

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

William A. Goddard III[#], Qingsong Zhang, Mustafa Uludogan, Alejandro Strachan, Tahir Cagin

*Materials and Process Simulation Center (139-74),
California Institute of Technology, Pasadena CA 91125*

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) [Rappe and Goddard, J. Phys. Chem. 95, 3358 (1991)]. 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) of cubic and tetragonal BaTiO₃ in a wide pressure range obtained using QM methods. 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 the experimental value.

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To whom correspondence should be addressed

INTRODUCTION

A great deal of progress has been made in using methods of quantum mechanic (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 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. When the temperature is lowered BaTiO₃ undergoes three phase 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 core and shell widths) 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 on the development of a 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,

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

Nonbonded interactions are represented through a Morse term to account short range Pauli Repulsion plus the dispersion, E^{vdW} . The valence terms, E^{Valence} , are based on bond order which allows smooth dissociation, the expression is based on Quantum mechanically calculated, Bond distance \rightarrow Bond order \rightarrow Bond energy, relationship. The most general form of valence terms allows the angle, torsion, and inversion terms when needed. In this description the atomic valency term when summed over bond orders gives the valency of the element.

2.1 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 atoms are allowed (shell charges) through the use of self-consistent charge equilibration model. Figure A1 shows the charge distribution in an atom. The gaussian charge distribution is given by

$$\begin{aligned} r_i^c(\vec{r}) &= \left(\frac{h_i^c}{p}\right)^{3/2} Q_i^c \exp(-h_i^c \cdot |\vec{r} - \vec{r}_i^c|^2) \\ r_i^s(\vec{r}) &= \left(\frac{h_i^s}{p}\right)^{3/2} Q_i^s \exp(-h_i^s \cdot |\vec{r} - \vec{r}_i^s|^2) \end{aligned}$$

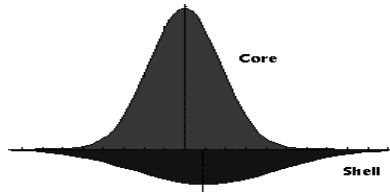


FIGURE A1. CHARGE DISTRIBUTION IN AN ATOM.

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

$$\begin{aligned} E^{\text{Elec}}(\{r_i\}, \{Q_i^{C,S}\}) &= \sum_{i=1}^N E_i^{\text{self}}(Q_i^{C,S}) + \frac{1}{2} \sum_{i,j:k,l}^N E^{\text{Int}}(r_{ij}, Q_i^k, Q_j^l) \\ E^{\text{Int}}(r_{ij}, Q_i^k, Q_j^l) &= \frac{\text{Erf}\left(\sqrt{\frac{h_i^k h_j^l}{h_i^k + h_j^l}} r_{ij}\right)}{r_{ij}} Q_i^k Q_j^l \\ E_i^{\text{self}}(Q_i^s) &= E_{i0} + c_i(Q_i^c + Q_i^s) + \frac{1}{2} J_i(Q_i^c + Q_i^s)^2 \end{aligned}$$

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

2.1.2 The physical properties from polarizable Reax FF

In this subsection we will give the expressions we are using to determine the physical properties of the ferroelectrics: The dipole moment of the crystal is given by:

$$\begin{aligned}
 d\bar{\mathbf{m}} &= \sum_{i=1}^N d\bar{\mathbf{m}}_i \\
 d\bar{\mathbf{m}}_i &= (d\bar{r}_i^c \cdot q_i^c + d\bar{r}_i^s \cdot q_i^s) \\
 &\quad + \bar{r}_i^s \cdot \sum_{j=1}^N (\nabla_{\bar{r}_j^c} q_i^s \cdot d\bar{r}_j^c + \nabla_{\bar{r}_j^s} q_i^s \cdot d\bar{r}_j^s) \\
 &\quad + \bar{r}_i^s \cdot (\nabla_{\bar{E}} q_i^s \cdot d\bar{E})
 \end{aligned}$$

