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Strain dependent polarization and dielectric properties of epitaxial BaTiO$_3$ from first-principles

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Using first-principles calculations, we investigated the strain dependences of the polarization and dielectric properties of epitaxial BaTiO$_3$ crystals over a wide range of misfit strains. We predict stabilization of the monoclinic r-phase over a wide range of strained states in the epitaxial BaTiO$_3$. The lowest energy [111] phonons in the r-phase become softened as the misfit strain approaches the transition boundaries towards the c- and aa-phases, but incomplete at the boundaries, in contrast to strained SrTiO$_3$. The strain dependence of the dielectric constant shows broadened peaks and considerable deviation from the Curie-Weiss-type law near critical strains, which are attributed to the incomplete phonon softening. © 2012 American Institute of Physics.

I. INTRODUCTION

Most of the perovskite ferroelectrics and dielectrics used in electronic devices are in the form of thin films deposited on rigid substrates. Due to differences of the lattice parameters, the thermal expansion coefficients between the films and the substrates, and/or energetics of the deposition process, large strains are often induced in the thin films. The physical properties of strained thin films can be substantially modified compared to those of strain-free systems. The strain caused by the constraint of the substrate has become ever more important because recent integrated devices require very thin films down to the order of 10 nm, where the strain is often not relaxed. Barium titanate BaTiO$_3$ (BTO) is of particular interest. BTO thin films grown on germanium or silicon with a cocommensurate interface are considered a breakthrough, opening a path to a variety of new applications. BTO thin films present the possibility of applications in microelectronics, nonlinear optics, and recently photonics. Such a wide variety of applications has resulted in a resurgence of interest in BTO thin film properties and strain effects. Previous investigations have covered a variety of subjects, including critical film thickness for ferroelectricity and the influence of thin film-electrode interface on polarization.

On the other hand, the epitaxial strain has been used as a tuning factor to enhance functional properties, i.e., polarization, or nonlinear optical susceptibility. Although phase diagrams of epitaxial BTO(001) with the misfit strain have been theoretically predicted from first-principles, or the phenomenological theory, the strain effect on the polarization, soft mode dynamics, and dielectric behavior of epitaxial BTO is far from being completely investigated. The strain-dependent polarization has been studied by the phenomenological theory. However, existing thermodynamic analysis of dielectric behavior in epitaxial BTO thin films is limited to small strains as present thermodynamic potentials are not applicable to strains larger than 0.4%. Experimentally, BTO thin film can suffer compressive epitaxial strains as large as 1.6%, or even 2.3% when it is deposited on SrTiO$_3$ (STO) substrate, or large tensile strains of at least 0.4% when deposited on Ge or Si substrates which current semiconductor technology primarily relies on. Moreover, it was reported that the different sets of parameters used in Refs. and resulted in completely different low-temperature phase behaviors. Despite extensive research, no reports have been published on the phonon and dielectric behaviors of epitaxially strained BTO from a microscopic and/or parameter-free computational scheme. Contrary to BTO, STO has been extensively studied in terms of its strain-induced phase stability, phonon softening, polarization, and dielectric behavior by several approaches such as the first-principles, phenomenology, and experiments. The first-principles studies have shown that STO exhibits complete optical phonon softening and dielectric anomaly at phase boundaries. Comparison of the phonon and dielectric behaviors of these epitaxially strained oxides is of fundamental and technological interest.

Using an *ab initio* approach, it is possible to perform parameter-free calculations. In addition, a rich variety of microscopic information on the polarization and soft mode behaviors over a wide range of misfit strain can be obtained. Here, we present the strain effects on polarization, soft mode dynamics and dielectric constant of epitaxially strained BTO...
crystals, in comparison with STO. The roles of strain and the A-site atomic size, which is characterized by a tolerance factor, as critical factors modifying the dielectric and ferroelectric properties of these perovskite oxide films are presented. Broad maxima appear in the strain dependence of the dielectric permittivity, which is a quite contrast to STO. The dielectric susceptibility deviates considerably from the so-called Curie-Weiss-type law for the epitaxial strain when approaching phase boundaries. The results show that the only A-site substitution can lead to significant changes of the soft mode dynamics and functional properties as well as critical behaviors of these epitaxially strained oxides.

