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EVALUATION AND EXTENSION OF REAXFF REACTIVE FORCE FIELD METHOD FOR APPLICATIONS TO DIELECTRIC OXIDES AND THEIR MULTI-MATERIAL INTERFACES

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14. ABSTRACT

The ReaxFF reactive force field method was extended to $BaTiO_3$. This extension combines earlier published ReaxFF descriptions for Ba and Ti oxides with additional training for a Ba/Ti/O/H force field against Density Functional Theory (DFT) data describing volume/energy relations, defect formation and migrations, and deformations of $BaTiO_3$ crystal structures. We reproduce the DFT data without requiring change to the ReaxFF formulism, which means that these parameters are fully transferable with all earlier ReaxFF sets, including those for organic molecules and different inorganic systems.

This parameter set was used in molecular dynamics (MD) simulations. We observe clear ferroelectric (FE) to non-ferroelectric transition for bulk $BaTiO_3$, and show how different surface terminations can affect the FE response. ReaxFF provides a unique, computational efficient, tool for studying FE response in realistic, complex materials.

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ReaxFF; BaTiO3; Ferroelectric; Dielectric; Reaction; Force Field; DFT; Materials; Modeling; Simulation

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1.0 SUMMARY

In order to develop a computational inexpensive atomistic-scale method to simulate ferroelectric response for realistic materials – including defects and interfaces – we have extended the ReaxFF reactive force field method to $BaTiO_3$ based materials. This extension was performed by combining earlier published ReaxFF descriptions for barium oxides and titanium oxides and by training this combined Ba/Ti/O/H force field against Density Functional Theory (DFT) data describing, amongst others, volume/energy relations for various $BaTiO_3$ crystal morphologies, oxygen vacancy energies and vacancy migration barriers and barriers for asymmetric/symmetric/asymmetric deformations of $BaTiO_3$ crystal structures. We found that ReaxFF can successfully reproduce these DFT data – without the necessity for changing the ReaxFF formulism, which means that these ReaxFF Ba/Ti/O/H parameters are fully transferable with all earlier ReaxFF parameter sets – including those for organic molecules and different inorganic systems.

After completing the training, we applied this ReaxFF Ba/Ti/O/H parameter set in a series of molecular dynamics (MD) simulations. We observed a clear ferroelectric to non-ferroelectric transition for $BaTiO_3$ bulk phases and observed how different surface terminations can affect the ferroelectric response. As such, we argue that ReaxFF provides a unique, computationally efficient, tool for studying ferroelectric response in realistic, complex materials.

2.0 INTRODUCTION

Ferroelectric phase transitions of perovskite-based oxides represent an important class of structural phase transitions that have significant technological implications related to piezoelectric and pyroelectric response [1-2]. Ferroelectric perovskites exhibit a spontaneous electric polarization that can be reoriented by an external electric field.

To improve our understanding of the dielectric properties of the oxides and their interfaces, we need to obtain detailed, atomistic-scale insight in the key events at this interface. Given typical operation conditions include elevated temperatures and relatively long time-scales, a simulation tool is required that can evaluate dynamics and properly describe reaction barriers and reaction energies. Furthermore, defects and domain boundaries in the oxide materials will play a key role in their dielectric response – which means that relatively large systems will need to be used in the simulations so that such large structural features can be considered. This combination of system size and dynamics indicates that quantum mechanical (QM) based methods by themselves will not be sufficient to fully evaluate the activity of a catalyst. While QM-based methods have become key tools in the evaluation of reaction barriers and reaction energies, the high computational cost associated with these methods renders QM-based dynamical descriptions only viable for relatively small systems and short time scales. For a fully dynamical description of events at piezoelectric metal oxide interfaces and boundaries, we require a computational method that is a number of magnitudes faster but retains the quality of QM-results for reaction energetics. Force field (FF) based approaches can provide the computational speed required to perform molecular dynamics (MD) simulations on system sizes sufficiently large to describe the full chemistry of the metal oxide and their interfaces. For this reason, a number of FF-based concepts related to ferroelectric materials have been formulated – ranging from relatively straightforward core-shell $BaTiO_3$ models[3] – aiming to capture the atomic dipole connected with ferroelectric response – to bond-valence models, as developed by Rappe and co-workers[1, 4-6], which capture the ferroelectric response through bond orders rather than atom polarizability. Beyond these relatively simple – and relatively fast – force field approaches there also exist more sophisticated force field approaches that allow charge flow through polarizable charges – either through a single point charge model, as applied in the COMB-potential[2, 7] – or even through a polarizable core-shell concept, as developed by Zhang, Goddard and co-workers[8-9]. These concepts all share a significant lack of transferability – they have demonstrated success within a single ferroelectric formulation, but cannot be straightforwardly extended to study interactions of ferroelectric materials in multi-material interfaces – for example, a ferroelectric nanocluster on a metal support, or ferroelectric clusters suspended in an organic polymer. In this project, we evaluated the ability of the ReaxFF method – which shares many features with the COMB potential and has demonstrated transferability to a wide range of materials (Figure 1) – for describing ferroelectric material response.

