Molecular Dynamics Simulations of Chemically Disordered Ferroelectric (Ba,Sr)TiO$_3$ with a Semi-Empirical Effective Hamiltonian

Takeshi Nishimatsu$^1$, Anna Grünebohm$^2$, Umesh V. Waghumare$^3$, and Momoji Kubo$^1$

$^1$Institute for Materials Research (IMR), Tohoku University, Sendai 980-8577, Japan
$^2$Faculty of Physics and Center for Nanointegration, CENIDE, University of Duisburg-Essen, 47048 Duisburg, Germany
$^3$Theoretical Sciences Unit, Jawaharlal Nehru Centre for Advanced Scientific Research (JNCASR), Bangalore-560064, India

We present a semi-empirical effective Hamiltonian to capture effects of disorder associated with Ba and Sr cations occupying A sites in (Ba$_x$Sr$_{1-x}$)TiO$_3$ on its ferroelectric phase transition. Averaging between the parameters of first-principles effective Hamiltonians of end members BaTiO$_3$ and SrTiO$_3$, we include a term with an empirical parameter to capture the local polarization and strains arising from the difference between ionic radii of Ba and Sr. Using mixed-space molecular dynamics of the effective Hamiltonian, we determine $T$-dependent ferroelectric phase transitions in (Ba$_x$Sr$_{1-x}$)TiO$_3$ which are in good agreement with experiment. Our scheme of determination of semi-empirical parameters in effective Hamiltonian should be applicable to other perovskite-type ferroelectric solid solutions.

I. INTRODUCTION

Barium (Ba) and strontium (Sr) belong to the same column of the periodic table and are chemically very similar. However, ternary perovskites $ABO_3$ based on Ba and Sr at their A site can be quite different in their properties: barium titanate (BaTiO$_3$) is ferroelectric at room temperature, while strontium titanate (SrTiO$_3$) is paraelectric. It is thought that this is largely because of the difference in their ionic radii of Ba and Sr. Using mixed-space molecular dynamics of the effective Hamiltonian, we determine $T$-dependent ferroelectric phase transitions in (Ba$_x$Sr$_{1-x}$)TiO$_3$ which are in good agreement with experiment. Our scheme of determination of semi-empirical parameters in effective Hamiltonian should be applicable to other perovskite-type ferroelectric solid solutions.

Perovskite-type ferroelectric solid solutions such as (Ba$_x$Sr$_{1-x}$)TiO$_3$ are of great interest in the field of dielectrics, since many commercial high-dielectric-constant material structures consist of such solid solutions and the composition parameter ($x$ here) is adjusted to get desired properties. Therefore, offering a recipe of computational simulations of such solid solutions is important.

In 2006, Walizer et al. presented Monte Carlo simulations with an effective Hamiltonian determined from first-principles calculations of (Ba$_{1/2}$Sr$_{1/2}$)TiO$_3$ within a virtual crystal approximation (VCA) and local inhomogeneous strains determined from fully disordered ionic configurations of Ba and Sr of (Ba$_x$Sr$_{1-x}$)TiO$_3$. They successfully reproduced the temperature–composition ($T$–$x$) phase diagram, though with a large underestimation of polarization. That underestimation basically came from a local-density approximation (LDA). Moreover, because local inhomogeneous strains around each site were fixed in their analysis and were not allowed to fluctuate thermally, temperature dependence of the effect from ionic configuration was not so clear.

Here, we newly determine a set of parameters for an effective Hamiltonian for (Ba$_x$Sr$_{1-x}$)TiO$_3$ from more accurate first-principles calculations, and perform molecular-dynamics (MD) simulations. In our MD simulations, local inhomogeneous strains around each site are not fixed but can fluctuate thermally. We report not only a temperature–composition ($T$–$x$) phase diagram, but also the dependence of polarization and lattice constants on composition.