The polarizability of the system is calculated using

$$\begin{aligned}
 \mathbf{a}_{bg} &= \frac{\partial}{\partial E_g} \mathbf{m}_b \\
 &= \sum_{i,k=1}^N \sum_{j,l=c,s} q_i^j \cdot H^{-1}_{ijb,klg} \cdot q_k^l \\
 &\quad + \sum_{i=1}^N \bar{r}_{ib}^s \cdot \sum_{k=1}^N \sum_{l=c,s} \frac{\partial}{\partial r_{kg}^l} q_i^s \cdot H^{-1}_{isb,klg} \cdot q_k^l \\
 &\quad + \sum_{i=1}^N \bar{r}_{ib}^s \cdot \frac{\partial}{\partial E_g} q_i^s
 \end{aligned}$$

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

$$\mathbf{e}_{bg} = \mathbf{d}_{bg} + \frac{4\pi}{V} \cdot \mathbf{a}_{bg}$$

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

$$\begin{aligned}
 Q_{k,ab} &= \frac{\partial P_b}{\partial r_{ka}^c} \\
 &= \frac{1}{\partial r_{ka}^c} \sum_{i=1}^N (q_i^s dr_{ib}^s + dq_i^s r_{ib}^s + q_k^c dr_{kb}^c) \\
 &= \sum_{i=1}^N q_i^s \frac{\partial r_{ib}^s}{\partial r_{ka}^c} + \sum_{i=1}^N \frac{\partial q_i^s}{\partial r_{ka}^c} r_{i,b}^s + \mathbf{d}_{ab} q_k^c
 \end{aligned}$$

2.2 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 and replaced the core electrons with ultrasoft pseudopotentials. The calculations correspond to zero temperature except that zero point energy is not included. Figure A2 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.

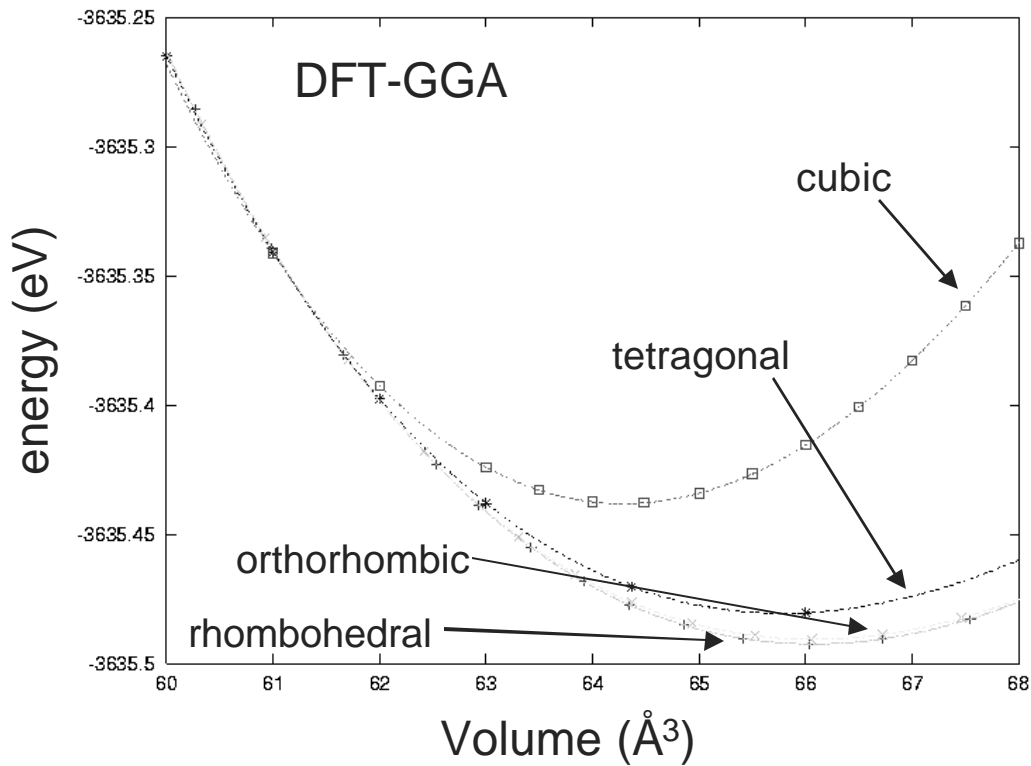


FIGURE A2: ZERO TEMPERATURE ENERGY-VOLUME CURVES FOR RHOMBOHEDRAL, ORTHORHOMBIC, TETRAGONAL AND CUBIC PHASES OF BaTiO₃ FROM DFT-GGA CALCULATIONS.

