

The ReaxFF Polarizable Reactive Force Fields for Molecular Dynamics Simulation of Ferroelectrics

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Abstract. We use *ab initio* Quantum Mechanical (QM) calculations to derive a force field that accurately describes the atomic interactions in BaTiO₃ allowing, via Molecular Dynamics (MD), the simulation of thousands of atoms. A key feature of the force field (denoted ReaxFF) is that charge transfer and atomic polarization are treated self-consistently. The charge on each atom is separated into a core, described as a Gaussian distribution with fixed total charge (e.g. +4 for Ti), and a valence charge, also described as a Gaussian distribution. The valence charges can flow in response to its environment as described via Charge Equilibration (QEq). The restoring force between a core and its valence electrons is given by the electrostatic interaction between the two charge distributions. Thus each atom has four universal parameters describing the electrostatics which are determined once from fitting to the QM charge distributions on a representative set of finite clusters. The nonelectrostatic interactions (Pauli repulsion, dispersion) are described with a Morse potential, leading to 3 additional universal parameters for each pair of atoms. We optimized the Morse parameters to reproduce the zero temperature Equation of State (energy- and pressure-volume curves) obtained using QM methods of cubic and tetragonal BaTiO₃ over a wide pressure range. We then use the ReaxFF with MD to study thermal properties of BaTiO₃, in particular the cubic to tetragonal phase transition. Our MD simulations indicate that the transition temperature obtained using ReaxFF is in good agreement with experiment.

INTRODUCTION

A great deal of progress has been made in using methods of quantum mechanics (QM) to study the structures, polarizations, domain boundaries, and other properties of ferroelectrics. However, QM is often impractical for studying phase transitions, complex domain walls and their mobility, cracks and failure, impurities, defects, and alloys that are important in many devices. For this reason we have been developing force field (FF) methods that could be suitable for the simulation of millions of atoms. The demands on obtaining a suitable FF for ferroelectrics are especially severe. It is imperative that the FF properly describes polarization and charge transfer and the response (local structures and polarization) to external and internal fields. Also the parameters should be transferable to new environments (changes in coordination, defect structures, alloying). In addition it must describe the structural, thermal and mechanical properties and how these change upon alloying, oxidation, processing. Moreover it would be desirable for the FF to correctly describe the chemical processes used in

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synthesizing the materials and the processes involved in aging. Most fundamental in determining the FF is that its parameters be derivable unambiguously from theory without using the experimental data available; thus *all* experimental data can be used for validation. It is not obvious that any FF could correctly and reliably describe all of these properties and phenomena. Nevertheless we have been developing the ReaxFF to satisfy these criteria and will report the progress and some applications.

In this paper we focus on BaTiO₃ as an important member of the family of ferroelectric perovskites; BaTiO₃ is particularly challenging since it exhibits three solid-solid phase transitions. At high temperatures it has the cubic perovskite structure with Ba atoms in the corners, Ti in the center, and O on the faces. As the temperature is lowered BaTiO₃ undergoes three transitions to ferroelectric phases:

- i) at T=393 K the cubic phase transforms to a tetragonal phase with polarization in the [100] direction;
- ii) at T=278 K it becomes orthorhombic with polarization in a [110] cubic direction;
- iii) finally at T=183 K a rhombohedral phase becomes stable with polarization along a [111] cubic direction.

Fundamental to a Force Field description of ferroelectrics is the treatment of charge and polarization. In the ReaxFF each atom is described in terms of a fixed core charge (e.g. +4 for Ti) in the shape of a Gaussian distribution and a variable valence charge, again as a Gaussian shape. Thus all the coulomb interactions are shielded. The valence charge can flow as described by the Charge Equilibration method (QEq) [1]. Each atom has four universal parameters describing the electrostatics (Electronegativity, hardness, and the sizes of the core and shell) which are determined once by fitting to *ab initio* charge distributions on a representative set of finite clusters. The nonelectrostatic interactions (Pauli repulsion, dispersion) are described with a Morse potential, leading to 3 additional universal parameters for each pair of atoms. These parameters are derived from QM data on various bulk phases that include many different coordination numbers.

We report here the development of the ReaxFF for BaTiO₃ (Section 2). We then use the ReaxFF with MD to study the cubic to tetragonal phase transition in BaTiO₃ (Section 3). Our results indicate that the ReaxFF correctly describes the cubic-tetragonal phase transition leading to an estimate of the phase transition temperature in good agreement with experiments.