In Sec. II, we briefly describe the first-principles methods we employ and the formalism and conditions of our MD simulations. In Sec. III, we present results of our MD simulations, and finally summarize our work in Sec. IV.
A. First-Principles Methods

Our first-principles calculations are based on the density functional theory (DFT) as implemented in ABINIT code.\textsuperscript{[13,14]} Bloch wave functions of electrons are expanded in the plane wave basis truncated with a cut-off energy of 60 Hartree, and are sampled on an 8 × 8 × 8 grid of \( k \)-points in the first Brillouin zone. We do not use LDA but use “Wu and Cohen”\textsuperscript{[15]} GGA functional, along with Rappe’s optimized pseudopotentials\textsuperscript{[16]} generated with Opim code.\textsuperscript{[17]} A valley-line tracing method\textsuperscript{[18]} is used to determine total energy surface of BaTiO\textsubscript{3} and SrTiO\textsubscript{3}. We basically use results of first-principles calculations of BaTiO\textsubscript{3} and SrTiO\textsubscript{3} in Ref.\textsuperscript{[17]}

B. Effective Hamiltonian

We use an effective Hamiltonian, obtained with input from first-principles calculations, for MD simulations. It is essentially the same as that in Refs.\textsuperscript{[17] and 18]}

\[
H^{\text{eff}} = \frac{M^*_\text{dipole}}{2} \sum_{R,\alpha} \hat{u}_{\alpha}^2(R) + \frac{M^*_\text{acoustic}}{2} \sum_{R,\alpha} \hat{u}_{\alpha}^2(R) + V^{\text{self}}(\{u\}) + V^{\text{dip}}(\{u\}) + V^{\text{short}}(\{u\}) + V^{\text{elas}, \text{homo}}(\eta_1, \ldots, \eta_6) + V^{\text{elas}, \text{inho}}(\{w\}) + V^{\text{coupl}, \text{homo}}(\{u\}, \eta_1, \ldots, \eta_6) + V^{\text{coupl}, \text{inho}}(\{u\}, \{w\}) ,
\]

(2)

where the phase space of atomic motion is reduced to a subspace spanned by local soft mode vectors \( u(R) \) and local acoustic displacement vectors \( w(R) \) of each unit cell at \( R \) in a simulation supercell. \( \eta_1, \ldots, \eta_6 \) are the six components of homogeneous strain in Voigt notation \((\eta_1 = e_{xx}, \eta_4 = e_{yz})\). \( M^*_\text{dipole} \sum_{R,\alpha} \hat{u}_{\alpha}^2(R) \) and \( M^*_\text{acoustic} \sum_{R,\alpha} \hat{u}_{\alpha}^2(R) \) are the kinetic energies of local soft modes and local acoustic displacements along with their effective masses of \( M^*_\text{dipole} \) and \( M^*_\text{acoustic} \). \( V^{\text{self}}(\{u\}) \) is the local-mode self-energy, \( V^{\text{dip}}(\{u\}) \) is the long-range dipole-dipole interaction, \( V^{\text{short}}(\{u\}) \) is the short-range harmonic interaction between local soft modes, \( V^{\text{elas}, \text{homo}}(\eta_1, \ldots, \eta_6) \) is the elastic energy from homogeneous strains, \( V^{\text{elas}, \text{inho}}(\{w\}) \) is the elastic energy from inhomogeneous strains, \( V^{\text{coupl}, \text{homo}}(\{u\}, \eta_1, \ldots, \eta_6) \) is the coupling between the local soft modes and the homogeneous strain, and \( V^{\text{coupl}, \text{inho}}(\{u\}, \{w\}) \) is the coupling between the soft modes and the inhomogeneous strains. Detailed explanation of symbols in the effective Hamiltonian can be found in Refs.\textsuperscript{[17,18] and 19] To decrease the computational time, forces exerted on \( \{u\} \) are calculated in reciprocal space using fast-Fourier transform (FFT) methods\textsuperscript{[15,21,22].

