

FIRST-PRINCIPLES MODELING OF FUNCTIONAL PEROVSKITE MATERIALS AND SUPERLATTICES

By

QIBIN ZHOU

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Karin M. Rabe

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ABSTRACT OF THE DISSERTATION

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By QIBIN ZHOU

Dissertation Director:

Karin M. Rabe

This thesis discusses first-principles modeling of functional perovskite oxides and perovskite superlattices. In the past few decades, first-principles density functional theory has driven tremendous advances in the theoretical study of materials. However, it does not give us a conceptual understanding of the physics of these materials, which makes the first-principles modeling necessary.

In the first project, we use the first-principles method to study the epitaxial strain-induced ferroelectricity in the orthorhombic CaTiO_3 structure and construct the energy expansion from first principles to illustrate the mechanism of the induced ferroelectricity. We also discover an unexpected polar phase of CaTiO_3 with in-plane polarization under compressive strain. Symmetry analysis shows that this phase is a realization of a new mechanism of geometric ferroelectricity. In the second project,

we collaborate with an experimental group at SUNY Stony Brook to study the perovskite superlattices $\text{PbTiO}_3/\text{BaTiO}_3$. A variety of properties, including electric polarization, tetragonality, piezoelectricity and dielectric constant, have been studied from first principles. We also construct a slab model, in which different constituents are treated as bulk-like materials with appropriate electrostatic constraints, to investigate the origin of the enhanced piezoelectricity in PTO/BTO superlattices. The third project is our first-principles study of the $\text{BaTiO}_3/\text{CaTiO}_3$ superlattices, in which the oxygen octahedron rotations play a substantial role. We observe the phase transitions among three competing phases and enhanced piezoelectricity in all of the three phases at intermediate BaTiO_3 concentration. The slab models of BTO/CTO superlattices consistently underestimate the polarization, which indicates the interfacial enhancement of polarization.

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Chapter 1

Introduction

In the past few decades, the first-principles method has driven tremendous advances in the theoretical study of materials. It is a powerful tool for obtaining information at the atomic scale and computing physical properties of materials of technological interest, such as functional materials and superlattices. First-principles calculations can thus provide theoretical input to the design of new materials with desired properties for technological applications or novel physical behavior.

However, the direct results of first-principles calculations do not give us a conceptual understanding of the physics of these materials; they can be considered as analogous to the experimental measurements of properties. For physical insight and to provide guidance in the materials design process, we need to construct models to describe the first-principles results, analogous to phenomenological modeling of experimental measurements. This thesis presents the first-principles modeling of functional perovskites and superlattices. In these materials, functional behaviors are derived from competing structures, whose relative energies can be tuned by the application of epitaxial strain or chemical substitutions. First-principles modeling sheds light on the competition between the candidate structures and helps to guide the search for the novel functional materials.

Perovskites form a large class of crystal materials with chemical formula ABO_3 , where A and B represent metal atoms of different sizes. The ideal cubic-symmetry perovskite structure has a five-atom unit cell of space group $Pm\bar{3}m$, as shown in Fig. 1.1. The B atom is at the center of an oxygen octahedron. These octahedra are

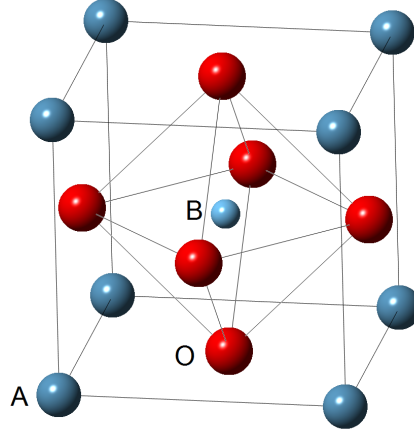


Figure 1.1: Perovskite cubic $Pm\bar{3}m$ structure. B cation sits at the center of the oxygen octahedron O_6 while A cation fills the space between the oxygen octahedra.

corner-linked to form a simple cubic network.

The ideal cubic perovskite structure is inherently unstable and prone to distortion due to the incompatibility of the ions with the crystal structure, as quantified by the tolerance factor (1). At low temperature, the perovskites can have different lower-symmetry structures, such as orthorhombic, tetragonal and rhombohedral. The variety of perovskite compositions and structures leads to various functional properties exhibited in the perovskite oxides, such as (anti-)ferroelectricity, piezoelectricity and (anti-)ferromagnetism, which makes perovskites an intensively studied family of functional materials.

The lower-symmetry structures of perovskites can be obtained by freezing in various distortion modes, such as polarization and oxygen octahedron rotations and tilts, as shown in Fig. 1.2, in the high-symmetry cubic structure (2; 3; 4). These distortion modes in the low-symmetry structures of perovskites are the origin of the functional behavior in perovskites. For example, in ferroelectrics such as BaTiO_3 , the instability of the polar mode Γ_4^- in the ideal cubic structure leads to ferroelectricity and large static dielectric response. In piezoelectric materials, the piezoelectric response also originates from the coupling of the polar mode and elastic strain. Models that take the polar mode and strain as the fundamental degrees of freedom can describe these

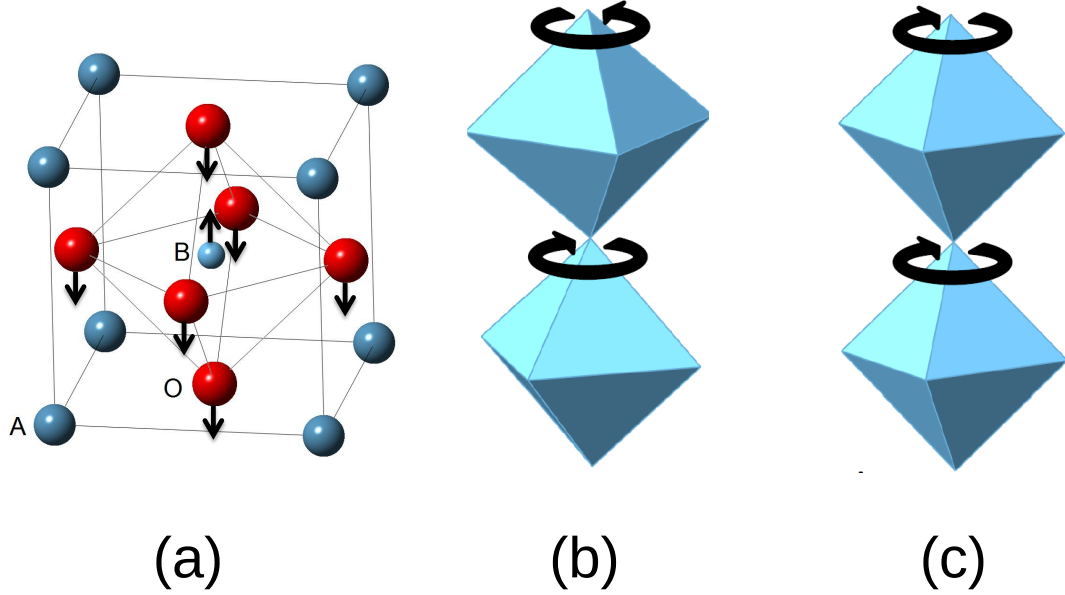


Figure 1.2: Distortion modes: (a) polar mode Γ_4^- , (b) out-of-phase rotational mode R_4^+ , (c) in-phase rotational mode M_3^+

properties well (5) and have also formed the basis for simulations of the temperature-driven ferroelectric-paraelectric transition.

Besides the polar mode Γ_4^- , instability of the oxygen octahedron rotational modes in the ideal cubic structure is also very common, for example, in CaTiO_3 . CaTiO_3 has a nonpolar orthorhombic $Pbnm$ structure with in-phase oxygen octahedron rotations ($M_3^+[001]$) and out-of-phase oxygen octahedron tilts ($R_4^+[110]$) frozen in the cubic $Pm\bar{3}m$ structure. The existence of the rotational modes greatly increases the complexity of the structures as well as the first-principles modeling.

In this thesis work, I have studied several functional perovskite materials and superlattices, and developed approaches to model their behavior as observed in first principles calculations, to obtain physical insight into their functional properties and

to assist in the design of new functional superlattices through interactions with experimental collaborators.

In the second chapter, I review the formalism of first principles calculations, including both the fundamental approximations of density functional theory and aspects of the numerical implementation. I show how functional properties such as electric polarization, dielectric response and piezoelectric response are obtained in the first-principles framework. The second half of this chapter is devoted to the formulation of my first-principles models, with a review of the fundamentals of polynomial expansions of the energy in symmetry invariants in the spirit of Landau theory, and a general overview of how the coefficients in such an expansion can be obtained from first-principles calculations.

In the third chapter, I present first-principles calculations and modeling for CaTiO_3 under epitaxial strain. First, I consider the epitaxial phases derived from the low-symmetry nonpolar bulk structure of CaTiO_3 , and develop a model to describe the structural energetics over a wide range of strain. Then, I examine an intriguing metastable structure that appears at compressive strain (6). From modeling of the first-principles results, I show that this phase is a realization of a new mechanism for geometric ferroelectricity.

In the fourth chapter, I consider superlattices of BaTiO_3 and PbTiO_3 (7). In previous first-principles investigation, it was observed that for certain stacking sequences, the piezoelectric response of the superlattices is substantially enhanced over the piezoelectric response of the pure compounds. Working with an experimental group at SUNY Stony Brook, I performed additional first-principles calculations and worked on developing a model that would describe the observed enhancement and provide guidance for optimizing the piezoelectric response of these superlattices, with the possibility of extension to other superlattice systems.

In the fifth chapter, I consider superlattices of BaTiO_3 and CaTiO_3 (8). The

oxygen octahedron rotations of CaTiO_3 , discussed in the third chapter, play an important role in determining the structure and properties of these superlattices. I discuss models that describe various aspects of the structure and properties of these superlattices as a function of overall composition and individual layer thicknesses.

Finally, I conclude with a summary of the most important lessons learned, and some avenues for further investigation.

Chapter 2

Formalism

“The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble. It therefore becomes desirable that approximate practical methods of applying quantum mechanics should be developed, which can lead to an explanation of the main features of complex atomic systems without too much computation.” P. A. M. Dirac, Proceedings of the Royal Society of London. Series A, Vol. 123, No. 792 (Apr. 6, 1929)

2.1 First-principles calculations

In the past thirty years, first-principles quantum-mechanical methods have achieved impressive success in analyzing and predicting the structures and properties of a wide range of materials, allowing a comprehensive understanding of the origin of macroscopic properties at the atomic scale. As established in the well-known quote from Dirac at the beginning of this chapter, the key ingredients in this success have been the exponential growth of computational power and the development of suitable approximations and highly efficient algorithms.

First, starting from elementary nonrelativistic quantum mechanics, I review the mapping to an equivalent non-interacting electron system through the Born- Oppenheimer approximation and density functional theory. Then, I discuss the numerical solution of the non-interacting electron system for a periodic arrangement of the nuclei, including pseudopotentials, plane wave basis set, and Brillouin zone averages. The central quantities are the total energy (electronic ground state for a given arrangement of the nuclei), the forces on the atoms through the Hellman-Feynman

theorem, and the stress on the unit cell. From these, Equilibrium structure, phonon frequencies, and elastic constants can be computed. The modern theory of polarization also allows us to compute the spontaneous polarization of ferroelectric materials and response functions such as the dielectric response and piezoelectric response. Practical aspects of these computations are described. I conclude this section with a discussion of the precision and accuracy of the first principles results.

2.1.1 Quantum-mechanical description of solids

In quantum mechanics, a solid is a system of interacting electrons and nuclei described by the Hamiltonian

$$\begin{aligned}
 H = & -\frac{\hbar^2}{2m_e} \sum_i \nabla_i^2 + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_{i,I} \frac{Z_I e^2}{|\mathbf{r}_i - \mathbf{R}_I|} \\
 & - \frac{\hbar^2}{2M_I} \sum_I \nabla_I^2 + \frac{1}{2} \sum_{I \neq J} \frac{Z_I Z_J e^2}{|\mathbf{R}_I - \mathbf{R}_J|}
 \end{aligned} \tag{2.1}$$

where $\hbar$ is the reduced Planck constant, m_e and M_I are the masses of electrons and ions, Z_I is the atomic number of the I -th ion and e is the electron charge. Because of the large difference between the electron and ion masses ($m_e \ll M_I$), electrons respond immediately to the motion of the ions. Therefore we can separate the motion of electrons and nuclei and only consider the dynamics of the electrons with frozen-in nuclei, which is called the Born-Oppenheimer approximation. In this way, the electronic Hamiltonian is simplified to

$$H = -\frac{\hbar^2}{2m_e} \sum_i \nabla_i^2 + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_i V_{\text{ext}}(\mathbf{r}_i) \tag{2.2}$$

where $V_{\text{ext}}(\mathbf{r}) = \sum_I \frac{Z_I e^2}{|\mathbf{r} - \mathbf{R}_I|}$. The electron-nuclei interaction is treated as the external potential to the electron. Even this simplification, it is still extremely difficult to achieve an exact solution to Eq. 2.2, because of the electron-electron interaction

$\frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}$. In the electron-electron interaction, besides the classic Coulomb interaction, there is also exchange and correlation energy which is due to the antisymmetry of the electron wave function. It is straightforward to include exchange in a total energy calculation, but the calculation of correlation energy can be formidable in a complex system. Therefore, further treatment is needed to perform accurate total energy calculation of solids.

2.1.2 Density functional theory

Density functional theory (9; 10) provides a simple way to include the exchange and correlation energy in the total energy calculation of solids. It reduces a system of strongly interacting electrons to a system of non-interacting electrons in an effective external potential. As described in more detail in this section, density functional theory has been proved to be extremely useful in the theoretical study of functional materials and successfully reproduced the ground-state properties of various materials.

Hohenberg-Kohn theorem

Hohenberg and Kohn (9) proved that there exists a universal functional of the electron density $F[n(\mathbf{r})]$, independent of the external potential V_{ext} , for the sum of the electron kinetic energy and electron-electron interaction potential. It is evident that the ground-state electron density $n(\mathbf{r})$ is uniquely determined by the external potential V_{ext} . In their paper, Hohenberg and Kohn showed that conversely V_{ext} is also a unique functional of $n(\mathbf{r})$, as will be briefly discussed in the following.

Hohenberg and Kohn preserved a proof by contradiction. Assume that there are no degenerate ground states and two different external potentials $V(\mathbf{r})$ and $V'(\mathbf{r})$, with ground states, Ψ and Ψ' respectively, give rise to the same electron density $n(\mathbf{r})$. Excluding the trivial case that $V - V' = \text{const}$, the two wave functions, Ψ and Ψ' , are different. If we combine the kinetic energy K and electron-electron interaction

V_{e-e} as F , for the two Hamiltonian $H = F + V$ and $H' = F + V'$, we have:

$$\langle \Psi | H | \Psi \rangle < \langle \Psi' | H | \Psi' \rangle \quad (2.3)$$

because Ψ is the wave function of the ground state of H . Then we have

$$E < E' + \langle \Psi' | V - V' | \Psi' \rangle \quad (2.4)$$

$$E < E' + \int [V(\mathbf{r}) - V'(\mathbf{r})] n(\mathbf{r}) d\mathbf{r} \quad (2.5)$$

If initially we switched Ψ and Ψ' , we would get

$$E' < E + \int [V'(\mathbf{r}) - V(\mathbf{r})] n(\mathbf{r}) d\mathbf{r} \quad (2.6)$$

Summing up Eq. 2.5 and Eq. 2.6 leads to the contradiction

$$E + E' < E + E' \quad (2.7)$$

Therefore, the external potential $V_{\text{ext}}(\mathbf{r})$ is a unique functional of electron density $n(\mathbf{r})$. Since $V_{\text{ext}}(\mathbf{r})$ defines the whole Hamiltonian H , the total energy, including the kinetic energy and electron-electron interaction, is also a unique functional of the density. According to the Hohenberg and Kohn theorem, the total energy of a system with wave function $\{\psi_i\}$ can be written as:

$$\begin{aligned} E[\{\psi_i\}] = & \sum_i \int \psi_i^* \left(-\frac{\hbar^2}{2m_e} \right) \nabla^2 \psi_i d^3\mathbf{r} + \int V_{\text{ext}}(\mathbf{r}) n(\mathbf{r}) d^3\mathbf{r} \\ & + \frac{e^2}{2} \int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3\mathbf{r} d^3\mathbf{r}' + E_{XC}[n(\mathbf{r})], \end{aligned} \quad (2.8)$$

where

$$n(\mathbf{r}) = \sum_i |\psi_i(\mathbf{r})|^2 \quad (2.9)$$

and $E_{XC}[n(\mathbf{r})]$ is the exchange and correlation energy functional. Because of the one-to-one mapping between the total energy functional and electron density, the electron density that yields the minimum of the total energy functional is exactly the ground state electron density, which provides some hope of solving the problem of strongly interacting electron gas.

Kohn-Sham equations

The Hohenberg-Kohn theorem provides an exact solution to the many-body problem of interacting electron gas. However, it does not show how to obtain the electron density that minimizes the total energy functional. Kohn and Sham (10) developed a self-consistent approach to determine the set of wave functions ψ_i that minimize the total energy functional, which are the solutions to the Kohn-Sham equations:

$$\left[-\frac{\hbar^2}{2m_e} + V_{\text{ext}}(\mathbf{r}) + V_H(\mathbf{r}) + V_{XC}(\mathbf{r}) \right] \psi_i(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r}) \quad (2.10)$$

Where

$$V_H(\mathbf{r}) = e^2 \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3\mathbf{r}' \quad (2.11)$$

$$V_{XC}(\mathbf{r}) = \frac{\delta E_{XC}[n(\mathbf{r})]}{\delta n(\mathbf{r})} \quad (2.12)$$

$V_H(\mathbf{r})$ is the Hartree potential which represents the classic Coulomb interaction between the electrons. $V_{XC}(\mathbf{r})$ is the effective exchange-correlation potential given by the functional derivative of the exchange-correlation energy $E_{XC}[n(\mathbf{r})]$. ψ_i is the wave function of the electronic state i , which is obtained through a set of self-consistent calculations. ε_i is the Kohn-Sham eigenvalue of electronic state i . The electron density $n(\mathbf{r})$ corresponding to the solutions to the single-particle Schrödinger-like equation, ψ_i , is the exact ground state density. The value of the corresponding Kohn-Sham functional is the total energy of the ground state. The Kohn-Sham equations reduce the

strongly interacting electron gas to independent electrons in effective potential caused by all the other electrons. If the exchange-correlation potential V_{XC} is described exactly, the electron density corresponding to eigenstates of Kohn-Sham Hamiltonian ψ_i is the exact electron density of the electron gas ground state. With the ground state electron density $n(\mathbf{r})$ known, the total energy of the ground state can then be obtained by the Kohn-Sham functional $E[n(\mathbf{r})]$.

Approximate forms for the exchange-correlation functional

As previously discussed, in principle, the solution to the Kohn-Sham equations is the exact solution of the ground state, as long as the exchange-correlation functional is exact. However, there is no way to obtain a simple exact functional to describe the exchange-correlation energy for arbitrary electron density $n(\mathbf{r})$. Therefore, some approximation is needed to describe the exchange-correlation functional in Kohn-Sham equations. It has been shown that if the electron density is sufficiently slowly varying, we have (11):

$$E_{XC}[n(\mathbf{r})] = \int n(\mathbf{r})\varepsilon_{XC}(n(\mathbf{r}))d\mathbf{r}, \quad (2.13)$$

where ε_{XC} is the exchange and correlation energy density of a uniform electron gas of density n . Kohn and Sham (10) applied this approximation with

$$V_{XC}(\mathbf{r}) = \frac{\delta E_{XC}[n(\mathbf{r})]}{\delta n(\mathbf{r})} = \varepsilon_{XC}(n(\mathbf{r})), \quad (2.14)$$

which is now commonly known as the local density approximation (LDA). The LDA is a local approximation of exchange-correlation energy and ignores the contributions of the inhomogeneities in the electron density. However, over the past few decades, the LDA has reproduced a variety of physical properties in many successful theoretical investigations of many types of materials and systems within a few percent of errors compared with the experimental data. The high accuracy of the LDA is partly due

to the fact that the LDA gives the correct sum rule for the exchange-correlation hole (12; 13; 14).

Generalized gradient approximation (GGA) is another exchange-correlation functional commonly utilized in many first-principles studies. The GGA is an improvement of LDA, which includes the contributions of nearby electrons by adding the gradient of electron density $\nabla n(\mathbf{r})$

$$V_{XC}(\mathbf{r}) = \varepsilon(n(\mathbf{r}), \nabla n(\mathbf{r})) \quad (2.15)$$

However, the corrections of electron density gradient have not shown the expected improvement over the results from the LDA. This is partially because the sum rule for the exchange-correlation hole is not obeyed in the GGA.

2.1.3 Lattice periodicity of crystals

As previously discussed, the density functional theory simplifies the strongly interacting electron gas to independent particles. However, in real materials, there are an infinite number of electrons whose wave functions extend over infinite space, which makes the Kohn-Sham equations still unsolvable. In periodic system, like crystals, the infinite number of electronic states can be mapped through the application of Bloch's theorem to an infinite number of $\mathbf{k}$ points with a finite number of electron states at each $\mathbf{k}$ point, which changes the notation of ψ_i in Eq.(2.10) to $\psi_{n\mathbf{k}}$. $\mathbf{k}$ is the wave vector of the electron wave function and n is the index which distinguishes the multiple electron states at the same $\mathbf{k}$ point. Mapping to $\mathbf{k}$ -space does not reduce the number of Equations to solve, but it provides the foundation for the further simplification based on Bloch's theorem, such as cutoff of plane-wave basis sets and the k -sampling.

Bloch's theorem

Bloch's theorem states that in a periodically-repeating system, the wave function of a particle, such as an electrons in a solid, can be written as a product of two parts:

$$\psi_{n\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}}u_{n\mathbf{k}}(\mathbf{r}), \quad (2.16)$$

where ψ is a wave function at an arbitrary wave vector $\mathbf{k}$, $\mathbf{r}$ is the position and u is a periodic function which has the period of crystal lattice with $u_{\mathbf{k}}(\mathbf{r}) = u_{\mathbf{k}}(\mathbf{r} + \mathbf{R})$. The periodic part of wave function, u , can be expanded using a discrete set of reciprocal lattice vectors $\{\mathbf{G}\}$ ($\mathbf{G} \cdot \mathbf{R} = 2\pi m$, $m=0,1,2,\dots$):

$$u_{n\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} C_{n,\mathbf{k}+\mathbf{G}} e^{i\mathbf{G}\cdot\mathbf{r}} \quad (2.17)$$

Combine Eq.(2.16) and Eq.(2.17) and we have:

$$\psi_{n\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} C_{n,\mathbf{k}+\mathbf{G}} e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}} \quad (2.18)$$

Substitution of Eq.(2.18) into Eq.(2.10) gives the plane-wave representation of the Kohn-Sham equations

$$\begin{aligned} \sum_{\mathbf{G}'} \left[\frac{\hbar^2}{2m_e} |\mathbf{k} + \mathbf{G}|^2 \delta_{\mathbf{G}\mathbf{G}'} + V_{\text{ext}}(\mathbf{G} - \mathbf{G}') \right. \\ \left. + V_H(\mathbf{G} - \mathbf{G}') + V_{XC}(\mathbf{G} - \mathbf{G}') \right] C_{n,\mathbf{k}+\mathbf{G}'} \\ = \varepsilon_{n\mathbf{k}} C_{n,\mathbf{k}+\mathbf{G}}. \end{aligned} \quad (2.19)$$

By solving the eigenvalues and eigenvectors of the Hamiltonian matrix whose matrix elements are given by the terms in the brackets above, we can obtain the energy and wave function of each electron state.

2.1.4 Pseudopotential approximation

Using Bloch’s theorem, the electron wave function in a periodic external potential can be expanded in a discrete set of plane-waves. In the core region, the wave function of the valence electrons oscillate rapidly to maintain the orthogonality with the core wave function. To accurately represent the oscillation of valence electron wave function, a large set of plane waves is required, which makes the all-electron (AE) calculations greatly time-consuming.

To make possible accurate calculations with a small set of plane waves, the pseudopotential approximation (15; 16; 17; 18; 19; 20) has been devised. Most of the physical properties of materials are determined by the valence electrons. The pseudopotential(PS) approximation remove the electron orbitals within the core region and replace the strongly attractive ionic potential and the core orbitals with a much weaker effective potential, which greatly improves the smoothness of the valence electron wave functions and hence reduces the size of the plane-wave basis set required.

To guarantee that the PS calculations accurately reproduce the results of the AE calculations, several requirements have to be fulfilled during the process of the pseudopotential construction. The construction of the pseudopotential starts with the AE calculation of a chosen atomic configuration. The PS electron state should have the same eigenenergy as the AE electron state. Outside a certain cutoff radius r_c , the PS wave function should match with the AE wave function, as shown in Fig. 2.1.4. Since, in the compounds, bonding or banding shifts eigenenergies away from the atomic levels, optimum transferability among a variety of chemical environments should also be guaranteed. This leads to the requirement that the logarithmic derivatives of the AE and PS wave functions and their first energy derivatives agree beyond the cutoff radii r_c , which minimizes the error due to the bonding or band shifts.

In the following part, I will discuss about three schemes to construct the pseudopotentials, which are the norm-conserving pseudopotentials, ultrasoft pseudopotentials (19) and projector augmented waves method (20). The three methods adapted

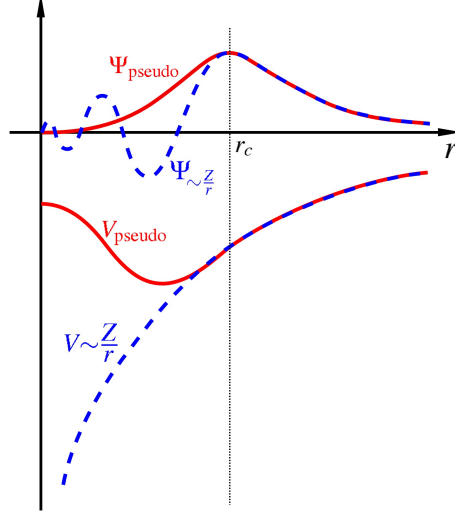


Figure 2.1: Schematic illustration of all-electron and pseudoelectron potentials and their wavefunctions

different strategies for the pseudopotential construction to reduce the size of the plane-wave basis set in the first-principles calculations and to maintain the optimum transferability.

Norm-conserving pseudopotentials

The norm-conserving pseudopotentials were first introduced in Ref (17). Besides having the same eigenenergy and the same wave function for $r > r_c$ as the AE calculation in a chosen atomic configuration, the most important property of the norm-conserving pseudopotentials is that the total charges of the PS and AE wavefunctions within the core region, $r < r_c$, are the same. This property, through Gauss's law, guarantees that the electrostatic potential outside the core region is the same for the PS and AE calculations. Due to the identity

$$2\pi \left[(r\phi)^2 \frac{d}{d\varepsilon} \frac{d}{dr} \ln \phi \right]_R = 4\pi \int_0^R \phi^2 r^2 dr, \quad (2.20)$$

the norm-conserving property is equivalent to the requirement for the logarithmic derivatives of the AE and PS wave functions, which guarantees the optimum

transferability.

The process of generating norm-conserving pseudopotentials is as follows. First, first-principles AE calculations with real spherical potential $V(r)$ is performed to obtain the radial part of the wave function for each angular momentum l , $\phi_l(r)$. The quantity $u_l(r)$ is defined as the product of the radius r and radial wave function $\phi_l(r)$. For each l , a cutoff radius r_{cl} is chosen to be typically 0.5 to 1.0 times of the radius of the outermost peak of $u_l(r)$. A trial effective potential V_{1l}^{PS} is constructed, utilizing an analytic function $f(x)$ which approaches 0 as $x \rightarrow \infty$ and approaches 0 at least as fast as x^3 as $x \rightarrow 0$,

$$V_{1l}^{\text{PS}}(r) = [1 - f(r/r_{cl})]V(r) + c_l f(r/r_{cl}). \quad (2.21)$$

The parameter c_l can be tuned so that the eigenenergy $\varepsilon_{1l}^{\text{PS}}$ of the radial Schrödinger equation with effective potential V_{1l}^{PS} is equal to the eigenenergy ε_l from the AE calculations, and the solution is a smooth wave function ω_{1l} without any nodes within the core region. Outside the core region, $r > r_{cl}$, ω_{1l} converges to $u_l(r)$. To satisfy the norm-conserving property, the intermediate PS wave function ω_{1l} is modified to

$$\omega_{2l}(r) = \gamma_l [\omega_{1l}(r) + \sigma_l g_l(r/r_{cl})], \quad (2.22)$$

where $g_l(x)$ is a function which equals to 0 for $x > 1$ and behaves as x^{l+1} for small x .

The parameter σ_l is adjusted to satisfy the norm-conserving requirement,

$$4\pi\gamma_l^2 \int_0^{r_{cl}} [\omega_{1l}(r) + \sigma_l g_l(r/r_{cl})]^2 dr = 4\pi \int_0^{r_{cl}} |\phi_l(r)|^2 r^2 dr. \quad (2.23)$$

With the modified PS wave function $\omega_{2l}^{\text{PS}(r)}$, the final pseudopotential V_{2l}^{PS} is then numerically calculated by inverting the radial Schrödinger equation.

The construction of norm-conserving pseudopotentials is easy and straight forward. However, good transferability requires that the cutoff radius r_{cl} is at around

the outmost maximum of the AE wave function. In the systems containing highly localized valence orbitals, such as first-row and transition-metal atoms, the norm-conserving condition requires that the PS wave function is also highly localized, which makes it impossible to construct a PS wave function which is much smaller than the AE one.