II. COMPUTATIONAL METHOD AND MODEL

First-principles density functional calculations were performed with the local density approximation (LDA) as implemented in the PWSCF package. The exchange correlation energy was approximated using the Ceperley-Alder form with Perdew-Zunger parameterization. Ultrasoft pseudopotentials were employed with the cutoff energy of 700 eV. Semicore states were included in Ba (5s^25p^66s^2), Sr(4s^24p^65s^2), and Ti(3s^23p^64s^23d^2), while O(2s^22p^6) were treated as valence states. Brillouin zone integration was performed with an 8x8x8 Monkhorst-Pack k-point mesh.

The epitaxial strain of the lattices is defined as

\[ \eta = \frac{a - a_0}{a_0} \times 100, \]

where \( a \) is the in-plane lattice parameter and \( a_0 \) is the stable cubic lattice constant of BTO. To determine the strain dependence of the equilibrium structure, we performed total-energy optimization of the BTO perovskite unit cell in four possible phases: the \( p \)-phase with zero polarization components \( P_z = P_x = P_y = 0 \), the \( c \)-phase with \( P_x = P_y = 0 \) and \( P_z \neq 0 \), the \( aa \)-phase with \( P_x = P_y \neq 0 \) and \( P_z = 0 \), and the \( r \)-phase with \( P_z = P_x \neq 0 \) and \( P_y \neq 0 \). As mentioned above, the existing phenomenological theory is limited to small strains. For a full understanding of epitaxially strained BTO, we considered a wide range of misfit strains from -2.0% to +2.0%. For each strain state, the structures were relaxed until the Hellman-Feynman forces on atoms were reduced to 0.0005 eV/Å. Once the ground state structure at each strain state was obtained, the phonon frequencies were calculated using the density functional perturbation theory (DFPT). The dielectric constant was then calculated by the following equation:

\[ \epsilon(\omega) = \epsilon_{\infty} + \sum_k \frac{Z_k^2}{\omega_k^2 - \omega^2}, \]

where \( \omega_k \) and \( Z_k \) are the phonon frequencies and mode dynamical charge, respectively, and \( \epsilon_{\infty} = 4\pi\varepsilon_c/m_0V \) (mass \( m_0 \), charge \( e \), and primitive cell volume \( V \)). The polarization was calculated by the Berry phase formalism applying

\[ P_z = \frac{1}{V} \sum_i Z_{z,i} u_{z,i}, \]

in which \( Z_{z,i} \) is the Born effective charge and \( u_{z,i} \) is the displacement of atom along \( z \).

III. RESULTS AND DISCUSSION

A. Structural behavior

Optimization of total energy results in the most stable structure of the BTO lattice for each strain state between the compressive -2.00% to the tensile +2.00%. In compressive states with misfit strains less than -0.90%, the \( c \)-phase, in which polarization is directed along the \( z \)-axis, is the most stable. At a strain of -0.90%, there is a second order phase transition from the \( c \)-phase to \( r \)-phase. The \( r \)-phase extends until the strain reaches a tensile strain of +1.00%, above which a continuous transition from the \( r \)-phase to \( aa \)-phase occurs. At the transition, the polarization switches to the in-plane direction. Although this transition sequence is consistent with that obtained by Diéguez et al., our result shows significantly larger critical strains. The former showed much earlier transitions at -0.64% for the \( c \rightarrow r \) transition and +0.65% for the \( r \rightarrow aa \) transition. Since important setup parameters in the former calculation, such as cutoff energy and atomic states treated in the pseudopotentials, are virtually the same as those used in the current work, the difference would arise from the use of a larger \( k \)-mesh (6 \times 6 \times 6) previously compared to 8 \times 8 \times 8 mesh used in the present work.