C. Effects of A-site Ordering with Ba or Sr Ions

To include the effects of alloying Ba and Sr with different ionic radii, according to Ref.\textsuperscript{[9]} we count the number of Ba or Sr ions at the 8 \( A \)-sites surrounding a given \( B \)-site at \( R \).

\[
s(R) = \sum_{i=1}^{8} \sigma_i \tag{3}
\]

as shown in Fig. 1 where \( \sigma_i = +1 \) or \(-1\) corresponds to the presence of a Ba or Sr ion, respectively. Consequently, value of \( s(R) \) ranges \(-8, -6, -4, -2, 0, +2, +4, +6, +8 \). In contrast to Ref.\textsuperscript{[9]} we introduce a term for modulation in local inhomogeneous strains by adding

\[
V^{\text{modulation}, \text{inho}}(\{w\}, \{s\}) = c \sum_{R} \sum_{\alpha=1,2,3} s(R) \eta_{\alpha}(R)
\]

\[
= \frac{c}{N} \sum_{\mathbf{k}} \sum_{\alpha=x,y,z} \tilde{w}_{\alpha}^*(\mathbf{k}) k_{\alpha} \tilde{s}(\mathbf{k}) \tag{4}
\]

to \( H^{\text{eff}} \) of Eq. (2). Here, \( c \) is strength of the modulation, \( N \) is the number of unit cells in the supercell, \( \mathbf{k} \) is wave vector, \( \tilde{w}_{\alpha}^*(\mathbf{k}) \) is complex conjugate of Fourier transform of \( w(R) \), \( \tilde{s}(\mathbf{k}) \) is Fourier transform of \( s(R) \). To simplify the computation, \( V^{\text{modulation}, \text{inho}}(\{w\}, \{s\}) \) is calculated in reciprocal space.

Effective hydrostatic pressure of

\[
p = b(\frac{1}{2} - x) \tag{5}
\]

is applied to capture the homogeneous strain that alters the lattice constants as a function of \( x \), because the modulation of Eq. (4) does not include alternation of the homogeneous strain. Here, \( b \) is a constant. Temperature-dependent negative effective pressure \( p = -0.0057 \) GPa for BaTiO\textsubscript{3}, which was applied in Ref.\textsuperscript{[17]} to mimic thermal expansion, is not applied in present work.
In the present MD simulations, only the parameters $\Gamma_{\text{modulation,inhо}}\{\{w\},\{s\}\}$ and $p$ are $x$-dependent, and other parameters in the effective Hamiltonian of Eq. (2) are kept constant. Such simplification can be successfully employed because Ba and Sr are chemically very similar and different only in their ionic radii. Determination and exact values of the parameters $c$ and $b$ will be discussed in Sec. III.B.

D. Molecular-Dynamics (MD) Simulations

MD simulations of (Ba$_x$Sr$_{1-x}$)TiO$_3$ ($x = 0.0, 0.1, \ldots, 0.9, 1.0$) with the effective Hamiltonian are performed with our original MD code feram$^{28}$ Input files for present simulations are in its free software package of feram-0.26.01/src/34example-BST/, and details of the code can be found in Ref. 18. Temperature is kept constant in each temperature step within a canonical ensemble using the velocity-scaling thermostat constant in each temperature step of simulation within a time step of $\Delta t = 2$ fs. We use a supercell with size of $N = L_x \times L_y \times L_z = 32 \times 32 \times 32$ unit cells and temperature steps of ±1 K/step in heating-up and cooling-down simulations. In every temperature step, we thermalize the system for 20,000 time steps, after which we use 20,000 time steps to average the properties. The initial configurations of $\{u\}$ are generated randomly: $\langle u_\alpha \rangle = 0.11\AA$ ($\alpha = x, y, z$) for heating-up simulations, $\langle u_\alpha \rangle = 0.00\AA$ for cooling-down simulations, and variance of $\langle u_\alpha^2 \rangle - \langle u_\alpha \rangle^2 = (0.02)\AA^2$ for the both. In the initial configurations, $\{w\}$ are set to zero. We have checked that the results of these simulations do not depend on initial configurations. A set of $s(R)$ for each $x$ of (Ba$_x$Sr$_{1-x}$)TiO$_3$ is generated from random configurations of $xN$ Ba and $(x-1)N$ Sr ions.