Ultrasoft pseudopotentials

Vanderbilt (19) developed the method of ultrasoft pseudopotential, in which the norm-conserving constraint is released and a much larger cutoff, usually almost half of the distance between the nearest neighbors, is allowed without hurting the transferability. The ultrasoft pseudopotential method is not only a replacement of the strong ionic potential and core orbitals with a weaker effective potential, but also a change of the Kohn-Sham equation Eq.(2.10). In the ultrasoft pseudopotential method, the PS electronic state $\tilde{\psi}_{n\mathbf{k}}$ is obtained by the solution of the following equation in Heisenberg representation

$$(T + V_{\text{loc}}^{\text{ion}} + V_{\text{NL}}^{\text{ion}} + V_H[n_v] + V_{\text{xc}}[n_v + n_c] - S\varepsilon_{n\mathbf{k}})|\tilde{\psi}_{n\mathbf{k}}\rangle = 0, \quad (2.24)$$

where T is the kinetic energy operator $-\frac{1}{2}\nabla^2$, $V_{\text{loc}}^{\text{ion}}$ is an appropriately chosen local potential which is independent of the angular momentum l and matches the real ionic potential beyond a cutoff radius r_c , V_H is the Hartree energy density functional, V_{xc} is the exchange-correlation density functional and $n_{v(c)}$ is the valence (core) charge density. $V_{\text{NL}}^{\text{ion}}$ and S are two operators, which depend on the angular momentum lm . The construction of the two operators will be discussed later. The wave function can be obtained by $\tilde{\psi}_{n\mathbf{k}}(\mathbf{r}) = \langle \mathbf{r} | \tilde{\psi}_{n\mathbf{k}} \rangle$ and the solution of Eq.(2.24) should be normalized according to

$$\langle \tilde{\psi}_{n\mathbf{k}} | S | \tilde{\psi}_{n'\mathbf{k}} \rangle = \delta_{nn'}. \quad (2.25)$$

Unlike the construction of norm-conserving pseudopotentials, in the ultrasoft pseudopotential method, for each angular momentum lm , the AE calculations in the reference atomic configuration are performed at several, usually two, energy levels ε_i . The AE electron state $\phi_i(\mathbf{r}) = \langle \mathbf{r} | \phi_i \rangle$ is the solution of the Schrödinger equation

$$(T + V_{\text{AE}} - \varepsilon_i) |\phi_i\rangle = 0, \quad (2.26)$$

where i is a composite index, $i = \{\varepsilon_i lm\}$ and V_{AE} is the original reference screened potential. Then a smooth pseudo-wave-function $\tilde{\phi}_i(\mathbf{r})$ is constructed with one single constraint, matching with $\phi_i(\mathbf{r})$ beyond the cutoff radius r_{cl} . A set of local wave functions $|\beta_i\rangle$ is defined as

$$|\beta_i\rangle = \sum_j (B^{-1})_{ji} |\chi_j\rangle, \quad (2.27)$$

where

$$|\chi_j\rangle = (\varepsilon_j - T - V_{\text{loc}}) |\tilde{\phi}_j\rangle, \quad (2.28)$$

$$B_{ij} = \langle \tilde{\phi}_i | \chi_j \rangle \quad (2.29)$$

The nonlocal pseudopotential operator V_{NL} and the nonlocal overlap operator S are constructed via the set of local wave functions $|\beta_i\rangle$,

$$V_{\text{NL}} = \sum_{i,j} D_{ij} |\beta_i\rangle \langle \beta_j|, \quad (2.30)$$

$$S = 1 + \sum_{i,j} |\beta_i\rangle \langle \beta_j|, \quad (2.31)$$

with the two quantities D_{ij} and Q_{ij} defined as

$$D_{ij} = B_{ij} + \varepsilon_{ij} Q_{ij}, \quad (2.32)$$

$$Q_{ij} = \langle \phi_i | \phi_j \rangle_{r_{cl}} - \langle \tilde{\phi}_i | \tilde{\phi}_j \rangle_{r_{cl}}. \quad (2.33)$$

The special notation $\langle \phi_i | \phi_j \rangle_R$ denotes the integral of $\phi_i^*(\mathbf{r})\phi_j(\mathbf{r})$ inside the sphere of radius R . From the definition of the quantity D_{ij} and Q_{ij} , we can easily see that

$$T + V_{\text{loc}} + V_{\text{NL}} - \varepsilon_i S|\tilde{\phi}_i\rangle = 0, \quad (2.34)$$

$$\langle \tilde{\phi}_i | S | \tilde{\phi}_j \rangle_{r_{cl}} = \langle \phi_i | \phi_j \rangle_{r_{cl}}. \quad (2.35)$$

It can be derived from the identity

$$\left(\frac{d}{d\varepsilon} \langle \tilde{\phi}_\varepsilon | T + V_{\text{loc}} + V_{\text{NL}} - \varepsilon S | \tilde{\phi}_\varepsilon \rangle_{r_{cl}} \right)_{\varepsilon=\varepsilon_i} = 0 \quad (2.36)$$

that

$$\left(-\frac{1}{2} u_i^2 \frac{d}{d\varepsilon} \frac{d}{dr} \ln u_\varepsilon(r) \right)_{R=r_{cl}} = \langle \tilde{\phi}_i | \tilde{\phi}_i \rangle_{r_{cl}} + Q_{ii} = \langle \phi_i | \phi_i \rangle_{r_{cl}}. \quad (2.37)$$

With a sufficient set of reference states ε_i , the scattering property of the pseudo wave function would match with that of the real wave function for a large range of energy ε . Therefore even for a large cutoff radius r_{cl} , a good transferability can still be maintained.

The PS wave function $\tilde{\psi}_{n\mathbf{k}}(\mathbf{r})$ is obtained by iterative solution of Eq.(2.24). The normalization constraint Eq.(2.25) is automatically satisfied. In the evaluation of the energy density functionals, V_H and V_{xc} , the deficit of valence charge due to the pseudization of electron states should be compensated. To make up the charge deficit, the valence charge density is defined to be

$$n_v(\mathbf{r}) = \sum_{n,\mathbf{k}} \tilde{\psi}_{n\mathbf{k}}^*(\mathbf{r}) \tilde{\psi}_{n\mathbf{k}}(\mathbf{r}) + \sum_{i,j} \rho_{ij} Q_{ji}(\mathbf{r}), \quad (2.38)$$

where

$$\rho_{ij} = \sum_{n,\mathbf{k}} \langle \beta_i | \tilde{\psi}_{n\mathbf{k}} \rangle \langle \tilde{\psi}_{n\mathbf{k}} | \beta_j \rangle, \quad (2.39)$$

$$Q_{ij}(\mathbf{r}) = \Psi_i^*(\mathbf{r})\Psi_j(\mathbf{r}) - \tilde{\psi}_i^*(\mathbf{r})\tilde{\psi}_j(\mathbf{r}). \quad (2.40)$$

The total energy is calculated by

$$E_{\text{tot}} = \sum_{n,\mathbf{k}} \langle \tilde{\psi}_{n\mathbf{k}} | \left(T + V_{\text{loc}} + \sum_{ij} D_{ij} |\beta_i\rangle \langle \beta_j| \right) | \tilde{\psi}_{n\mathbf{k}} \rangle \quad (2.41)$$

$$+ E_H[n_c] + E_{\text{xc}}[n_c + n_v]. \quad (2.42)$$

Projector augmented wave (PAW) potentials

The third pseudopotential method that I will discuss is the projector augmented wave (PAW) method that was developed by Blöchl (20).

The valence electron wave functions, which are physically relevant, oscillate rapidly in the core region and makes the plane-wave expansion difficult in the first-principles calculations. In the PAW method, the physically relevant AE wave functions $|\psi\rangle$ are transformed from computationally convenient PS wave functions $|\tilde{\psi}\rangle$,

$$|\psi\rangle = \mathcal{T}|\tilde{\psi}\rangle, \quad (2.43)$$

where $\mathcal{T}$ is a linear operator which will be discussed later. We can obtain physical quantities, represented as the expectation value $\langle \mathcal{O} \rangle = \langle \psi | \mathcal{O} | \psi \rangle$ of some operator $\mathcal{O}$ from the expectation value $\langle \tilde{\psi} | \tilde{\mathcal{O}} | \tilde{\psi} \rangle$ of a PS operator $\tilde{\mathcal{O}} = \mathcal{T}^\dagger \mathcal{O} \mathcal{T}$.

Now, let us consider the transformation $\mathcal{T}$, which is represented by the sum of identity and a set of local, atom-centered transformation operators $\hat{\mathcal{T}}_R$ such that

$$\mathcal{T} = 1 + \sum_R \hat{\mathcal{T}}_R. \quad (2.44)$$

The local operator $\hat{\mathcal{T}}_R$ acts only within some augmentation region Ω_R enclosing the atom, which is equivalent to the core region within cutoff radius r_{cl} in other pseudopotential methods. From Eq.(2.44), it is obvious that the AE and PS wave functions

coincide outside the augmentation region Ω_R . The local operator $\hat{\mathcal{T}}_R$ is defined as the transformation from the PS partial wave $|\tilde{\phi}_i\rangle$ to the AE partial wave $|\phi_i\rangle$

$$|\phi_i\rangle = (1 + \hat{\mathcal{T}}_R)|\tilde{\phi}_i\rangle \quad (2.45)$$

The AE partial waves are obtained by radially integrating the Schrödinger equation

$$\left(-\frac{1}{2}\nabla^2 + v_{\text{at}} - \varepsilon_i^1\right)|\phi_i\rangle = 0 \quad (2.46)$$

outward for the atomic AE potential v_{at} and a set of energy ε_i^1 . The construction of the PS partial waves is similar to the other pseudopotential approaches. An appropriate PS potential $\tilde{v}_{\text{at}}$ is selected to match the AE potential v_{at} outside the augmentation region. The PS partial wave $|\tilde{\phi}_i\rangle$ is obtained by the solution of the Schrödinger equation

$$\left(-\frac{1}{2}\nabla^2 + \tilde{v}_{\text{at}} - \varepsilon_i^1\right)|\tilde{\phi}_i\rangle = 0 \quad (2.47)$$

for the energy of the corresponding AE partial wave.

The set of PS partial waves form a complete basis of the PS Hilbert space, therefore every PS wave function can be expanded by the PS partial waves:

$$|\tilde{\psi}\rangle = \sum_i |\tilde{\phi}_i\rangle \langle \tilde{p}_i | \tilde{\psi} \rangle \text{ within } \Omega_R, \quad (2.48)$$

where $|\tilde{p}_i\rangle$ is a projector satisfying

$$\langle \tilde{p}_i | \tilde{\phi}_j \rangle = \delta_{ij}. \quad (2.49)$$

Utilizing the relation $|\phi_i\rangle = \mathcal{T}|\tilde{\phi}_i\rangle$, the corresponding AE wave function is calculated

by

$$|\psi\rangle = \mathcal{T}|\tilde{\psi}\rangle = \sum_i |\phi_i\rangle \langle \tilde{p}_i | \tilde{\psi}\rangle \text{ within } \Omega_R. \quad (2.50)$$

From Eqs.(2.48) and (2.50), we can get

$$|\psi\rangle = |\tilde{\psi}\rangle + \sum_i (|\phi_i\rangle - |\tilde{\phi}_i\rangle) \langle \tilde{p}_i | \tilde{\psi}\rangle, \quad (2.51)$$

which is a linear transformation from the PS wave function $\tilde{\psi}$ to the AE wave function ψ .

For a certain operator $\mathcal{O}$, its expectation value can be calculated as

$$\langle \mathcal{O} \rangle = \sum_n f_n \langle \psi_n | \mathcal{O} | \psi_n \rangle = \sum_n f_n \langle \tilde{\psi}_n | \tilde{\mathcal{O}} | \tilde{\psi}_n \rangle, \quad (2.52)$$

where f_n is the occupation of the state n . Using Eq.(2.51), the PS operator is of the form

$$\begin{aligned} \tilde{\mathcal{O}} &= \mathcal{T}^\dagger \mathcal{O} \mathcal{T} \\ &= \mathcal{O} + \sum_{ij} |\tilde{p}_i\rangle (\langle \phi_i | \mathcal{O} | \phi_j \rangle - \langle \tilde{\phi}_i | \mathcal{O} | \tilde{\phi}_j \rangle) \langle \tilde{p}_j|. \end{aligned} \quad (2.53)$$

Hence, the charge density, which is the expectation value of the real-space projection operator $|r\rangle\langle r|$, is given by

$$n(r) = \tilde{n}(r) + n^1(r) - \tilde{n}^1(r), \quad (2.54)$$

where

$$\tilde{n}(r) = \sum_n f_n \langle \tilde{\psi}_n | r \rangle \langle r | \tilde{\psi}_n \rangle, \quad (2.55)$$

$$n^1(r) = \sum_{nij} f_n \langle \tilde{\psi}_n | \tilde{p}_i \rangle \langle \phi_i | r \rangle \langle r | \phi_j \rangle \langle \tilde{p}_j | \tilde{\psi}_n \rangle, \quad (2.56)$$

$$\tilde{n}^1(r) = \sum_{nij} f_n \langle \tilde{\psi}_n | \tilde{p}_i \rangle \langle \tilde{\phi}_i | r \rangle \langle r | \tilde{\phi}_j \rangle \langle \tilde{p}_j | \tilde{\psi}_n \rangle. \quad (2.57)$$

Compared with the charge density in the ultrasoft pseudopotentials, Eq.(2.38), in principle, the charge density in the PAW method is equivalent as long as the projectors $|\beta_i\rangle$ and $|\tilde{p}_i\rangle$ are the same (21). Knowing the charge density $n(r)$, the energy density functional in the Kohn-Sham equations can be evaluated and the energy and wave function of each single-electron state can be obtained by the solution of the Kohn-Sham equation.

Cutoff of plane-wave basis sets

The size of the Hamiltonian matrix represented in Eq.(2.19) is determined by the number of the reciprocal lattice vectors $\{\mathbf{G}\}$. In principle, an infinite number of vectors $\{\mathbf{G}\}$ are required to represent the electron wave function, and the size of the Hamiltonian matrix is hence also infinite. In Bloch's theorem, the electron wave function is expanded by a plane-wave basis set of $e^{i\mathbf{k}+\mathbf{G}}$. In fact, only the wave vectors with small kinetic energy $(\hbar^2/2m_e)|\mathbf{k} + \mathbf{G}|^2$ have large coefficients $C_{i,\mathbf{k}+\mathbf{G}}$. Therefore, we can truncate the plane-wave basis and only include the wave vector whose kinetic energy is lower than a certain cutoff energy. Through this approximation, the dimension of Hamiltonian matrix is made finite and Eq.(2.19) is no longer unsolvable. Such truncation would certainly lead to errors in the calculations. Therefore, in the DFT calculations, the cutoff energy should be increased until the calculated total energy converges.

k -point sampling

Given the energy $\varepsilon_{n\mathbf{k}}$ and wave function $\psi_{n\mathbf{k}}(\mathbf{r})$ obtained through the solution of Eq.(2.19), the total energy and electron density can be calculated via averaging over

the Brillouin zone

$$E = \frac{\Omega}{(2\pi)^3} \int_{BZ} \left(\sum_n \varepsilon_{n\mathbf{k}} \right) d\mathbf{k} \quad (2.58)$$

$$n(\mathbf{r}) = \frac{\Omega}{(2\pi)^3} \int_{BZ} \left(\sum_n \psi_{n\mathbf{k}}^*(\mathbf{r}) \psi_{n\mathbf{k}}(\mathbf{r}) \right) d\mathbf{k}, \quad (2.59)$$

where Ω is the volume of the primitive unit cell. In general, integration over a certain area can be numerically calculated via determination of the function values at a set of points and interpolation for the other points. However, to obtain sufficient accuracy in the general numerical integration, usually it is necessary to know the functional values over a large set of points.

To avoid the use of the general numerical integration, efficient methods (22; 23; 24; 25; 26) have been developed utilizing the point group symmetry of the reciprocal lattice. Those methods make possible simpler and more accurate calculations of average over the Brillouin zone. The main idea underlying those methods is to represent the function values over a region of $\mathbf{k}$ space by the values at a single or several special $\mathbf{k}$ points. To illustrate this idea, we assume a smooth function $f(\mathbf{k})$ with the complete symmetry of the lattice

$$f(T_i \mathbf{k}) = f(\mathbf{k}), \quad (2.60)$$

where T_i is an element of the operations of the reciprocal lattice point group T . Both the energy $\varepsilon_{n\mathbf{k}}$ and wave function $\psi_{n\mathbf{k}}$ satisfy that condition. We can express $f(\mathbf{k})$ in the form

$$f(\mathbf{k}) = f_0 + \sum_{m=1}^{\infty} f_m A_m(\mathbf{k}), \quad (2.61)$$

where

$$A_m(\mathbf{k}) = \sum_{|\mathbf{R}|=R_m} e^{i\mathbf{k}\cdot\mathbf{R}}, m = 1, 2, \dots \quad (2.62)$$

$A_m(\mathbf{k})$ is obtained via a sum over equivalent lattice vectors $\mathbf{R}$ related to each other through the operations of T . It has the following property:

$$\frac{\Omega}{(2\pi)^2} \int_{BZ} A_m(\mathbf{k}) d\mathbf{k} = 0, m = 1, 2, \dots \quad (2.63)$$

The average of $f(\mathbf{k})$ over the Brillouin zone, $\bar{f}$, is given by

$$\bar{f} = \frac{\Omega}{(2\pi)^2} \int_{BZ} f(\mathbf{k}) d\mathbf{k}. \quad (2.64)$$

Substitution of Eq.(2.62) into Eq.(2.64) gives that $\bar{f} = f_0$. Therefore if we could a single point $\mathbf{k}_0$, which satisfied

$$A_m(\mathbf{k}_0) = 0, m = 1, 2, \dots, N, \quad (2.65)$$

for $N = \infty$, then we could use the function value at $\mathbf{k}_0$ to represent the average over the Brillouin zone, $f(\mathbf{k}_0) = \bar{f}$. Unfortunately, such a point with $N = \infty$ does not exist. However, since the coefficients f_m in Eq.(2.61) decreases rapidly as m increases, an estimate with required accuracy can be obtained as long as the condition(2.65) is satisfied for sufficient large N . Moreover, the condition(2.65) is not necessary for a single $\mathbf{k}$ point. We can use the linear combination of a set of carefully selected $\mathbf{k}$ points, which satisfy

$$\sum_i \alpha_i A_m(\mathbf{k}_i) = 0, m = 1, 2, \dots, N, \quad (2.66)$$

$$\sum_i \alpha_i = 1, \quad (2.67)$$

for the estimation of $\bar{f}$. This is a systematic way of sampling in $\mathbf{k}$ -space and arbitrary large N can be achieved given that a sufficient dense $\mathbf{k}$ -grid is used.

2.1.5 Crystal structure prediction through total energy minimization

The prediction of the ground-state crystal structure and quantitative values for the structural parameters are obtained by minimizing the total energy with respect to the lattice vectors and atomic positions in the unit cell. As in the minimization of any function of many variables, direct information about the derivatives of the total energy is extremely valuable for rapid location of local and global minima. In first principles calculations, first derivatives of the total energy are obtained through application of the Hellmann-Feynman theorem for forces on the atoms in the unit cell

$$F_I = - \left\langle \psi(\{\mathbf{R}\}) \left| \frac{\partial H(\{\mathbf{R}\})}{\partial \mathbf{R}_I} \right| \psi(\{\mathbf{R}\}) \right\rangle, \quad (2.68)$$

and through the Nielsen-Martin stress expressions for changes in energy with changes in lattice parameters.

These optimization approaches preserve the symmetry of the starting configuration. Thus, for each choice of space group, they will identify the lowest energy structure with that symmetry. A strength of first principles methods is the capability for computing properties of hypothetical materials and materials under constraints. For example, in the study of BaTiO₃/SrTiO₃ (27), the effect of epitaxial strain on structure is studied in a first-principles framework through “strained bulk” calculations, in which the in-plane lattice constant of each superlattice is matched to the lattice constant of the substrate materials so that the interfacial effect is excluded.

For the total-energy formalism described above, the accuracy of the computation of lattice constants depends on the choice of approximation for the exchange-correlation functional. Use of the local density approximation gives lattice constants typically about 1% too small compared with experimental values, while use of the

GGA tends to give lattice constants that are typically about 1% too large; this is the case for simple semiconductors and for oxides.

2.1.6 Phonon dispersion relations from first principles

Phonon dispersion relations reveal important information about the structures. For a system near its equilibrium energy, the harmonic approximation applies. The frequencies ω and eigenvectors $\{U_I^\alpha\}$ for the α th Cartesian component of the I th atom of the normal modes are determined by Equation:

$$\sum_{J,\beta} (C_{IJ}^{\alpha\beta} - M_I \omega^2 \delta_{IJ} \delta_{\alpha\beta}) U_J^\beta = 0,$$

where $C_{IJ}^{\alpha\beta}$ is the matrix of interatomic force constants (IFCs):

$$C_{IJ}^{\alpha\beta} = \frac{\partial^2 E(\{\mathbf{R}\})}{\partial R_I^\alpha \partial R_J^\beta} = -\frac{\partial F_I^\alpha}{R_J^\beta}.$$

Unstable normal modes, which have imaginary frequencies, indicate the lattice modes that if frozen in, will lower the energy.

The IFCs can be obtained by the calculation of the change of Hellmann-Feynman forces with a small atomic displacement. This is called the frozen-phonon method. The frozen-phonon approach is straightforward for the calculation of the zone-center modes ($\mathbf{q} = 0$). An enlarged unit cell, or “supercell”, is required for the calculation of IFC at any $\mathbf{q} \neq 0$.

An alternative approach for phonon dispersion calculations is density functional perturbation theory (DFPT) (28). The DFPT uses the perturbation theory to calculate the second derivatives of the energy with respect to the atomic displacements

$$\frac{\partial^2 E(\{\mathbf{R}\})}{\partial R_I^\alpha \partial R_J^\beta} = 2 \sum_n \frac{\langle \psi_0 | \frac{\partial H}{\partial R_I^\alpha} | \psi_n \rangle \langle \psi_n | \frac{\partial H}{\partial R_J^\beta} | \psi_0 \rangle}{\epsilon_0 - \epsilon_n}, \quad (2.69)$$

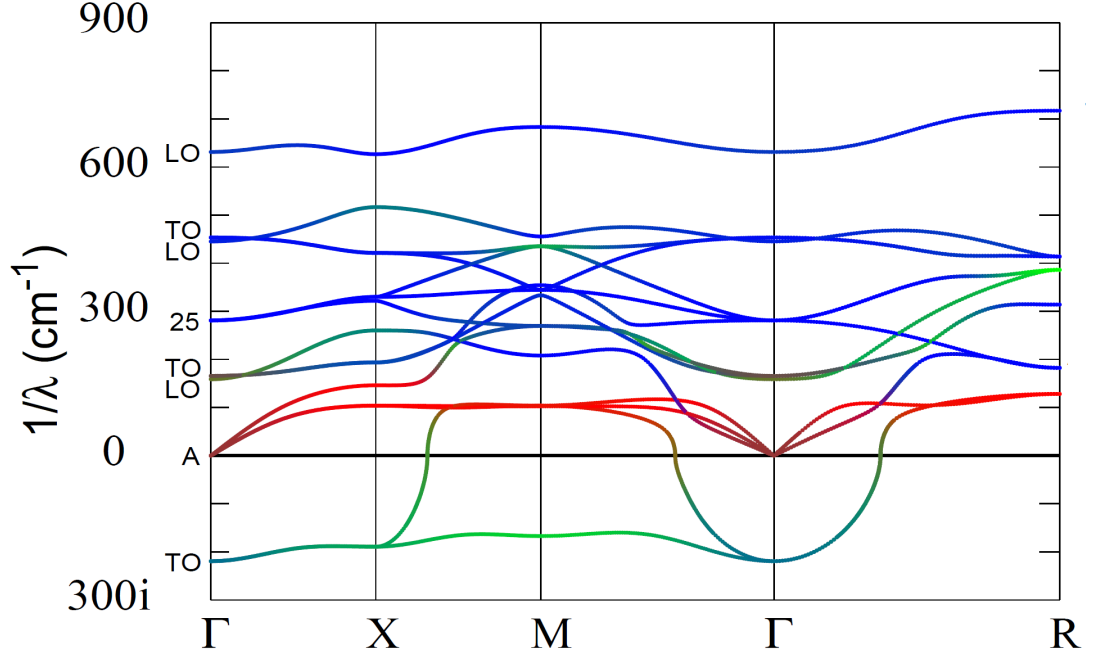


Figure 2.2: The phonon dispersion of BaTiO₃ from Ref (29). Imaginary frequency indicates the instability of the mode.

where $\{\psi_i\}$ are the states in the unperturbed system. In DFPT, the calculation of the dynamical matrix can be performed for any $\mathbf{q}$ vector without introducing supercells.

The phonon dispersion calculations can reveal the instabilities in the high-symmetry structure. The unstable phonon modes have imaginary frequencies and lead to structures of lower symmetry. Fig. 2.2 shows the phonon dispersion of cubic BaTiO₃ structure. The unstable mode at Γ point indicates the polar instability in the cubic BaTiO₃ structure.

2.1.7 Electric polarization from first principles

In periodic solids, the classical definition of electric dipole moment $p = \int e n(\mathbf{r}) d\mathbf{r}$ is not appropriate to calculate the polarization as the electric dipole moment of the unite cell, because the value of the integral depends on the choice of the unit cell. We use the Berry-phase method to calculate electric polarization from first principles. For more details, please refer to Ref. (30; 31; 32).

With the electric polarization calculated from first principles, we can calculate the Born effective charge Z_{ij}^* for each atom as

$$Z_{ij}^* = \frac{\Omega}{e} \frac{\delta P_i}{\delta u_j}, \quad (2.70)$$

where Ω is the volume of the unit cell, e is the charge of the electron, P_i is the polarization in i -direction and u_j is the displacement in j -direction.

2.1.8 Static dielectric response from first principles

With the modern theory of polarization, the static dielectric response

$$\varepsilon_{ij} = \varepsilon_0 \delta_{ij} + \frac{dP_i}{dE_j}, \quad (2.71)$$

can be calculated from first principles (33). In the Born-Oppenheimer approximation the macroscopic polarization $\mathbf{P}$ can be expressed as

$$P_i = P_i^0 + P_i^{\text{lat}} + P_i^{\text{E}}, \quad (2.72)$$

where P_i^0 is the spontaneous polarization of Equilibrium structure in zero field, P_i^{lat} is the polarization induced by lattice response and P_i^{E} is the electronic screening polarization. With this relation, the static dielectric constant can be calculated as

$$\varepsilon_{ij} = \varepsilon_0 \delta_{ij} + \varepsilon^\infty + \frac{\partial P_i^{\text{lat}}}{\partial E_j}, \quad (2.73)$$

where $\varepsilon^\infty = \frac{\partial P_i^{\text{E}}}{\partial E_j}$ is the electronic component of the dielectric tensor. The contribution of lattice response is calculated as

$$\frac{\partial P_i^{\text{lat}}}{\partial E_j} = \sum_{\omega_\mu^2 \neq 0} \frac{\overline{Z}_{\mu i}^* \overline{Z}_{\mu j}^*}{V \varepsilon_0 m_0 \omega_\mu^2} + \sum_{kl} V^{-1} \frac{\partial P_i}{\partial \eta_k} (C^{-1})_{kl} \frac{\partial P_j}{\partial \eta_l}. \quad (2.74)$$

The first term describes the phonon contribution to the dielectric tensor. The summation is over all of the optical phonons ω_μ and the mode effective charge $\overline{Z}_{\mu i}^*$ is defined as

$$\overline{Z}_{\mu i}^* = \sum_{nk} Z_{nik}^* (m_0/m_n)^{\frac{1}{2}} (u_\mu)_{nk}, \quad (2.75)$$

where Z_{nik}^* is the Born effective charge component of n th atom, m_n is its mass and $(u_\mu)_{nk}$ is the displacement of n th atom in k -direction. The second term includes the effect of changes in the lattice on the dielectric response, where C is the elastic tensor

$$C_{ij} = -\frac{\partial^2 E}{\partial \eta_i \partial \eta_j}. \quad (2.76)$$

2.1.9 Piezoelectric response from first principles

In 1880 (34), Pierre and Jacques Curie published their observation of the accumulated surface charges on a set of crystals when they were mechanically stressed. This phenomenon was later termed as piezoelectricity. Later the converse effect was mathematically predicted from fundamental laws of thermodynamics (35). The piezoelectric coefficients are defined as

$$d_{ij} = \left(\frac{\partial P_i}{\partial \sigma_j} \right)_E = \left(\frac{\partial \eta_j}{\partial E_i} \right)_\sigma, \quad (2.77)$$

where P is the electric polarization, σ is the stress, E is the electric field and η is the elastic strain. In first-principles calculations, d_{33} was computed from the expression

$$d_{33} = \frac{dP(\eta_{33})/d\eta_{33}}{d\sigma_{33}/d\eta_{33}} \quad (2.78)$$

where $d\sigma_{33} = -dE_{tot}(\eta_{33})/d\eta_{33}$ is the relevant stress, E_{tot} is the energy per volume and all derivatives are computed with electric field held to zero. The derivatives are computed by choosing five or more values of c near the optimized value, obtaining

the total energy and polarization for c constrained to each of these values, and fitting $E_{tot}(\eta_{33})$ and $P(\eta_{33})$ to quadratic and linear order polynomials, respectively; the minimizing value of η_{33} and the derivatives are computed from the fits.

2.1.10 Discussion of accuracy

As previously discussed, the accuracy of the computation of lattice constants depends on the choice of approximation for the exchange-correlation functional. Experience shows that these are usually about 1% too small compared with experimental values for LDA and about 1% too large for GGA. The errors of calculated phonon frequencies and the related response functions, such as piezoelectricity, are typically within 10% of experimental values. Because density functional theory is strictly applicable only to the properties of the ground state, calculations of excited state properties, such as band gap, from the Kohn-Sham band structure are not generally accurate. The deficits and effect of temperature can also lead to discrepancy between the DFT calculations and the experiment.