In a first-principles-based Monte Carlo simulation using a very large periodic supercell of 10 \times 10 \times 10, large critical strains of -1.2% and +1.2% were obtained for the \( c \rightarrow r \) and \( r \rightarrow aa \) transitions, respectively, at low temperatures. It is worth mentioning that in the Berry phase based calculations of the polarization and dielectric constant, a very dense \( k \)-mesh is required. Indeed, the Berry phase approach is hindered by a slow \( O(L^{-2}) \) convergence, where \( L \) is the supercell size or equally the resolution of the \( k \)-mesh. Our result obtained using a dense \( k \)-mesh implies that the \( r \)-phase is stabilized over a much wider range of the misfit strain at low temperatures. This result combined with the high strain sensitivity of the polarization orientation in the \( r \)-phase leads to severe modification of the functional behavior of the epitaxially strained BTO. The symmetry analysis performed on the optimized atomic structures shows that the \( c \)-phase, \( r \)-phase, and \( aa \)-phase belong to crystallographic space groups of tetragonal \( P4mm \), monoclinic \( Cm \), and orthorhombic \( Amm2 \), respectively. Optimized atomic structures with polarized directions of the epitaxially strained BTO lattice at compressive strains of -1.5% and -0.5% and a tensile strain of 1.5% are shown in Figs. 1(a)–1(c), respectively. In the \( c \)-phase, the cation Ti and anion O atoms displace oppositely along a [001] direction, determining the direction of polarization [Fig. 1(a)]. In the \( r \)-phase, the Ti’ and O’ relatively displace along a direction which forms an angle with the \( z \)-axis [Fig. 1(b)]. With increasing tensile strain, the displacements are stabilized along the [110] direction, causing the transition to the [110]-polarized \( aa \)-phase [Fig. 1(c)].

B. Polarization and dielectric properties

As mentioned in Sec. I, the strain-induced modification of polarization has been predicted but for the \( z \)-component
only. Given that the monoclinic $r$-phase is stabilized over a wide range of misfit strains, the $x$- and $y$-components will severely modify the strain-dependent polarization of the epitaxial BTO. Therefore, the behavior of the $z$-component of polarization only would be far from sufficient and is not experimentally significant. In the current work, within the Berry phase approach the strain effect on the polarization and all of its Cartesian components were calculated. Figure 2(a) shows the strain dependence of the polarization over the full range of epitaxial strain. The calculated polarization is in good agreement with the experimental polarization obtained from BTO thin films of various thicknesses on several substrates. It may be argued that the thickness can act as an additional factor to modify the polarization behavior. However, in general, due to the difficulties of growing thin films with a constant thickness but in different strain states, systematic behaviors of the polarization and thin film properties as a function strain are still not experimentally available. As seen in Fig. 2(a), epitaxially strained BTO has an enhanced polarization compared to that of a single unstrained crystal (26 $\mu$C/cm$^2$). The polarization of strained STO, which was predicted by Antons et al., was reproduced for comparison. It is found that the polarization of the epitaxial BTO crystal is significantly less sensitive to strain than STO. Experimental results have shown that the difference of the A-site atom could cause a considerable change in the strain dependence of the polarization in perovskite oxide thin films. This has been attributed to the suppressed strain sensitivity of highly polar perovskites, compared with less polar perovskites. This argument can account for the low strain sensitivity of highly polar PbTiO$_3$ or similar oxides, in which the hybridization between the lone pair ($ns^2$) state and a low-lying state induces a large displacement of the A-site. However, this becomes irrelevant in the present case because Sr and Ba have the same valence electronic configuration. Instead, the effect of the atomic size would be dominant.

The perovskite $ABO_3$ structure can be characterized by a tolerance factor, $t$ as follows:

$$t = \frac{r_A + r_O}{\sqrt{2}(r_B + r_O)},$$

(4)

where $r_A$, $r_B$, and $r_O$ are the ionic radii of the A, B, and O ions, respectively. The large atomic size of Ba$^{2+}$ results in a significantly larger $t = 1.0706$, compared with $t = 1.0091$ for STO. This implies that there is a large space available for Ti in BTO, which allows the Ti ion to rattle into off-center positions. As a result, the Ti$^{4+}$ displaces from the cubic center even in the strain-free state. The ferroelectric displacement changes weakly with the misfit strain under the off-center states of the Ti ion. Consequently, the polarization is less sensitive to strain. The variation of the polarization components are shown in the inset of Fig. 2(a). With increasing tensile strain, the $x$- and $y$-components continuously increase and become the only components present with tensile strains larger than +1.00%. Figure 2(b) shows the orientation evolution of the polarization. The polarization rotates from a tetragonal orientation [001] to an orthorhombic orientation [110] through the (110) plane as the misfit strain changes from the compressive to tensile state. It was shown that such a rotation path is the minimum energy path and can induce an enormous piezoelectric response with the piezo-
The calculated soft-mode behaviors of STO and BTO, regarded as the extreme ends of the Ba$_x$Sr$_{1-x}$TiO$_3$ solution, are consistent with the experimental results.