III. RESULTS AND DISCUSSION

A. Results of First-principles Calculation and Determination of Parameters of $H_{\text{eff}}$ of (Ba$_{1/2}$Sr$_{1/2}$)TiO$_3$

Using the systematic procedure described in Ref. 17, we perform first-principles calculations to determine a set of parameters of $H_{\text{eff}}$ for SrTiO$_3$ (See Table I). We averaged the parameters of $H_{\text{eff}}$ of BaTiO$_3$ in Ref. 17 and those of $H_{\text{eff}}$ of SrTiO$_3$ (See Table I). It is found that this set of parameters indeed reproduces the three transition temperatures of (Ba$_{1/2}$Sr$_{1/2}$)TiO$_3$ as depicted in Fig. 2(a).

In contrast to the parameters in effective Hamiltonian of Ref. 9 obtained using LDA-based VCA, the present procedure gives improved estimation of equilibrium cubic lattice constant $a_0$, and allow simple analysis of the effects of cationic disorder on ferroelectric transitions (See Table II).

| Parameter | Ref. 17 | Present work | Ref. 9 |
|-----------|---------|--------------|--------|
| $p$ [GPa] | $-0.0057^\star$ | 0.0 | 6.0(0.5 - $x$) | $-5.2$ |
| $a_0$ [Å] | 3.986 | 3.901 | 3.944 | 3.901 |
| $B_{11}$ [eV] | 126.73 | 131.33 | 129.03 | 129.96 |
| $B_{12}$ [eV] | 41.76 | 36.26 | 39.01 | 43.81 |
| $B_{44}$ [eV] | 49.74 | 41.30 | 45.27 | 46.94 |
| $c$ [eV] | | | | $-0.279$ |
| $B_{1xx}$ [eV/Å$^2$] | $-185.35$ | $-102.09$ | $-143.72$ | $-191.72$ |
| $B_{1yy}$ [eV/Å$^2$] | $-3.289$ | 0.5299 | $-1.3755$ | $-3.98$ |
| $B_{4zz}$ [eV/Å$^2$] | $-14.550$ | $-15.494$ | $-15.022$ | $-5.73$ |
| $\alpha$ [eV/Å$^4$] | 78.99 | 22.39 | 50.69 | 97.44 |
| $\gamma$ [eV/Å$^4$] | $-115.48$ | $-28.88$ | $-72.18$ | $-143.25$ |
| $k_1$ [eV/Å$^6$] | $-267.98$ | $-65.14$ | $-166.56$ | $-166.56$ |
| $k_2$ [eV/Å$^6$] | 197.50 | 117.00 | 157.25 | $-166.56$ |
| $k_3$ [eV/Å$^6$] | 830.20 | 201.68 | 515.94 | $-166.56$ |
| $k_4$ [eV/Å$^8$] | 641.97 | 139.35 | 390.66 | $-166.56$ |
| $M_{\text{mole}}^z$ [amu] | 38.24 | 43.61 | 40.93 | $-166.56$ |
| $M_{\text{acoustic}}^z$ [amu] | 46.64 | 36.70 | 41.67 | $-166.56$ |
| $Z^*$ [eV] | 10.33 | 9.28 | 9.81 | 9.66 |
| $\epsilon_{\infty}$ | 6.87 | 6.46 | 6.66 | 5.21 |
| $\kappa$ [eV/Å$^2$] | 8.534 | 10.316 | 9.425 | 6.287 |
| $\kappa$ [eV/Å$^2$] | $-2.084$ | $-2.012$ | $-2.048$ | $-2.334$ |
| $j_1$ [eV/Å$^2$] | $-1.129$ | $-1.815$ | $-1.472$ | 4.318 |
| $j_3$ [eV/Å$^2$] | 0.689 | 0.590 | 0.640 | 0.817 |
| $j_5$ [eV/Å$^2$] | $-0.611$ | $-0.567$ | $-0.589$ | $-0.461$ |
| $j_7$ [eV/Å$^2$] | 0.000 | 0.000 | 0.000 | 0.000 |
| $j_9$ [eV/Å$^2$] | 0.000 | 0.000 | 0.000 | 0.000 |
| $\kappa$ [GPa] | $-1.518$ | $-0.126$ | $-1.906$ | $-0.254$ |
| $\kappa$ [GPa] | 17.128 | 19.215 | $-1.422$ | 0.711 |
| $\kappa$ [GPa] | 16.333 | 18.142 | $-1.143$ | 1.191 |
| $\kappa$ [GPa] | 13.871 | 16.300 | $-1.143$ | 1.191 |