2.2 Polynomial expansions of the energy

Density functional theory has been proved to be extremely useful in the investigation of functional materials, giving detailed information about atomic arrangements and the atomic-scale origin of macroscopic properties such as the dielectric and piezoelectric responses. For the physical interpretation of the wealth of information available from a first-principles study, it can be very useful to focus on one or a few important degrees of freedom and develop a simple model for the structural energetics.

For the functional perovskite materials considered in this thesis, the important degrees of freedom are the lattice modes described in Chapter 2. A model of the structural energetics can be obtained by expanding the energy as a function of these modes around the cubic perovskite structure as a reference structure. The allowed

terms are constrained by symmetry considerations, following the prescriptions of the analogous expansions of free energy in Landau theory in terms of order parameters defined through symmetry analysis.

There are four parts in the following part. First, I will briefly explain the most essential aspects of the theory of finite groups; a fuller description of group theory can be found in Ref (36). The second part is the mode description of crystal structures. Then I will discuss the construction of the polynomial expansion of the energy following the procedures of Landau theory. The last part is how to determine the coefficients in the energy polynomial expansions from first-principles calculations.

2.2.1 Introduction to group theory

Basic concepts of group theory

In mathematics, an abstract group G is a collection of elements $A, B, C, \dots$ and a binary operation AB , which satisfy the following four conditions:

1. The group is closed, i.e., if $A, B \in G$ then $AB \in G$
2. The associative law is valid, i.e., $(AB)C = A(BC)$.
3. There is an identity element E , so that, for $\forall A \in G$, $AE = EA = A$.
4. For $\forall A \in G$ there exists an inverse element A^{-1} so that $AA^{-1} = A^{-1}A = E$.

The number of elements in the group is called the order of the group. In a group with a finite order, the identity E can be obtained by multiplying an arbitrary element X by itself enough times, $X^n = E$. The number n is called the order of the element X .

A subgroup is a collection of elements within a group that by themselves form a group.

The conjugation of element A is defined as $B = XAX^{-1}$, where X is an arbitrary element of the group. Conjugation is a transitive relation, since if $B = XAX^{-1}$

	E	C_2^1	C_2^2	C_2^3	C_3^1	C_3^2
E	E	C_2^1	C_2^2	C_2^3	C_3^1	C_3^2
C_2^1	C_2^1	E	C_3^1	C_3^2	C_2^2	C_2^3
C_2^2	C_2^2	C_3^2	E	C_3^1	C_2^3	C_2^1
C_2^3	C_2^3	C_3^3	C_3^1	E	C_2^1	C_2^2
C_3^1	C_3^1	C_2^3	C_2^1	C_2^2	C_3^2	E
C_3^2	C_3^2	C_2^1	C_2^2	C_2^3	E	C_3^1

Table 2.1: Multiplication table for the point symmetry operations of an equilateral triangle

and $C = YAY^{-1}$, then $B = (XY^{-1})C(XY^{-1})^{-1}$. A class is defined as the totality of elements which can be obtained from a given group element by conjugation. The elements of the same class are of the same order, because if $B = XAX^{-1}$ and $A^n = E$, then $B^n = (XAX^{-1})^n = XAX^{-1} \dots XAX^{-1} = XA^nX^{-1} = E$.

The elements of a point group are point symmetry operations $\{R\}$, such as rotations and reflections, which transform the system into an equivalent state. Fig. 2.2.1 shows an equilateral triangle, which has six point symmetry operations: one identity element (E), the rotations by $\pm 2\pi/3$ about the origin (C_3^1, C_3^2) and the rotations by π about the three twofold axes (C_2^1, C_2^2, C_2^3). The multiplication Table (2.2.1) shows the product of each pair of the six symmetry operations. It is obvious that the four conditions of the abstract group are satisfied and the six point symmetry operations form a 2- D point group. The point group of an equilateral triangle has three classes:

1. E ;
2. C_2^1, C_2^2, C_2^3 ;
3. C_3^1, C_3^2 .

It is easy to show that the symmetry operations of the same class have the same order.

In principle, there are continuous point groups in two or three dimensional space. However, the crystallographic restriction theorem limits the rotational symmetries

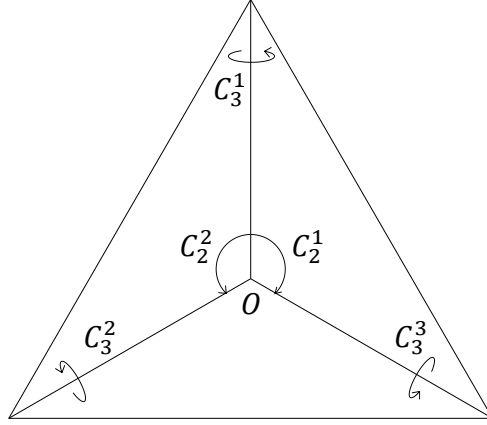


Figure 2.3: The symmetry operations of a equilateral triangle

of a crystal to only 2-fold, 3-fold, 4-fold, and 6-fold. Therefore there are only 10 two-dimensional and 32 three-dimensional crystallographic point groups.

The symmetry group of the crystal lattice is called a space group, and consists of both translational symmetry operations and point group operations. A space group operation is denoted as

$$\{R_{\alpha}|\tau\}, \quad (2.79)$$

where R_{α} denotes point group operations and τ denotes translation operations. There are three special types of space group operations: identity, pure point group operations and pure translations, which are denoted as $\{\varepsilon|0\}$, $\{R_{\alpha}|0\}$ and $\{\varepsilon|\tau\}$, respectively. In the space group G , all of the elements of the form $\{\varepsilon|\tau\}$ form the translation group T . The translation group T defines the Bravais lattice of the crystal. For the three-dimensional crystal structures, there are in total 14 possible Bravais lattices, which are obtained by combining one of the 7 lattice systems with one of the lattice centerings. By replacing the different atomic structures in the Bravais lattice sites, a total of 230 space groups, 73 symmorphic and 157 nonsymmorphic, can be formed. If all of the symmetry operations in a space group can be expressed as of the form

$\{R_\alpha|\tau\} = \{\varepsilon|R_n\}\{R_\alpha|0\}$, where R_α denotes the translation vector of the Bravais lattice, by selecting the correct origin, then the space group G is called a symmorphic group. Otherwise, G is called a nonsymmorphic group. In the symmorphic group, the entire point group is a subgroup of the space group, while in the nonsymmorphic group, the point group is not a subgroup.

Representation theory

Representation theory is essential for developing the group theoretical framework for the applications of group theory to solid state physics. A representation of an abstract group is a matrix group with square matrices, whose elements have a one-to-one correspondence to the elements of the abstract group. The assigned matrices follow the multiplication relation of the original abstract group. We denote $D(A)$ as the corresponding matrix for the element A . Then we should have $D(A)D(B) = D(AB)$. The following is a representation $\Gamma_R(A)$ of each element A in the point group of the previously discussed equilateral triangle.

$$\begin{array}{ccc}
 E & C_3^1 & C_3^2 \\
 \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} & \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ 0 & 0 & -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} & \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ 0 & 0 & \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} \\
 C_2^1 & C_2^2 & C_2^3 \\
 \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} & \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & \frac{1}{2} & -\frac{\sqrt{3}}{2} \\ 0 & 0 & -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} & \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & \frac{1}{2} & \frac{\sqrt{3}}{2} \\ 0 & 0 & \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}
 \end{array} \tag{2.80}$$

It is easy to prove that the above representations with matrices follow the multiplication relation in the Table 2.2.1. We can also see that all of the representation matrices

$\Gamma_R(A)$ are block matrices of the form

$$\begin{pmatrix} \Gamma_1 & 0 & 0 \\ 0 & \Gamma_{1'} & 0 \\ 0 & 0 & \Gamma_2 \end{pmatrix} \quad (2.81)$$

. where Γ_1 and $\Gamma_{1'}$ are 1×1 matrices and Γ_2 is a 2×2 matrix. If the representation matrices for all elements in the group can be brought into the same block form by similarity transformation,

$$\hat{\Gamma}_R = U^{-1} \Gamma_R U, \quad (2.82)$$

the representation is called reducible representations. Each block corresponds to an irreducible representation (irrep) of the point group. The representation (2.80) is a reducible representation containing three irreps, which is denoted as:

$$\Gamma_R = \Gamma_1 + \Gamma_{1'} + \Gamma_2. \quad (2.83)$$

The irreps, $\Gamma_n(A)$, for each element A in the point group of Equilateral triangle are as follows:

$$\begin{array}{lll}
 & E & C_3^1 & C_3^2 \\
 \Gamma_1: & \begin{pmatrix} 1 \end{pmatrix} & \begin{pmatrix} 1 \end{pmatrix} & \begin{pmatrix} 1 \end{pmatrix} \\
 \Gamma_{1'}: & \begin{pmatrix} 1 \end{pmatrix} & \begin{pmatrix} 1 \end{pmatrix} & \begin{pmatrix} 1 \end{pmatrix} \\
 \Gamma_2: & \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} & \begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} & \begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} \\
 & C_2^1 & C_2^2 & C_2^3 \\
 \Gamma_1: & \begin{pmatrix} 1 \end{pmatrix} & \begin{pmatrix} 1 \end{pmatrix} & \begin{pmatrix} 1 \end{pmatrix} \\
 \Gamma_{1'}: & \begin{pmatrix} -1 \end{pmatrix} & \begin{pmatrix} -1 \end{pmatrix} & \begin{pmatrix} -1 \end{pmatrix} \\
 \Gamma_2: & \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix} & \begin{pmatrix} \frac{1}{2} & -\frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} & \begin{pmatrix} \frac{1}{2} & \frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}
 \end{array} \tag{2.84}$$

It can be shown that every representation with matrices with nonzero determinants can be brought into unitary form,

$$\Gamma_n^{-1}(A) = \Gamma_n^\dagger(A), \tag{2.85}$$

by a similarity transformation (36).

Now I will introduce the orthogonality theorem, or “Wonderful Orthogonality Theorem,” which is essential to the application of the group theory to solid state physics. All of the inequivalent irreps of a group obey the orthogonality relation

$$\sum_R \Gamma_n(R)_{\mu\nu} \Gamma_{n'}(R^{-1})_{\nu'\mu'} = \frac{h}{l_n} \delta_{nn'} \delta_{\mu\mu'} \delta_{\nu\nu'}, \tag{2.86}$$

where the summation is over all h group elements $A_1, A_2, \dots, A_h$ and l_n and $l_{n'}$ are the dimensionalities of representations Γ_n and $\Gamma_{n'}$. If the irreps are of unitary form,

the orthogonality relation becomes

$$\sum_R \Gamma_n(R)_{\mu\nu} \Gamma_{n'}^*(R)_{\mu'\nu'} = \frac{h}{l_n} \delta_{nn'} \delta_{\mu\mu'} \delta_{\nu\nu'}. \quad (2.87)$$

For the proof of the orthogonality relation, please refer to Ref (36).

Character of a representation

The character of the matrix representation $\chi^{\Gamma_n}(R)$ for a symmetry operation R is the trace of the matrix representation $\Gamma_n(R)$:

$$\chi^{\Gamma_n}(R) = \sum_{\mu=1}^{l_n} \Gamma_n(R)_{\mu\mu}, \quad (2.88)$$

where l_n is the dimensionality of the irrep Γ_n . The character of the representation has an important property: the representation matrices for the elements in the same class have the same character. Because all elements in the same class can be brought to each other through similarity transformation,

$$A = U^{-1}BU, \quad (2.89)$$

a similarity transformation does not change the trace of the representation matrices.

There is also a Wonderful Orthogonality Theorem for the character,

$$\sum_R \chi^{\Gamma_n}(R) \chi^{\Gamma_{n'}}(R^{-1}) = h \delta_{\Gamma_n \Gamma_{n'}}, \quad (2.90)$$

which for the unitary representations becomes

$$\sum_R \chi^{\Gamma_n}(R) \chi^{\Gamma_{n'}}(R)^* = h \delta_{\Gamma_n \Gamma_{n'}}. \quad (2.91)$$

Thus can be easily proved by summation of the Wonderful Orthogonality Theorem

(2.86) and (2.87) over the diagonal elements. Since the elements of the same class have the same character, the Wonderful Orthogonality Theorem for character can be expressed as

$$\sum_k N_k \chi^{\Gamma_n}(\mathcal{C}_k) \chi^{\Gamma_{n'}}(\mathcal{C}_k)^* = h \delta_{\Gamma_n \Gamma_{n'}}, \quad (2.92)$$

where $\mathcal{C}_k$ denotes a class with index k and N_k is the order of the class. The Wonderful Orthogonality Theorem for character indicates that the character vector, $\{\chi^{\Gamma_n}(\mathcal{C}_k)\}$, is unique for each irrep Γ_n , because if two inequivalent irreps had the same character, the vectors could not be orthogonal and the Wonderful Orthogonality Theorem for character would be violated. Moreover, there is a second orthogonality relation for character:

$$\sum_{\Gamma_n} N_k \chi^{\Gamma_n}(\mathcal{C}_k) \chi^{\Gamma_{n'}}(\mathcal{C}_{k'})^* = h \delta_{kk'}. \quad (2.93)$$

The two orthogonality relations (2.92) and (2.93) provide an efficient way to determine whether a representation is reducible. The characters of a reducible representation will generally violate the two orthogonality relations.

The characters of representations encode many important properties of both classes and irreps and greatly help the study of structures. The property of a group can be summarized in a compact form as a character table, a two-dimensional table whose rows correspond to the irreps and whose columns correspond to the classes of group elements. Table 2.2.1 shows the character table for the previous example of Equilateral triangle. The character table is a useful tool for the classification of finite groups.

	E	$3C_2$	$2C_3$
Γ_1	1	1	1
$\Gamma_{1'}$	1	-1	1
Γ_2	2	0	-1

Table 2.2: The character table of the point group of an equilateral triangle.

Basis functions

For a group G with symmetry elements R and symmetry operator $\hat{P}_R$, we can define a set of basis functions $|\Gamma_n \alpha\rangle$ with index α for each irrep Γ_n . The symmetry operator $\hat{P}_R$ and its matrix representation $\Gamma_n(R)$ are related through the relation

$$\hat{P}_R |\Gamma_n \alpha\rangle = \sum_j \Gamma_n(R)_{j\alpha} |\Gamma_n j\rangle. \quad (2.94)$$

The basis functions should obey the orthonormality relation

$$\langle \Gamma_n i | \Gamma_{n'} j \rangle = \delta_{nn'} \delta_{ij}. \quad (2.95)$$

The orthonormality relation (2.95) provides a way to construct the representation matrix by using the basis functions and symmetry operator:

$$\Gamma_n(R)_{j\alpha} = \langle \Gamma_n j | \hat{P}_R | \Gamma_n \alpha \rangle. \quad (2.96)$$

We can also define a projection operator $\hat{P}_{kl}^{(\Gamma_n)}$, which transform a basis function $|\Gamma_n l\rangle$ to another basis function $|\Gamma_n k\rangle$ with the same representation Γ_n :

$$\hat{P}_{kl}^{(\Gamma_n)} |\Gamma_n l\rangle \equiv |\Gamma_n k\rangle. \quad (2.97)$$

The projection operator $\hat{P}_{kl}^{(\Gamma_n)}$ can be expanded in terms of the symmetry operators

$\hat{P}_R$:

$$\hat{P}_{kl}^{(\Gamma_n)} = \sum_R A_{kl}^{(\Gamma_n)}(R) \hat{P}_R. \quad (2.98)$$

Plugging Eq.(2.94) and (2.98) into the definition of the projection operator (2.97), we have

$$\sum_{R,j} A_{kl}^{(\Gamma_n)}(R) \Gamma_n(R)_{jl} |\Gamma_n j\rangle = |\Gamma_n k\rangle. \quad (2.99)$$

According to the orthonormality relation (2.95) between the basis functions, we can derive that

$$\sum_R A_{kl}^{(\Gamma_n)}(R) \Gamma_n(R)_{jl} = \delta_{jk}. \quad (2.100)$$

Comparing with the Wonderful Orthogonality Theorem (2.87), we can get the expression of the coefficient $A_{kl}^{(\Gamma_n)}(R)$,

$$A_{kl}^{(\Gamma_n)}(R) = \frac{l_n}{h} \Gamma_n(R)_{kl}^*. \quad (2.101)$$

Then we have the explicit form of the projection operator, which is

$$\hat{P}_{kl}^{(\Gamma_n)} = \frac{l_n}{h} \sum_R \Gamma_n(R)_{kl}^* \hat{P}_R. \quad (2.102)$$

The special case $\hat{P}_{kk}^{(\Gamma_n)}$ only contains the diagonal elements of the representation matrix,

$$\hat{P}_{kk}^{(\Gamma_n)} = \frac{l_n}{h} \sum_R \Gamma_n(R)_{kk}^* \hat{P}_R. \quad (2.103)$$

Utilizing the special projection operator $\hat{P}_{kk}^{(\Gamma_n)}$, we can construct another projection

operator $\hat{P}^{(\Gamma_n)}$, where

$$\begin{aligned}
 \hat{P}^{(\Gamma_n)} &= \sum_k \hat{P}_{kk}^{(\Gamma_n)} \\
 &= \frac{l_n}{h} \sum_{k,R} \Gamma_n(R)_{kk}^* \hat{P}_R \\
 &= \frac{l_n}{h} \sum_R \chi^{(\Gamma_n)}(R)^* \hat{P}_R.
 \end{aligned} \tag{2.104}$$

For an arbitrary function F ,

$$F = \sum_{\Gamma_{n'}} \sum_{j'} f_{j'}^{(\Gamma_{n'})} |\Gamma_{n'} j'\rangle, \tag{2.105}$$

and the effect of application of projection operator $\hat{P}^{(\Gamma_n)}$ is

$$\begin{aligned}
 \hat{P}^{(\Gamma_n)} F &= \frac{l_n}{h} \sum_{k,R} \Gamma_n(R)_{kk}^* \sum_{\Gamma_{n'}} \sum_{j'} f_{j'}^{(\Gamma_{n'})} \hat{P}_R |\Gamma_{n'} j'\rangle \\
 &= \frac{l_n}{h} \sum_k \sum_{\Gamma_{n'}} \sum_j \sum_{j'} \sum_R f_{j'}^{(\Gamma_{n'})} \Gamma_n(R)_{jj'} \Gamma_{n'}(R)_{kk}^* |\Gamma_{n'} j'\rangle \\
 &= \sum_k \sum_{\Gamma_{n'}} \sum_j \sum_{j'} f_{j'}^{(\Gamma_{n'})} \delta_{\Gamma_n \Gamma_{n'}} \delta_{jk} \delta_{j'k} |\Gamma_{n'} j'\rangle \\
 &= \sum_k f_k^{(\Gamma_n)} |\Gamma_n j\rangle.
 \end{aligned} \tag{2.106}$$

We can see that the projection operator $\hat{P}^{(\Gamma_n)}$ projects out an arbitrary function F to a function transforming as Γ_n . In a later section, we will utilize this property to construct the invariant polynomial expansions.

Space groups in reciprocal space and representations

The previously discussed representation theory and projection operators are for general abstract groups. Therefore, they also apply to the space groups of crystals. In the following, I will discuss how to incorporate the point group symmetry and translational symmetry of the crystal lattice.

For lattice periodic system, it is convenient to study the properties of the materials in reciprocal space. Therefore it is natural to choose functions with wave vectors $\mathbf{k}$ as a set of basis functions. The symmetry properties at each $\mathbf{k}$ point is described by the group of wave vector $G_{\mathbf{k}}$. $G_{\mathbf{k}}$ is defined as the collection of all symmetry operations that bring the wave vector $\mathbf{k}$ into itself or an equivalent wave vector of the form

$$\mathbf{k}' = \mathbf{k} + \mathbf{K}_m, \quad (2.107)$$

where $\mathbf{K}_m$ is a reciprocal lattice vector satisfying

$$e^{i\mathbf{K}_m \cdot \mathbf{R}_n} = 1, \quad (2.108)$$

for all lattice vectors $\mathbf{R}_n$. Not all elements in the space group of the crystal lattice G are necessarily included in $G_{\mathbf{k}}$ when $\mathbf{k} \neq 0$. Therefore $G_{\mathbf{k}}$ might be the same as G or its subgroup.

Now let's consider a certain function $F_{\mathbf{k}}$ at wave vector $\mathbf{k}$. The symmetry operator $\hat{P}_{\{R|\tau\}}^{\mathbf{k}}$ corresponds to the symmetry operation $\{R|\tau\}$, which is in the group of wave vector $G_{\mathbf{k}}$. For the symmorphic group, the symmetry operation $\{R|\tau\}$ can be decomposed into a pure translational operation $\{\varepsilon|\mathbf{R}_n\}$ and a pure point group operation $\{R|0\}$. Therefore the effect of application of $\hat{P}_{\{R|\tau\}}^{\mathbf{k}}$ on $F_{\mathbf{k}}$ is as follows:

$$\hat{P}_{\{R|\tau\}}^{\mathbf{k}} F_{\mathbf{k}} = \hat{P}_{\{\varepsilon|\mathbf{R}_n\}}^{\mathbf{k}} \hat{P}_{\{R|0\}}^{\mathbf{k}} F_{\mathbf{k}}. \quad (2.109)$$

$\hat{P}_{\{R|0\}}^{\mathbf{k}} F_{\mathbf{k}}$ is also a function at wave vector $\mathbf{k}$. According to Bloch's theorem,

$$\hat{P}_{\{\varepsilon|\mathbf{R}_n\}}^{\mathbf{k}} \hat{P}_{\{R|0\}}^{\mathbf{k}} F_{\mathbf{k}} = e^{i\mathbf{k} \cdot \mathbf{R}_n} \hat{P}_{\{R|0\}}^{\mathbf{k}} F_{\mathbf{k}}. \quad (2.110)$$

Therefore, we have

$$\hat{P}_{\{R|\tau\}}^{\mathbf{k}} F_{\mathbf{k}} = e^{i\mathbf{k} \cdot \mathbf{R}_n} \hat{P}_{\{R|0\}}^{\mathbf{k}} F_{\mathbf{k}}. \quad (2.111)$$

The case of a nonsymmorphic group is more complicated. For detailed description, please refer to Ref (36).

2.2.2 Mode description of crystal structures

A crystal structure that is obtained by a continuous distortion of a higher symmetry structure can be described with reference to that structure by specifying the nonzero amplitudes of the modes that generate the deformation. For example, the tetragonal BaTiO₃ structure can be described by a single unique mode Γ_4^- and elastic strain η_3 . A mode amplitude of 1 a.u. corresponds to a displacement eigenvector with norm 1.00 Å. For example, the analysis of ISOTROPY shows that the bulk $Pbnm$ structure of CaTiO₃ consists of in-phase rotational mode M_3^+ , out-of-phase rotational mode R_4^+ , X_5^+ mode and R_5^+ mode. The first two modes are the primary order parameters of the phase transition from the cubic $Pm\bar{3}m$ to orthorhombic $Pbnm$ structure. The other two modes, which are stable in the ideal cubic structure, are induced by the combination of M_3^+ and R_4^+ breaking symmetry.

2.2.3 Symmetry analysis in Landau theory

Landau introduced a mean field method to estimate the free energy of the system and simulate the phase transition between the low and high symmetry states. In Landau theory, the free energy is approximately described by an analytic function in terms of order parameters, which describe the structural and physical properties of the system. Typically the Landau free energy is a polynomial expansion with terms respecting the symmetry of the order parameter. In the original Landau theory, the free energy was described by a fourth-order polynomial with a single order parameter, the primary order parameter, which breaks the symmetry and induces the phase transition:

$$F = F_0 + \alpha\psi^2 + \kappa\psi^4, \quad (2.112)$$

where the coefficients are functions of external constraints, such as temperature. This fourth-order energy expansion successfully captures the physics in some transitions, such as the appearance of the polarization P , the order parameter in para- and ferroelectric phase transition. In those systems, inversion of the primary order parameter: $\psi \rightarrow -\psi$, i.e., flipping of the polarization P , does not change the energy of the system. Therefore the symmetry of the order parameter only allow even order terms existing in the energy expansion. However, for some systems, other order parameters are necessary to appropriately describe the energy surface of the system, which leads to a more complicated Landau energy function. In the following part, I will explain how to construct the Landau energy function through symmetry analysis.

In all groups, there is a special irrep, Γ_1 , with character of 1 for all group elements. It means that the basic functions of irrep Γ_1 are invariant under all group elements. As a scalar quantity, the free energy of the system does not change under any symmetry operations. Therefore the free energy is a basic function that transforms as the irrep Γ_1 of the space group of crystal lattice. To construct an energy polynomial satisfying that symmetry requirement, we can apply the projection operator of irrep Γ_1 ,

$$\hat{P}^{(\Gamma_1)} = \frac{1}{h} \sum_{\{R|\mathbf{R}_n\}} P_{\{R|\mathbf{R}_n\}}, \quad (2.113)$$

to each term in the Taylor expansion of the free energy function. The projection operator $\hat{P}^{(\Gamma_1)}$ will project out each term to zero or a function transforming as irrep Γ_1 .

I will use the case of the orthorhombic perovskite CaTiO_3 to illustrate the process of energy function construction. The ground state of CaTiO_3 is of space group $Pbnm$, which is obtained by freezing the phonon modes R_4^+ (twofold, R_{4x}^+ and R_{4y}^+) and M_3^+ in the high-symmetry $Pm\bar{3}m$ structure. The coupling of the R_4^+ and M_3^+ modes also induces another mode X_5^+ (twofold, X_{5x}^+ and X_{5y}^+). R_4^+ , M_3^+ and X_5^+ are the three dominant distortion modes in the CaTiO_3 $Pbnm$ structure and we will construct the

energy function in terms of the three distortion modes. The three distortion modes are denoted according to their corresponding zone-boundary wave vectors $R(\frac{\pi}{a}, \frac{\pi}{a}, \frac{\pi}{a})$, $M(\frac{\pi}{a}, \frac{\pi}{a}, 0)$ and $X(0, 0, \frac{\pi}{a})$, where a is the lattice constant of cubic $Pm\bar{3}m$ unit cell. The symmetry of the three distortion modes are also the same as their corresponding wave vectors'. Because the space group $Pm\bar{3}m$ is a symmorphic group, the translational and point group operations commute with each other. The application of the space group symmetry operator on one distortion mode M , $M = R_{4x}, R_{4y}, M_3, X_{5x}, X_{5y}$, is given by

$$\begin{aligned} P_{\{R|\mathbf{R}_n\}}M &= P_{\{R|0\}}P_{\{\varepsilon|\mathbf{R}_n\}}M \\ &= e^{i\mathbf{k}_M \cdot \mathbf{R}_n} P_{\{R|0\}}M, \end{aligned} \quad (2.114)$$

where $\mathbf{R}_n$ is a lattice vector and R is the point group symmetry operation of the group $G_{\mathbf{k}_M}$. For an arbitrary term in the Taylor expansion of free energy function, $R_{4x}^{N_{Rx}} R_{4y}^{N_{Ry}} M_3^{N_M} X_{5x}^{N_{Xx}} X_{5y}^{N_{Xy}}$, the effect of the projection operator $\hat{P}^{(\Gamma_1)}$ is:

$$\begin{aligned} &\hat{P}^{(\Gamma_1)} R_{4x}^{N_{Rx}} R_{4y}^{N_{Ry}} M_3^{N_M} X_{5x}^{N_{Xx}} X_{5y}^{N_{Xy}} \\ &= \frac{1}{h} \sum_{\{R|\mathbf{R}_n\}} P_{\{R|\mathbf{R}_n\}} (R_{4x}^{N_{Rx}} R_{4y}^{N_{Ry}} M_3^{N_M} X_{5x}^{N_{Xx}} X_{5y}^{N_{Xy}}) \\ &= \frac{1}{h} \left(\sum_{\mathbf{R}_n} e^{[(N_{Rx}+N_{Ry})\mathbf{k}_R + N_M\mathbf{k}_M + (N_{Xx}+N_{Xy})\mathbf{k}_X] \cdot \mathbf{R}_n} \right) \\ &\quad \times \left(\sum_R P_{\{R|0\}} \left(R_{4x}^{N_{Rx}} R_{4y}^{N_{Ry}} M_3^{N_M} X_{5x}^{N_{Xx}} X_{5y}^{N_{Xy}} \right) \right), \end{aligned} \quad (2.115)$$

where h is the number of the symmetry operations, $h = N_{\mathbf{R}_n} \cdot N_R$ and R is chosen from the largest common subgroup of $G_{\mathbf{k}_R}$, $G_{\mathbf{k}_M}$ and $G_{\mathbf{k}_X}$. Eq.(2.115) is ill-defined, because a space group have infinite number of translational vector $\mathbf{R}_n$. However, only if the sum of wave vectors, $(N_{Rx} + N_{Ry})\mathbf{k}_R + N_M\mathbf{k}_M + (N_{Xx} + N_{Xy})\mathbf{k}_X$, equals to a certain reciprocal lattice vector K_m , the term in the first parenthesis is nonzero, otherwise the summation over $\mathbf{R}_n$ would cancel out. This symmetry requirement is

called translational invariance. The summation in the second parenthesis is nonzero only if the target function contains basis functions invariant under the point group symmetry operations. Replacing the summation over the infinite lattice vectors $\mathbf{R}_n$ with a delta function, Eq.(2.115) changes to the following form:

$$\begin{aligned} & \hat{P}^{(\Gamma_1)} R_{4x}^{N_{Rx}} R_{4y}^{N_{Ry}} M_3^{N_M} X_{5x}^{N_{Xx}} X_{5y}^{N_{Xy}} \\ &= \delta_{[(N_{Rx}+N_{Ry})\mathbf{k}_R+N_M\mathbf{k}_M+(N_{Xx}+N_{Xy})\mathbf{k}_X],\mathbf{K}_m} \\ & \times \frac{1}{N_R} \left(\sum_R P_{\{R|0\}} \left(R_{4x}^{N_{Rx}} R_{4y}^{N_{Ry}} M_3^{N_M} X_{5x}^{N_{Xx}} X_{5y}^{N_{Xy}} \right) \right). \end{aligned} \quad (2.116)$$

Now I will use Eq.(2.115) to check the symmetry of some terms in the energy expansion. First, let's look at the coupling term $R_{4x}R_{4y}$. The sum of the wave vectors $(1+1)\mathbf{k}_R = (\frac{2\pi}{a}, \frac{2\pi}{a}, \frac{2\pi}{a})$ is a reciprocal lattice vector. Therefore the translational invariance is satisfied. Since both of the two modes are of point group O_h , the point group of this term is also O_h . According to the Table A.1 in Appendix A, we have

$$\hat{P}^{(\Gamma_1)} R_{4x} R_{4y} = 0. \quad (2.117)$$

Therefore, the term $R_{4x}R_{4y}$ contains no component transforming irrep Γ_1 . Then let's try the coupling term $R_{4x}MX_{5x}$. Again the translational invariance is satisfied, since the sum of wave vectors, $\mathbf{k}_R + \mathbf{k}_M + \mathbf{k}_X = (\frac{4\pi}{a}, \frac{4\pi}{a}, \frac{4\pi}{a})$, is also a reciprocal lattice vector. The point group of this term is D_{4h} , because $M_3^+ X_5^+$ are of point group D_{4h} . According to the Table A.2 in Appendix A, we have

$$\hat{P}^{(\Gamma_1)} R_{4x} M X_{5x} = \frac{1}{2} (R_{4x} M X_{5x} + R_{4y} M X_{5y}). \quad (2.118)$$

Therefore the term $R_{4x}MX_{5x} + R_{4y}MX_{5y}$ is an invariant term under all symmetry operations and is a valid term in the Landau free energy expansion.