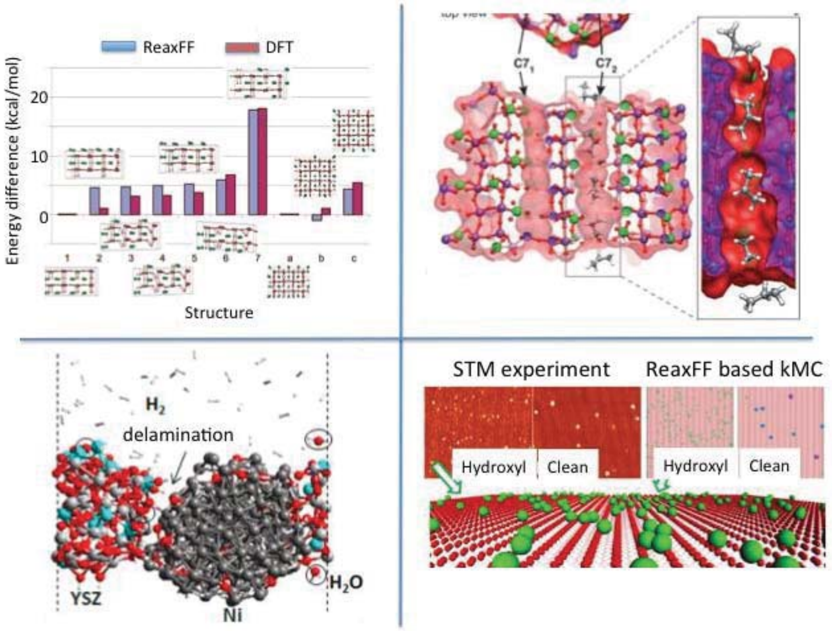

Figure 1 Overview of Some Previous ReaxFF Applications to Mixed Metal Oxide Systems (a) Comparison of DFT and ReaxFF Surface Energies for Yttrium-stabilized BaZrO3 surfaces[10] (b) ReaxFF Application to Reactive Diffusion of Hydrocarbons in the Pore of a Bi/Mo/V-mixed Metal Oxide Catalyst[11]. (c) ReaxFF Application to H2 Dissociation on a YSZ-supported Ni- Nanoparticle[12] (d) Comparison of Experimental and ReaxFF/DFT Informed kMC Structures of a Clean and Hydroxylated TiO2 Surface with Pd-metal Clusters[13]