| Parameter | Value |
|-----------|-------|
| $\xi_1$ | 0.166 |
| $\xi_2$ | 0.770 |
| $\xi_3$ | 0.202 |
| $\xi_4$ | 0.202 |
| $\xi_5$ | 0.546 |
| $Z_{xx}^A$ [eV] | 2.741 |
| $Z_{xx}^B$ [eV] | 7.492 |
| $Z_{xx}^C$ [eV] | $-2.150$ |
| $Z_{xx}^D$ [eV] | $-5.933$ |
FIG. 2. (Color online) Simulated temperature-dependence of lattice constants of (Ba$_{1/2}$Sr$_{1/2}$)TiO$_3$ for four different strength of the modulation, $c = 0, -0.279, -0.7, -1.0$, (a)–(d), respectively. The larger $|c|$, the lower $T_{O\leftrightarrow R}$.

**B. Determination of Parameters for (Ba$_x$Sr$_{1-x}$)TiO$_3$ Alloy**

To simulate an alloy or solid solution (Ba$_x$Sr$_{1-x}$)TiO$_3$, we determine the modulation strength $c$ in Eq. (4) as

$$
c = -\frac{1}{16} \frac{a_{BTO} - a_{STO}}{a_{BST}} (B_{11} + 2B_{12}) = -0.279 \text{ [eV]}. \quad (6)
$$

When $s(R) = \pm 8$, local inhomogeneous strains of

$$
\eta_1 = \eta_2 = \eta_3 = \pm \frac{1}{2} \frac{a_{BTO} - a_{STO}}{a_{BST}} \quad (7)
$$

minimize the energy:

$$
E(\{\eta_i\}_\text{local}) = \frac{1}{2} B_{11}(\eta_1^2 + \eta_2^2 + \eta_3^2) + B_{12}(\eta_2\eta_3 + \eta_3\eta_1 + \eta_1\eta_2) + \frac{1}{2} B_{44}(\eta_1^2 + \eta_2^2 + \eta_3^2) + cs(\eta_1 + \eta_2 + \eta_3). \quad (8)
$$

Here, $a_{BTO} = 3.986$ Å is the calculated cubic lattice constant of BaTiO$_3$, $a_{STO} = 3.901$ Å is that of SrTiO$_3$, and $a_{BST} = (a_{BTO} + a_{STO})/2 = 3.944$ Å, and $B_{11}$, $B_{12}$, and $B_{44}$ are the elastic constants of (Ba$_{1/2}$Sr$_{1/2}$)TiO$_3$ expressed in energy unit ($B_{11} = a_{BST}^2 C_{11}$, $B_{12} = a_{BST}^2 C_{12}$, and $B_{44} = a_{BST}^2 C_{44}$). In Fig. 2 results of heating-up and cooling-down MD simulations with four different values of $c = 0, -0.279, -0.7$, and $-1.0$ [eV] are given for $x = 1/2$, i.e. (Ba$_{1/2}$Sr$_{1/2}$)TiO$_3$ for which the largest influence of disordered ionic configurations has to be expected. We find lower transition temperature between orthorhombic and rhombohedral structures, i.e. $T_{O\leftrightarrow R}$, for larger $|c|$. The other two transition temperatures $T_{C\leftrightarrow T}$ and $T_{T\leftrightarrow O}$ remain almost unchanged. This may be because $T_{O\leftrightarrow R}$ is the lowest transition temperature among the three, and local inhomogeneous strains around each site are almost frozen into the lowest energy structure. However, the difference in $T_{O\leftrightarrow R}$ between $c = 0$ and $c = -0.279$ eV is only 3 K. In Fig. 2(d), we find strange behavior in tetragonal phase for $c = -1.0$ which may be unrealistically negatively large.