2.2.4 First principles computation of coefficients in energy expansion

Previous work (37; 38; 39) can be used as the starting point for the construction of an effective Hamiltonian for nonzero T simulation. To determine the coefficients in the energy polynomial, we freeze in one or more modes in the high symmetry structure with other modes set as zero or minimized over, which depends on the project. The amplitudes of the frozen-in distortion modes are varied and the coefficients are fitted to the total energy calculated from first principles.

Chapter 3

First-principles study of epitaxially strained CaTiO_3

3.1 Introduction

As described in the Introduction, the equilibrium bulk structure of CaTiO_3 is a nonpolar orthorhombic Pbnm structure, generated by strongly unstable oxygen octahedron rotations. The first principles phonon dispersion for CaTiO_3 in the cubic perovskite structure (Fig. 3.1) includes not only the unstable oxygen octahedron modes R_4^+ and M_3^+ that generate the nonpolar bulk orthorhombic structure, but also a unstable polar mode. The fact that the polar mode is not present in the bulk structure can be understood as the result of the competition between oxygen octahedron modes and polar modes, which has been discussed in a number of perovskite systems (40). In CaTiO_3 , the oxygen octahedron instabilities are strong enough to eliminate the polar instability completely in the bulk phase.

One way to enhance the strength of the polar instability is through the polarization-strain coupling discussed in the Introduction. Indeed, elastic strains have been an extremely powerful means of stabilizing electric polarization of perovskite oxides (41), one example being the epitaxial-strain induced ferroelectricity in SrTiO_3 (42; 43). Furthermore, elastic strains also have a significant effect on the rotational modes, and thus indirectly influence the competition between the rotational and polar modes, hence changing the stability of the polar modes. Strain-induced ferroelectric phases were reported in the first-principles study of epitaxially-strained bulk CaTiO_3 (44).

Above approximately 1.5% tensile strain, four competing ferroelectric phases exhibiting in-plane polarizations with different orientations were observed, with the $Pmn2_1$ structure having the lowest total energy among the four polar structures over the range of strain considered. First-principles calculations were also performed up to 2% compressive strain; however, no polar structures were stabilized in that range of epitaxial strain.

In this chapter, I report calculations that extend the previously considered range of strain to higher values of compressive strain (6%). My structure search included all structures derived from the Pbnm bulk phase. The polar instability was revealed by frozen-phonon calculations. Previously unreported polar phases at compressive strain were discovered and characterized. Next, I discuss the construction of a model that reproduces the epitaxial strain dependence of the distortions in the epitaxial phases derived from the bulk orthorhombic Pbnm structure, with the focus on the coupling and competition between the oxygen octahedron rotation distortions and the polarization. The large amplitude of the distortions in the structures presents a substantial challenge to modeling with a polynomial form, which I address below. In the last part of the chapter, I focus on a distinct metastable ferroelectric epitaxial phase identified in the first principles calculations in the compressive strain regime. In most perovskites, compressive strain favors a polarization along the normal (the long direction for the tetragonal unit cell). The phase I discuss has, surprisingly, a polarization in the epitaxial plane. A model for the structural energetics of this phase shows it is a geometric ferroelectric driven by a previously unrecognized mechanism.

3.2 First principles computational details

In this study, the first-principles calculations were performed using density functional theory within the local density approximation as implemented in VASP 5.2 (46; 47). We used the Ceperley and Alder functional (48), with projector-augmented wave

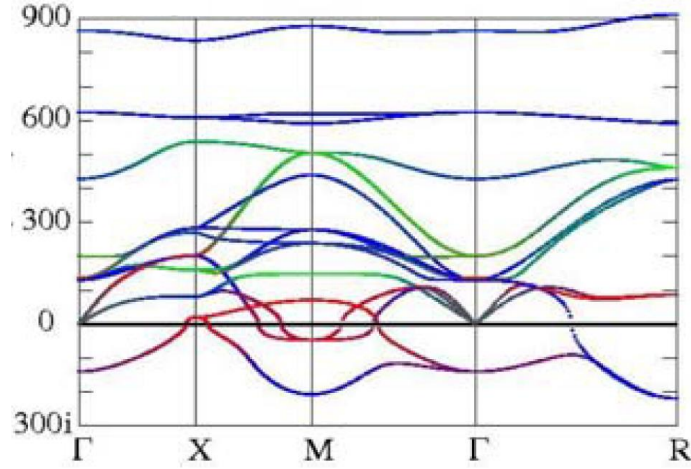


Figure 3.1: Phonon dispersion for CaTiO_3 in the ideal cubic perovskite structure from Ref. (45).

potentials (20; 21). We considered 3p and 4s as valence states to build the Ca pseudopotential, 3p, 3d and 4s valence states for the Ti pseudopotential and 2p valence states for the O pseudopotential. A plane-wave energy cut-off of 680 eV was used. The Brillouin zone of the twenty-atom unit cell was sampled by a $8 \times 8 \times 6$ Monkhorst-Pack k -point mesh (25). The electric polarization is computed using the Berry-phase method (30) with a $8 \times 8 \times 6$ Monkhorst-Pack k -point mesh.

3.2.1 Structural optimizations and epitaxially strained calculations

To investigate the effect of epitaxial strain, we performed “strained bulk” calculations matched to a square lattice substrate. The zero-strain lattice constant is taken as $a_0 = 3.77\text{\AA}$, the cube root of the volume per formula unit of the relaxed $Pbnm$ structure. As shown in Fig. 3.2, there are two ways to fit the $Pbnm$ structure to the matching plane, which lead to two different epitaxially strained structures, c - $ePbnm$ and ab - $ePbnm$ (44), respectively. In c - $ePbnm$, the $Pbnm$ space group is retained, while in ab - $ePbnm$, the symmetry is lowered to $P2_1/m$. In the structural optimization, both the lattice and internal structural parameters were relaxed until forces on atoms were less than $1\text{ meV/\AA}$. For all of the relaxed non-polar structures,

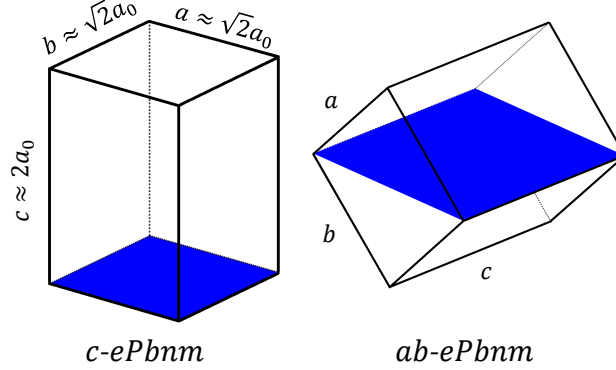


Figure 3.2: The two ways to fit the $Pbnm$ structure of CaTiO_3 to a square (001) substrate. The shaded plane represents the matching plane.

frozen phonon calculations were carried out to determine the stability against zone-center modes. In the frozen phonon calculations, the force constant matrices were calculated by displacing each atom by $0.01 \text{ \AA}$. The eigenvector and the frequencies of the zone-center modes were computed via the diagonalization of the force constant matrices and a imaginary frequency indicates the instability of the corresponding phonon mode. Unstable zone center modes were frozen in and the resulting structures relaxed to obtain the observed polar phases.

3.3 First-principles results

3.3.1 First principles results

The energies of various structures are plotted as a function of epitaxial strain in Fig. 3.3. Consistent with previous investigations of the strain range from -2 to 4% (44), the two non-polar structures show different trends with epitaxial strain, with an orientational phase transition point at approximately +1.5%. Above +1.5 % tensile strain, the frozen phonon calculations reveal four unstable polar modes, two for each orientational structure, which lead to four polar structures with in-plane polarization:

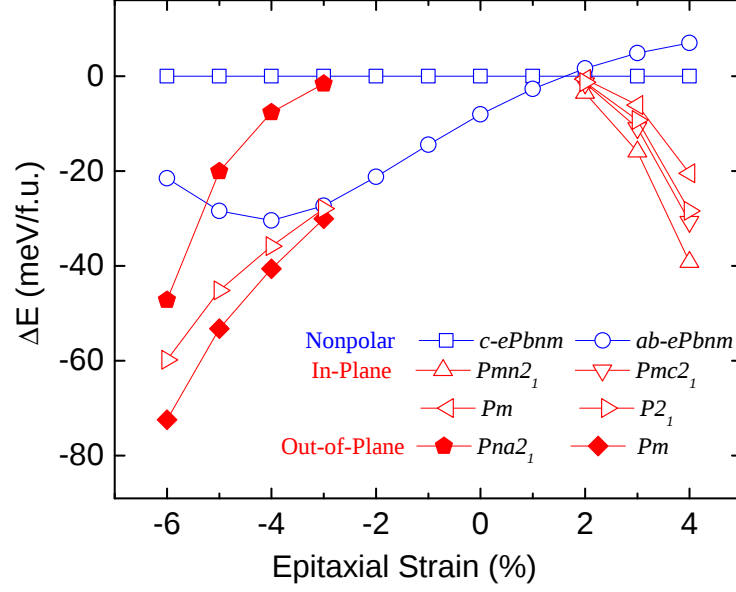


Figure 3.3: Total energy per formula unit from first principles for various epitaxially constrained structures as a function of square misfit strain. At each strain, the energy of the *c-ePbnm* structure is taken as the zero of energy.

*Pmn*₂₁ ([100]) and *Pmc*₂₁ ([010]) in *c-ePbnm* (matching plane (001)) and *P2*₁ ([001]) and *Pm* ($\bar{1}10$) in *ab-ePbnm* (matching plane (110)). Of the four polar structures, the *Pmn*₂₁ structure is the lowest in energy, which is consistent with previous work.

By extending the range of compressive strain considered to 6%, polar instabilities are also observed in the frozen phonon calculations of corresponding strained CaTiO₃. In the compressively strained *c-ePbnm* structure, there is one polar instability, which leads to the polar structure *Pna*₁, while in the *ab-ePbnm* structure, two polar instabilities are observed, which generate two distinct polar structures: *Pm* and *P2*₁. In both the *Pm*([110]) and *Pna*₂₁([001]) phases, the direction of the polarization is out of the matching plane, consistent with the fact that polarization-strain coupling generally favors polarization along the elongation direction of the unit cell. In contrast, in the *P2*₁([001]) phase the polarization is one order smaller than that in other structures, as shown in Fig. 3.4, and unexpectedly lies in plane. This suggests that the ferroelectricity of the *P2*₁ phases is driven by a different mechanism, which will

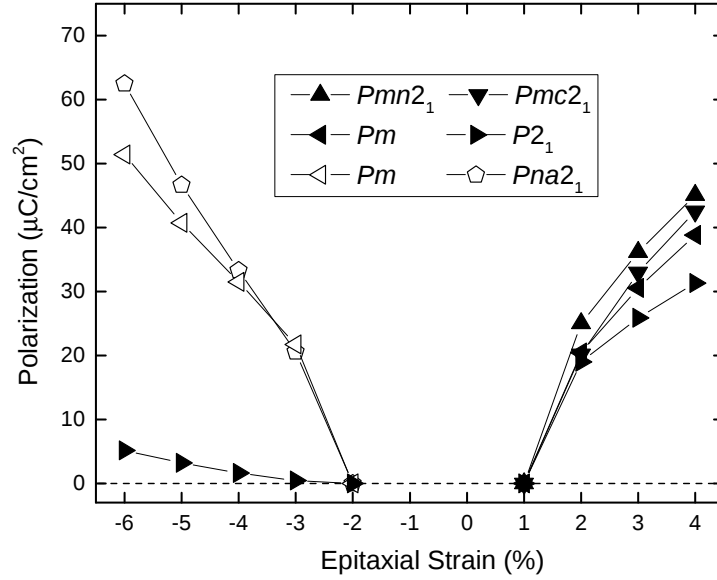


Figure 3.4: First-principles calculated polarization in various polar structures.

be discussed further below.

We performed mode decomposition for the various computed structures at compressive strain using ISOTROPY (49). Fig. 3.5 shows that the dominant distortion modes in both the c - $Pbnm$ ($Pbnm$) and ab - $Pbnm$ ($P2_1/m$) structures are R_4^+ , M_3^+ and X_5^+ (Fig. 3.6), the same modes that dominate the bulk $Pbnm$ structure. While many of the mode amplitudes vary relatively little with epitaxial strain, a few modes show strong strain dependence, which will be discussed further below. In the polar structures, besides the zone-center mode Γ_{4z}^- , which produces the polarization, many other nonpolar modes are also introduced by the symmetry lowering, but most of their amplitudes are very small. Table 3.1 shows the dominant modes in the mode decomposition of various structures at 5% compressive strain. The Pm phase has a large amplitude for the polar mode Γ_{4xy}^- , as expected for a proper ferroelectric. In contrast, in $P2_1$, the largest additional mode amplitude is not Γ_{4z}^- , but X_5^- , the alternating displacements of Ti and O atoms, and the amplitude of Γ_{4z}^- is much smaller than that in other polar phases. Moreover, the eigenvector of Γ_{4z}^- in $P2_1$ is quite different from

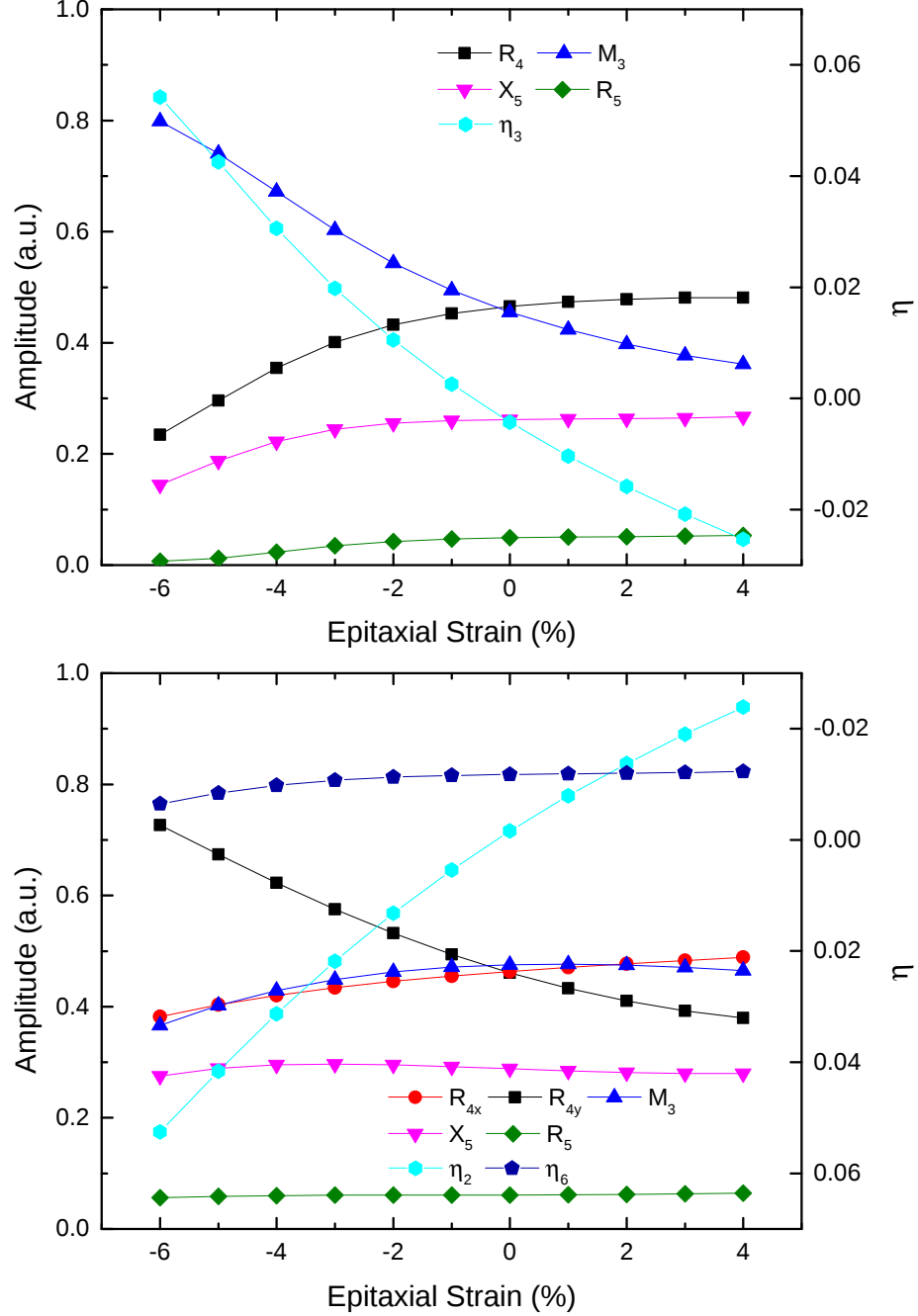


Figure 3.5: Mode decomposition of nonpolar CaTiO_3 structure. Top: mode decomposition of $c\text{-}ePbnm$. Bottom: mode decomposition of $ab\text{-}ePbnm$. 1 a.u. of distortion mode is defined as that the norm of the corresponding displacement eigenvector is 1.00 Å. All of the superscripts of the distortion modes are omitted. In $c\text{-}ePbnm$, symmetry requires that $R_{4x}^+ = R_{4y}^+ = R_4$. In $ab\text{-}ePbnm$, the space group is lowered from orthorhombic to monoclinic. Therefore, shearing strain component η_6 should be considered.

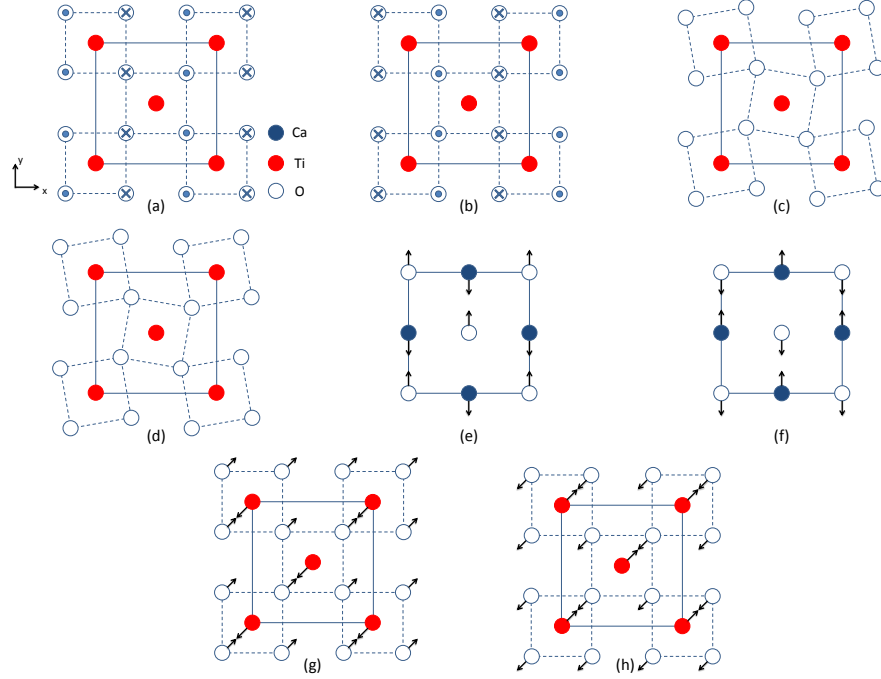


Figure 3.6: Schemes of distortion modes. (a), (b) R_4^+ mode in Ti-O layers at $z = 0.0$ and $0.5c$. (c), (d) M_3^+ mode in Ti-O layers at $z = 0.0$ and $0.5c$. (e), (f) X_5^+ mode in Ca-O layers at $z = 0.25c$ and $0.75c$. (g), (h) X_5^- mode in Ti-O layers at $z = 0.0$ and $0.5c$.

that in Pm . At 5% compressive strain, in $P2_1$, $[Ca, Ti, O_{\parallel}, O_{\perp}] = [-0.76, 0.19, 0.13, 0.60]$, in Pm , $[Ca, Ti, O_{\parallel}, O_{\perp}] = [-0.10, -0.65, 0.55, 0.51]$. In $P2_1$, the polarization is A -site dominated, while in Pm it is B -site dominated, as in the other epitaxial-strain-induced ferroelectric phases. The difference between eigenvectors is additional evidence of the different mechanism for the in-plane polarization in $P2_1$, which will be discussed in Section 3.5.

Mode	$Pbnm$	$P2_1/m$	$Pna2_1$	Pm	$P2_1$
R_4^+	0.418	0.785	0.530	0.762	0.778
M_3^+	0.740	0.402	0.657	0.451	0.434
X_5^+	0.187	0.289	0.205	0.305	0.308
Γ_4^-	0.000	0.000	0.184	0.153	0.048
X_5^-	0.000	0.000	0.147	0.000	0.143

Table 3.1: Amplitudes of modes, which are greater than 0.1 a.u., in different structures at 5% compressive strain. The information about the components is not included in this table.

3.4 Construction of polynomial energy expansion for CaTiO_3

In order to illuminate the mechanism of the strain-induced ferroelectricity in the orthorhombic CaTiO_3 , we constructed a polynomial expansion to describe the energy surface of CaTiO_3 . The total energy of CaTiO_3 was expanded in terms of distortion modes and elastic strains with respect to the high-symmetry cubic $Pm\bar{3}m$ structure. One obstacle in the construction of the CaTiO_3 energy function is the existence of multiple distortions, which greatly increases the complexity of the expression. In the $c\text{-}ePbnm$ structure, which retains the space group of $Pbnm$, there are a total of five distortion modes, including the two oxygen octahedron rotations, $M_3^+[001]$ and $R_4^+[110]$, and three other modes, X_5^+ , R_5^+ and M_2^+ . In the $ab\text{-}ePbnm$ structure and in the strain-induced ferroelectric phases, the space group is further lowered and more modes have non-zero amplitudes. The amplitudes of most of these additional distortion modes are very small. Therefore, to preserve the simplicity of the model, we only include the distortion modes with significant amplitudes, which are M_3^+ , R_4^+ , X_5^+ , Γ_4^- and X_5^- , and elastic strain components, η_1 , η_2 and η_3 , in the construction of the energy function.

In the polynomial energy expansion for systems with small distortions, such as BaTiO_3 and SrTiO_3 , the energy is expanded up to 4th order in the polar mode, which is sufficient to describe the para- and ferroelectric phase transition. However, in CaTiO_3 , because of the large amplitudes of the distortion modes, the truncation error at 4th order is non-negligible and higher order terms need to be included in order to precisely reproduce the response of CaTiO_3 to the application of epitaxial strain. In our study, we expanded the energy series up to 8th order to reduce the truncation errors. However, including the full set of terms up to 8th order is cumbersome and not necessary for a useful description of the energy surface. Therefore, we developed a systematic method for the selection of terms with significant contributions to the total energy, as follows.

The total energy is decomposed into the sum of various coupling terms,

$$E(S) = \sum_{A \subset S} \Delta E(A), \quad (3.1)$$

where $E(S)$ is the total energy of the structure described by S , the full set of structural parameters that determines the structural configuration, the summation is over all of the subgroups of S , A 's and $\Delta E(A)$ represents the coupling term including only and all of the elements in the subgroup A . The value of the coupling term $\Delta E(A)$ can be determined iteratively by the following relations:

$$\Delta E(A) = E(A) - \sum_{A' \subset A} \Delta E(A'), \quad (3.2)$$

where $E(A)$ is the total energy of the configuration in which only structural parameters in A are of nonzero value and $E(\emptyset)$ is the total energy of the high-symmetry cubic structure, E_0 , or

$$\Delta E(A) = E(A) + \sum_{A' \subset A} (-1)^{k-k'} E(A'), \quad (3.3)$$

where k and k' are the sizes of group A and its subgroup A' . We performed first-principles calculation to compute the total energy of configurations of various sets of structural parameters A and the values of nonzero parameters are set as their average values in epitaxially-strained CaTiO_3 . Then we used the relation (3.2) or (3.3) to estimate the value of each coupling term and selected the terms with most significant impact (specifically, the largest absolute value) in the energy expansion.

One advantage of decomposing the total energy into coupling terms is that we can fit each coupling term separately without any interference of the fitting errors from other terms. We used an 8th-order polynomial for all terms with only one distortion mode, such as $\Delta E(\{R_4^+\})$ and $\Delta E(\{\Gamma_4^-\})$, and 4th-order polynomials for the pure strain terms. For the terms including more than one structural parameter, we fitted

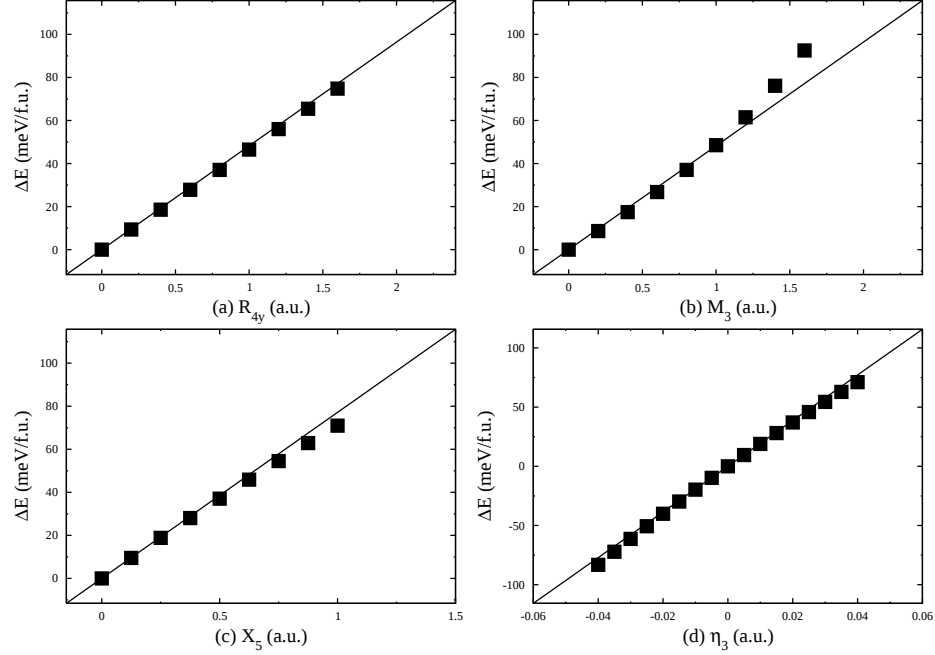


Figure 3.7: Fitting of the coupling term $\Delta E(R_{4x}^+, M_3^+, X_5^+, \eta_3)$ to the energy expansion $C\eta_3 R_{4x} M_3 X_5$, where C is the coefficient and the superscripts of the distortion modes are omitted.

them with polynomials with appropriately selected order, which is no higher than 8th-order. For a given energy polynomial, we chose a natural grid of sampling points, in which each structural parameter was varied in turn with others fixed at the average value, as shown in Fig. 3.7. The coefficients in the energy expansion are adjusted to minimize the cost function:

$$L = \sum_A (\Delta E(A) - \hat{\Delta E}(A))^2, \quad (3.4)$$

where the summation is over all of the sampling configurations and $\hat{\Delta E}(A)$ is the value estimated by the energy polynomial. In principle, the fitting error L can be eliminated by choosing a fitting polynomial with sufficient coefficients or fitting parameters. We also impose another requirement that the fitted polynomial does not have any spurious minima or divergence outside the range of the sampling, otherwise we reduce the order of the polynomial until it is satisfied.