3.0 METHODS, ASSUMPTIONS, AND PROCEDURES

While originally primarily designed for non-reactive systems, in recent years a number of FF-approaches have been formulated that can also be used to model reactive events (Reactive Force Field (RFF)). At this moment, RFFs have been reported for metallic [e.g. [14-15]], covalent [e.g. [16-17]] and fully/partially ionic materials [e.g. [7, 18]]. One of the more widely employed reactive force field schemes is the ReaxFF reactive force field approach[19], which combines a bond order/ bond distance relationship with a polarizable charge description. This combination has made ReaxFF applicable to a wide range of materials, including covalent [e.g. [19-20]], metallic[21-22], and metal oxide/hydride/carbide systems [e.g. [23],[24]]. The ReaxFF transferability enables us to not only study the oxide materials in this project, but it also allows for a straightforward extension to a wide range of interactions with surfaces and organic materials. At this moment, we already have ReaxFF parameters available for various oxide materials, including zirconates[25-27], zinc oxides[28-30], aluminum oxides, silica and iron oxides[29, 31-32], as well as a range of noble metals, including Pt, Pd, Ni and Cu[33-35]. These ReaxFF descriptions are fully transferable, which means that only a limited number of new ReaxFF angle parameters need to be developed to enable simulations of oxide interactions with other materials. ReaxFF has been successfully employed to a number of mixed-metal oxide systems (Figure 1), including Ba/Y/Zr-oxides[36] as well as Bi/Mo/V-oxides[11, 23, 37-39], where we demonstrated an ability to predict the structure of complex multi-metal, multi-oxidation materials. Given the considerable success of the bond/valence force fields developed by Rappe and co-workers[1, 4-6], as well as the COMB-polarizable force field method[2, 7], in reproducing QM-results for ferroelectric materials we would expect the ReaxFF concept to be capable of predicting ferroelectric response, and our earlier work on copper ions in water supports this expectation. For these clusters, we clearly observe the ReaxFF capability to reproduce the complex, asymmetric, behavior of transition metal oxides. In this project, we seek to extend the ReaxFF method to ferroelectric materials, in particular $BaTiO_3$, by training against a DFT derived training set containing, amongst others, equations of state for ferroelectric (tetragonal, orthorhombic and rhombohedral) and non-ferroelectric (cubic) $BaTiO_3$ phases, oxygen vacancy energies and their migration barriers and asymmetric-symmetric-asymmetric $BaTiO_3$ unit cell distortions. In addition to these $BaTiO_3$ specific data, we also included the Ti- and Ba-metal data and TiO_2 and BaO oxide data from previous work[10, 40] into the ReaxFF training set, thus extending the transferability of the $BaTiO_3$ force field to BaO and TiO_2 materials and their surface chemistry.

Force field optimization was performed using the standalone, open-source ReaxFF code. MD-simulations were performed using the ADF/ReaxFF code – using multiple processors for the larger (8192 atom) systems. In our NPT simulations we employed Berendsen thermostats and barostats with relatively weak coupling (100 fs for the thermostat, 2500 fs for the barostat coupling).

4.0 RESULTS AND DISCUSIONS

A central part of the ReaxFF training set consisted of DFT/PBE derived volume/energy equations of state for various asymmetric (tetragonal, rhombohedral and orthogonal, all ferroelectric phases) and symmetric (cubic, non-ferroelectric phase) $BaTiO_3$ crystal morphologies. Figure 2 compares the ReaxFF and DFT results for these four phases – showing that ReaxFF captures their energy/volume trend and, most importantly, reproduces that the cubic phase is significantly less stable at zero pressure than the three asymmetric phases.