We first set the constant $b$ in the effective pressure of Eq. (5) so that average lattice constant becomes the same as BaTiO$_3$ for $x = 1.0$ and SrTiO$_3$ for $x = 0.0$ as

$$
b = \frac{a_{BTO} - a_{STO}}{a_{BST}} 3K = 11.65 \text{ [GPa]}, \quad (9)
$$

where $K = (B_{11} + 2B_{12})/(3a_{BST}^3)$ is bulk modulus. However, $b = 11.65 \text{ [GPa]}$ gives too high transition temperatures for $x = 1$, i.e. BaTiO$_3$. Therefore, we determine this $b$ empirically, as $b = 6.0 \text{ [GPa]}$. The reason for this may be the overestimation of the coupling between homogeneous strain and polarization.

**C. Results of Molecular-Dynamics Simulations**

Using the set of parameters determined above, we perform heating-up and cooling-down MD simulations. In Fig. 3 a calculated temperature–composition ($T$–$x$) phase diagram is presented. Heating-up and cooling-down transition temperatures are averaged when corresponding transition has temperature hysteresis between the heating-up and cooling-down simulations. For $x > 0.25$, the almost linear $x$-dependence of all three transition temperatures is well reproduced by our approach. For $x$ below 0.25 the experimentally observed transition temperatures decrease with a larger slope and the alloy is no longer ferroelectric for $x < 0.094$. In this concentration range of $x < 0.25$, the antiferrodistortive
instability found in pure SrTiO$_3$ may play an important role and the instability reduces transition temperatures non-linearly, and finally for pure SrTiO$_3$ the system is a quantum paraelectric. Both effects are not accessible in our classical MD simulations neglecting rotations of octahedra.

Simulated $x$-dependence of lattice constants $a$ and $c$ at room temperature (300 K) is compared with experimental values$^{25}$ in Fig. 3. Though the absolute values have good agreement, more moderate $x$-dependence of lattice constants of our simulations than the experiment is coming from the empirical correction to $b$ from 11.65 to 6.0 GPa used here. Overestimation of $c/a$ of this MD simulation is coming from the error in first-principles calculations and unavoidable within current techniques of DFT theories.

Simulated $x$-dependence of polarization $|P|$ is also compared with the experimentally observed values$^{25}$ in Fig. 3. It is seen that our simulation slightly overestimates $|P|$ for the whole range of $x$ and for any phases, but trends for $x > 0.094$ are quite reasonable. The main reason for this may come from the unavoidable overestimation of $c/a$ and resulting overestimation of $|P|$ in first-principles calculations. Moreover, as shown in Fig. 6, true dipole moment per unit cell $P(u)$ deviates from lineararity at large $u$ both in BaTiO$_3$ and SrTiO$_3$, and it may also explain the overestimation of $|P|$ in Fig. 3. In Fig. 5, true dipole moment as a function of $u$ for atomic displacements along [001] distortion calculated with the Berry-phase theory$^{25}$ is compared with $Z^* u$ in $H_{\text{eff}}$ of Eq. (2).

IV. SUMMARY

In this work, we presented a new set of parameters of an effective Hamiltonian for (Ba$_x$Sr$_{1-x}$)TiO$_3$ solid-solution with input largely from the results of first-principles calculations, including the modulation in local inhomogeneous strains due to Ba: Sr disorder. Using heating-up and cooling-down MD simulations we have obtained $x-T$ phased diagram. Though two parameters have been determined semi-empirically, results of our simulations and experimentally observed values are in good agreement for the dependence of transition temperatures, lattice constants $a$ and $c$, and polarization on composition $x$. It is found that $x$-dependent properties of (Ba$_x$Sr$_{1-x}$)TiO$_3$ are determined mainly through the change in homogeneous lattice constants and that influence of modulation on local inhomogeneous strains is relatively weak.