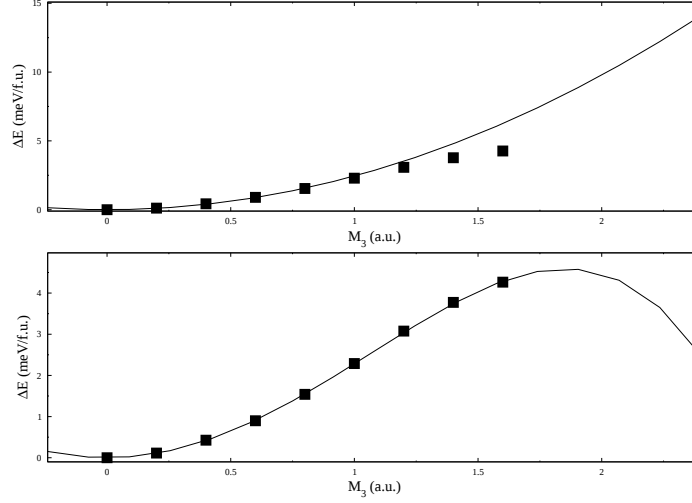


Figure 3.8: Comparison the fitting of coupling term $\Delta E(\{R_{4x}^+, M_3^+, X_5^-\})$ with polynomials of different orders. Top: fitting with 6th-order polynomial $C_6^{(1)} R_{4x}^2 M_3^2 (X_5^-)^2$; Bottom: fitting with 8th-order polynomial $C_6^{(2)} R_{4x}^2 M_3^2 (X_5^-)^2 + C_{8,1}^{(2)} R_{4x}^4 M_3^2 (X_5^-)^2 + C_{8,2}^{(2)} R_{4x}^2 M_3^4 (X_5^-)^2 + C_{8,3}^{(2)} R_{4x}^2 M_3^2 (X_5^-)^4$. The superscripts of distortion modes are omitted when there is no ambiguity.

3.4.1 Construction of CaTiO_3 energy function

To simplify the energy function, we only included the distortion modes with significant amplitudes in the energy function of CaTiO_3 . The ground state of orthorhombic bulk CaTiO_3 structure are obtained by freezing R_4^+ and M_3^+ modes in the high-symmetry cubic structure. Therefore, the two rotational modes are the most important structural parameters in the energy expansion. Moreover, the lowered symmetry of $ab-ePbnm$ makes the out-of-phase tilting modes around two directions, R_{4x}^+ and R_{4y}^+ , no longer equivalent. The two components of R_4^+ mode should be separately considered. Since the goal of the construction of the energy function is to quantitatively reproduce the induced ferroelectricity under epitaxial strain, the polar mode Γ_4^- , which yields the electric polarization, is also essential ingredient in construction of the energy expansion. The polar CaTiO_3 structures are characterized by the direction of the polarization. Therefore, it is necessary to include the three components of the polar Γ_4^- mode. Besides the primary distortion modes, we also included the two zone-boundary modes X_5^+ and X_5^- , which have large amplitudes comparable with

that of the polar mode, as shown in Fig. 3.5 and Table 3.1. For selection of the strain components, we artificially suppressed the shearing strain η_6 and only include the diagonal elements of the strain matrix in Voigt notation, $\eta_1 \sim \eta_3$. In our energy function, there are in total 11 structural parameters, including 8 distortion modes, $\Gamma_{4x}^- \sim \Gamma_{4y}^-, M_3^+, R_{4x}^+, R_{4y}^+, X_5^+$ and X_5^- , and 3 elastic strain components, $\eta_1 \sim \eta_3$.

With 11 structural parameters included, the decomposition of the total energy Eq. 3.1 contains $2^{11} = 2048$ coupling terms. We calculated the value of each term near the ground state of orthorhombic CaTiO_3 and sorted them in descending order of the absolute value. We chose the first several terms, whose sum of absolute values accounts for over 90% of the sum over all coupling terms, $\sum_A |\Delta E(A)|$. There are a total of 169 independent coupling terms included in the energy function. For the application of point group symmetry operations on the distortion modes and elastic strain, please refer to Table A.1 and A.2 in Appendix A.

The energy function with coefficients fitted to the first principles calculations by least square error mode is shown in Appendix B. The application of epitaxial strain was simulated by fixing the appropriate elastic strain components and optimizing the energy function with conjugate gradient method. Fig. 3.9 shows the total energy of various structures estimated by the energy function. The simulation with the energy function successfully reproduces the orientational phase transition between the two non-polar structures, $c\text{-}ePbnm$ and $ab\text{-}ePbnm$. The critical point in the energy function simulation is near 0% strain, while in the first principles calculations it is at 1.5%. This discrepancy between first-principles calculations and energy function simulations is due to the fact that the shearing strain component η_6 was omitted in the energy function. The four ferroelectric phases with in-plane polarization at tensile strains are also observed in the simulations of the energy function, with the same ground state $Pmn2_1$ as in the first-principles calculations. However, at compressive strains, only the two ferroelectric phases with out-of-plane polarization, $Pna2_1$ and Pm , are stabilized by the epitaxial strain. The strain-induced geometric ferroelectric phase

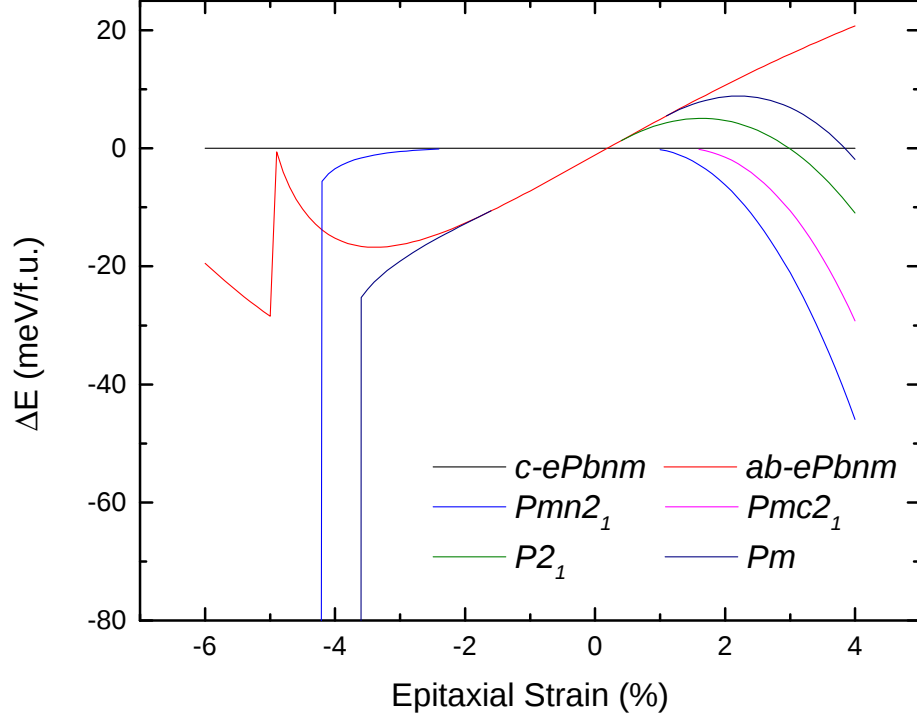


Figure 3.9: Total energy per formula unit estimated by the energy function for various epitaxially constrained structures as a function of square misfit strain. At each strain, the energy of *c-ePbnm* structure is taken as the zero of energy.

$P2_1$ is not observed in the energy function simulation, even though the multilinear coupling terms $\Gamma_4^- R_4^+ M_3^+ X_5^-$ and $\Gamma_4^- X_5^+ X_5^-$ are included in the energy function. The missing of $P2_1$ phase in the simulation is because the eigenvector of the polar mode in $P2_1$, which is *A*-cation dominated, is different from the eigenvector of the polar mode in other phases, which is *B*-cation dominated and used in the determination of the energy function coefficients. At large compressive strain, there exist several spurious low-energy states, which results from poor behavior of extrapolation of the polynomial expansion for outside the physical reference region.

The energy expansion in Appendix B quantitatively describes the energy surface of bulk CaTiO_3 . As will be discussed in Chapter 4 and 5, it is useful in the investigation of long-period superlattices, in which the direct first-principles calculations is not feasible. The energy expansion also helps us understand the coupling or competition between the distortion modes and elastic strains. For example, as previously

discussed, the energy function of CaTiO_3 indicates that the geometric ferroelectric phase $P2_1$ arises from the multilinear coupling term $\Gamma_4^- R_4^+ M_3^+ X_5^-$ and $\Gamma_4^- X_5^+ X_5^-$. The energy expansion also shows that all of the coupling terms between X_5^+ and rotational modes have positive coefficients, which indicates the mutual competition between the X_5^+ and rotational modes. Similarly, from the energy expansion, we can see that the X_5^+ mode also arises from a trilinear term $(R_{4x} + R_{4y})M_3X_5$.

The energy expansion of bulk CaTiO_3 also illuminate the interactions between the polar model, which yields spontaneous polarization, and the oxygen octahedron rotational modes. As previously discussed, the corresponding phonons of the polar and rotational modes are all unstable in the ideal cubic $Pm\bar{3}m$ structure, while in the bulk orthorhombic $Pbnm$ structure, there are only the rotational modes, R_4^+ and M_3^+ . It is widely known that the absence of the polar mode Γ_4^- in bulk CaTiO_3 is because of the inhibition of the oxygen octahedron rotations and tilts. However, in our energy expansion, both the coupling terms $(\Gamma_x^2 R_y^2 + \Gamma_y^2 R_x^2 + \Gamma_z^2 R_x^2 + \Gamma_z^2 R_y^2)$ and $((\Gamma_x^2 + \Gamma_y^2)M^2)$ have negative coefficients, which indicates that the rotational mode enhances the polar modes perpendicular to its rotational axis (50). This rotational enhancement of polarization is because with fixed lattice constant the rotations and tilts increase the volume of the oxygen octahedra and favor the polar mode perpendicular to their rotational axes. One thing should be mentioned is that our observation does not contradict the conclusions of previous work that rotational modes suppresses the polar instability in the bulk CaTiO_3 . Previous work studied the impact of the rotational modes on the spontaneous polar instability in the cubic $Pm\bar{3}m$ structure, whose eigenvector is A -cation dominated, while in our study the strain-induced polar mode is B -cation dominated. Therefore, whether the rotational modes enhance or suppress the polar mode depends on the eigenvector of the polar mode.

3.5 Geometric ferroelectricity in CaTiO_3

Ferroelectricity produced by a primary polar instability of a paraelectric high-symmetry reference structure is characteristic of prototypical perovskite ferroelectrics such as BaTiO_3 and PbTiO_3 (51), and is referred to as proper ferroelectricity. In improper ferroelectrics (52; 53; 54; 55; 56; 57; 58; 59; 60; 61), the primary instability is nonpolar, and polarization P is induced through a coupling of the nonpolar instability Φ to a polar lattice distortion. Improper ferroelectrics can be further classified by the form of the coupling and the nature of the nonpolar instability. In conventional improper ferroelectrics, the coupling has the form $P\Phi^\gamma$ where $\gamma \geq 2$. In hybrid improper ferroelectrics, two nonpolar instabilities Φ_1 and Φ_2 combine to induce the polarization through a trilinear coupling $P\Phi_1\Phi_2$. In a pseudoproper ferroelectric (REF TOLEDANO BOOK), a stable polar lattice mode and a nonpolar instability have the same transformation property with respect to the symmetry of the paraelectric phase and are coupled by a bilinear term $P\Phi$, so that the nonpolar instability induces a polarization. The nonpolar instability may be physically distinct from a lattice distortion, for example it may be a magnetic ordering instability (REFS), or it may itself be a lattice distortion. In the latter case, for pseudoproper ferroelectrics, the paraelectric phase must itself be a nonpolar distortion of a higher-symmetry reference phase, so that the distinction between the polar lattice mode and the nonpolar distortion can be made on the basis of transformation properties under the symmetry operations of the reference phase. We will collectively refer to pseudoproper, improper and hybrid improper ferroelectrics with nonpolar lattice instabilities as geometric ferroelectrics.

To investigate the origin of the polarization in $P2_1$, we adopted the approach in the YMnO_3 study of Fennie and Rabe (52). As shown in Fig. 3.10, we plotted the energy functions of X_5^- and Γ_{4z}^- with $ab\text{-}ePbnm$ at 5% compressive strain as the reference structure. We can see that in the reference structure, X_5^- is unstable while Γ_{4z}^- is stable, which indicates that the X_5^- mode drives the polar-nonpolar phase transition.

Fig. 3.11 shows that with increasing X_5^- mode amplitude, the energy curve of the Γ_{4z}^- mode remains a single well, but the position of its minimum shifts from zero to a non-zero position. This means that X_5^- distortion induces the polar Γ_{4z}^- mode in the $ab-ePbnm$ structure. Thus, this is an example of geometric ferroelectricity.

Now using the high-symmetry cubic structure as the reference structure, we expand the total energy function E as a 4th-order polynomial in distortion modes $R_4^+, M_3^+, X_5^+, \Gamma_4^-$ and X_5^- (see Figure 3.6) and elastic strains η_1, η_2 and η_3 :

$$\begin{aligned}
E = & E_{Pbnm}(R, M, X, \eta_1, \eta_2, \eta_3) \\
& + \kappa(\Gamma_x^2 + \Gamma_y^2 + \Gamma_z^2) + \alpha(\Gamma_x^2 + \Gamma_y^2 + \Gamma_z^2)^2 \\
& + \lambda(\Gamma_y^2\Gamma_z^2 + \Gamma_x^2\Gamma_y^2 + \Gamma_z^2\Gamma_x^2) + \kappa_5 X_5^2 + \alpha_5 X_5^4 \\
& + \bar{B}_x(\Gamma_x^2 + \Gamma_y^2)R^2 + \bar{B}_z\Gamma_z^2 R^2 + B'_x(\Gamma_x^2 + \Gamma_y^2)M^2 \\
& + B'_z\Gamma_z^2 M^2 + \tilde{B}_x(\Gamma_x^2 + \Gamma_y^2)X^2 + \tilde{B}_z\Gamma_z^2 X^2 \\
& + \bar{B}_5 X_5^2 R^2 + B'_5 X_5^2 M^2 + \tilde{B}_5 X_5^2 X^2 \\
& + B_{5x}(\Gamma_x^2 + \Gamma_y^2)X_5^2 + B_{5z}\Gamma_z^2 X_5^2 + B_{15}(\eta_1 + \eta_2)X_5^2 \\
& + B_{35}\eta_3 X_5^2 + B_{1x}(\eta_1\Gamma_x^2 + \eta_2\Gamma_y^2 + \eta_3\Gamma_z^2) \\
& + B_{1z}((\eta_2 + \eta_3)\Gamma_x^2 + (\eta_1 + \eta_3)\Gamma_y^2 + (\eta_1 + \eta_2)\Gamma_z^2) \\
& + C_1 X X_5 \Gamma_z + C_2 R M X_5 \Gamma_z
\end{aligned} \tag{3.5}$$

For simplicity, the sub- and superscripts are omitted when there is no ambiguity; to distinguish the two X modes, X is used for X_5^+ and X_5 is used for X_5^- . To keep the energy polynomial concise, only terms involving Γ_4^- and X_5^- are shown explicitly and a single term E_{Pbnm} represents the energy function of non-polar structures. The determination of coefficients from first-principles results, which will be discussed later, shows that all biquadratic terms, such as $(\Gamma_{4z}^-)^2(X_5^-)^2$, have positive coefficients, which indicates the mutual competition between any pair of distortion modes. We see that the coupling between Γ_{4z}^- and X_5^- originates from the higher order terms $X_5^+ X_5^- \Gamma_{4z}^-$ and $R_4^+ M_3^+ X_5^- \Gamma_{4z}^-$, which is the signature of geometric ferroelectricity.

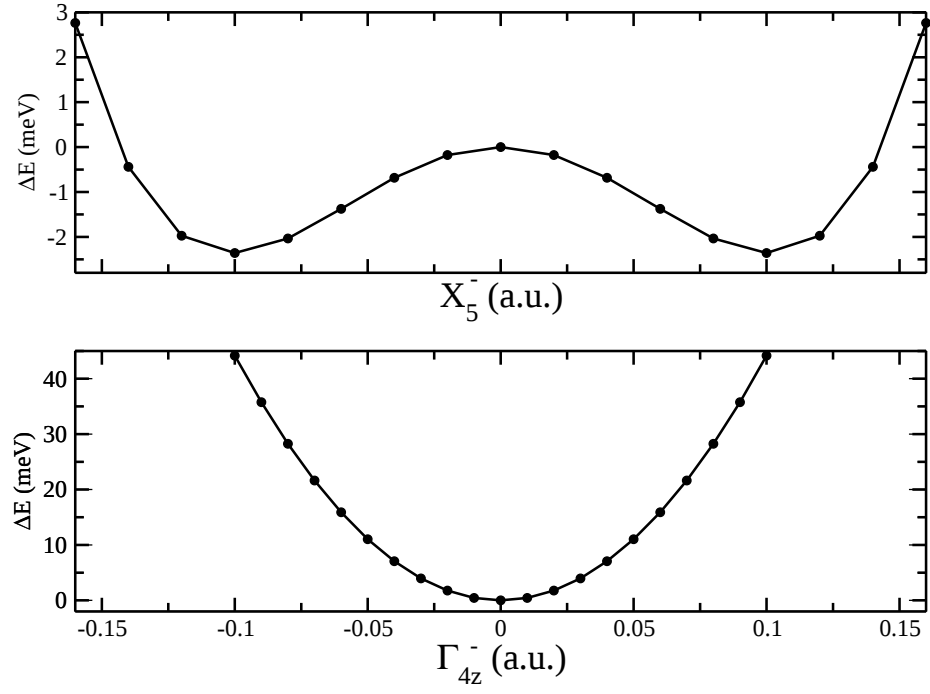


Figure 3.10: Energy as a function of X_5^- and Γ_{4z}^- . The reference structure is *ab-ePbnm* at 5% compressive strain.

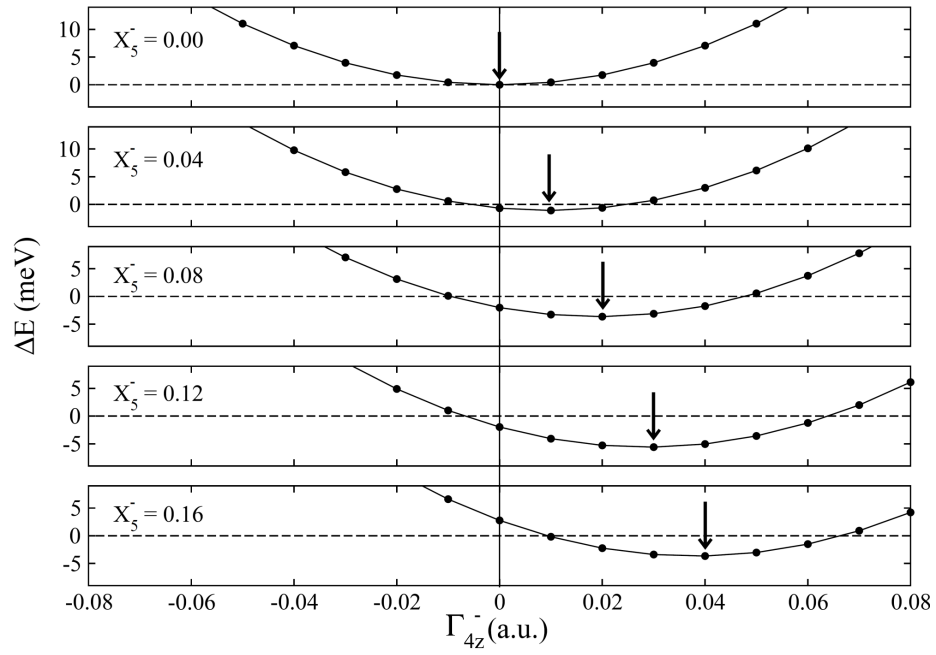


Figure 3.11: Energy as a function of Γ_{4z}^- at fixed X_5^- .

The coefficients of $X_5^+ X_5^- \Gamma_{4z}^-$ and $R_4^+ M_3^+ X_5^- \Gamma_{4z}^-$ are 0.46 eV/a.u. and 1.93 eV/a.u.. In the $Pbnm$ phase, R_4^+ , M_3^+ and X_5^+ are all nonzero. According to Table 3.1, the product $R_4^+ M_3^+$ has an amplitude (0.33 a.u.) similar to that of X_5^+ (0.31 a.u.), so that the contributions of the two terms to the induced polarization are comparable. This analysis provides a natural way of understanding the instability of the epitaxially-strained nonpolar $Pbnm$ phase to the polar $P2_1$ phase observed in first-principles identification of low-symmetry phases described above. The unstable distortion is a mixture of a nonpolar X_5^- mode and a polar Γ_{4z}^- mode of the cubic reference structure; we see from the discussion that this coupling results from the pre-existing R_4^+ , M_3^+ and X_5^+ distortions in the $Pbnm$ phase. While a transition from the $Pbnm$ phase to the $P2_1$ phase would be accompanied by a divergence in the dielectric constant, following the study of TbMnO_3 (56) this would be characterized as a geometric, rather than a conventional proper, ferroelectric transition (62).

In geometric ferroelectrics, the multilinear coupling term couples the switching of the zone-center and zone-boundary modes. In the $P2_1$ phase, switching of polarization would result in switching of either a single mode X_5^- or both X_5^+ and the product $R_4^+ M_3^+$. Switching of a rotation mode has an estimated energy barrier of several hundred meV. Fig. 3.10 shows that the well depth of the X_5^- mode is only 2.0 meV, so the X_5^- switching path would be preferred. However, detection of the switching of X_5^- is difficult. It would be possible if there was magnetic order in the system that coupled to X_5^- , suggesting further study of other compounds with magnetic order.

In CaTiO_3 , the geometric ferroelectric phase is not the ground state at any value of epitaxial strain in our “strained bulk” calculation. However, for out-of-plane polarized thin films there are depolarization field effects, which in general would be expected to produce domain structures (63), at a cost of free energy increasing with domain wall density. Since for the large polarizations predicted for the out-of-plane polar phases in compressively strained CaTiO_3 the domain wall density should be rather high, it might be that the in-plane polarized $P2_1$ phase in ultrathin perovskite films is lower

in free energy for some range of strain. In addition, the set of perovskites exhibiting the $Pbnm$ structure is quite large, and it might be possible to find a system in which the geometric ferroelectric phase is in fact the ground state for some range of epitaxial strain.

3.6 Summary

Our first-principles study of epitaxially strained CaTiO_3 revealed the existence of two polar phases with out-of-plane polarization and an unexpected metastable polar phase with in-plane polarization at compressive strain. Detailed symmetry analysis indicated that the unusual polarization is due to geometric ferroelectricity and is induced by a strain-induced nonpolar instability at the X point combined with distortion modes present in the nonpolar orthorhombic structure. This discovery of a novel strain-induced ferroelectric phase in the simple perovskite CaTiO_3 provides a new mechanism for the design of functional materials with improper ferroelectricity. We also expanded the total energy of CaTiO_3 with the cubic $Pm\bar{3}m$ structure as reference and the energy expansion semi-quantitatively reproduces the strain-induced para- and ferroelectric phase transitions in CaTiO_3 . The study of the coefficients in the energy function also reveals that rotational distortion modes enhance the B -cation dominated polar distortion modes.

Chapter 4

Interface-driven enhancement of piezoelectricity in PbTiO₃/BaTiO₃ superlattices

4.1 Introduction

Artificially structured oxides present exciting opportunities for the design of functional materials with specified and/or novel properties.(64; 65; 66) With dramatic advances in epitaxial growth techniques allowing atomic-scale control, there has been much experimental and theoretical attention focused on multicomponent strained-layer superlattices. The strain in the layers, which is controlled both by the lattice mismatch between the constituents and by the epitaxial constraint to the substrate, the electrostatic boundary conditions and atomic and electronic reconstruction at the interfaces all play important roles in determining the properties of superlattices. These features can produce desirable functional properties, such as switchable electric polarization, dielectric response and piezoelectricity, distinct from those of their bulk constituents. (64; 65; 66; 67; 68; 69; 70; 71; 72; 73; 74; 75; 76; 77; 78; 79)

Previous work indicates that the d_{33} piezoelectric response of these superlattices is of interest, despite the clamping by the substrate. First-principles calculations on ferroelectric/ferroelectric PbTiO₃/BaTiO₃ (PTO/BTO) superlattices on a SrTiO₃ (STO) substrate indicate an enhanced piezoelectricity at a PTO concentration of $\geq 50\%$ (80). Subsequent first-principles calculations for unclamped superlattices showed dramatic enhancements achievable by tuning uniaxial stress or pressure. A previous experimental study used MgO ($a = 4.213\text{\AA}$) as the substrate, so that both BTO and PTO were under tensile strain, promoting an in-plane direction for

the polarization. In the present case, we consider PTO-BTO on STO, in which the a lattice parameter of tetragonal PTO layer is a close match to the substrate, favoring out-of-plane polarization. Further, growth on STO puts the BTO under compressive strain, enhancing its tetragonality and its polarization normal to the layers. Due to electrostatic coupling, the larger polarization of tetragonal PTO leads to a further enhancement of the polarization of BTO.

The first-principles calculation and modeling described in this chapter is motivated by recent synthesis and measurements on PTO/BTO superlattices on STO that confirm the prediction of enhanced piezoelectricity at a PTO concentration of $\geq 50\%$.⁽⁸⁰⁾ An experimental-theoretical team including myself, Valentino Cooper, Tahir Yusufaly, Premi Chandra, Karin Rabe and the group of Matthew Dawber at Stony Brook has studied the origin of this enhancement using a phenomenological model in conjunction with additional first-principles calculations. The model can address questions such as the maximum d_{33} achievable in the superlattices by varying composition and epitaxial strain. We find that the piezoelectric enhancement is interface-driven, and thus these results suggest a new pathway towards developing nanocomposites with high piezoelectric coefficients by design.

4.2 First-principles computational details

Our first-principles calculations are performed using the same methodology as that of the previous study (80); we use density functional theory for PTO/BTO superlattices $PmBn$ with m and n layers of PTO and BTO respectively. The superlattices considered were P1Bn ($n=1-9$), P2Bn ($n=1-7$), P3Bn ($n=1-5$), P4Bn ($n=1-4$), P5Bn ($n=1-3$).¹ Experimental measurements were carried out for P8B2, P7B3, P6B5 and P2B4 by the group of Matthew Dawber at SUNY Stony Brook (7). First-principles calculations of crystal structure, polarization, d_{33} and dielectric constant for these

¹Crystal structure, polarization, and d_{33} for these superlattices were computed by Tahir Yusufaly.

four superlattices were performed for comparison with experiment.

All calculations used projector augmented wave (PAW) potentials with the Vienna ab initio simulation package (VASP v4.6.26), with the local density approximation for the exchange correlation functional. A 700 eV (22 Ha) cutoff and a $8 \times 8 \times 1$ k-point mesh were used. For BTO in the tetragonal $P4mm$ five-atom unit-cell structure, the computed lattice constants are $a = 3.947\text{\AA}$ and $c = 3.996\text{\AA}$. The tetragonal PTO constants were computed as $a = 3.987\text{\AA}$ and $c = 4.033\text{\AA}$. In all superlattice calculations, the in-plane lattice constant was constrained to that of the theoretical value for an STO substrate ($3.863\text{\AA}$) while the structure, including the c lattice parameter, was optimized within the $P4mm$ space group with 1×1 in-plane periodicity; we note that with the STO substrate, both BTO and PTO are under compressive strain so that polarizations in both are expected to be aligned along the $\hat{z}$ direction.⁽⁸⁰⁾ All ionic coordinates were relaxed until the Hellmann-Feynman forces on the ions were less than $5 \text{ meV/\AA}$.

4.3 Results

In Fig. 4.1 and 4.2 we display the measured polarization (P) and the tetragonality ($\frac{1}{n+m} \frac{c}{a}$) in PTO/BTO superlattices as a function of PTO concentration (x), plotted together with the first principles results for the full set of superlattices considered. The agreement between theory and experiment for the polarization is excellent. As has been seen in many previous first-principles studies of PbTiO_3 , the tetragonality of PbTiO_3 is substantially underestimated in the local density approximation; however, the trend in which a minimum occurs for superlattices at high PbTiO_3 concentrations observed in the experiments is well reproduced by the calculations. Both the polarization and tetragonality depend primarily on the concentration x . Where multiple superlattices at the same x are considered (e.g. 1:1, 2:2, 3:3), there is little dependence of polarization or tetragonality

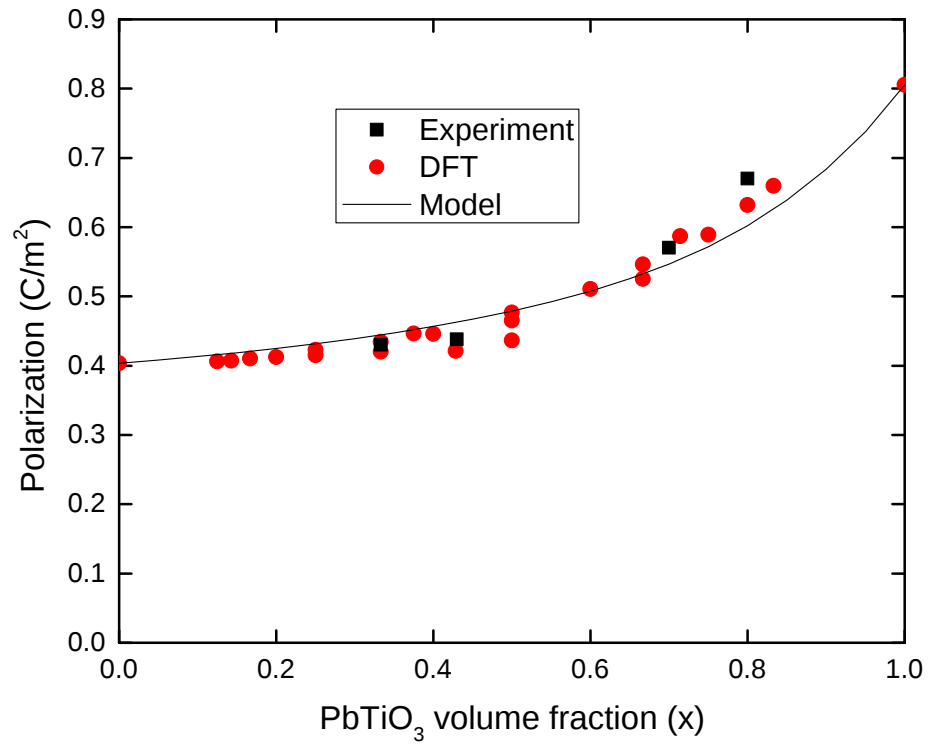


Figure 4.1: Polarization of PTO/BTO superlattices from experiment, first-principles and slab model prediction, from Ref (81).

