension (e.g., bulk, films, nanowires, nanodots, etc.) at *any* finite temperature (with the exception of low temperature for which quantum effects would have to be taken into account) with *any* dipole pattern (i.e., homogeneous versus inhomogeneous) and for a wide frequency
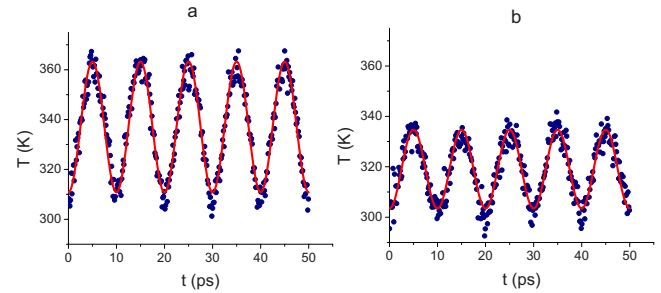

FIG. 1. (Color online) Predicted time dependency of the temperature in bulk PZT under an ac electric field $E(t) = [0.6 - 0.5 \cos(2\pi\nu t)] \times 10^9$ V/m with $\nu = 100$ GHz. Panels (a) and (b) display the unclamped and clamped cases, respectively. The filled dots show the raw data while the solid line represents $T(t) = T_0 + \alpha E(t)$, where α is the time-independent coefficient that allows for the best fit of the raw data.

range of applied electric fields (namely, 0.1 GHz–10 THz). Inhomogeneous electric field can also be easily incorporated in the proposed scheme. Moreover, one can "play" with some parameters or degrees of freedom of our approach to reveal their effect on the electrocaloric coefficient. For instance, it is possible to freeze or not the response of the volume to an electric field, that is, to perform *clamped versus unclamped* calculations, in order to quantify the role of the field-induced change in volume on the electrocaloric effect.

Let us first check the accuracy of our method by applying along the x axis an ac electric field given by $E(t) = [0.6 - 0.5 \cos(2\pi\nu t)] \times 10^9$ V/m with $\nu = 100$ GHz in a bulk PZT that is initially at an equilibrium temperature of $\simeq 300$ K (Ref. 20) under a constant field of 10^8 V/m. (Such field insures that the polarization's direction never switches during the whole MD simulations and, thus, prevents irreversible heating of the sample.[21]) Figures 1(a) and 1(b) display the temperature as a function of time for unclamped conditions (for which the volume is allowed to vary under the field, as it should be in reality) versus clamped conditions, respectively. Figure 1 reveals that the temperature follows the ac electric field for both the unclamped and clamped cases, that is, $\Delta T(t) = \alpha \Delta E(t)$, where $\Delta T(t)$ and $\Delta E(t)$ are the change in temperature (with respect to the initial temperature) and the change in the electric field (with respect to the initial electric field of 0.1×10^9 V/m) at time t, respectively, and where α is *independent of time*. α is numerically found to be equal to 0.52×10^{-7} and 0.31×10^{-7} K m/V for the unclampled and clamped cases, respectively. Our numerical value of $\simeq 0.52 \times 10^{-7}$ K m/V agrees rather well with the experimental data of $0.6 \pm 0.05 \times 10^{-7}$ K m/V given in Ref. 4 for (unclamped) PZT bulks near room temperature, which reveals the high accuracy of our proposed scheme. [Note that we numerically checked that our simulated electrocaloric coefficient of 0.52×10^{-7} K m/V is nearly unchanged when varying by several order of magnitudes the frequency (but still below the resonant frequency) and amplitudes of the applied electric field near room temperature. For frequencies near the resonant frequency, which is numerically found[22] to be around 8 THz in bulk PZT at room temperature under zero field, the temperature does not follow the ac field anymore, leading to an
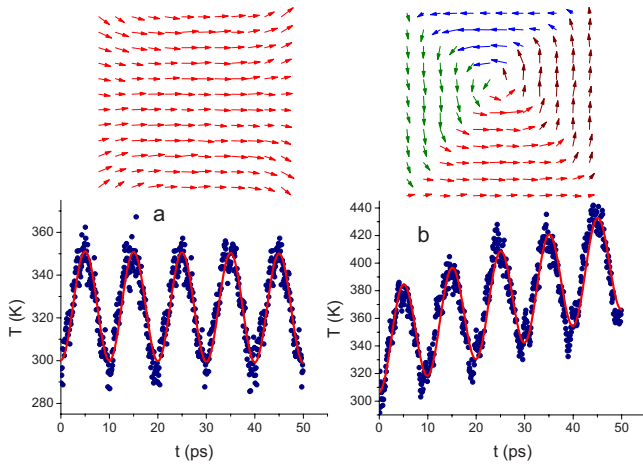
FIG. 2. (Color online) Predicted time dependency of the temperature in a cubic dot of 4.8 nm lateral size and made of PZT under an ac electric field $E(t)=[0.6-0.5\cos(2\pi\nu t)]\times10^9$ V/m with ν =100 GHz for [panel (a)] $\beta=0.95$ and [panel (b)] $\beta=0.80$. The filled dots show the raw data while the solid line represents $T(t)=T_0+\alpha E(t)$ in panel (a) versus $T(t)=T_0+\alpha E(t)+\gamma t$ in panel (b), where α and β are time-independent coefficients that allow for the best fit of the raw data. The insets display a cross section in the (x,y) plane of the initial dipole configuration.

