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The influence of mechanical and electrical boundary conditions on electrocaloric response in $(Ba_{0.50}Sr_{0.50})TiO_3$ thin films

S. Bin-Omran

Department of Physics and Astronomy, College of Science, King Saud University, P.O. Box 2455, Riyadh 11451, Saudi Arabia

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ABSTRACT

The Wang-Landau Monte Carlo algorithm, implemented within an effective Hamiltonian approach, is used to investigate the effect of mechanical and electrical boundary conditions on electrocaloric (EC) properties in $(Ba_{0.50}Sr_{0.50})TiO_3$ thin films. The results indicate that the EC response maximizes near the paraelectric-to-ferroelectric (respectively, ferroelectric-to-ferroelectric) phase transition is suppressed (respectively, enhanced) by activating the depolarizing field inside the films. On the other hand, the EC response shows strong dependence on both the compressive and tensile strains. Interestingly, $(Ba_{0.50}Sr_{0.50})TiO_3$ thin films are expected to show a giant EC effect near room temperature when the applied tensile strain is properly controlled. Our predictions also reveal that all observed phase transitions in the BST films are of second order and lead to an enhancement of refrigerant efficiency.

1. Introduction

Ferroelectric materials are currently attracting considerable interest because of their numerous potential applications in miniaturized devices, such as nonvolatile and dynamic random-access memories, sensors, wireless communications, actuators, and electrocaloric (EC) devices [1]. Particular attention has been devoted to improving the EC effect, defined as a reversible change in temperature and entropy obtained by applying an external electric field under adiabatic or isothermal conditions. In low-dimensional systems, researchers have observed low EC strength, represented by the change in temperature (ΔT) with respect to the change in the applied electric field (ΔE), compared with those of the corresponding bulk [2–5]. As a matter of fact, the characteristics of ferroelectric thin films—the film's thickness, the strain imposed by the substrate and the depolarizing field arising from incomplete compensation of the polarization-induced charges at the surfaces/interfaces—substantially affect their properties.

Several theoretical predications [5–15] and experimental measurements [3,16–25] have been used to investigate and determine the EC effects in various ferroelectric materials. When a high electric field, which is unachievable in ferroelectric bulk or relatively thick films, was applied, giant electrocaloric effect described as temperature change (ΔT) was observed in PZT films [15] and organic P(VDF-TrFE) thin films [16]. Mechanical boundary conditions controlled by varying epitaxial misfit strain, which has a well-known influence on the symmetry of the crystallographic phases, the spontaneous polarization in nominally paraelectric materials, and transition temperature, can also dramatically affect the EC response in ferroelectric materials [2,4,6,8,12–14,26]. Recently, an atomistic first-principles-based computational approach used to reveal that the residual depolarizing field enhances the EC response in $PbTiO_3$ film [11]. The nature of the phase transition and its diffuseness character, described as a broadening of the dielectric-dispersion curve in a rather wide temperature interval around the phase-transition temperature, making it technologically promising for solid-state coolers to efficiently operate over a large temperature range, are key properties for maximizing the EC response. It has also been shown that the EC response peaks near the phase transition and is enhanced when the transition is of first-order association with a finite latent heat [2,5].

For practical cooling devices, it is of desirable to select a type of material that is environmentally friendly and operates at room temperature. Barium strontium titanate $(Ba,Sr)TiO_3$ (BST) ferroelectric material is a solid solution of lead-free $BaTiO_3$ and $SrTiO_3$ parent compounds. As a matter of fact, the transition temperature for $Ba_{0.50}Sr_{0.50}TiO_3$ bulk is very close to room temperature, which leads to high dielectric permittivity and tenability. Interestingly, a giant electrocaloric effect was reported in ferroelectric BST alloys [12,27–30].

In this article, the first-principles-derived scheme combined with the Wang-Landau algorithm is performed to investigate the

E-mail address: somran@ksu.edu.sa (S. Bin-Omran).

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precise effects of electrical and mechanical boundary conditions on the EC effect of $(Ba_{0.50},Sr_{0.50})TiO_3$ thin films. The article is organized as follows. Section II describes the numerical method we used. Section III presents our computation results and discusses them in detail. Finally, Section IV summarizes our findings.

2. Methodology

The first-principles-derived effective Hamiltonian [31,32] is considered as an efficient tool to predict the properties of large (~20,000 atoms) supercells of ferroelectric systems at finite-temperature and has been successfully used to predict and determine several properties for disordered and ordered $(Ba_{1-x}, Sr_x)TiO_3$ systems. The general framework for the construction of the effective Hamiltonian approach is to (i) define a reduced number of degrees of freedom per unit cell and (ii) construct a model Hamiltonian, written as a function of these reduced degrees of freedom, which reproduces the spectrum of low-energy excitations (ferroelectric soft-modes and strains) for the given material as determined from first-principles calculations. This transverse optical phonon mode (soft-mode) and the long-wavelength acoustic modes (strain variables) are relevant degrees of freedom for the phase transition since the ferroelectric phase transitions are accompanied by a softening of the phonon soft-mode and by the appearance of a strain. In fact, the total energy of this effective Hamiltonian depends on two different degrees of freedom: (i) the local soft mode (u_i) in each 5-atom unit cell (i) (which is directly proportional to the electrical polarization) and (ii) the homogeneous (η_H) and inhomogeneous (η_I) strains, where it describes the local deformation of the unit cells [31].