FIRST-PRINCIPLES-BASED REAXFF FOR BATIO3

The energy expression for the crystal is expressed as the sum of electrostatic interactions, van der Waals interactions and valence interactions,

$$E = E^{\text{Coulomb}} + E^{\text{vdW}} + E^{\text{Valence}}$$

Such a partition into Valence, Coulomb, and vdW nonbond terms is common to most force fields (e.g. DREIDING [9] and UFF [10]). Also for ionic crystals such as BaTiO₃, successful calculations have been carried out with only vdW and coulomb terms (e.g. SiO₂ [7] and MgO [14]). There are four unique aspects of ReaxFF:

- The charges are determined by an extended Charge Equilibration (XQEq) scheme described in section 2.1 that includes both charge transfer and polarization self

consistently and instantaneously. This represents an extension of standard QEq [1], which did not allow polarization on the atoms.

- The valence terms, E^{Valence} , are expressed in terms of partial bond orders that go to zero as each bond is dissociated. The bond energy is determined by the bond order using an expression on QM calculations. Thus Bond distance \rightarrow Bond order \rightarrow Bond energy. In addition we define the atomic valence as the sum over all bond orders to a particular atom, and provide an energy penalty if this valence exceeds the expected valence of the atom (4 for Ti, 2 for O, 2 for Ba). Although the ReaxFF formulation [8] allows additional valence terms to describe the dependence of energy on bond angle (3-body), dihedral torsion (4-body), and inversion angle (4-body), we did not find the multibody valence terms to be necessary for BaTiO₃.
- Nonbonded interactions are represented through a Morse term to account short range Pauli Repulsion plus the dispersion, E^{vdW} . More commonly Lennard Jones 12-6 or 9-6 or exponential-6 forms are used.
- All parameters are optimized to fit QM calculations on clusters (with Jaguar [11,12] and solids (with CASTEP [13])).

Self-consistent charge transfer and polarization

The electrostatic interaction between all atoms, E^{Coulomb} , is computed by taking into account the fact that it is shielded when the charges overlap. In order to take into account the polarizability of the atoms an extended form of shell model is employed. In this model the charges are distributed over the atoms (Gaussian distribution functions are used). In this model the shell charge can move with respect to core and the charge transfer between the shells on different atoms is allowed through the use of the self-consistent charge equilibration model (QEq). Figure 1 shows the charge distribution in an atom. The Gaussian charge distribution is given by

$$\rho_i^c(r)^K = \left(\frac{\eta_i^c}{\pi}\right)^{3/2} Q_i^c \exp(-\eta_i^c \cdot |r - r_i^c|^2)$$

$$\rho_i^s(r)^K = \left(\frac{\eta_i^s}{\pi}\right)^{3/2} Q_i^s \exp(-\eta_i^s \cdot |r - r_i^s|^2)$$

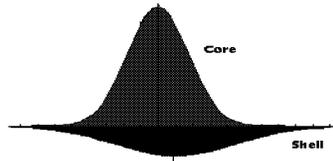


FIGURE 1. Charge distribution in an atom.

The electrostatic energy of the crystal is given by the sum of atomic self-energy and the pair-wise interaction energy

$$E^{Elec}(\{r_i\}, \{Q_i^{C,S}\}) = \sum_{i=1}^N E_i^{self}(Q_i^{C,S}) + \frac{1}{2} \sum_{i,j;k,l}^{N'} E^{Int}(r_{ij}, Q_i^k, Q_j^l)$$

$$E^{\text{int}}(r_{ij}, Q_i^k, Q_j^l) = \frac{\text{Erf}\left[\frac{\sqrt{\eta_{ij}\eta_{kl}} \cdot r_{ij}}{\eta_{ij} + \eta_{kl}}\right]}{r_{ij}} Q_i^k Q_j^l$$

$$E_i^{\text{self}}(Q_i^s) = E_{io} + \chi_i(Q_i^c + Q_i^s) + \frac{1}{2} J_i (Q_i^c + Q_i^s)^2$$

The charges in the system are dynamically updated as the configuration of the system changes using the QEq method.