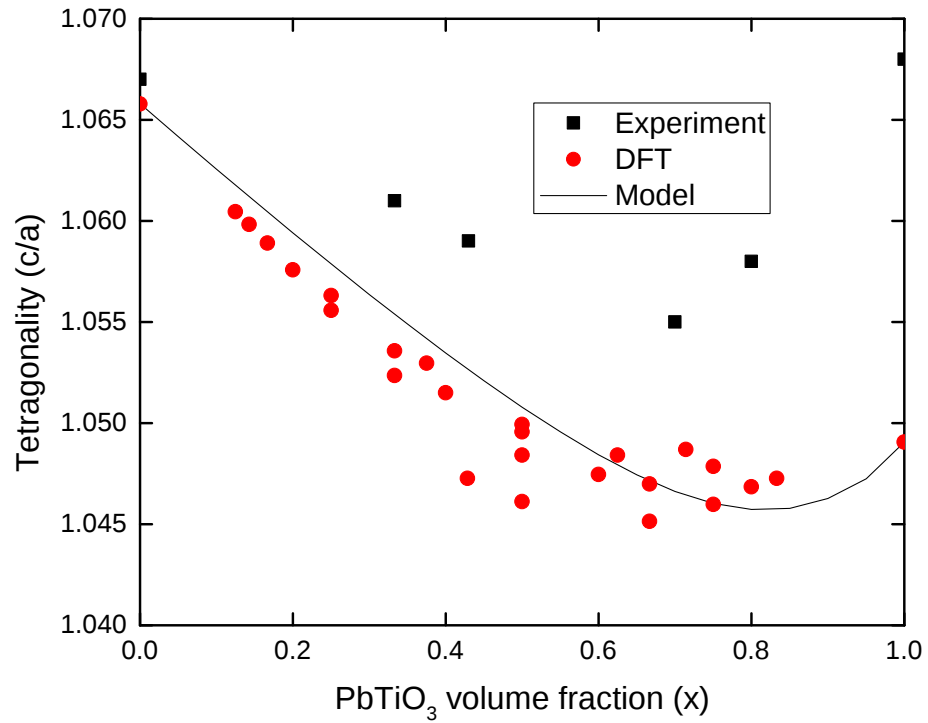


Figure 4.2: Tetragonality of PTO/BTO superlattices from experiment, first-principles and slab model prediction, from Ref (81).

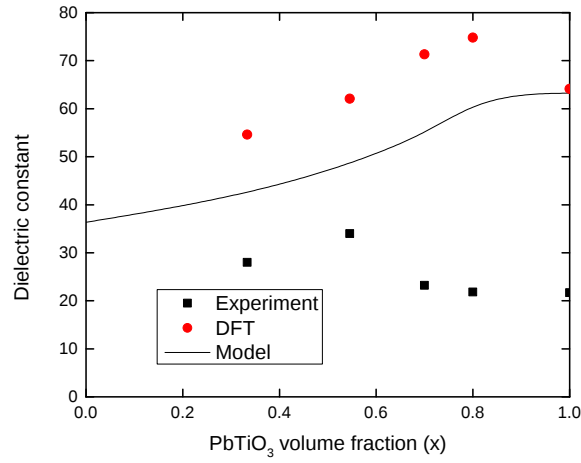


Figure 4.3: The measured dielectric coefficient ϵ_{33} with the first-principles results for the same set of superlattices.

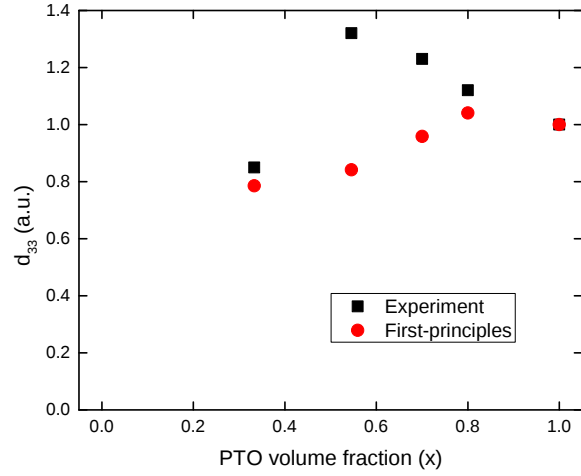


Figure 4.4: The measured piezoelectric coefficient d_{33} with the first-principles results for the same set of superlattices. All d_{33} are normalized by the value of d_{33} in pure PbTiO₃ material.

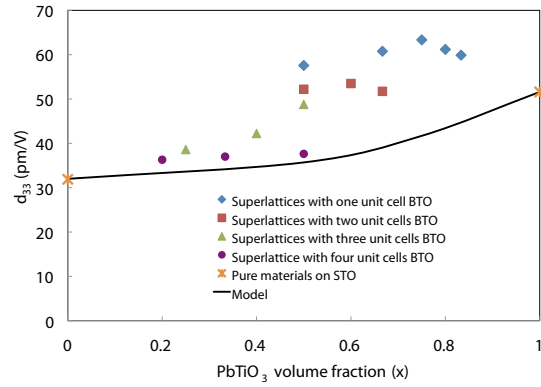


Figure 4.5: d_{33} of PTO/BTO superlattices from first principles and slab model predictions.

The measured dielectric coefficient (ϵ_{33}) is presented in Fig. 4.3 with the first-principles results for the corresponding superlattices (7). A peak in ϵ_{33} at intermediate values of x is seen both in the experimental and first principles results. Fig. 4.4 shows the comparison of the measured piezoelectric response d_{33} with the experimental measurements for the same set of superlattices. The enhancement of d_{33} observed at intermediate values of x in the experiments is substantially greater than that obtained by first-principles calculations. However, for shorter period superlattices, the first-principles results presented in Fig. 4.5 show a comparable enhancement of d_{33} over pure PTO, consistent with previous first-principles calculations (80). According to the first-principles results, d_{33} depends rather strongly on interface density, with the d_{33} decreasing as the thicknesses of constituent layers increase at fixed PbTiO_3 fraction. The results for polarization and tetragonality for the full set of superlattices considered were shown in Fig. 4.1 and 4.2. In Fig. 4.5, we present the piezoelectric response for the full set of superlattices. The enhancement at intermediate x is seen to be strongest for the superlattices with the thinnest layers. As the layer thicknesses increase at a given x , the piezoelectric responses decreases; this can in particular be seen at $x=0.50$ (1:1, 2:2, 3:3, 4:4) and $x=2/3$.

4.4 Discussion

There are several aspects of this piezoelectric response enhancement that demand further study, including the atomic-scale mechanism for the enhancement, and identification of the superlattice layer sequence and epitaxial strain that will maximize the d_{33} achieved. Here, we explore these questions using first principles calculations and modeling.

Our first step in the construction of a model is the dielectric slab model (27). In this model, each layer is treated as strained bulk material with the electric boundary conditions imposed by the superlattices.(80; 75; 66) In particular, the absence of

free charge (short-circuit boundary conditions) implies continuity of the electrical displacement field across the interfaces. Combined with the assumption of short-circuit boundary conditions, this relates the polarizations and the electric fields in the various layer. Details of the energy function and determination of the model parameters from bulk first-principles calculations on bulk PTO and BTO are discussed in Appendix C.

The model results for the polarization and tetragonality are shown in Figs. 4.1 and 4.2. The dielectric slab model describes the polarization and tetragonality of the superlattices remarkably well. Since bulk PTO has higher polarization than does BTO, the tendency of electrostatics to equalize polarization of the layers will drive a decrease in the PTO polarization and an increase in the BTO polarization. Thus, we expect $P(x)$ to increase with x in PTO/BTO superlattices. The monotonic behavior of $\frac{1}{n+m} \varepsilon(x)$ is more surprising, but can be understood within the slab model through polarization-strain coupling. At low x , the polarization of the PTO layer is suppressed, and the tetragonality is reduced. In this regime, with increasing x , the average tetragonality is reduced. However, as the polarization increases with higher values of x , the tetragonality of the PTO layer increases towards its pure value, while the tetragonality of the BTO layer increases above its pure value, though not strongly enough to yield any superlattice polarizations greater than that of pure PTO.

The dielectric and piezoelectric responses for the dielectric slab model are shown in Figs. 4.3 and 4.5. Examination of the first-principles results at fixed x suggest that they converge to the dielectric slab results as the thickness of the layers increases. This is expected, as the dielectric slab model incorporates only the bulk-like responses of the layers and is scale invariant (that is, depends only on x and not on individual layer thicknesses). It should be noted that for the dielectric slab limit, there is no enhancement of the responses at intermediate concentrations. This supports the idea that the enhancement is due to the interfaces.

These results have stimulated discussion about how to develop a model that can

better describe the dielectric and piezoelectric response as a function of layer thickness. A natural approach is to extend the model to include degrees of freedom associated with the interfaces. Specially addition to a polar degree of freedom for each interface would yield four polar modes instead of two. Analysis is in progress to understand how to parametrize the extended energy function to reproduce the contributions of the polar modes to the dielectric and piezoelectric responses.

4.5 Conclusions

Using a synergy of experiment and theory, we have investigated the origin of the predicted enhancement of the piezoelectric coefficient in PTO/BTO superlattices as a function of PTO concentration x . Motivated by prior DFT studies,⁽⁸⁰⁾ our experimental collaborators have performed polarization, tetragonality and piezoelectric measurements on PTO/BTO superlattices and have confirmed the predicted dielectric and d_{33} enhancement. These measurements have in turned inspired us to perform further theoretical investigations into the origin of the d_{33} enhancement. Subsequent DFT studies have filled out the $P(x)$, $\frac{\epsilon}{a}(x)$ and $d_{33}(x)$ curves; furthermore we have found that both the tetragonality and particularly the piezoelectricity are not only dependent on PTO concentration (x), but also on the interfacial density. Indeed the development of an effective energy functional describing only the layer degrees of freedom cannot explain any of the observed piezoelectric enhancement. First principles calculations of the atomic positions in the constituent layers and at the interfaces, as well as the eigenvectors, frequencies and mode effective charges of the polar modes that contribute to the dielectric and piezoelectric response, provide valuable guidance in our ongoing efforts to extend the model to include interface degrees of freedom and a successful description of the functional properties with varying layer thicknesses.

Continuing the synergy between experiment and theory, further piezoelectric measurements on BTO/PTO superlattices at fixed PTO concentration of $x = 0.5$ with

varying period would be an excellent way to test our proposal; this value of x has the largest variation of interfacial densities. In parallel, first-principles and associated modeling studies of the permittivity as a function of PTO concentration and interfacial density would also be very useful.

An overall goal of this study is to design new materials with novel and/or enhanced functionalities. Previous pathways to enhanced piezoelectricity in ferroelectric superlattices have been polarization rotation or compositional inversion, but neither are applicable to the BTO/PTO superlattices we are studying here. By contrast, here we are proposing that the observed piezoelectric enhancement is interface-driven and is strongly dependent on the interfacial density at a given component concentration. study closely the effects of interfaces on the piezoelectricity that is most likely present in others as well. Once we have understood the details and mechanism of this interfacial-driven enhancement in BTO/PTO, then we will be able to propose specific heterostructure systems for future integrated theoretical and experimental study where such piezoelectric enhancement is optimized.

Chapter 5

First-principles modeling of piezoelectric response of perovskite superlattices: the case of $\text{BaTiO}_3/\text{CaTiO}_3$

5.1 Introduction

In multicomponent ABO_3 superlattices, instabilities belonging to individual bulk constituents strongly interact with each other through the interfaces. Such interactions in superlattices lead to rich behavior beyond that of simple perovskites (82; 27; 73; 83; 75; 54; 84), and in particular can lead to enhanced piezoelectric response (80). The superlattice $\text{BaTiO}_3/\text{CaTiO}_3$ has been studied both experimentally (84) and theoretically (85; 86; 87; 88; 89). One important feature of BTO/CTO superlattices is the corner-shared oxygen octahedron rotations and tilts that suppress the polar instability in bulk CaTiO_3 structure. However, until recently, the oxygen octahedron rotations and tilts were neglected in the first-principles studies of BTO/CTO superlattices. Even in the recent two first-principles studies, either only oxygen octahedron rotations were considered (88) or only the superlattices at one specific BaTiO_3 concentration were computed (89).

In this study, we use first-principles method to study the BTO/CTO superlattices with both oxygen octahedron rotations and tilts at various compositions ($n_{\text{BTO}}, n_{\text{CTO}} = 1, 2, 3, 4$). We find phase transitions of BTO/CTO superlattices that depend on both the constituent fractions and layer thicknesses. In particular, the

polarization in the stacking direction (z -axis) becomes nonzero at BaTiO₃ concentrations over 25%. An enhancement of piezoelectricity is also observed, with piezoelectric constant d_{33} diverging at the phase transition point between zero and nonzero P_z states.

First-principles methods have been extremely useful for the theoretical study of superlattices. However, despite of the rapid development of computer hardware and algorithms, the direct first-principles study of large superlattices is still prohibitively computationally demanding. Therefore, first-principles modeling, which enables us to study superlattices with arbitrary stacking sequences and helps us understand the physics behind the novel properties of superlattices, is necessary for guiding high throughput searches for novel superlattices. Previous work (27) shows that the superlattices can be described as layers of bulk-like materials connected by appropriate electrostatic boundary conditions. This dielectric slab model appropriately describes the electrostatic interactions between different constituents, but neglects the interfacial effects, which might be important in certain systems (88). In this study, we used the slab model to predict the polarization and the enhanced piezoelectricity in BTO/CTO superlattices, and to identify cases in which interfacial effects are essentially important.

5.2 First-principles computational details

In this study, the first-principles calculations were performed in the framework of density functional theory within the local density approximation using VASP5.2 package. (46; 47) We used the Ceperley and Alder functional (48) and projector-augmented wave potentials (20; 21) with a plane-wave energy cut off of 500 eV. We used $\sqrt{2} \times \sqrt{2} \times (n_{\text{BTO}} + n_{\text{CTO}})$ supercells with epitaxial strain $a_0 = 3.864\text{\AA}$, the computed lattice constant of SrTiO₃. The Brillouin zone of the unit cell was sampled by a $4 \times 4 \times l$ Monkhorst-Pack k -point mesh (25) ($l = 3$ for B1C1 and $l = 1$ for

others). Structural relaxations were performed until the force on each atom is less than 1 meV/Å. The Berry-phase method was used to calculate the polarization in the superlattices.

In perovskite superlattices $AA'BO_3$, the cation ordering lowers the symmetry of the crystal structure and increases the complexity of the system. Due to the existence of multiple metastable states, the search for the ground state of perovskite superlattices can be challenging. In our study, we used the stacking method (90) to search for the ground states of BTO/CTO superlattices. In the stacking method, the structural optimization starts from the combinations of strained low-energy bulk structures of the constituents. The strained bulk $BaTiO_3$ structure is simple and has only one low-energy state, which is of space group $P4mm$. Because of the large Goldschmidt tolerance factor, $BaTiO_3$ is resistant to any oxygen octahedron rotations or tilts and the only distortion mode is the out-of-plane polarization. However, the coexistence of the oxygen octahedron rotations and tilts makes the strained bulk $CaTiO_3$ more complicated. The lattice constant of relaxed bulk $CaTiO_3$ is 3.77Å. So in our study the $CaTiO_3$ constituents are under tensile strain. Previous work (44) shows that tensile-strained bulk $CaTiO_3$ has two low-energy orthorhombic states, $Pmn2_1(a^-a^-c^+/uu0)$ and $Pmc2_1(a^-a^-c^+/\bar{u}u0)$ (we introduce notation to show the rotations and polarizations in the three directions with respect to the five-atom cubic cell. Plus or minus superscripts indicate the in/out-of-phase rotations or the direction of polarization). Of the two orthorhombic states, the $Pmn2_1$ structure has a lower energy at all tensile strains ($\Delta E = E_{Pmc2_1} - E_{Pmn2_1} = 3.0\text{meV/f.u.}$ with $a_s = 3.864\text{\AA}$). The bulk $CaTiO_3$ has another metastable structure $R3c$ ($a^-a^-a^-/uuu$) with out-of-phase rotations along $[111]$ direction and polarization in $[111]$ direction, whose space group is lowered to Cc under square misfit strain. The energy of the Cc is higher than the other two orthorhombic structures, ($\Delta E = E_{Cc} - E_{Pmn2_1} = 36.4\text{meV/f.u.}$ with $a_s = 3.864\text{\AA}$). In all, there are three starting structures, $P4mm + Pmn2_1(P_a/c^+$ phase, space group $P1$), $P4mm + Pmc2_1(P_b/c^+$ phase, space group Pc) and $P4mm + Cc(P_b/c^-$ phase,

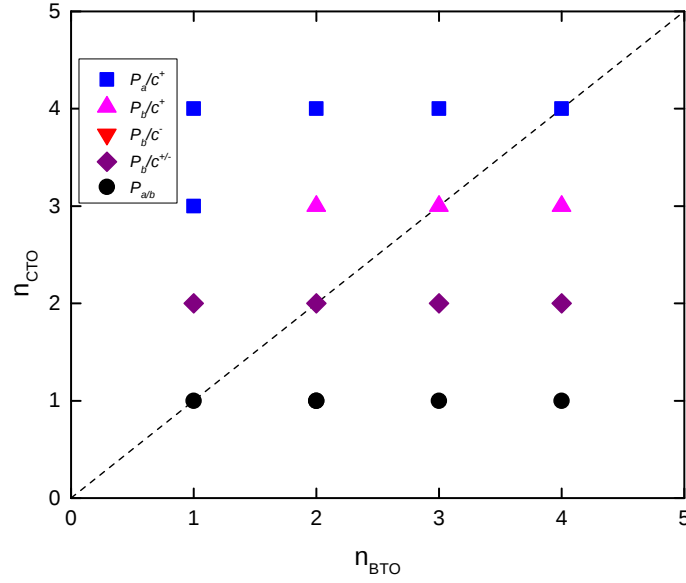


Figure 5.1: Ground state structures of various BTO/CTO superlattices. The dashed line represents 50% BTO concentration.

space group $P1$). The notations, P_a/c^+ , P_b/c^+ and P_b/c^- , are referred to the direction of the in-plane polarization with respect to the lattice vectors of the superlattice unit cell ($a = (\sqrt{2}, \sqrt{2}, 0)$, $b = (-\sqrt{2}, \sqrt{2}, 0)$, $c = (0, 0, n_{\text{BTO}} + n_{\text{CTO}})$) and in- or out-of-phase of the rotation along c -direction within the CTO constituent, regardless of the interface layers. In the superlattices with thin CaTiO_3 layers ($n_{\text{CTO}} < 3$), P_b/c^+ and P_b/c^- phases are indistinguishable by symmetry, since the in-/out-of-phase rotations along c -axis are undefined, denoted as $P_b/c^{+/-}$. When $n_{\text{CTO}} = 1$, the in-plane oxygen octahedron tilts within the CTO constituents also are undefined and the two directions of in-plane polarization are actually equivalent. Therefore there is only one single phase, denoted as $P_{a/b}$, in the superlattices with a single CTO layer. For each combination of $n_{\text{BTO}} : n_{\text{CTO}}$, we optimized all distinct structures and compared the energy of the relaxed structures to determine the ground state.

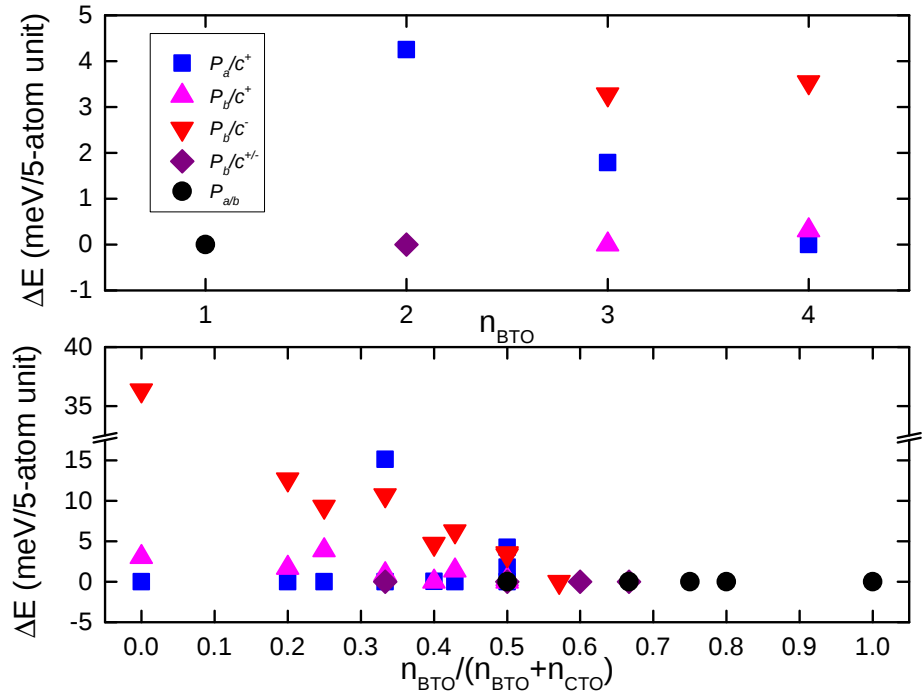


Figure 5.2: Dependence of the BTO/CTO total energy on the thicknesses of constituents (top) and BTO concentrations (bottom) with the energy of the corresponding ground state structure as the reference.

5.3 Results

The ground state structures in various BTO/CTO superlattices are shown in Fig. 5.1. Those results indicate that the both the BTO concentration and thicknesses of constituent layers affect the configurations of the BTO/CTO ground states. At 50% BTO concentration, as shown in the top panel of Fig. 5.2, the P_b/c^- phase has higher energy than the other two phases in BTO/CTO superlattices with short period, e.g. $n = 2$. As the thicknesses of both constituent layers increase, the energy difference between P_b/c^- phase and the ground states decreases and P_a/c^+ phase becomes the ground state in B4C4 superlattices. The bottom panel of Fig. 5.2 indicates that at low BTO concentration the ground state of BTO/CTO superlattices is the P_a/c^+ phase, which corresponds to the ground state of the pure bulk CTO materials. As the BTO concentration rises, the energy of P_b/c^+ and P_b/c^- phases is lowered with respect to that of P_a/c^+ phase. Above approximately 30% BTO fraction, P_b/c^+ phase is the ground states for some sequences. At high BTO concentration, e.g. B3C2, P_a/c^+ phase becomes unstable. The P_b/c^- phase is not the ground state in any of the superlattices considered. However the decreasing of the energy difference between P_b/c^- phase and the ground state suggests that at high BTO concentration, the P_b/c^- phase will be favored.

Fig. 5.3-5.5 show the computed polarization of various BTO/CTO superlattices in the three directions. In most structures, the in-plane polarization, such as $P[100]$ in P_a/c^+ phase, $P[100]$ and $P[010]$ in P_b/c^+ and P_b/c^- phases, changes almost linearly as the BTO fraction changes. However, $P[010]$, which does not exist in the bulk materials of the either constituent, rises at high BTO concentration. The $P[010]$ in P_a/c^+ phase is due to the incomplete cancellation of the antipolar mode X_5^+ in the CTO constituent at the interfaces (54). The inset graph of Fig. 5.4 also shows that $P[010]$ in all of the three structures decreases as the constituent thickness increases, which indicates the interfacial enhancement of $P[010]$.

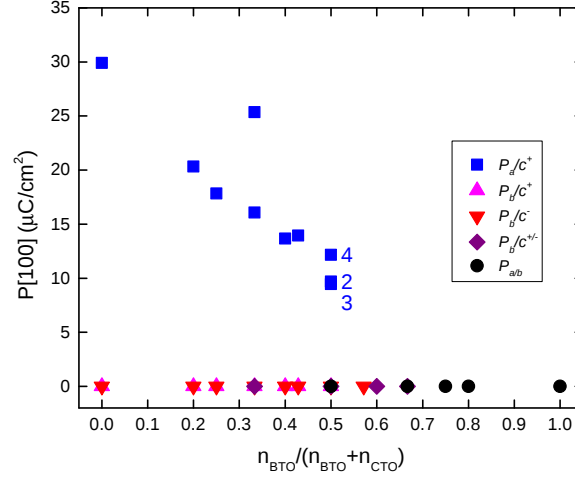


Figure 5.3: Computed polarization of various BTO/CTO superlattices in [100] direction

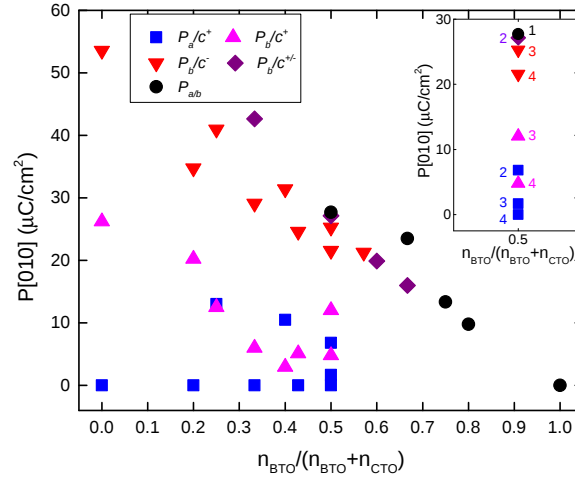


Figure 5.4: Computed polarization of various BTO/CTO superlattices in [010] direction

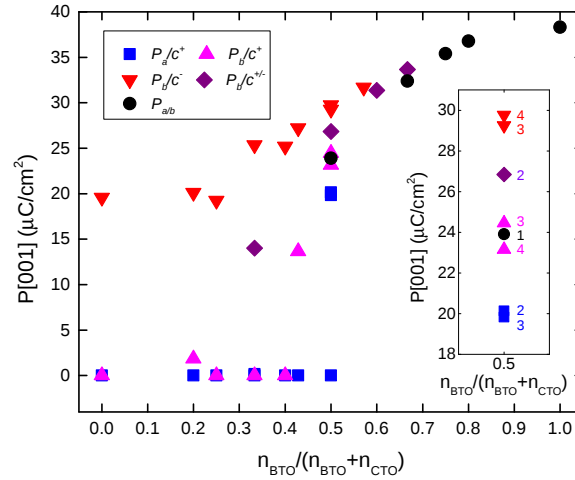


Figure 5.5: Computed polarization of various BTO/CTO superlattices in [001] direction

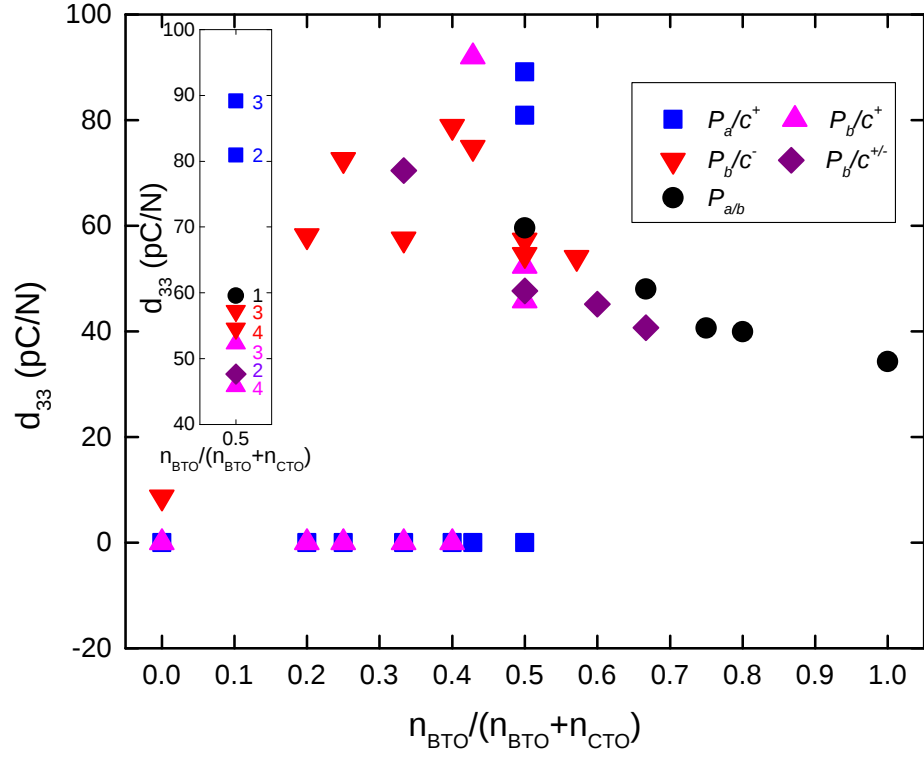


Figure 5.6: d_{33} of the three phases at various BTO concentrations.

Fig. 5.5 shows how the polarization in [001] direction varies in the three phases as the BTO concentration and thicknesses of constituents change. In both P_a/c^+ and P_b/c^+ phases, the polarization in [001] direction monotonically increases with the BTO concentration and both phases exhibit a transition from zero to nonzero $P[001]$ state. The inset graph of the Fig. 5.5 shows the $P[001]$ in various BTO/CTO superlattices at 50% BTO concentration and indicates that the interfacial effect enhances the out-of-plane polarization in P_a/c^+ and P_b/c^+ phases, except for B1C1 P_b/c^+ structure. The P_b/c^- structures have nonzero out-of-plane polarization at all epitaxial strains in our study. The $P[001]$ in P_b/c^- phase decreases as the density of interfaces decreases, as shown in the results for the superlattices of 50% BTO concentration.