In this work, we investigate the EC properties of defect-free thin films made of disordered $(Ba_{0.50},Sr_{0.50})TiO_3$ grown along the [001] pseudo-cubic direction (chosen to be along the z-axis) and A-O terminated at all surfaces/interfaces (where A denotes either Ba or Sr). These films are mimicked by $12 \times 12 \times 12$ supercells that are periodic along the x- and y-axes but finite along the z-axis. The x-, y- and z-axes lie along the [100], [010], and [001] pseudo-cubic directions, respectively. Typically, supercells of 48 Å thickness (12 unit cells) along the z-periodic direction are used in such studies. The total energy of such a supercell can be written as

$$E_{tot}(\{u_i\},\eta_H,\{v_i\},\{\sigma_j\},\{\eta_{loc}\}) = E_{Heff}(\{u_i\},\eta_H,\{v_i\},\{\sigma_j\},\{\eta_{loc}\}) + \frac{1}{2}\cdot\beta\cdot\sum_i < E_{dep} > \cdot Z^* \cdot u_i, \quad (1)$$

where u_i represents the local soft modes at the site I of the supercell (Z^*u_i gives the local electrical dipole, where Z^* is the Born effective charge); η_H and v_i are parameters that describe the homogeneous strain tensor and inhomogeneous strain-related variables [31]; $\{\sigma_j\}$ indicates the species of atoms, that is, $\sigma_j = +1$ (respectively, -1) if there is a Ba (respectively, Sr) atom at the A-lattice site j of the $(Ba_xSr_{1-x})TiO_3$ system; and $\{\eta_{loc}\}$ is the strain generated from the difference between the sizes of Ba and Sr ions [32].

E_{Heff} denotes the intrinsic-alloy effective Hamiltonian energy. Its first-principles-derived parameters and analytical expression are given in Ref. [32] for bulk BST, with the exception of the dipole–dipole interactions, the formula for which was derived in Refs. [33,34] for thin films under ideal open-circuit (OC) electrical boundary conditions, under which the depolarizing field attains its maximum value.

Practically, such electrical boundary conditions can be simulated by changing the value of the screening coefficient β. More precisely, $\beta = 0$ and $\beta = 1$ stand for the ideal open-circuit (OC) conditions and short-circuit (SC) conditions, respectively, under which polarization-bound charges are induced at the film surfaces and the depolarizing field is generated, which is screened by non-polar systems sandwiching such films (to simulate, e.g., air, vacuum, electrodes and/or non-ferroelectric substrate). To obtain a more realistic electrical-boundary situation, the value of β can be varied between 0 and 1 (or, equivalently, the magnitude of the residual depolarizing field inside the film can be controlled).

On the other hand, mechanical boundary conditions can also be simulated [35,36] owing to the homogeneous strain $\{\eta_H\}$. In the effective Hamiltonian, the form of the strain tensor η is relevant to two cases of interest: stress-free and epitaxially strained (001) films. In the stress-free case, all the components of the strain tensor are fully relaxed. On the other hand, mimicking an epitaxial strain leads to the freezing of three components of η, namely, $\eta_6 = 0$ and $\eta_1 = \eta_2 = \delta$ (in Voigt notation, with $\delta = (a_{sub} - a_{lat})/a_{lat}$), where a_{sub} symbolizes the in-plane lattice parameter of the substrate while $a_{lat} = 3.90$ Å is the 0 K cubic-lattice constant of stress-free $Ba_{0.50}Sr_{0.50}TiO_3$ bulk, as predicted by LDA calculations [32]. At the same time, the other homogeneous strain variables are relaxed during the simulation. (Note that a pressure $P = -4.8$ GPa was applied to $BaTiO_3$ to overcome the well-known LDA underestimation of the lattice constant [32].)

To better understand the behavior of the EC response in the investigated films and calculate thermodynamic quantities at any given temperature, the total energy of the effective Hamiltonian is technically applied within the so-called Wang-Landau algorithm [37]. This algorithm calculates the density of states Ω(E), which is defined as the number of all possible states (or configurations) for an energy E of the system of interest, by performing random walks in the energy space. This technique has proven to be efficient in predicting several static and dynamic properties of different ferroelectric materials [38–41].

3. Results and discussion

(a) Electrocaloric effect versus electrical boundary conditions

Fig. 1(a) shows the absolute value of the polarization (|P|) versus temperature (T) for a stress-free BST thin film with a thickness of 48 Å under different electrical boundary conditions (namely, the screening parameter β is chosen to be 1.00, 0.975, and 0.95). Practically, the electrical polarization can be determined as in [40]:

$$|P| = \frac{Z^* \sum_E |u|\Omega(E)e^{-\alpha E}}{a_{lat.}^2 \sum_E \Omega(E)e^{-\alpha E}}, \quad (2)$$

where $\alpha = \frac{1}{k_B T}$ and k_B is the Boltzmann constant.

The results reveal that at any given β, the polarization is always zero at high temperature, indicating the presence of a paraelectric phase (denoted by p). As the temperature is and passes through a critical temperature, the planarization jumps and then increases as the temperature decreases further. For $\beta = 1.00$ and 0.975, our calculations show that BST films undergo two phase transitions. The first transition is associated with an increase in P_z (while P_x and P_y remain nearly zero) at $T \approx 680$ K (respectively, 420 K) for $\beta = 1$ (respectively, 0.975), indicating that the system goes from a paraelectric phase to a ferroelectric tetragonal phase (denoted by c). Note that such high value of transition temperature is due to the enhancement of the surface/interface polar modes which arises from the truncation of short-range interactions that oppose the onset of local dipoles [31,33,34]. The second phase transition is characterized by increases in P_x and P_y (in addition to P_z) at $T \approx 110$ K (respectively, 170 K) for $\beta = 1$ (respectively, 0.975), indicating that the BST film