The physical properties from polarizable Reax FF

In this subsection we provide the expressions used to determine the physical properties of the ferroelectrics: The dipole moment of the crystal is given by:

$$d\mu = \sum_{i=1}^N d\mu_i$$

$$d\mu_i^K = (dr_i^{cK} \cdot q_i^c + dr_i^{sK} \cdot q_i^s)$$

$$+ r_i^{sK} \cdot \sum_{j=1}^N (\nabla_{r_j^s} q_i^s \cdot dr_j^{cK} + \nabla_{r_j^s} q_i^s \cdot dr_j^{sK})$$

$$+ r_i^{sK} \cdot (\nabla_E \mathcal{E}_i^s \cdot dE)^K$$

The polarizability of the system is calculated using

$$\alpha_{\beta\gamma} = \frac{\partial}{\partial E_\gamma} \mu_\beta$$

$$= \sum_{i,k=1}^N \sum_{j,l=c,s} q_j^l \cdot H^{-1}_{ij\beta,kl\gamma} \cdot q_k^l$$

$$+ \sum_{i=1}^N r_{i\beta}^s \cdot \sum_{k=1}^N \sum_{l=c,s} \frac{\partial}{\partial r_{ky}^l} q_j^l \cdot H^{-1}_{is\beta,kl\gamma} \cdot q_k^l$$

$$+ \sum_{i=1}^N r_{i\beta}^s \cdot \frac{\partial}{\partial E_\gamma} q_i^s$$

Here, H is the Hessian of the system. Using the polarizability we obtain can compute the dielectric constant from the following expression:

$$\epsilon_{\beta\gamma} = \delta_{\beta\gamma} + \frac{4\pi}{V} \cdot \alpha_{\beta\gamma}$$

The Born effective charges for the atoms are obtained using the expression:

$$\begin{aligned}
Q_{k,\alpha\beta} &= \frac{\partial P_\beta}{\partial r_{k\alpha}^c} \\
&= \frac{1}{\partial r_{k\alpha}^c} \int_{i=1}^N (q_i^s dr_{i\beta}^s + dq_i^s r_{i\beta}^s + q_k^c dr_{k\beta}^c) \\
&= \int_{i=1}^N q_i^s \frac{\partial r_{i\beta}^s}{\partial r_{k\alpha}^c} + \int_{i=1}^N \frac{\partial q_i^s}{\partial r_{k\alpha}^c} r_{i,\beta}^s + \delta_{\alpha\beta} q_k^c
\end{aligned}$$

Nonbond (Morse) parameters: equation of state of BaTiO₃

We used accurate QM methods (DFT with the GGA approximation) to calculate the zero temperature equation of state of the four experimentally known phases of BaTiO₃. We used the plane wave code CASTEP [13] and replaced the core electrons with ultrasoft pseudopotentials. The calculations correspond to zero temperature except that zero point energy is not included. Figure 2 shows energy-volume curves for cubic, tetragonal, orthorhombic and rhombohedral. The *ab initio* results show three pressure induced phase transitions:

- i) rhombohedral to orthorhombic at ~5 GPa,
- ii) orthorhombic to tetragonal at ~6 GPa, and
- iii) tetragonal to cubic at 7.5 GPa.

The order and transition pressures are in good agreement with experimental results, see [2] and references therein. The tetragonal phase is stable at room conditions and consequently of great technological importance.