As discussed in Chapter 2, the d_{33} of BTO/CTO superlattices is calculated according to the formula,

$$d_{33} = \frac{\partial P_z}{\partial \sigma_{33}} = -\frac{\partial P_z}{\partial \eta_{33}} \frac{\partial E}{\partial \eta_{33}},$$

where P_z is the polarization in $[001]$ direction, σ_{33} is a diagonal element of the stress matrix, E is the total energy density and η_{33} is a diagonal element of the strain matrix. The computed d_{33} of various BTO/CTO superlattices is shown in Fig. 5.6. All P_a/c^+ , P_b/c^+ and P_b/c^- phases with nonzero out-of-plane polarization show enhanced d_{33} , higher than that of either bulk constituent. In both P_a/c^+ and P_b/c^- phases, d_{33} increases as the thicknesses of constituent layers increase, which indicates that the interfacial effect enhances the piezoelectric constant d_{33} in BTO/CTO superlattices.

5.4 Discussion

To study the physics behind the functional properties, such as polarization and piezoelectric response, in the BTO/CTO superlattices, we constructed a first-principles-based dielectric slab model. Fig. 5.7 shows the total energy of various structures predicted by the slab model. In the simulation of the pure slab model, the P_a/c^+ phase is the ground state for all BTO concentrations. For $x \leq 0.5$, this is the case for the superlattices with the thickest layers, the limit in which the slab model is valid. For $x > 0.5$, it would be necessary to perform calculations for longer-period superlattices than those considered here to investigate this limit.

Fig. 5.8-5.10 shows the comparison of the out-of-plane polarization and piezoelectric constant d_{33} of the P_a/c^+ , P_b/c^+ and P_b/c^- phases at various BTO concentrations from first principles and model predictions. The slab model predicts the phase transition between zero and non-zero $P[001]$ phases at about 50% BTO concentrations in P_a/c^+ and P_b/c^+ phases. The slab model consistently underestimates the out-of-plane polarization in all of the three phases. In previous work (54; 73; 91; 92), the enhancement of polarization in perovskite superlattices has been reported. The recent work (93) shows that the suppression of the oxygen octahedron rotations at the interface causes the enhancement of polarization in BTO/CTO superlattices, which

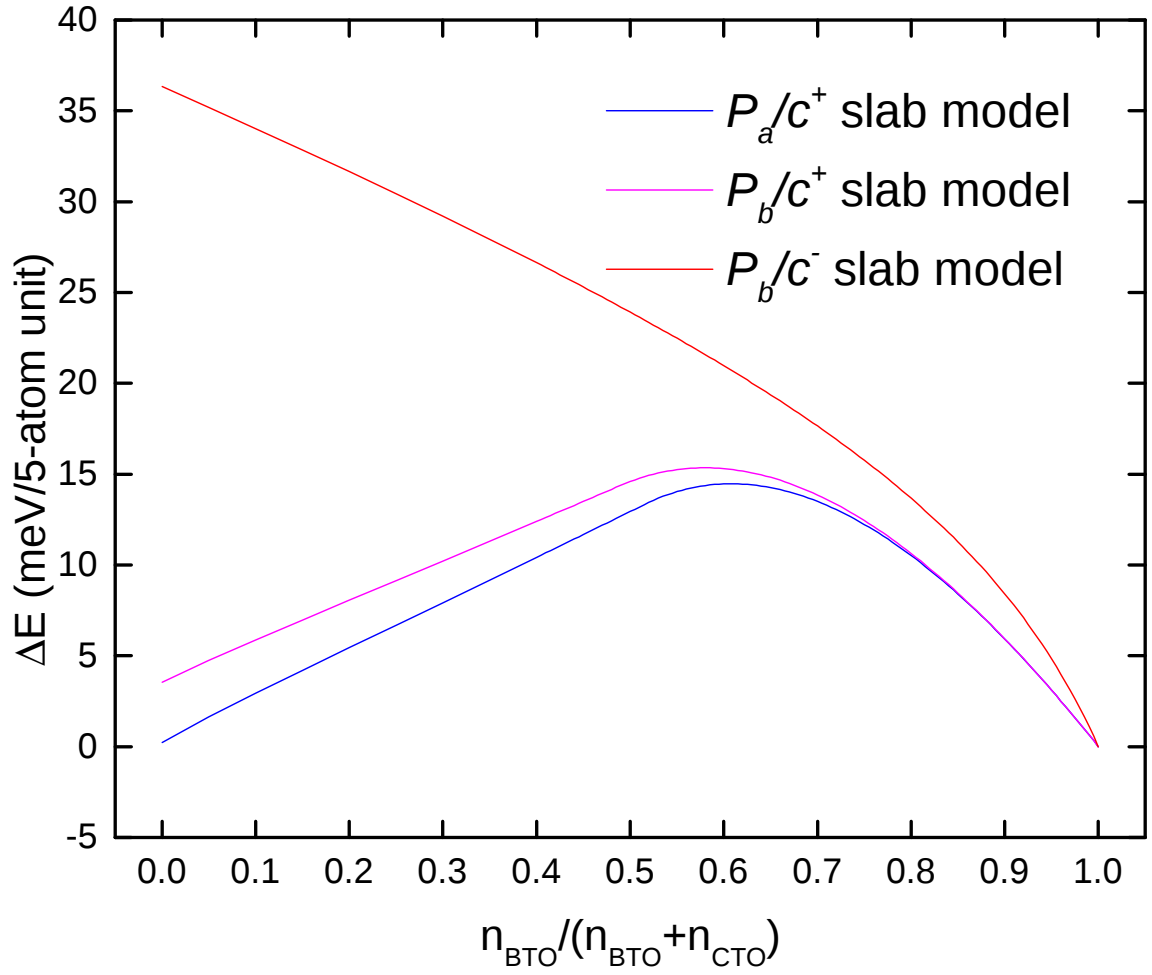


Figure 5.7: Total energy of various structures predicted by the slab model. The reference is the linear interpolation of the bulk material energy, $E_{\text{ref}} = (1-x)E_{Pmn2_1} + xE_{\text{CTO}}$, $x = n_{\text{BTO}}/(n_{\text{BTO}} + n_{\text{CTO}})$.

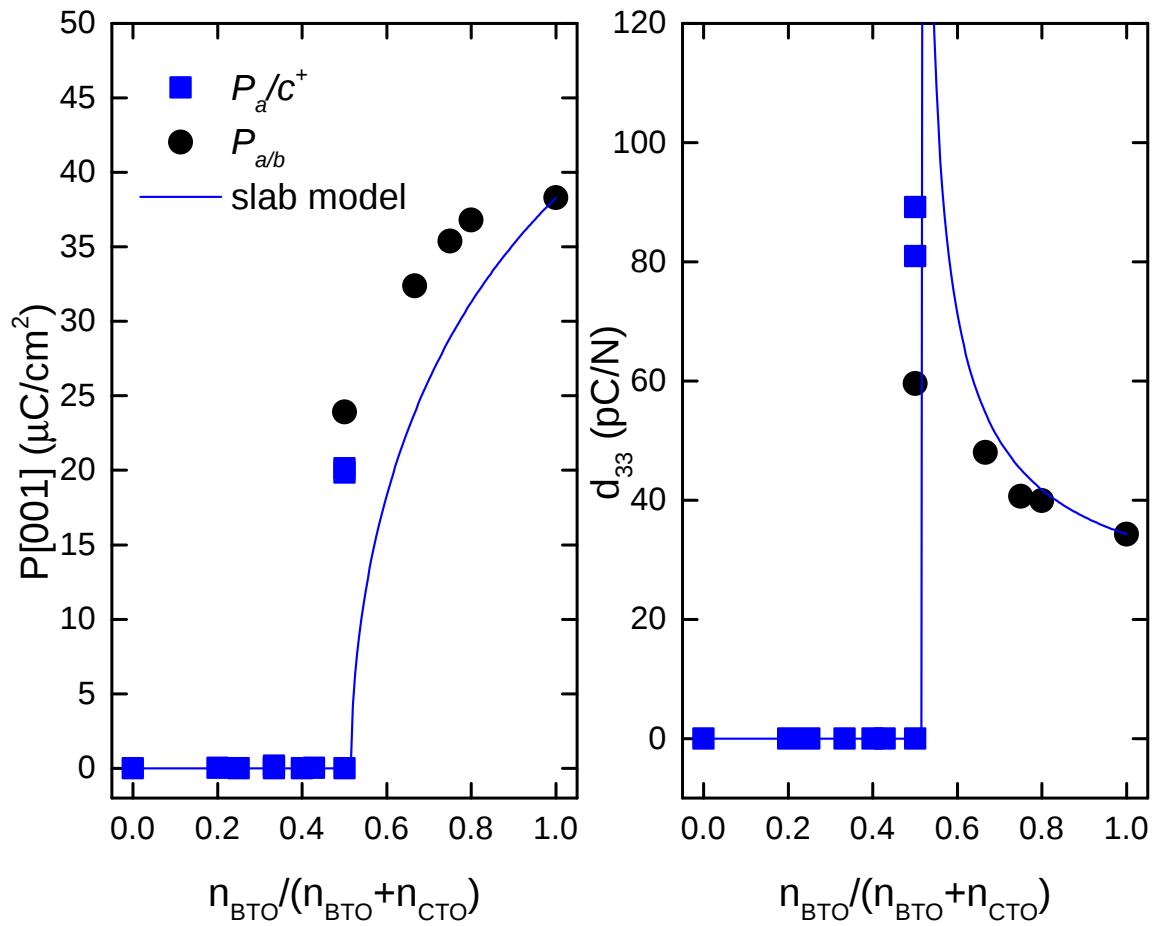


Figure 5.8: Comparison of out-of-plane polarization and d_{33} of P_a/c^+ phase from first principles and slab model.

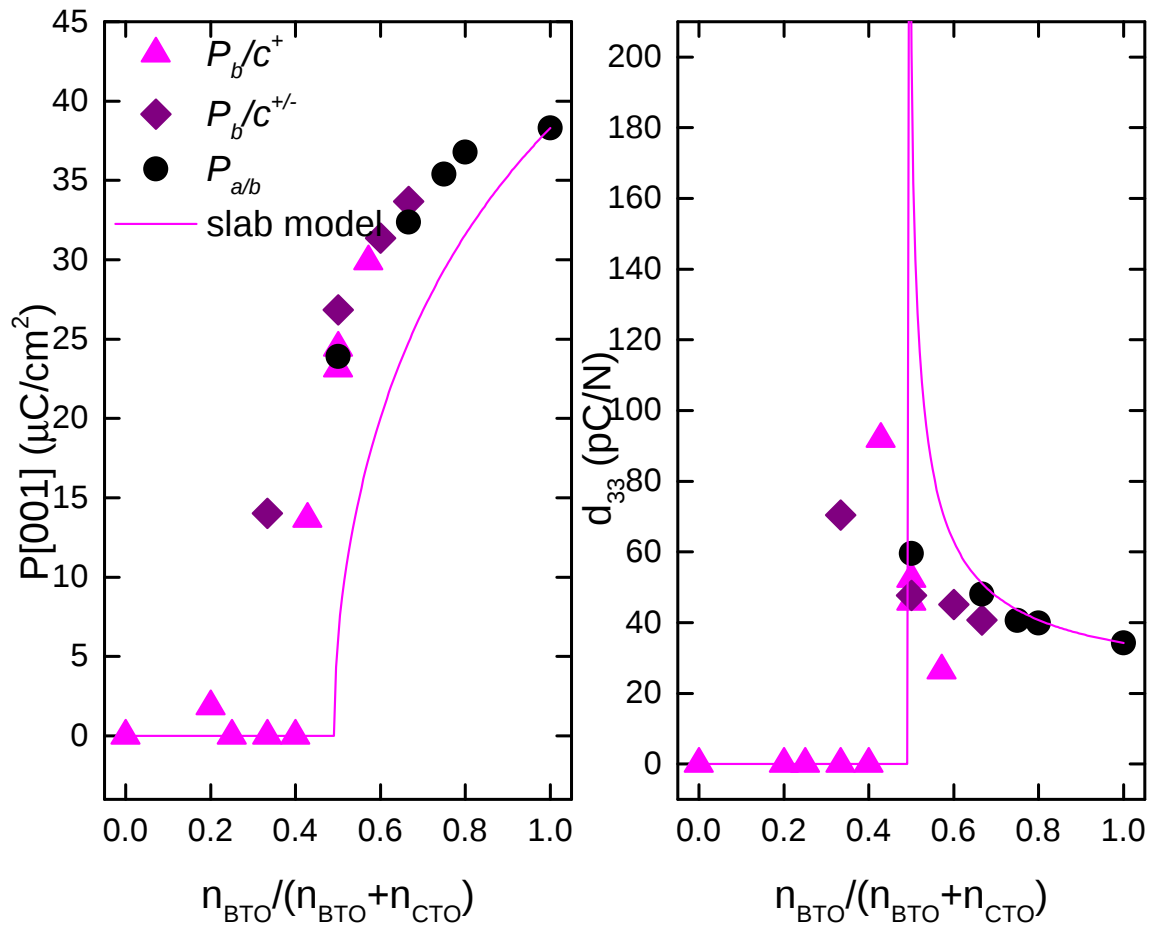


Figure 5.9: Comparison of out-of-plane polarization and d_{33} of P_b/c^+ phase from first principles and slab model.

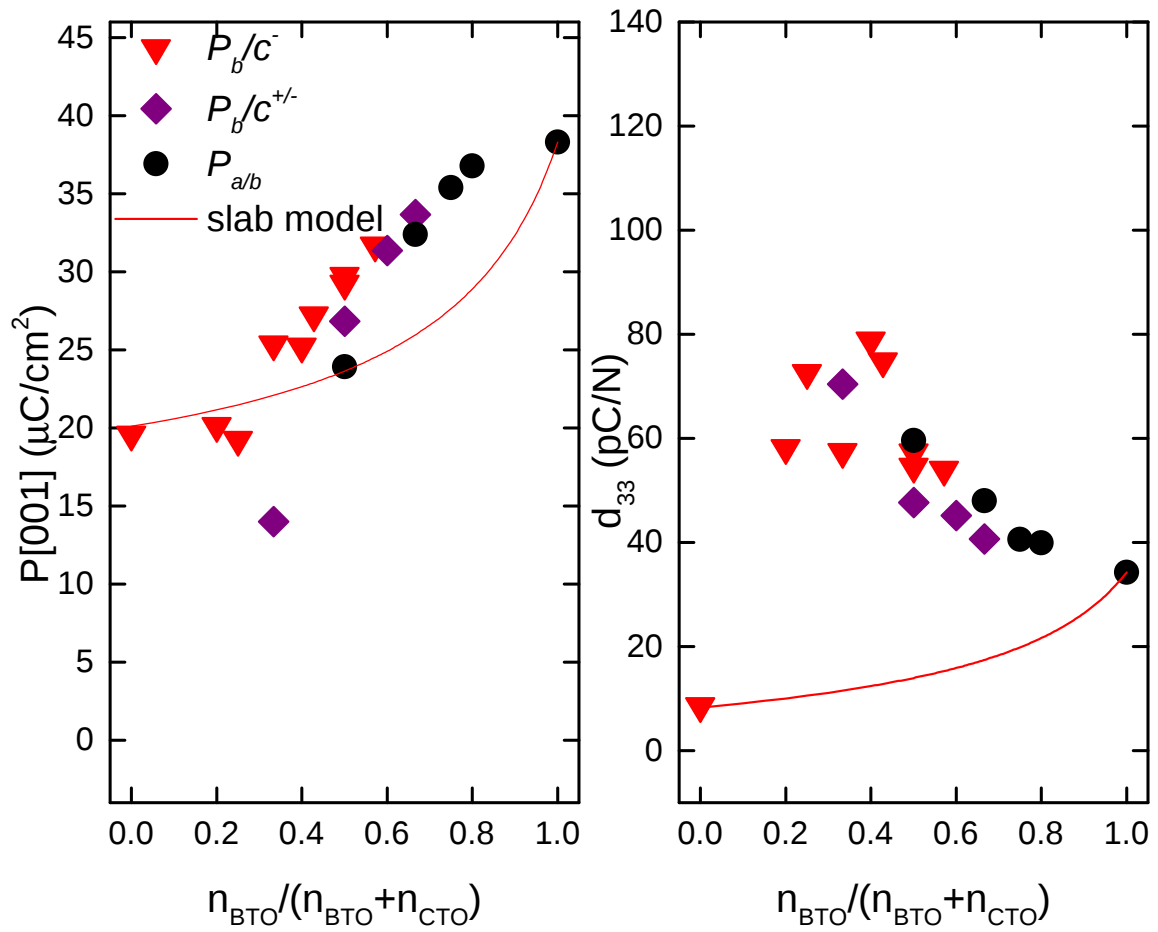


Figure 5.10: Comparison of out-of-plane polarization and d_{33} of P_b/c^- phase from first principles and slab model.

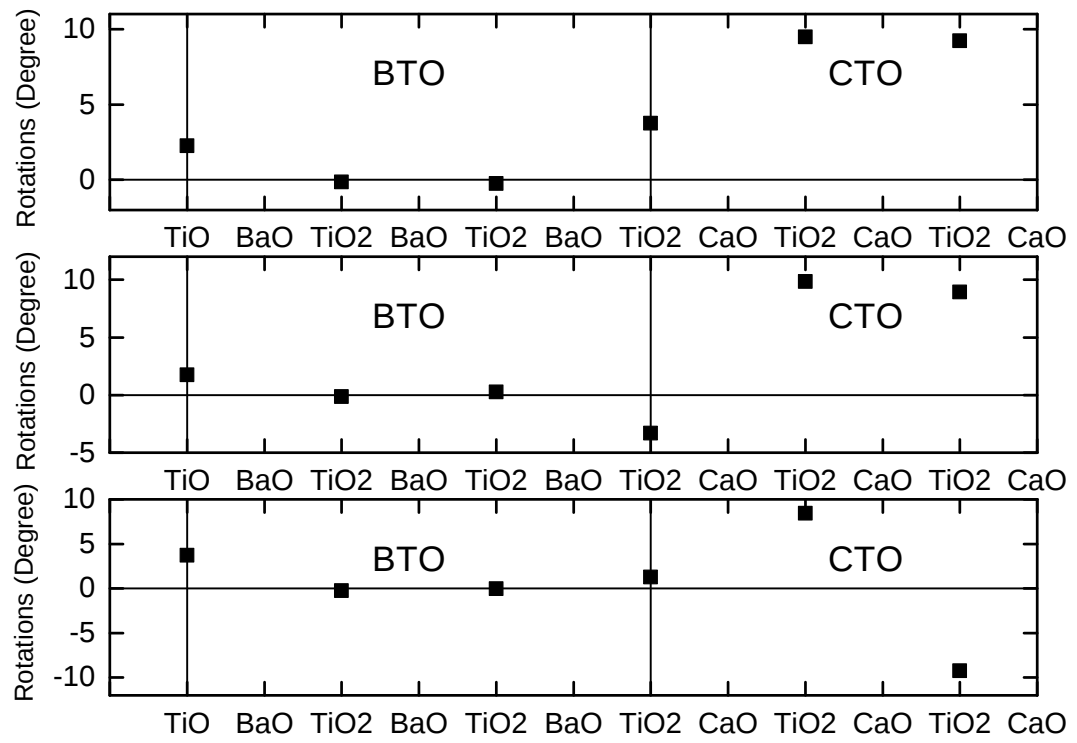


Figure 5.11: Oxygen octahedron rotations in B3C3 structures for P_a/c^+ (top), P_b/c^+ (middle) and P_b/c^- (bottom) phases.

is consistent with our first-principles calculations, as shown in Fig. 5.11 and our modeling. Especially, in P_b/c^+ phases, the out-of-phase rotation at one interface makes the CTO constituent a mixture of $Pmn2_1$ and $P1$ structures and the localized $P1$ CTO layer enhances the polarization in the superlattices.

In P_a/c^+ and P_b/c^+ phases, the slab model predicts a divergence of the piezoelectric constant d_{33} at the critical point of the zero and non-zero P[001] phase transition, which suggests that this phase transition contributes to the enhancement of the piezoelectricity in P_a/c^+ and P_b/c^+ phases. However, for the P_b/c^- phase, in which the out-of-plane polarization exists at all BTO concentrations, the slab model fails to reproduce the high piezoelectricity at intermediate BTO concentrations, which is greater than that of either bulk constituents. It indicates that the interfacial effect also lead to the enhancement of the piezoelectric constant d_{33} .

5.5 Summary

In conclusion, we calculated the energy and functional properties of the three candidate structures of BTO/CTO superlattices, P_a/c^+ , P_b/c^+ and P_b/c^- phases. As the BTO concentration increases, we observe two phase transitions, one from the P_a/c^+ to the P_b/c^+ phase and the other from the P_b/c^+ to the P_b/c^- phase. The critical points of the phase transitions depend on both BTO concentration and the thicknesses of the constituents. Enhancement of piezoelectricity is observed in all of the three phases. We also construct a first-principles slab model, which indicates that the interfacial effect enhances the out-of-plane polarization and the piezoelectricity in the BTO/CTO superlattices.

Chapter 6

Conclusions

The possibility of constructing simple models to describe the energetics of competing phases in perovskite materials and superlattices is strongly suggested by the fact that the mode decomposition of distorted perovskite structures generally shows only a small number of dominant modes. Mode amplitudes clearly emerge as the degrees of freedom for models of the energy landscape, to predict changes with electric field and epitaxial strain, relevant to response functions of thin films and to the structure and properties of superlattices.

First principles models are like phenomenological models in that they are fit to data, the data being obtained in a "computer experiment." An important difference, because the amount of experimental data is relatively limited, that phenomenological models fit to experimental data can only have a correspondingly small number of free parameters. This limitation is lifted in the first principles case, where an arbitrary number of coefficients can be determined by suitable first principles calculations, and therefore highly complex models with many degrees of freedom and coupling terms can be considered.

To get quantitative and predictive models still presents challenges. While polynomial expansions around a high-symmetry structure converge rapidly for systems where the phases involve small distortions, the description of the energy landscape for systems where there are only a small number of dominant modes but the amplitudes are large requires careful treatment, as exemplified in the case of epitaxially-strained CaTiO_3 discussed in Chapter 3. Even when the distortions are small, the fact that

there can be multiple modes of the same symmetry, most notably the polar mode in perovskites, creates difficulties in modeling a range of properties, since the eigenvector for the mode needed to describe the low energy structure might be different from the mode that describes the polar response to strain changes. In the case of superlattices, the polar modes that determine the dielectric and piezoelectric response might look quite different from the modes that are obtained within the slab model, which assumes uniform distortion in the layer.

Development of successful procedures for constructing models for these systems relies first on the careful analysis of individual systems that require addressing these issues. This is what has been the central work of my thesis. My hope is that the techniques and insights that have been worked out in these case-by-case studies will, in the near future, form the basis for the systematic modeling of a wider range of materials and superlattices, and that the models thus obtained will provide valuable guidance in the design, laboratory realization and deployment of novel high-performance functional materials for technologically important devices.

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Appendix A

Tables of action of symmetry operations on selected distortion modes

Table A.1: Application of symmetry operations of the point group O_h on the elastic strain components and the distortion modes whose corresponding $\mathbf{k}$ vectors have the star of O_h .

O_h	Γ_{4x}^-	Γ_{4y}^-	Γ_{4z}^-	R_{4x}^+	R_{4y}^+	R_{4z}^+	η_1	η_2	η_3
xyz	x	y	z	x	y	z	1	2	3
xzy	x	z	y	$-x$	$-z$	$-y$	1	3	2
yxz	y	x	z	$-y$	$-x$	$-z$	2	1	3
yzx	z	x	y	z	x	y	3	1	2
zxy	y	z	x	y	z	x	2	3	1
zyx	z	y	x	$-z$	$-y$	$-x$	3	2	1
$xy\bar{z}$	x	y	$-z$	$-x$	$-y$	z	1	2	3
$xz\bar{y}$	x	$-z$	y	x	$-z$	y	1	3	2
$yx\bar{z}$	y	x	$-z$	y	x	$-z$	2	1	3
$yz\bar{x}$	$-z$	x	y	z	$-x$	$-y$	3	1	2
$zx\bar{y}$	y	$-z$	x	$-y$	z	$-x$	2	3	1
$zy\bar{x}$	$-z$	y	x	$-z$	y	x	3	2	1
$x\bar{y}z$	x	$-y$	z	$-x$	y	$-z$	1	2	3
$x\bar{z}y$	x	z	$-y$	x	z	$-y$	1	3	2
$y\bar{x}z$	$-y$	x	z	$-y$	x	z	2	1	3

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Table A.1 – continued from previous page

O_h	Γ_{4x}^-	Γ_{4y}^-	Γ_{4z}^-	R_{4x}^+	R_{4y}^+	R_{4z}^+	η_1	η_2	η_3
$y\bar{z}x$	z	x	$-y$	$-z$	$-x$	y	3	1	2
$z\bar{x}y$	$-y$	z	x	y	$-z$	$-x$	2	3	1
$z\bar{y}x$	z	$-y$	x	z	$-y$	x	3	2	1
$x\bar{y}z$	x	$-y$	$-z$	x	$-y$	$-z$	1	2	3
$x\bar{z}y$	x	$-z$	$-y$	$-x$	z	y	1	3	2
$y\bar{x}z$	$-y$	x	$-z$	y	$-x$	z	2	1	3
$y\bar{z}x$	$-z$	x	$-y$	$-z$	x	$-y$	3	1	2
$z\bar{x}y$	$-y$	$-z$	x	$-y$	$-z$	x	2	3	1
$z\bar{y}x$	$-z$	$-y$	x	z	y	$-x$	3	2	1
$\bar{x}yz$	$-x$	y	z	x	$-y$	$-z$	1	2	3
$\bar{x}zy$	$-x$	z	y	$-x$	z	y	1	3	2
$\bar{y}xz$	y	$-x$	z	y	$-x$	z	2	1	3
$\bar{y}zx$	z	$-x$	y	$-z$	x	$-y$	3	1	2
$\bar{z}xy$	y	z	$-x$	$-y$	$-z$	x	2	3	1
$\bar{z}yx$	z	y	$-x$	z	y	$-x$	3	2	1
$\bar{x}y\bar{z}$	$-x$	y	$-z$	$-x$	y	$-z$	1	2	3
$\bar{x}z\bar{y}$	$-x$	$-z$	y	x	z	$-y$	1	3	2
$\bar{y}x\bar{z}$	y	$-x$	$-z$	$-y$	x	z	2	1	3
$\bar{y}z\bar{x}$	$-z$	$-x$	y	$-z$	$-x$	y	3	1	2
$\bar{z}x\bar{y}$	y	$-z$	$-x$	y	$-z$	$-x$	2	3	1
$\bar{z}y\bar{x}$	$-z$	y	$-x$	z	$-y$	x	3	2	1
$\bar{x}y\bar{z}$	$-x$	$-y$	z	$-x$	$-y$	z	1	2	3
$\bar{x}z\bar{y}$	$-x$	z	$-y$	x	$-z$	y	1	3	2
$\bar{y}x\bar{z}$	$-y$	$-x$	z	y	x	$-z$	2	1	3
$\bar{y}z\bar{x}$	z	$-x$	$-y$	z	$-x$	$-y$	3	1	2

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Table A.2 – continued from previous page

D_{4h}	Γ_{4x}^-	Γ_{4y}^-	Γ_{4z}^-	R_{4x}^+	R_{4y}^+	M_3^+	X_{5x}^+	X_{5y}^+	X_{5x}^-	X_{5y}^-	η_1	η_2	η_3
$xy\bar{z}$	x	y	$-z$	$-x$	$-y$	1	$-x$	$-y$	x	y	1	2	3
$y\bar{x}\bar{z}$	$-y$	x	$-z$	y	$-x$	1	y	$-x$	y	$-x$	2	1	3
$\bar{y}x\bar{z}$	y	$-x$	$-z$	$-y$	x	1	$-y$	x	$-y$	x	2	1	3
$\bar{y}\bar{x}z$	$-y$	$-x$	z	y	x	-1	$-y$	$-x$	$-y$	$-x$	2	1	3
yxz	y	x	z	$-y$	$-x$	-1	y	x	y	x	2	1	3

Appendix B

Energy function for CaTiO₃

The total energy of bulk CaTiO₃ is expanded with the ideal cubic $Pm\bar{3}m$ structure as reference in terms of structural parameters, $\Gamma_{4x\sim y}^-$, M_3^+ , $R_{4x\sim y}^+$, X_5^+ , X_5^- and $\eta_{1\sim 3}$. The unit of energy is meV/f.u. For simplicity all of the superscripts and subscripts are omitted. X_5^- mode is denoted as X_m in order to distinguish from X_5^+ mode.