Figure 4 shows the dielectric constant ($\varepsilon_r$) of strained BTO. Instead of sharp peaks at the phase transitions in STO (inset), broad maxima were found in the strain dependence of $\varepsilon_r$ in the epitaxially strained BTO. The out-of-plane dielectric constant, $\varepsilon_{33}$, reaches a broad maximum at the transition boundary between the $r$- and $aa$-phases in the tensile strained state. On the other hand, the in-plane dielectric constant, $\varepsilon_{11}$, shows a broad maximum at the transition boundary between the $r$- and $c$-phases in the compressive strained state. These broad maxima are caused by the incomplete softening of the lowest energy [111] phonons [Figure 3(b)]. Similarly, the difference of $\varepsilon_r$ between STO and BTO was also observed in their temperature dependence. Particularly, it has been shown that the dielectric constant of STO varies strongly with the thin film strain state and temperature.26,45

High $\varepsilon_r$ and a sharp peak in its temperature dependence were reported for a STO thin film in the tensile state on a DyScO$_3$ substrate, which was well described by the Curie-Weiss law.26 In contrast, broader peaks have been clearly observed in the temperature dependence of $\varepsilon_r$ in BTO thin films, and this behavior was attributed to the stress in the thin films.12,27,28 Although a clear atomic-scale mechanism remains elusive, there is increasing evidence that strain induced by the substrate is responsible for the broad maxima in the temperature dependent $\varepsilon_r$ in epitaxial BTO.

Essentially, the dielectric behavior is primarily determined by optical phonons of lowest frequencies. It has been shown that the frequency of optic phonons can be expressed in terms of the unit cell volume and the short-range repulsive force, which in turn varies with Ti-O bond lengths.46 Therefore, the strain-induced modifications of the Ti-O bond lengths would break the balance between the attractive long-range Coulomb force and repulsive short-range electronic force, inducing phonon hardening represented by the incomplete phonon softening at the transition boundary. In fact, this strain effect has been suggested to account for the broad transition as a function of temperature.4,47,48

![Figure 3](image-url)  
**FIG. 3.** The strain dependence of the three lowest optical modes in epitaxial (a) SrTiO$_3$ and (b) BaTiO$_3$. The square, triangle, and circle symbols represent the [001]-, [110]-, and [111]-polarized modes, respectively.

![Figure 4](image-url)  
**FIG. 4.** The in-plane ($\varepsilon_{11}$) and out-of-plane ($\varepsilon_{33}$) dielectric constants of BaTiO$_3$ at various misfit strains. The inset shows the components of the dielectric constant in SrTiO$_3$ as a function of the misfit strain. The square and circle symbols denote $\varepsilon_{33}$ and $\varepsilon_{11}$, respectively.
and temperature-driven phase transitions in epitaxial BTO are affected by the same stress-induced modifications of the delicate interactions in the Ti-O network. Therefore, the argument accounting for the temperature dependence of $\varepsilon_r$ may remain valid for its strain-induced behavior in epitaxial BTO. On the other hand, the epitaxial BTO and STO show distinctly different dielectric behaviors, as can be seen in our calculated and the experimental results for the strain and temperature dependences of $\varepsilon_r$, respectively. Experimentally, it is well known that the A-site substitution has severe effects on the lattice dynamics and dielectric and polarization behaviors of perovskite oxides.\(^{41,44,49}\) As discussed in Fig. 2, the A-site size effect, which can be characterized by the tolerance factor, acts as an additional factor to modify the Ti-O interactions, and hence the lattice dynamics in these perovskites. Therefore, the difference in the A-site would lead to rich diversification of the dielectric and ferroelectric properties in these titanate perovskites.