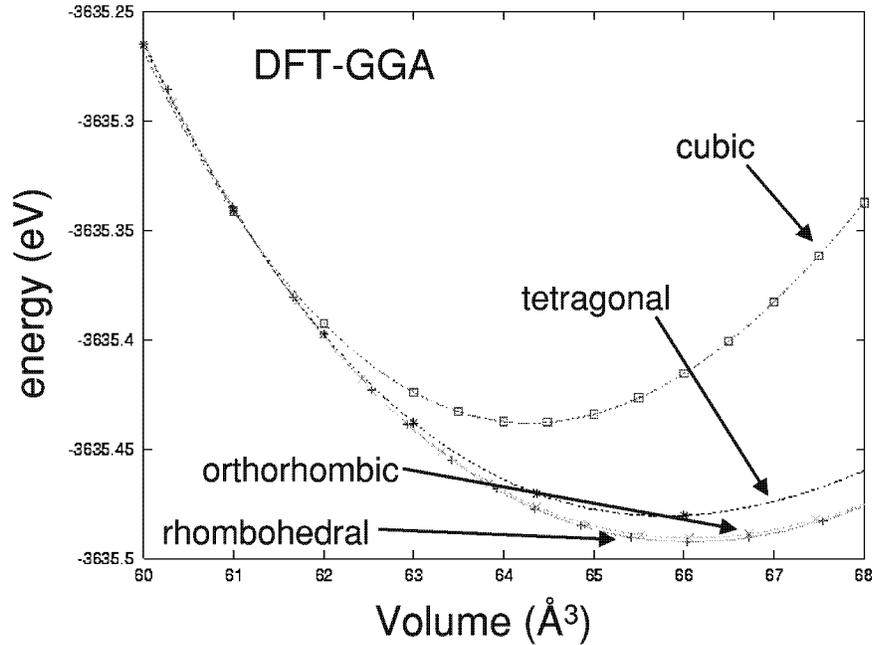


FIGURE 2: Zero temperature energy-volume curves for rhombohedral, orthorhombic, tetragonal and cubic phases of BaTiO₃ from DFT-GGA calculations.

Table 1 compares our *ab initio* results for the bulk properties of the tetragonal phase (zero pressure volume, c/a ratio, and internal atomic displacements: Δ_{Ti} , Δ_{O1} , Δ_{O2}) with experimental values. We see that DFT-GGA overestimates the zero pressure volume and for the experimental volume it overestimates the c/a ratio. In Table I, Δ_{Ti} denotes the displacement of the Ti atom in the z direction in cell coordinates, Δ_{O1} is the scaled displacement in the z displacement of the O atoms located in the same xy plane as the Ti, and Δ_{O2} is the scaled z displacement of the O in the same xy planes as the Ba atoms. The DFT-GGA atomic displacements are in good agreement with experiment [3]. As in previous studies, the *ab initio* results of the ferroelectric properties are very sensitive to the volume and better agreement with experiments is obtained using the experimental volume.

TABLE 1: Bulk properties (zero pressure volume and c/a ratio) of tetragonal BaTiO₃. *

	V_0 (Å ³)	c/a	Δ_{O2}	Δ_{O1}	Δ_{Ti}
DFT-GGA (exp. volume)	64.2555	1.03	0.0272	0.0156	0.0165
DFT-GGA (zero stress)	65.9118	1.049			
Experiment (300 K)*	64.2555	1.011	0.0244	0.0105	0.0224

We have also used DFT-GGA to calculate energy as a function of atomic displacements in the [100] ferroelectric mode, where we kept c/a fixed at 1.031. Starting from the relaxed tetragonal structure we moved the Ti and O atoms simultaneously towards their cubic positions at fixed lattice parameters. The dashed line in Figure 3 shows the energy as a function of displacement (circles represent results and the line is a guide for the eye).

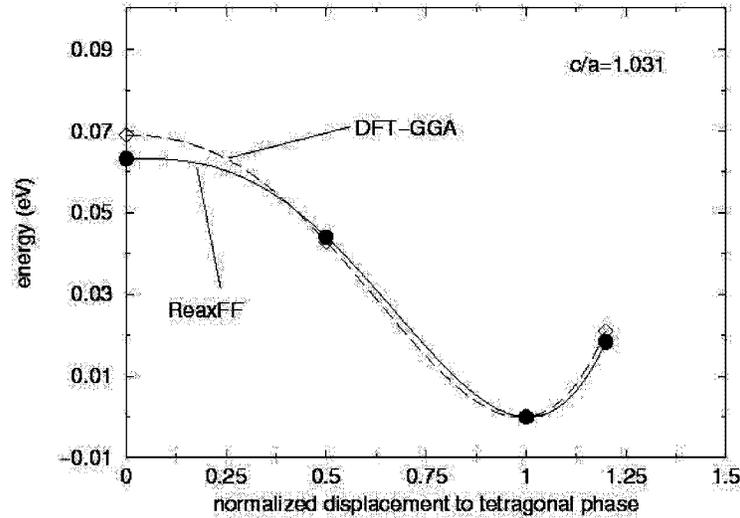


FIGURE 3: Energy as a function of atomic displacement in the z direction. Starting from the tetragonal positions (displacement equal to 1 in the Figure) we move the atoms towards their cubic positions (zero displacements in the Figure) keeping the lattice parameters fixed.