Our procedure of first-principles calculations, determination of parameters, and MD calculations should be applicable to other perovskite-type ferroelectric solid solutions such as (K,Na)NbO$_3$, (Ba,Sr,Ca)TiO$_3$, etc.
FIG. 5. (Color online) Simulated composition ratio \( x \)-dependence of polarization \(|P|\) (open marks). \(|P|\) is measured at the middle of the two transition temperatures, \((T_{C\rightarrow T} + T_{T\rightarrow O})/2\) for \(|P|_{(100)}\) of the tetragonal phase or \((T_{T\rightarrow O} + T_{O\rightarrow R})/2\) for \(|P|_{(110)}\) of the orthorhombic phase, or half of \(T_{O\rightarrow R}\) for \(|P|_{(111)}\) of the rhombohedral phase. For comparison, experimentally observed values by Ménoret et al.\(^7\) are also plotted (filled marks connected with lines).

FIG. 6. (Color online) Using the Berry-phase theory,\(^25\) dipole moments per unit cell as a function of \( u \) for atomic displacements along [001] distortion are calculated for (a) SrTiO\(_3\) and (b) BaTiO\(_3\). \( Z^*u \) in \( H_{\text{eff}} \) of Eq. (2) are also plotted for comparison. 1.0 \( \text{eÅ} \) in a unit cell of volume \((4.0 \text{ Å})^3\) corresponds 25 \( \mu \text{C} \cdot \text{cm}^{-2}\).

ACKNOWLEDGMENTS

Computational resources were provided by the Center for Computational Materials Science, Institute for Materials Research (CCMS-IMR), Tohoku University. We thank the staff at CCMS-IMR for their constant effort. This study is financially supported by the German Research Foundation, DFG SPP 1599. This study was also supported in part by MEXT as a social and scientific priority issue (Creation of new functional devices and high-performance materials to support next-generation industries) to be tackled by using post-K computer. U.V.W. acknowledges support from a JC Bose National Fellowship of the Department of Science and Technology, Government of India. We acknowledge collaboration and useful discussion with Anil Kumar.

1. R. D. Shannon, Acta Cryst. A 32, 751 (1976).

2. V. M. Goldschmidt, Akad. Oslo Math-Natur. 2, 7 (1926).
[58x734]D. Fu and M. Itoh, *Ferroelectrics – Material Aspects* (IN-TECH, Rijeka, 2011) chapter 20.

[58x734]H. Fujishita, Y. Shiozaki, and E. Sawaguchi, *J. Phys. Soc. Jpn.* **46**, 581 (1979).

[58x734]K. A. Müller and H. Burkard, *Phys. Rev. B* **19**, 3593 (1979).

[58x734]V. V. Lemanov, E. P. Smirnova, P. P. Syrnikov, and E. A. Tarakanov, *Phys. Rev. B* **54**, 3151 (1996).

[58x734]C. Ménoret, J. M. Kiat, B. Dkhil, M. Dunlop, H. Dammak, and O. Hernández, *Phys. Rev. B* **65**, 224104 (2002).

[58x734]M. McQuarrie, *J. Am. Ceram. Soc.* **38**, 444 (1955).

[58x734]L. Walizer, S. Lisenkov, and L. Bellaiche, *Phys. Rev. B* **73**, 144105 (2006).

[58x734]X. Gonze, J.-M. Beuken, R. Caracas, F. Detraux, M. Fuchs, G.-M. Rignanese, L. Sindic, M. Verstraete, G. Zerah, F. Jollet, M. Torrent, A. Roy, M. Mikami, P. Ghosez, J.-Y. Raty, and D. C. Allan, *Comput. Mater. Sci.* **35**, 478 (2006).