To further investigate the dielectric behavior of the epitaxial BTO near the critical strain, the inverse dielectric susceptibility, which is defined as $1/\chi = 1/(\varepsilon_r - 1)$ was calculated (Fig. 5). The data were fitted to the so-called Curie-Weiss-type law for the strain as follows:\(^{50}\)

$$\frac{1}{\chi} = C(S_m - S_m^t), \quad (5)$$

where $C$ is a constant, $S_m$ is the misfit strain, and $S_m^t$ is the critical misfit strain. As seen in Fig. 5(a), the strain induced phase transitions in STO are well described by the Curie-Weiss-type law. For each in-plane ($xx$-) or out-of-plane ($zz$-) component, there are changes of the slope, $C$, at the phase boundaries. As mentioned above, the temperature dependent transition in an epitaxial STO thin film was also found to obey the Curie-Weiss law.\(^{20}\) The strain dependent susceptibility of BTO exhibits linear behavior for large misfit strains in the $c$-phase and $aa$-phase as shown in Fig. 5(b). The linear dependence of the $aa$-phase agrees partly with phenomenological calculations used to study the behavior of the inverse dielectric susceptibility in the absence of strain-induced phase transitions.\(^{50}\) However, in the vicinity of the phase transitions, the in-plane and out-of-plane components show nonlinear behaviors when approaching the critical strains of $-0.90\%$ and $+1.00\%$, respectively, from the monoclinic $r$-phase. For example, the out-of-plane susceptibility deviates significantly from the Curie-Weiss-type law near the boundary between the $r$- and $aa$-phases, which was associated with the incomplete $[111]$ phonon softening. It should be emphasized that although pioneering works on the strain dependences of the ($z$-component) polarization\(^{15}\) and dielectric constant\(^{17,18,50}\) of epitaxial BTO crystals predicted general effects of strain on these quantities, they have the disadvantages of parameter dependence, a limited range of strain, and a lack of microscopic characterization\(^{17,18,50}\) or insufficient information.\(^{15,50}\) However, experiments and applications require not only full and accurate descriptions of strain-dependent magnitudes of the physical quantities to fabricate high-performance devices but also understanding of the microscopic properties and diversified behaviors among the complex oxides from a parameter-free theory to control and design the functionalities of the electronic devices. This current work based on a parameter-free computational scheme provides full and concrete strain dependences of the dielectric constant (Fig. 4) as well as polarization and its orientation (Fig. 2).

In addition, the out-of-plane dielectric constant, $\varepsilon_{z3}$, is of significant interest in semiconducting devices employing oxide thin films. For BTO thin films grown on Ge or Si substrates, the BTO film is rotated by $45^\circ$ on the (001) plane of the substrate and experiences tensile strain due to the thermal expansion mismatch.\(^{22,51}\) The $\varepsilon_{z3}$ increases with increasing tensile strain in a region that Si or Ge is most likely to induce into the BTO film, although its dependence is significantly less than that of STO. The differences of the strain dependences of the polarization and dielectric constant are accounted for in terms of microscopic characterization of the A-site size effect and soft mode dynamics. The strain dependent behavior of BTO and the comparison with STO would be of both great technological and fundamental interest.\(^{7,21,22}\)

IV. CONCLUSION

In summary, we present the strain dependent polarization and dielectric properties of epitaxially strained BTO crystals over a wide range of misfit strains from $-2.00\%$ to $+2.00\%$ from first-principles. With a more refined setup (i.e., denser k-point mesh), it was revealed that the structural transitions should occur at much larger critical epitaxial strains of $-0.90\%$ and $+1.00\%$, compared to the previously reported $-0.6\%$ and $+0.65\%$. This implies stabilization of the monoclinic $r$-phase in the epitaxial BTO lattice over a much wider...
range of misfit strains at low temperatures. More importantly, the optical phonons of strained BTO soften less than those of strained STO, giving rise to a broad maximum of the dielectric constant of the strained BTO. Consequently, the strained BTO films exhibit less sensitivity of the dielectric constant than STO films and significant deviation from the so-called Curie-Weiss-type law for epitaxial strain near the critical strains. The distinction between BTO and STO is quite noticeable in that both perovskite oxides differ only in the A-site substitution. Our results would provide useful information for experiments and applications of BTO thin films on a wide variety of substrates, in which the understanding of strain effects on polarization and dielectric properties is vitally important.

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