We used the *ab initio* data to obtain the Morse parameters of the ReaxFF; the parameters describing electrostatic interaction were fixed to the values obtained in the previous sub-section. A simplified version of the electrostatics interactions was used for this first version of the ReaxFF. We do not allow atomic polarization; i.e., the core and shell are forced to center in the same point in space. This simplified electrostatics is used for the optimization of Morse parameters as well as in the MD simulations described in Section 3.

We optimized the Morse interactions using the First Principles EOS of the cubic and tetragonal phases and the energy as a function of [100] displacements from the tetragonal phase (Figure 3). Figure 4 compares our *ab initio* EOS with those obtained using the optimized ReaxFF; the *ab initio* results are shown as symbols (squares for the cubic phase and circles for tetragonal) and ReaxFF is shown as lines (dashed for cubic and solid for tetragonal). The solid line in Figure 3 shows the energy as a function of atomic displacements using the ReaxFF. From Figures 3 and 4 we see that the ReaxFF accurately describes the atomic interactions in BaTiO_3 ; it correctly describes the cubic-tetragonal energy difference as a function of volume in a wide pressure range (a critical quantity to correctly describe the phase transition) and the energy as a function of atomic displacements in the [100] direction.

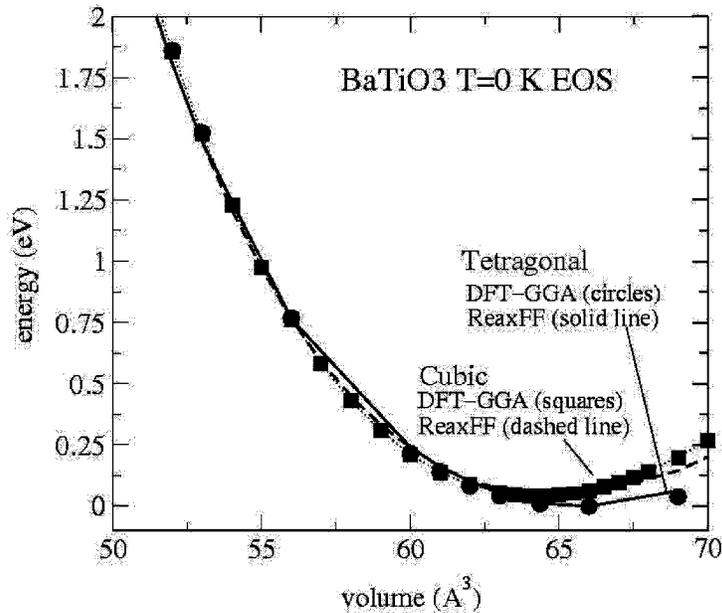


FIGURE 4: Zero temperature energy-volume curves for the tetragonal and cubic phases of BaTiO₃. DFT-GGA results are shown as symbols (squares for the cubic phase and circles for tetragonal) and ReaxFF is shown as lines (dashed for cubic and solid for tetragonal).

MD SIMULATION OF THE CUBIC TO TETRAGONAL PHASE TRANSITION

Using ReaxFF in MD simulations we studied the transition temperature for the cubic to tetragonal phase transition. These calculations used constant volume and temperature MD (TVN ensemble) at the experimental volume (64.2555 \AA^3 per formula unit) and $c/a=1.005$, which is half way between the experimental value for the tetragonal and cubic phases. We used a supercell obtained by replicating the cubic unit cell 4 times in the c direction and 2 in the a direction, leading to a 40 atom cell with periodic boundary conditions in all three directions. In order to estimate the cubic-tetragonal phase transition temperature we performed MD simulations at various temperatures of $T=600 \text{ K}$, 500 K , and 400 K .