Table A1 compares our *ab initio* results regarding 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 overestimated the zero pressure volume and for the experimental volume it overestimates the c/a ratio. In table A1, 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 A1: bulk properties (zero pressure volume and c/a ratio) of tetragonal BaTiO₃. *

	V_0 (Å ³)	c/a	D_{O2}	D_{O1}	D_{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 keep c/a fixed at 1.031. Starting from the relaxed tetragonal structure we march the Ti and O atoms towards their cubic positions at fixed lattice parameters. The dashed line in Figure A3 shows the energy as a function of displacement (circles represent results and the line is a guide for the eye).

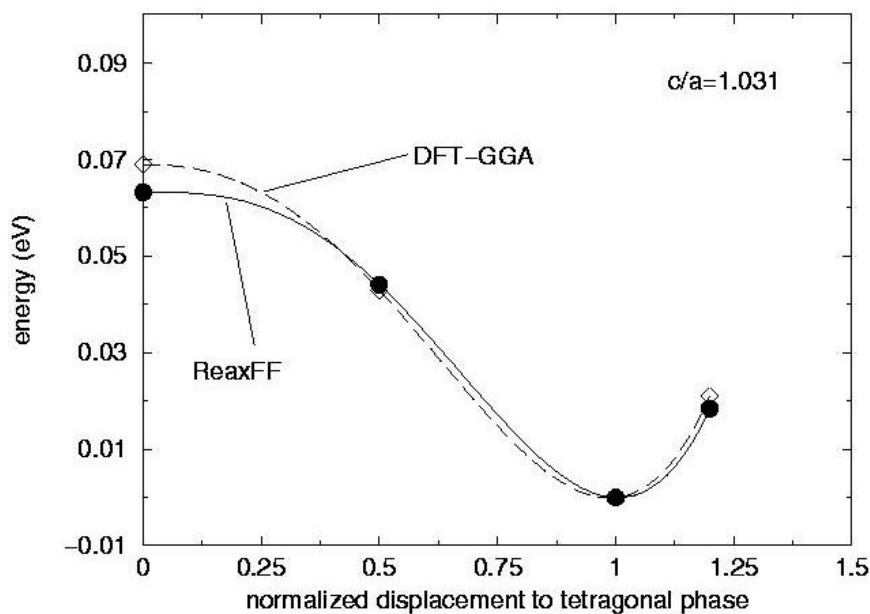


FIGURE A3: ENERGY AS A FUNCTION OF ATOMIC DISPLACEMENT IN THE Z DIRECTION. STARTING FROM THE TETRAGONAL POSITIONS (DISPLACEMENT EQUAL TO 1 IN THE FIGURE) WE MOVE THE ATOMS TOWARDS THEIR CUBIC POSITIONS (ZERO DISPLACEMENTS IN THE FIGURE) KEEPING THE LATTICE PARAMETERS FIXED

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 don't 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 A3). In Figure A4 we compare our *ab initio* EOS and that obtained with 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 A3 shows the energy as a function of atomic displacements using the ReaxFF. From Figures A3 and A4 we see that the ReaxFF accurately describes the atomic interactions in BaTiO₃; 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.