irreversible heating for these frequencies as a result of high values of the imaginary part of the dielectric permittivity.[21]] Similarly, our numerically found $\simeq1.7$-fold increase in the electrocaloric coefficient when allowing the volume to respond to an electric field is quantitatively similar to the $\simeq1.5$-fold increase for this coefficient predicted by the phenomenological work in Ref. 7 when going from epitaxial to stress-free BaTiO$_3$ films. Note also that the periodic time dependency of the temperature displayed in Fig. 1 may be of tremendous technological potential if one designs a device based on the *accumulation* of the absolute change in temperature over a long period of time [Fig. 1(a) implies that for the unclamped case, the accumulated absolute change in temperature over 1 s equals 52×10^{11} K for our chosen field].

We now turn our attention to PZT dots subject to an ac electric field applied along the x axis and given by $E(t)=[0.6-0.5\cos(2\pi\nu t)]\times10^9$ V/m with $\nu=100$ GHz. These dots are *initially* at an equilibrium temperature close to room temperature[20] and experience a dc field of 0.1×10^9 V/m. It is important to realize that the initial dipole configuration depends on the screening of the polarization-induced surface charges. More precisely, two types of equilibrium dipole pattern exist depending on the chosen value of the β parameter of Eq. (1): an homogeneous and polarized state,[8] displayed in the inset of Fig. 2(a), occurs when $\beta>0.9$, while an highly inhomogeneous state exhibiting a coexistence between a dipole vortex and a polarized part, as shown in the inset of Fig. 2(b), happens for $\beta<0.9$. Figures 2(a) and 2(b) show the time dependency of the temperature in these dots for β =0.95 and β=0.80, respectively, both for the unclamped case. For the dot under short-circuit-like conditions (that is, $\beta=0.95$), the change in temperature is once again provided

by $\Delta T(t)=\alpha\Delta E(t)$. Here, α is equal to 0.51×10^{-7} Km/V. An electrocaloric effect, which is both qualitatively and quantitatively similar to the one in the bulk, thus also exists in this dot. Interestingly, performing additional computations for various β ranging between 0.90 and the ideal-SC value of 1.0 leads to the discovery that α linearly behaves with the screening parameter in dots exhibiting the dipole configuration shown in Fig. 2(a). More precisely, $\alpha\simeq1.89-1.43\beta$, which implies that one can tune the electrocaloric coefficient from 0.46 (for $\beta=1.0$) to 0.60 (for $\beta=0.9$)—that is, an $\simeq30\%$ increase—by adjusting the electrical boundary conditions of the dots. Such tuning arises from the fact that decreasing β leads to a decrease in the Curie temperature in the dot. Moreover, the partly screened dot for which $\beta=0.8$ adopts a different behavior in the sense that its field-induced change in temperature is given by $\Delta T(t)=\alpha\Delta E(t)+\gamma t$. One thus need to add a variation linear with time to the usual electrocaloric effect of $\alpha\Delta E(t)$ to be able to represent the response of the temperature to an ac field when the initial dipole configuration is the one displayed in the inset of Fig. 2(b) (that is, for $\beta<0.9$). Such linear addition describes a continuous sample heating and is caused by the field-induced expansion/compression of the vortex part [see the top of the inset in Fig. 2(b)] with respect to the polarized part [see the bottom of the inset of Fig. 2(b)] in this configuration. As a matter of fact, such expansion/compression is accompanied by flipping of dipoles, which is known to induce heat.[21,23] Interestingly, for $\beta=0.8$, γ is numerically found to be around 1.2 K/ps—leading to an average increase in the temperature by 60 K every 50 ps—while $\alpha=0.72\times10^{-7}$ K m/V. We also further found that this γ coefficient increases when further decreasing β, revealing the increase in the vortex contribution (with respect to the polarized contribution) to the electrocaloric effect.