Figure 5 shows the time evolution of the average position of the Ti atoms along the c direction with respect to their cubic position for different temperatures. At $T=600 \text{ K}$ the Ti atoms fluctuate around the cubic position (zero in the Figure) with no net polarization. At $T=500 \text{ K}$ the Ti atoms spend most of the 20 ps of simulation on one side of the cubic position, i.e. in a tetragonal configuration, but at time $t \sim 17 \text{ ps}$ the polarization changes; thus we expect that at $T=500 \text{ K}$ the average polarization be zero. At $T=400 \text{ K}$ the Ti atoms choose one of the two possible tetragonal polarizations indicating a spontaneous polarization. Figure 6 shows the time evolution of the average

Ti positions along a direction for the same three MD runs; we see that for all temperatures the average polarization in the a direction is zero and we obtain the same results for the b direction. This indicates that the cubic-tetragonal phase transition temperature is around $T=400$ K, very close to the experimental value (393 K). To obtain an accurate prediction of the phase diagram for BaTiO_3 within ReaxFF, much more extensive MD simulations are essential. However, these preliminary results suggest that ReaxFF correctly describes the cubic-tetragonal phase transition.

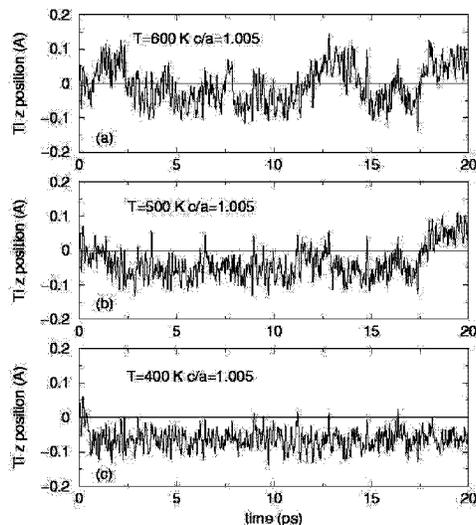


FIGURE 5: Time evolution of the average Ti position along the c direction with respect to its cubic position for different temperatures. We see no polarization for $T=600$ K and $T=500$ K while for $T=400$ K the Ti are displaced from their cubic positions.

The description of the phase transitions in BaTiO_3 has proved to be a challenge for theorists. Previous simulations tend to give transition temperatures lower than the experimental values. For example the First-Principles-based effective Hamiltonian approach [4, 5] gives the correct order of phases (cubic, tetragonal, orthorhombic, rhombohedral) but low transition temperatures (290 K, 230 K, and 197 K) compared with experimental values (403 K, 278 K, 183 K), see for example [2]. The non-linear Oxygen polarizability shell model [6] has been used with MD to calculate the phase transition temperatures. This model also gives the phase transitions in the correct order but with low transition temperatures (190 K; 120 K and 90 K).

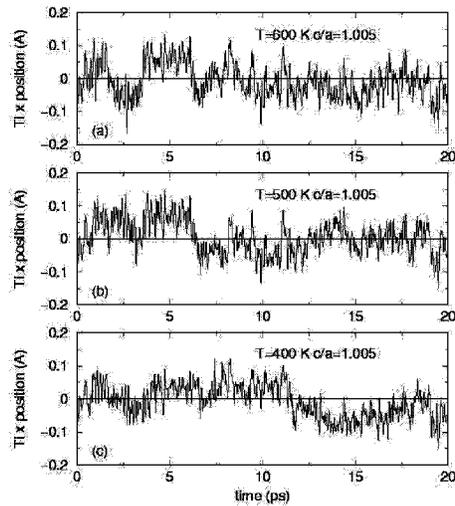


FIGURE 6: Time evolution of the average Ti position along the b direction with respect to its cubic position for different temperatures.

CONCLUSIONS

We describe a new generation of force field (denote as ReaxFF) based purely on ab initio QM calculations for BaTiO₃ and designed to describe the polarizations and reactions observed in the QM. ReaxFF treats charge transfer and atomic polarization self consistently. The charge on atom is described with two functions:

- the core charge is a Gaussian with fixed positive amplitude centered on the atom.
- the valence charge is a Gaussian with variable negative amplitude and allowed to move off the nuclear center

The valence charge of an atom depends on its environment, and is calculated using the Charge Equilibration (QEq) method. The restoring force that keeps the valence distribution near its core is simply the Coulomb interaction between the charge distributions. This simple model describes accurately the ab initio charge distributions for a variety of molecules and also reproduces the Born effective charges and dielectric properties of BaTiO₃. The non-electrostatic nonbond interactions are described with simple two-body Morse terms.

Using ReaxFF we carried out MD simulations to estimate the cubic to tetragonal phase transition temperature. Our results suggest reasonable agreement with the experimental transition temperature, but additional MD simulations are necessary to accurately characterize the calculated transition temperature.

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