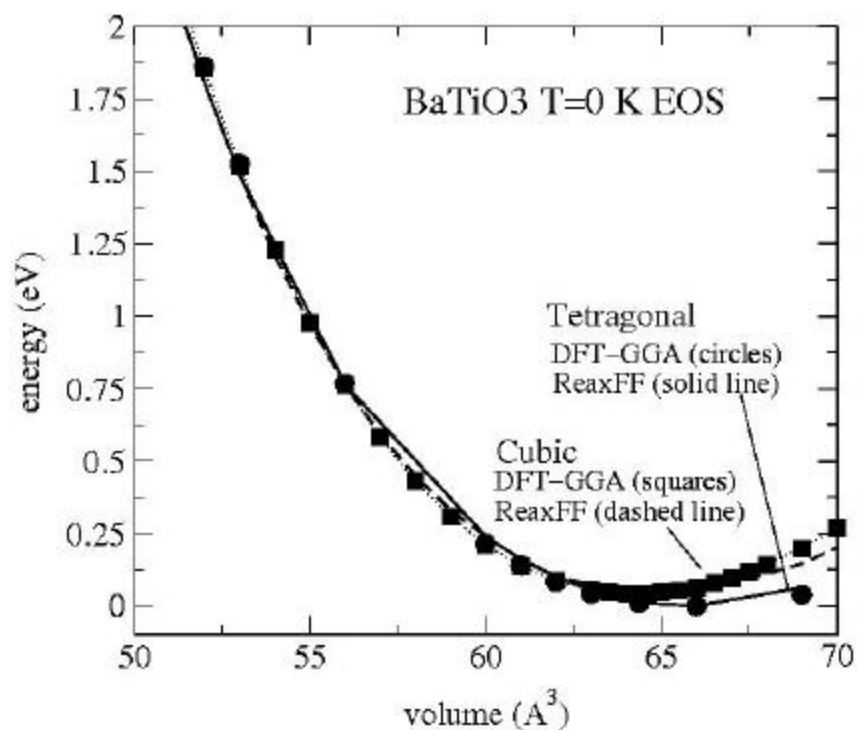


FIGURE A4: ZERO TEMPERATURE ENERGY-VOLUME CURVES FOR THE TETRAGONAL AND CUBIC PHASES OF BATIO3. DFT-GGA RESULTS ARE SHOWN AS SYMBOLS (SQUARES FOR THE CUBIC PHASE AND CIRCLES FOR TETRAGONAL) AND REAXFF IS SHOWN AS LINES (DASHED FOR CUBIC AND SOLID FOR TETRAGONAL).

MD SIMULATION OF THE CUBIC TO TETRAGONAL PHASE TRANSITION

We use the ReaxFF with MD simulations to study the transition temperature for the cubic to tetragonal phase transition. Our current ReaxFF MD code does not allow constant stress dynamics, the appropriate ensemble to study solid-solid phase transitions. Nevertheless, since the cubic to tetragonal transition does not involve large variations of the lattice parameters ($c/a \sim 1\%$) we can estimate the phase behavior with constant volume and temperature MD (TVN

ensemble). In order not to favor one phase over the other we decided to use the experimental volume (64.2555 \AA^3 per formula unit) and half the experimental c/a ratio ($c/a=1.005$). In order to estimate the cubic-tetragonal phase transition temperature we performed MD simulations at various temperatures: $T=600 \text{ K}$, 500 K , and 400 K . 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; periodic boundary conditions are applied in all directions.

Figure A5 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 A6 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 results indicate that the cubic-tetragonal phase transition temperature is around $T=400 \text{ K}$ very close to the experimental value (393 K). Constant stress simulations for longer times and larger systems are needed for an accurate calculation of the phase diagram of BaTiO_3 but our preliminary results indicate that ReaxFF correctly describes cubic-tetragonal phase transition.