[58x734]X. Gonze, B. Amadon, P.-M. Anglade, J.-M. Beuken, F. Bottin, P. Boulanger, F. Bruneval, D. Caliste, R. Caracas, M. Cote, T. Deutsch, L. Genovese, P. Ghosez, M. Giantomassi, S. Goedecker, D. R. Hamann, P. Hermet, F. Jollet, G. Jomard, S. Leroux, M. Mancini, S. Mazevet, M. J. T. Oliveira, G. Onida, Y. Pouillon, T. Rangel, G.-M. Rignanese, D. Sangalli, R. Shaltaf, M. Torrent, M. J. Verstraete, G. Zerah, and J. W. Zwanziger, *Comput. Phys. Commun.* **180**, 2582 (2009).

[58x734]X. Gonze, F. Jollet, F. Abreu Araujo, D. Adams, B. Amadon, T. Applencourt, C. Audouze, J.-M. Beuken, J. Bieder, A. Bokhanchuk, E. Bousquet, F. Bruneval, D. Caliste, M. Côté, F. Dahm, F. Da Pieve, M. Delaveau, M. Di Gennaro, B. Dorado, C. Espejo, G. Geneste, L. Genovese, A. Gerossier, M. Giantomassi, Y. Gillet, D. R. Hamann, L. He, G. Jomard, J. Laflamme Janssen, S. Le Roux, A. Levitt, A. Lherbier, F. Liu, I. Lukačević, A. Martin, C. Martins, M. J. T. Oliveira, S. Poncé, Y. Pouillon, T. Rangel, G.-M. Rignanese, A. H. Romero, B. Rousseau, O. Rubel, A. A. Shukri, M. Stankovski, M. Torrent, M. J. Van Setten, B. Van Troeye, M. J. Verstraete, D. Waroquiers, J. Wiktor, B. Xu, A. Zhou, and J. W. Zwanziger, *Comput. Phys. Commun.* **205**, 106 (2016).

[58x734]Z. G. Wu and R. E. Cohen, *Phys. Rev. B* **73**, 235116 (2006).

[58x734]A. M. Rappe, K. M. Rabe, E. Kaxiras, and J. D. Joannopoulos, *Phys. Rev. B* **41**, 1227 (1990).

[58x734]Opium - pseudopotential generation project, http://opium.sourceforge.net/ (1998–2014).

[58x734]T. Hashimoto, T. Nishimatsu, H. Mizuseki, Y. Kawazoe, A. Sasaki, and Y. Ikeda, *Jpn. J. Appl. Phys.* **43**, 6785 (2004).

[58x734]T. Nishimatsu, M. Iwamoto, Y. Kawazoe, and U. V. Waghmare, *Phys. Rev. B* **82**, 134106 (2010).

[58x734]T. Nishimatsu, U. V. Waghmare, Y. Kawazoe, and D. Vanderbilt, *Phys. Rev. B* **78**, 104104 (2008).

[58x734]R. D. King-Smith and D. Vanderbilt, *Phys. Rev. B* **49**, 5828 (1994).

[58x734]W. Zhong, D. Vanderbilt, and K. M. Rabe, *Phys. Rev. B* **52**, 6301 (1995).

[58x734]U. V. Waghmare, E. J. Cockayne, and B. P. Burton, *Ferroelectrics* **291**, 187 (2003).

[58x734]U. V. Waghmare, *Acc. Chem. Res.* **47**, 3242 (2014).

[58x734]T. Nishimatsu, feram at SourceForge.net, http://loto.sourceforge.net/feram/ (2007–2016).

[58x734]J. Sun, R. C. Remsing, Y. Zhang, Z. Sun, A. Ruzsinszky, H. Peng, Z. Yang, A. Paul, U. Waghmare, X. Wu, M. L. Klein, and J. P. Perdew, *Nat. Chem.* **2**, 2535 (2016).

[58x734]R. D. King-Smith and D. Vanderbilt, *Phys. Rev. B* **47**, 1651 (1993).