$$\begin{aligned}
E = & (-44.080) + (-0.127)(\eta_1 + \eta_2 + \eta_3) + 70.089(\eta_1^2 + \eta_2^2 + \eta_3^2) \\
& + (-252.107)(\eta_1^3 + \eta_2^3 + \eta_3^3) + 566.767(\eta_1^4 + \eta_2^4 + \eta_3^4) \\
& + 36.187(\eta_1\eta_2 + \eta_1\eta_3 + \eta_2\eta_3) + (-37.448)\eta_1\eta_2\eta_3 + 0.393X_m^2 + 0.052X_m^4 \\
& + (-0.021)X_m^6 + 0.012X_m^8 + (-1.998)(\eta_1X_m^2 + \eta_2X_m^2) + 1.551\eta_1\eta_2X_m^2 + 0.000X^2 \\
& + 0.296X^4 + 0.059X^6 + 0.004X^8 + (-1.107)\eta_3X^2 + 1.410(\eta_1\eta_3X^2 + \eta_2\eta_3X^2) \\
& + (-2.531)(\eta_1X^2 + \eta_2X^2) + 9.905\eta_1\eta_2X^2 + 0.002X^2X_m^2 + (-0.340)M^2 + 0.132M^4 \\
& + (-0.012)M^6 + 0.001M^8 + (-0.069)\eta_3M^2 + 2.518\eta_3^2M^2 + 1.390(\eta_1M^2 + \eta_2M^2) \\
& + 2.427(\eta_1\eta_3M^2 + \eta_2\eta_3M^2) + (-7.009)\eta_1\eta_2M^2 + (-14.131)\eta_1\eta_2\eta_3M^2 \\
& + (-0.008)M^2X_m^2 + (-0.112)\eta_3M^2X_m^2 + 0.086M^2X^2 + (-0.221)\eta_3M^2X^2 \\
& + 0.162(\eta_1M^2X^2 + \eta_2M^2X^2) + (-0.854)(\eta_1\eta_3M^2X^2 + \eta_2\eta_3M^2X^2) \\
& + 0.800\eta_1\eta_2M^2X^2 + (-0.018)M^2X^2X_m^2 + 0.148\eta_3M^2X^2X_m^2 + (-0.377)(R_x^2 + R_y^2) \\
& + 0.142(R_x^4 + R_y^4) + (-0.015)(R_x^6 + R_y^6) + 0.001(R_x^8 + R_y^8) \\
& + 1.398(\eta_1R_y^2 + \eta_2R_x^2 + \eta_3R_x^2 + \eta_3R_y^2) + 0.140(\eta_1R_x^2 + \eta_2R_y^2) + 1.546(\eta_1^2R_x^2 + \eta_2^2R_y^2) \\
& + 2.104(\eta_1\eta_2R_x^2 + \eta_1\eta_2R_y^2 + \eta_1\eta_3R_x^2 + \eta_2\eta_3R_y^2) + (-5.570)(\eta_1\eta_3R_y^2 + \eta_2\eta_3R_x^2)
\end{aligned}$$

$$\begin{aligned}
& + (-19.113)(\eta_1\eta_2\eta_3R_x^2 + \eta_1\eta_2\eta_3R_y^2) + 0.001(R_x^2X_m^2 + R_y^2X_m^2) \\
& + 0.343(R_x^2X^2 + R_y^2X^2) + 0.117(R_x^2X^4 + R_y^2X^4) + (-0.009)(R_x^4X^2 + R_y^4X^2) \\
& + (-0.547)(\eta_3R_x^2X^2 + \eta_3R_y^2X^2) + (-1.785)(\eta_1R_x^2X^2 + \eta_2R_y^2X^2) \\
& + 1.513(\eta_1\eta_3R_x^2X^2 + \eta_2\eta_3R_y^2X^2) + (-0.153)(\eta_1R_y^2X^2 + \eta_2R_x^2X^2) \\
& + 0.449(\eta_1\eta_2R_x^2X^2 + \eta_1\eta_2R_y^2X^2) + (-0.016)(R_x^2X^2X_m^2 + R_y^2X^2X_m^2) \\
& + 0.165(R_x^2M^2 + R_y^2M^2) + (-0.412)(\eta_3R_x^2M^2 + \eta_3R_y^2M^2) \\
& + (-0.437)(\eta_1R_x^2M^2 + \eta_2R_y^2M^2) + 1.865(\eta_1\eta_3R_x^2M^2 + \eta_2\eta_3R_y^2M^2) \\
& + (-0.376)(\eta_1R_y^2M^2 + \eta_2R_x^2M^2) + 0.506(\eta_1\eta_2R_x^2M^2 + \eta_1\eta_2R_y^2M^2) \\
& + (-0.137)(R_xMX + R_yMX) + 0.012(R_xMX^3 + R_yMX^3) \\
& + (-0.033)(R_xM^3X + R_yM^3X) \\
& + (-0.036)(R_x^3MX + R_y^3MX) + 1.507(\eta_3R_xMX + \eta_3R_yMX) \\
& + 1.226(\eta_1R_xMX + \eta_2R_yMX) + (-6.821)(\eta_1\eta_3R_xMX + \eta_2\eta_3R_yMX) \\
& + 1.356(\eta_1\eta_2R_xMX + \eta_1\eta_2R_yMX) + (-0.434)(\eta_1R_xMXX_m^2 + \eta_2R_yMXX_m^2) \\
& + 0.011(R_x^2M^2X_m^2 + R_y^2M^2X_m^2) + 0.005(R_xMXX_m^2 + R_yMXX_m^2) + 0.174R_x^2R_y^2 \\
& + (-0.445)\eta_3R_x^2R_y^2 + (-0.444)(\eta_1R_x^2R_y^2 + \eta_2R_x^2R_y^2) + 2.292\eta_1\eta_2R_x^2R_y^2 \\
& + (-0.031)R_xR_yX_m^2 + 0.068(\eta_1R_xR_yX_m^2 + \eta_2R_xR_yX_m^2) + (-0.716)R_xR_yX^2 \\
& + 0.373\eta_3R_xR_yX^2 + 2.545(\eta_1R_xR_yX^2 + \eta_2R_xR_yX^2) + (-9.454)\eta_1\eta_2R_xR_yX^2 \\
& + (-0.012)R_x^2R_y^2M^2 + 0.025\eta_3R_x^2R_y^2M^2 + 0.018(\eta_1R_x^2R_y^2M^2 + \eta_2R_x^2R_y^2M^2) \\
& + 0.009R_xR_yM^2X_m^2 + (-0.031)(R_x^2R_yMX + R_xR_y^2MX) \\
& + 0.157(\eta_1R_x^2R_yMX + \eta_2R_xR_y^2MX) + (-0.000)(\eta_1R_xR_y^2MX + \eta_2R_x^2R_yMX) \\
& + 0.635(\Gamma_x^2 + \Gamma_y^2 + \Gamma_z^2) + 7.722(\Gamma_x^4 + \Gamma_y^4 + \Gamma_z^4) + (-5.913)(\Gamma_x^6 + \Gamma_y^6 + \Gamma_z^6) \\
& + 6.300(\Gamma_x^8 + \Gamma_y^8 + \Gamma_z^8) + (-34.974)(\eta_1\Gamma_x^2 + \eta_2\Gamma_y^2 + \eta_3\Gamma_z^2) \\
& + (-0.375)(\eta_1\Gamma_y^2 + \eta_1\Gamma_z^2 + \eta_2\Gamma_x^2 + \eta_2\Gamma_z^2 + \eta_3\Gamma_x^2 + \eta_3\Gamma_y^2) \\
& + (-33.743)(\eta_1^2\Gamma_y^2 + \eta_1^2\Gamma_z^2 + \eta_2^2\Gamma_x^2 + \eta_2^2\Gamma_z^2 + \eta_3^2\Gamma_x^2 + \eta_3^2\Gamma_y^2) \\
& + 8.228(\eta_1\eta_2\Gamma_x^2 + \eta_1\eta_2\Gamma_y^2 + \eta_1\eta_3\Gamma_x^2 + \eta_1\eta_3\Gamma_z^2 + \eta_2\eta_3\Gamma_y^2 + \eta_2\eta_3\Gamma_z^2)
\end{aligned}$$

$$\begin{aligned}
& + (-1.951)(\eta_1\eta_2\Gamma_z^2 + \eta_1\eta_3\Gamma_y^2 + \eta_2\eta_3\Gamma_x^2) + 0.124\Gamma_z^2X^2 + (-0.036)\Gamma_z^2X^4 \\
& + (-0.724)\Gamma_z^4X^2 + 0.134\Gamma_z^2M^2 + (-0.471)\eta_3\Gamma_z^2M^2 \\
& + (-1.057)(\eta_1\Gamma_z^2M^2 + \eta_2\Gamma_z^2M^2) + (-1.404)(\eta_1\eta_3\Gamma_z^2M^2 + \eta_2\eta_3\Gamma_z^2M^2) \\
& + 0.044\Gamma_zM^2XX_m + (-0.330)\eta_3\Gamma_zM^2XX_m \\
& + (-0.639)(\Gamma_x^2R_y^2 + \Gamma_y^2R_x^2 + \Gamma_z^2R_x^2 + \Gamma_z^2R_y^2) \\
& + 6.137(\eta_1\Gamma_x^2R_y^2 + \eta_2\Gamma_y^2R_x^2 + \eta_3\Gamma_z^2R_x^2 + \eta_3\Gamma_z^2R_y^2) \\
& + 0.513(\eta_1\Gamma_y^2R_x^2 + \eta_1\Gamma_z^2R_x^2 + \eta_2\Gamma_x^2R_y^2 + \eta_2\Gamma_z^2R_y^2) \\
& + 0.117(\Gamma_zR_x^2XX_m + \Gamma_zR_y^2XX_m) \\
& + (-0.153)(\eta_1\Gamma_z^2R_x^2M^2 + \eta_2\Gamma_z^2R_y^2M^2) + (-0.229)(\Gamma_zR_xMX_m + \Gamma_zR_yMX_m) \\
& + 0.580(\eta_3\Gamma_zR_xMX_m + \eta_3\Gamma_zR_yMX_m) + 0.820(\eta_1\Gamma_zR_xMX_m + \eta_2\Gamma_zR_yMX_m) \\
& + 0.532(\eta_1\Gamma_zR_yMX_m + \eta_2\Gamma_zR_xMX_m) + (-0.052)(\Gamma_z^2R_xMX + \Gamma_z^2R_yMX) \\
& + 0.178\Gamma_z^2R_x^2R_y^2 + (-0.047)\Gamma_z^2R_xR_yX_m^2 + 0.013\Gamma_zR_xR_yXX_m \\
& + (-0.025)\Gamma_zR_x^2R_y^2XX_m + 0.006\Gamma_zR_xR_yXX_m^3 + (-0.009)\Gamma_zR_xR_yX^3X_m \\
& + 0.025(\Gamma_zR_x^3R_yXX_m + \Gamma_zR_xR_y^3XX_m) + (-0.436)\Gamma_z^3R_xR_yXX_m \\
& + (-0.434)(\Gamma_x^2M^2 + \Gamma_y^2M^2) + 0.044(\Gamma_x^2M^4 + \Gamma_y^2M^4) + (-1.247)(\Gamma_x^4M^2 + \Gamma_y^4M^2) \\
& + 0.648(\eta_3\Gamma_x^2M^2 + \eta_3\Gamma_y^2M^2) + 5.731(\eta_1\Gamma_x^2M^2 + \eta_2\Gamma_y^2M^2) \\
& + (-1.571)(\eta_1\Gamma_y^2M^2 + \eta_2\Gamma_x^2M^2) + 10.168(\eta_1\eta_2\Gamma_x^2M^2 + \eta_1\eta_2\Gamma_y^2M^2) \\
& + 0.136(\Gamma_x^2R_x^2 + \Gamma_y^2R_y^2) + (-1.080)(\eta_1\Gamma_y^2R_y^2 + \eta_2\Gamma_x^2R_x^2 + \eta_3\Gamma_x^2R_x^2 + \eta_3\Gamma_y^2R_y^2) \\
& + (-0.496)(\eta_1\Gamma_x^2R_x^2 + \eta_2\Gamma_y^2R_y^2) + 0.240(\eta_1\Gamma_x^2R_x^2M^2 + \eta_2\Gamma_y^2R_y^2M^2) \\
& + (-2.336)(\eta_1\Gamma_z^2R_y^2 + \eta_2\Gamma_z^2R_x^2 + \eta_3\Gamma_x^2R_y^2 + \eta_3\Gamma_y^2R_x^2) \\
& + 17.079(\eta_1^2\Gamma_z^2R_y^2 + \eta_2^2\Gamma_z^2R_x^2 + \eta_3^2\Gamma_x^2R_y^2 + \eta_3^2\Gamma_y^2R_x^2) + (-0.393)(\Gamma_x^2R_y^2X_m^2 + \Gamma_y^2R_x^2X_m^2) \\
& + 0.026(\Gamma_x^2R_y^2X^2X_m^2 + \Gamma_y^2R_x^2X^2X_m^2) + 0.178(\Gamma_x^2R_y^2M^2 + \Gamma_y^2R_x^2M^2) \\
& + 0.080(\Gamma_x^2R_y^2M^2X_m^2 + \Gamma_y^2R_x^2M^2X_m^2) + (-0.044)(\Gamma_x^2R_x^2R_y^2 + \Gamma_y^2R_x^2R_y^2) \\
& + 2.625(\Gamma_x^2\Gamma_y^2 + \Gamma_x^2\Gamma_z^2 + \Gamma_y^2\Gamma_z^2) \\
& + (-5.542)(\Gamma_x^4\Gamma_y^2 + \Gamma_x^4\Gamma_z^2 + \Gamma_x^2\Gamma_y^4 + \Gamma_x^2\Gamma_z^4 + \Gamma_y^4\Gamma_z^2 + \Gamma_y^2\Gamma_z^4)
\end{aligned}$$

$$\begin{aligned}
& + 6.423(\eta_1\Gamma_x^2\Gamma_y^2 + \eta_1\Gamma_x^2\Gamma_z^2 + \eta_2\Gamma_x^2\Gamma_y^2 + \eta_2\Gamma_y^2\Gamma_z^2 + \eta_3\Gamma_x^2\Gamma_z^2 + \eta_3\Gamma_y^2\Gamma_z^2) \\
& + 3.856(\eta_1\Gamma_y^2\Gamma_z^2 + \eta_2\Gamma_x^2\Gamma_z^2 + \eta_3\Gamma_x^2\Gamma_y^2) \\
& + (-20.912)(\eta_1\eta_2\Gamma_x^2\Gamma_z^2 + \eta_1\eta_2\Gamma_y^2\Gamma_z^2 + \eta_1\eta_3\Gamma_x^2\Gamma_y^2 + \eta_1\eta_3\Gamma_y^2\Gamma_z^2 + \eta_2\eta_3\Gamma_x^2\Gamma_y^2 + \eta_2\eta_3\Gamma_x^2\Gamma_z^2) \\
& + (-2.219)(\eta_1\Gamma_x^2\Gamma_z^2M^2 + \eta_2\Gamma_y^2\Gamma_z^2M^2) + 1.602(\Gamma_x^2\Gamma_z^2R_y^2 + \Gamma_y^2\Gamma_z^2R_x^2) \\
& + 0.568(\Gamma_x^2\Gamma_z^2R_y^2X_m^2 + \Gamma_y^2\Gamma_z^2R_x^2X_m^2) + 0.506\Gamma_x\Gamma_yX_m^2 + (-3.095)\Gamma_x^2\Gamma_y^2X_m^2 \\
& + (-0.132)\Gamma_x\Gamma_yX_m^4 + (-2.232)(\Gamma_x^3\Gamma_yX_m^2 + \Gamma_x\Gamma_y^3X_m^2) + 0.582\Gamma_x\Gamma_yX^2 \\
& + 1.464\Gamma_x^2\Gamma_y^2M^2 + 0.423\Gamma_x\Gamma_yM^2X_m^2 + (-0.275)\Gamma_x\Gamma_yR_xR_y + 1.878\eta_3\Gamma_x\Gamma_yR_xR_y \\
& + 0.166\Gamma_x\Gamma_yR_xR_yX_m^2 + (-0.296)\Gamma_x\Gamma_yR_xR_yX^2 + (-1.352)\Gamma_x\Gamma_y\Gamma_z^2R_xR_y
\end{aligned}$$

Appendix C

Energy functions for strained BaTiO₃ and PbTiO₃

In the dielectric slab model, the constituent layers of the superlattice are modeled as bulk materials responding to the changes in mechanical and electrical boundary conditions produced by the lattice matching at the interface, which here constrains the in-plane lattice parameter to that of the STO substrate, and the absence of free charge, which results in equal displacement field D in the two layers.

The constitutive relations for each constituent material are determined from first principles calculations and fit to a polynomial model. For the BTO/PTO superlattice, each layer is described by two degrees of freedom: the c-axis strain, defined as $\eta = \frac{c}{a} - 1$, and the zero-field polarization along the normal direction, represented here by u . The energy per formula unit for each constituent layer is expressed by the lowest order terms in a Taylor expansion:

$$E = \frac{1}{2}ku^2 + \frac{1}{4}\gamma u^4 + \frac{1}{2}\beta u^2\eta + \frac{1}{2}C\eta^2 + C'\eta^3 + C''\eta^4$$

The coefficients k , γ , β , C , C' and C'' are determined from first principles calculations, as follows. For both BTO and PTO, we consider the tetragonal $P4mm$ structure with five atoms per unit cell and the a parameter fixed to 3.86 Å, the lattice parameter computed for the cubic SrTiO₃ substrate. For a range of c values, we relax the internal structural parameters to obtain the total energy and the polarization as a function of η . This information, combined with the c lattice parameter and energy of the minimum-energy $P/4mmm$ structure (polarization zero), is sufficient to determine the coefficients. The model should reproduce d_{33} and ϵ_{33} computed for the pure

(strained) compounds.

The total energy of the superlattice is modeled as the sum of the energies of the two slabs, including the electrostatic work done in each slab, included as the term $-uE$ for each layer. With the imposed short circuit boundary conditions are imposed, corresponding to the periodic boundary conditions in the first principles calculations, the relation D is $\epsilon_{fs}E + u$ is sufficient to determine E_1 and E_2 , the electric fields in each constituent layer. Then the total energy is minimized to obtain u_1 , u_2 and $\frac{c}{a}$ for each slab and hence total polarization P and total $\frac{c}{a}$.

ϵ_{33} and d_{33} at $E = 0$ can be determined with a finite difference approach. we consider the system at $E = 0$ and apply an infinitesimal field ΔE . This leads to an infinitesimal change in the electric fields of the constituent layers. linearize the response of each constituent at nonzero E . This also yields a finite difference value for $d_{33} = d\eta/dE$ at zero stress (converse piezoelectric effect).

To determine $d_{33} = dP/d\sigma$ at $E = 0$ (direct piezoelectric effect), we optimized the structure for several values of fixed c , computing the total energies and polarization. Using the expression $d_{33} = dP/d\sigma(E = 0) = (dP/d\eta)/(d\sigma/d\eta)$ where $\eta = c/a - 1$, we fit $P(\eta)$ and $E(\eta)$, yielding $\sigma = -dE/d\eta$, and evaluate the d_{33} .

Appendix D

Energy functions for strained BaTiO₃ and CaTiO₃

In the slab model, the superlattice is treated as layers of bulk-like materials. The total energy of the superlattice is described by the weighted average of energy functions of bulk materials.

$$E^{\text{Slab}} = \frac{1}{n_B + n_C} (n_B E_B(P_{zB}, \eta_{3B}) + n_C E_C(P_{zC}, \eta_{3C}, \{\phi_C\}))$$

E_B and E_C are the energy function of strained bulk BTO and CTO. Tensile strained bulk CTO has multiple metastable states, so we constructed different E_C 's for each individual phase. $P_{z\alpha}$ is the polarization in z -direction and $\eta_{3\alpha}$, $\alpha = B, C$, is the elastic strain of the constituents. $\{\phi_C\}$ is the group of distortion modes in bulk CTO besides the P_z , such as oxygen octahedron rotations, tilts and in-plane polarization. Within the framework of slab model, different constituents are connected via appropriate electrostatic boundary condition. Strictly speaking, the correct boundary condition should be constant electric displacement in z -direction: $D_{zB} = D_{zC}$. In our modeling, we adapted an approximation of uniform polarization in z : $P_{zB} \sim P_{zC} = P$, since BTO and CTO have similar permittivity. Therefore the total energy of the superlattice changes to the following form:

$$E_{\text{Slab}} = \frac{1}{n_B + n_C} (n_B E_B(P, \eta_{3B}) + n_C E_C(P, \eta_{3C}, \{\phi_C\}))$$

As previously mentioned, the structure of bulk BTO is simple and the only distortion mode is the out-of-plane polarization P . According to the Landau theory, a

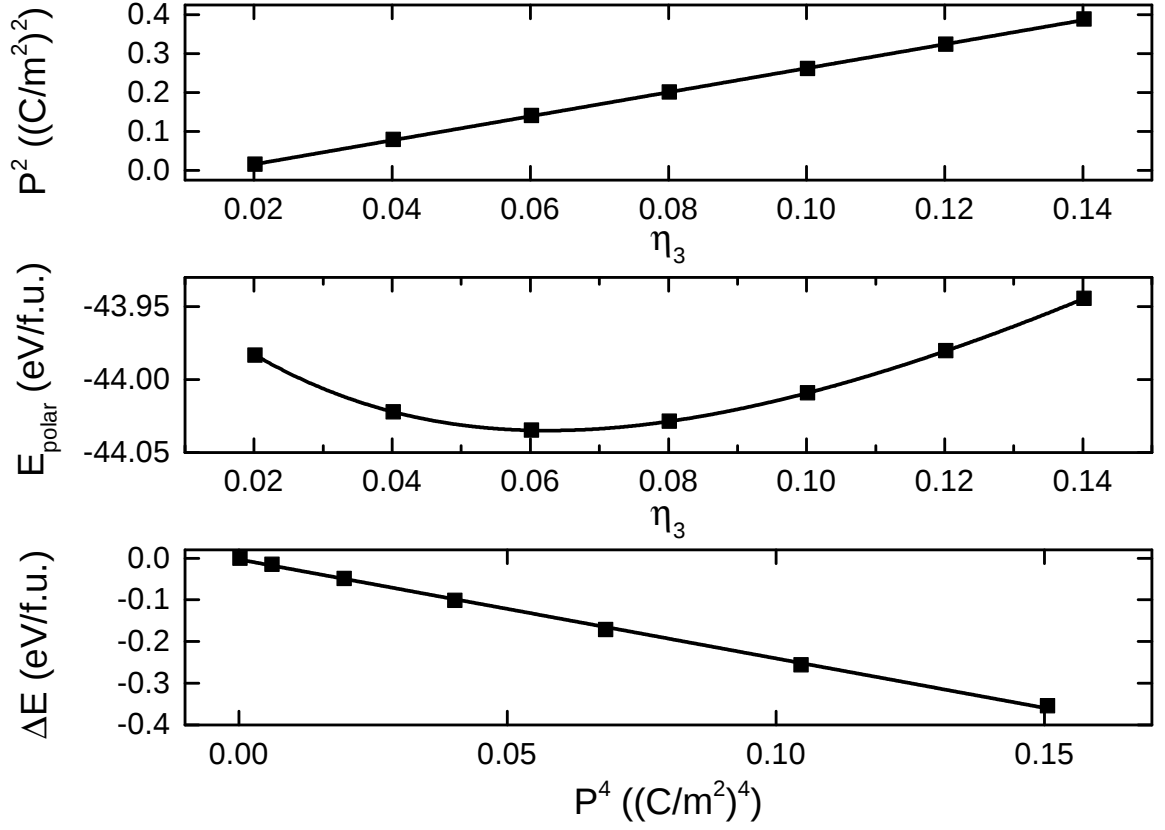


Figure D.1: Fitting of the coefficients in BTO energy function. Top: fit the polarization, $P^2 = -\frac{1}{2\kappa}(\alpha + B_{1xx}\eta_3)$; middle: fit the energy of polar structure, $E_{\text{polar}} = (E_0 - \frac{\alpha^2}{4\kappa}) + (B_1 - \frac{\alpha B_{1xx}}{2\kappa})\eta_3 + (B_{11} - \frac{\beta^2}{4\kappa})\eta_3^2$; bottom: fit the energy difference between the polar and nonpolar structures, $\Delta E = E_{\text{polar}} - E_{\text{nonpolar}} = -\kappa P^4$

forth order polynomial is sufficient to describe the anharmonic behavior of bulk BTO:

$$\begin{aligned}
 E_B(P, \eta_{3B}) &= E_{0B} + \alpha_B P^2 + \kappa_B P^4 + \frac{1}{2} B_{1xxB} \eta_{3B} P^2 \\
 &+ B_{1B} \eta_{3B} + \frac{1}{2} B_{11B} \eta_{3B}^2
 \end{aligned}$$

All of coefficients are determined via the response of polarization with respect to the change of elastic strain η_3 from first-principles calculations (7), which is shown in Fig. D.1. However, the energy function of bulk CTO is quite different from that of bulk BTO. Because of the existence of other distortion modes, such as oxygen octahedron rotations and tilts, increases the complexity of bulk CTO structure and makes the complete form of bulk CTO explicitly including all possible modes too complicated to be practical. Because the goal of our model is to reproduce P_z and piezoelectric constant d_{33} and within the framework of slab model the only interaction between the two constituents are via the polar instabilities P_z , we simplify the energy function of bulk CTO by explicitly considering P_z and η_3 only:

$$\begin{aligned}
 E_C(P, \eta_{3C}) &= E_{0C} + \alpha_C P^2 + \kappa_C P^4 + \frac{1}{2} B_{1xxC} \eta_{3C} P^2 \\
 &+ B_{1C} \eta_{3C} + \frac{1}{2} B_{11C} \eta_{3C}^2
 \end{aligned}$$

All of coefficients are renormalized by integrating over all the other distortion modes, such as rotations, tilts and in-plane polarization. So the energy function is different for each of the three phases. Meanwhile, the determination of the renormalized coefficients in bulk CTO is different from the process in bulk BTO, because there is no spontaneous out-of-plane polarization in CTO $Pmn2_1$ and $Pmc2_1$ structures. As shown in Fig. D.2, for the nonpolar structures $Pmn2_1$ and $Pmc2_1$, we applied sufficient elastic strain to induce out-of-plane polarization and studied the response of the induced polarization to the application of strain. The total energy of nonpolar structure is fitted as a quadratic function of strain to determine the coefficients, E_0 ,

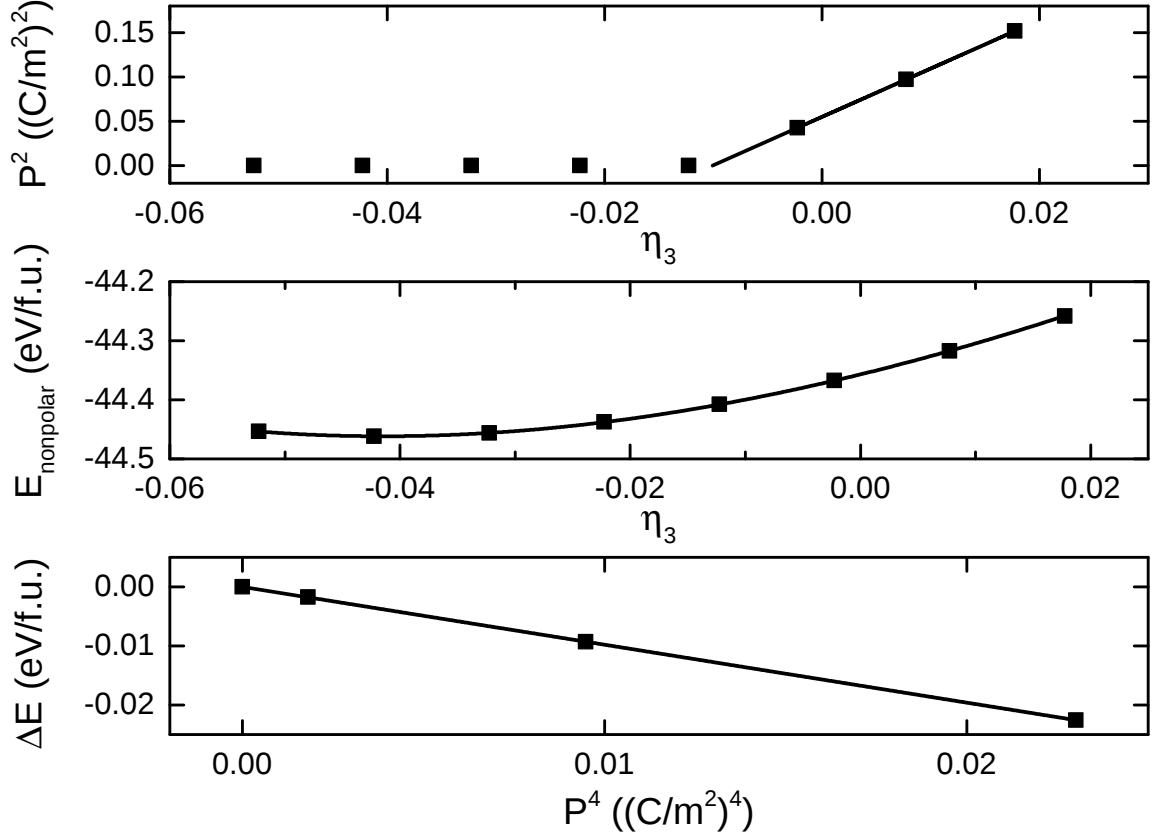


Figure D.2: Fitting of the coefficients in the energy function of CTO $Pmc2_1$ structure. Top: fit the polarization, $P^2 = -\frac{1}{2\kappa}(\alpha + B_{1xx}\eta_3)$; middle: fit the energy of nonpolar structure, $E_{\text{polar}} = E_0 + B_1\eta_3 + B_{11}\eta_3^2$; bottom: fit the energy difference between the polar and nonpolar structures, $\Delta E = E_{\text{polar}} - E_{\text{nonpolar}} = -\kappa P^4$

B_1 and B_{1xx} . The coefficient κ is determined by fitting the energy difference between the polar and nonpolar structures as a function of polarization. The determination of the coefficients of the energy function of CTO $P1$ structure is different from all of the other ones. The coefficients are adjusted so that the energy function reproduces the properties of the ground state such as total energy E , polarization in z -direction P , elastic strain η_3 , $\partial P^2/\partial\eta_3$ and $\partial^2 E/\partial\eta_3^2$. Table D.1 shows the coefficients of the energy function of the bulk materials, which is sufficient for the construction of the slab model.

Coefficients	BaTiO ₃	CaTiO ₃		
		<i>Pmn2₁</i>	<i>Pmc2₁</i>	<i>P1</i>
E_0 (eV/f.u.)	-43.942	-44.350	-44.345	-44.306
B_1 (eV/f.u.)	-3.495	5.569	5.617	5.384
B_{11} (eV/f.u.)	45.364	67.598	67.660	64.738
α (eV/f.u./(C^2m^{-4}))	0.221	-0.066	-0.108	-1.286
κ (eV/f.u./(C^4m^{-8}))	2.403	0.892	0.980	8.148
B_{1xx} (eV/f.u./(C^2m^{-4}))	-14.823	-10.635	-10.696	-17.343

Table D.1: Coefficients of energy function of bulk materials determined from first-principles calculations.