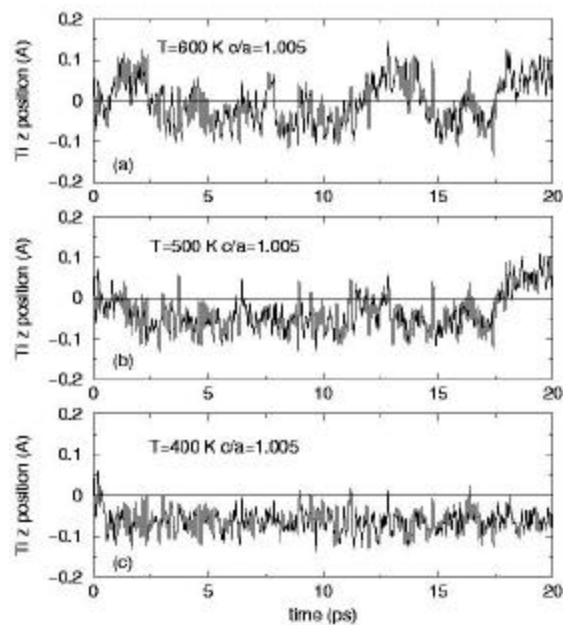


FIGURE A5: TIME EVOLUTION OF THE AVERAGE TI POSITION ALONG THE c DIRECTION WITH RESPECT TO ITS CUBIC POSITION FOR DIFFERENT TEMPERATURES. WE SEE NO POLARIZATION FOR $T=600 \text{ K}$ AND $T=500 \text{ K}$ WHILE FOR $T=400 \text{ K}$ THE TI ARE DISPLACED FROM THEIR CUBIC POSITIONS.

The description of the phase transitions in BaTiO_3 has proved to be a challenging problem 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).

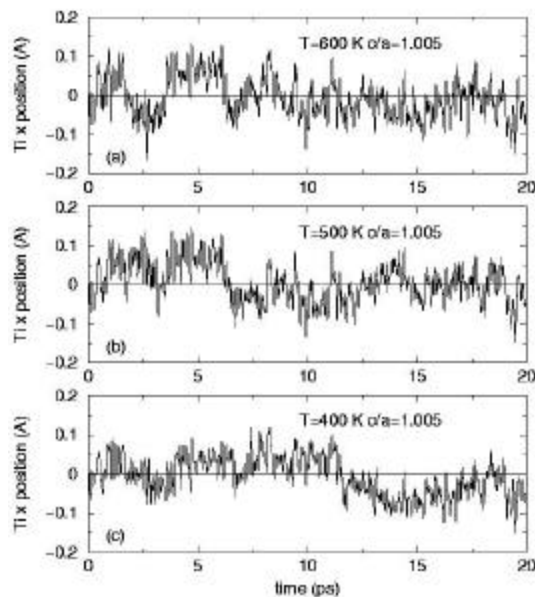


FIGURE A6: TIME EVOLUTION OF THE AVERAGE TI POSITION ALONG THE B DIRECTION WITH RESPECT TO ITS CUBIC POSITION FOR DIFFERENT TEMPERATURES.

CONCLUSIONS

We report a new generation of force fields (denote as ReaxFF) based purely on ab initio QM calculations for BaTiO₃ and designed to describe the polarizations observed in the QM. The ReaxFF treats charge transfer and atomic polarization self consistently. The charge on atom is described with two Gaussian distributions: a positive, fixed distribution represents the core and a variable charge, negative distribution represents the valence atoms. The valence charge of an atom depends on its environment as the Charge Equilibration method. The restoring force that keeps the valence distribution near its core is simply given by the interaction between the charge distributions. This simple model can describe correctly ab initio charge distributions on a variety of molecules, Born effective charges and dielectric properties of BaTiO₃. The non-electrostatic interactions are described with simple two-body Morse terms.

We applied this ReaxFF with MD to estimate the cubic to tetragonal phase transition temperature. Our results suggest reasonable agreement with experimental transition temperature, but additional MD simulations are necessary to accurately characterize the calculated transition temperature.

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REFERENCES

1. Rappe AK and Goddard WA, *J. Phys. Chem.* 95, 3358 (1991)
2. Ishidate T, Abe S, Takahashi H, and Mori N, *Phys Rev Lett.* 78, 2397-2400 (1997)
3. Kwei GH, Lawson AC, Billinge SJL, Cheong SW, *J. Phys. Chem.* 97, 2368-2377 (1993)
4. Zhong W, Vanderbilt D, Rabe KM, *Phys Rev Lett* 73, 1861-1864 (1994)
5. Zhong W, Vanderbilt D, Rabe KM, *Phys Rev B* 52, 6301-6312 (1995)
6. Tinte S, Stachiotti MG, Sepliarsky M, Migoni RL, Rodriguez CO, *J Phys-Condens Mat* 11, 9679-9690 (1999)