In summary, first-principles-derived effective Hamiltonians and nonequilibrium molecular dynamics have been combined to directly compute electrocaloric effects in ferroelectrics bulks and nanostructures under ac electric fields. Such scheme predicts that the temperature directly follows the ac electric field in PZT *bulk* near room temperature when the field frequency is far away from resonance with an electrocaloric coefficient that is in very good agreement with experimental data. Such periodic evolution of the temperature may lead to the design of original devices exploiting the (giant) absolute change in temperature over a time window that is much larger than the time period of the field. Moreover, freezing the field-induced change in volume leads to a significant decrease in the electrocaloric coefficient. Furthermore, PZT *dots* with large enough screening of the depolarizing field and under similar ac electric fields behave in the same fashion as in the bulk at the quantitative but important exception that the electrocaloric coefficient can be tuned by adjusting the magnitude of the residual depolarizing field. (Interestingly, one can also think of combining time-dependent mechanical/electrical boundary conditions with an ac field to produce an *asymmetric* time dependency of the temperature during each field period—that is, to, e.g., induce a temperature that decreases in average during each field cycle.) One may thus design original applications at the nanoscale such as self-cooling of nanoscale electric circuits.

Finally, PZT dots with smaller screening quality exhibit a different behavior for which the change in temperature at time t consists of the superposition of two terms: one term that is directly proportional to the applied ac field at that time t and another term that is linear in t. We are confident that our proposed scheme can be of further large benefits by, e.g., leading to a deep microscopic understanding of electrocaloric effects in various systems as well as to the design of optimized or original devices based on its predictions.

[1] O. Auciello, J. F. Scott, and R. Ramesh, Phys. Today **51** (7), 22 (1998).

[2] G. G. Wiseman and J. K. Kuebler, Phys. Rev. **131**, 2023 (1963).

[3] B. A. Strukov, Sov. Phys. Crystallogr. **11**, 757 (1967).

[4] P. D. Thacher, J. Appl. Phys. **39**, 1996 (1968).

[5] J. F. Nye, *Physical Properties of Crystals* (Oxford University Press, New York, 1957).

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

[7] G. Akcay, S. P. Alpay, J. V. Mantese, and G. A. Rossetti, Jr., Appl. Phys. Lett. **90**, 252909 (2007).

[8] I. Ponomareva, I. I. Naumov, I. Kornev, Huaxiang Fu, and L. Bellaiche, Phys. Rev. B **72**, 140102(R) (2005); I. Ponomareva, I. I. Naumov, and L. Bellaiche, *ibid.* **72**, 214118 (2005).

[9] L. Bellaiche, A. Garcia, and D. Vanderbilt, Phys. Rev. Lett. **84**, 5427 (2000); Ferroelectrics **266**, 41 (2002).

[10] A. García and D. Vanderbilt, in *First-Principles Calculations for Ferroelectrics: Fifth Williamsburg Workshop*, edited by R. E. Cohen (AIP, Woodbury, NY, 1998), p. 54.

[11] I. I. Naumov and H. Fu, arXiv:cond-mat/0505497 (unpublished).

[12] E. Almahmoud, Y. Navtsenya, I. Kornev, H. Fu, and L. Bellaiche, Phys. Rev. B **70**, 220102(R) (2004).

[13] I. Kornev, H. Fu, and L. Bellaiche, Phys. Rev. Lett. **93**, 196104 (2004).

[14] MD computations were performed for bulk PZT under zero external electric field to check the accuracy of the MD scheme. Such simulations exactly reproduce the transition temperatures of bulk PZT obtained in the Monte Carlo simulations (Ref. 9)

and provide a good agreement with experiments for the soft-mode frequency of bulk PZT (Ref. 24).

[15] D. Rapaport, *The Art of Molecular Dynamics Simulation* (Cambridge University Press, Cambridge, England, 2001).

[16] W. G. Hoover, A. J. C. Ladd, and B. Moran, Phys. Rev. Lett. **48**, 1818 (1982).

[17] D. J. Evans, J. Chem. Phys. **78**, 3297 (1983).

[18] M. A. Osman and D. Srivastava, Phys. Rev. B **72**, 125413 (2005).

[19] J. Íñiguez and D. Vanderbilt, Phys. Rev. Lett. **89**, 115503 (2002).

[20] All the theoretical temperatures given in this study have been decreased by a factor of 1.6125 from the temperatures given by our MD schemes in order that the theoretical Curie temperature of $Pb(Zr_{0.5}Ti_{0.5})O_3$ bulk matches its experimental value of 640 K (Ref. 25).

[21] R. J. Meredith, *Engineers' Handbook of Industrial Microwave Heating*, IEE Power Series 25 (The Institution of Electrical Engineers, London, UK, 1998), p. 19.

[22] I. Ponomareva, L. Bellaiche, T. Ostapchuk, J. Hlinka, and J. Petzelt, Phys. Rev. B **77**, 012102 (2008).

[23] Such assertion is also supported by subsequent calculations in the PZT *bulk* under ac fields that allow the polarization to *switch in direction*: in such cases, the temperature also increases in average after each field cycle.

[24] I. Fedorov, J. Petzelt, V. Zelezny, G. A. Komandin, A. A. Volkov, K. Brooks, Y. Huang, and N. Setter, J. Phys.: Condens. Matter **7**, 4313 (1995).

[25] Y. Yamamoto, Jpn. J. Appl. Phys., Part 1 **35**, 5104 (1996).