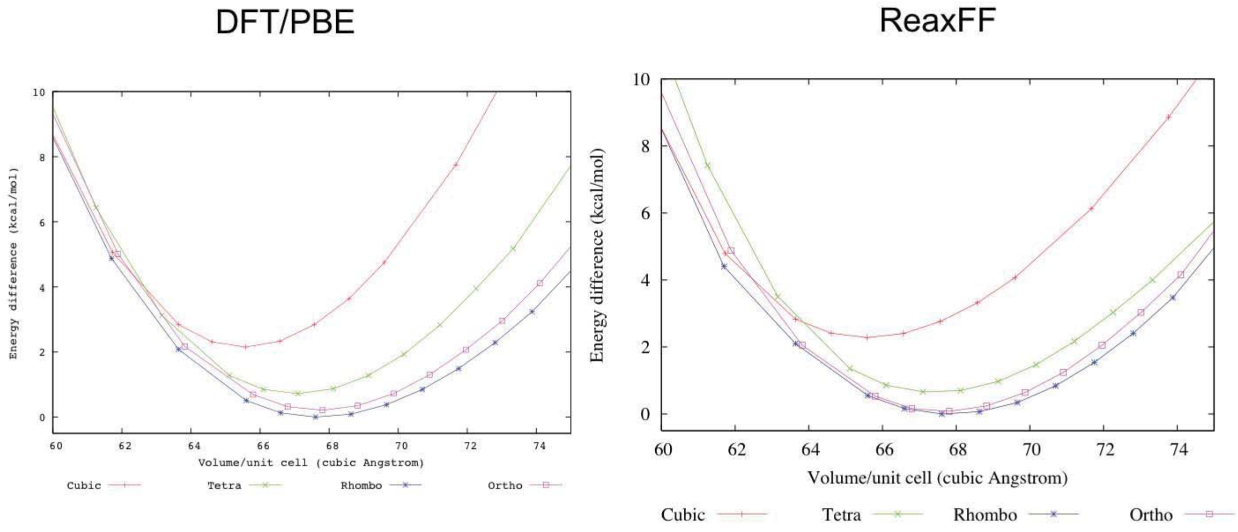

Figure 2 Comparison of DFT/PBE and ReaxFF Equations of State for Various BaTiO3 Crystal Morphologies.

In addition to these equations of state, we also included oxygen vacancy energy formation and the barrier for migration of these vacancies in the ReaxFF training set. Figure 3 shows the lowest energy path for O-vacancy migration in $BaTiO_3$. ReaxFF predicts a vacancy energy of+146.5 kcal/mol (relative to O_2) for $BaTiO_3$, which is in reasonable agreement with the DFT value (+182.6 kcal/mol) especially considering that DFT typically over-estimates the O_2 stability. More importantly, perhaps, ReaxFF reproduces the barrier for O-vacancy migration quite well (ReaxFF: 19.6 kcal/mol; DFT: 19.9 kcal/mol) which indicates that ReaxFF should be able to describe vacancy migration and re-organization. Furthermore, using local restraints we can force a BaTiO3 unit cell to transform from a tetragonal to a cubic structure – according to DFT calculations, the barrier for this asymmetric to symmetric conversion is 2.1 kcal/mol; ReaxFF finds a barrier of 2.0 kcal/mol – where the cubic, symmetric, state has the highest energy along the transformation path.

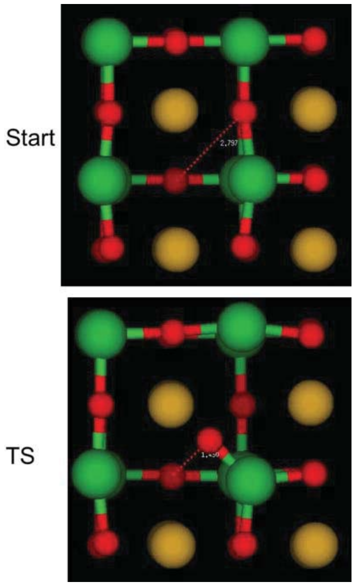

Figure 3 Initial, Energy Minimized Structure of the Oxygen Vacancy in BaTiO3 (start) and Transition State Structure for the Migration of this Vacancy (TS)

In order to validate the ReaxFF $BaTiO_3$ force field we performed a series of molecular dynamics (MD) simulations. The first of these simulations involved a heating/cooling of an initially tetragonal $BaTiO_3$ supercell (Figure 4). Here we found that around T=250K the crystal structure changes from a ferroelectric phase to a non-ferroelectric, cubic, phase. Subsequently, we took the 500K non-ferroelectric structure from Figure 4 and performed a cooldown simulation (Figure 5) where we saw, around T=280K, the reverse conversion from a non-ferroelectric to a ferroelectric phase (in this case, an orthogonal phase).

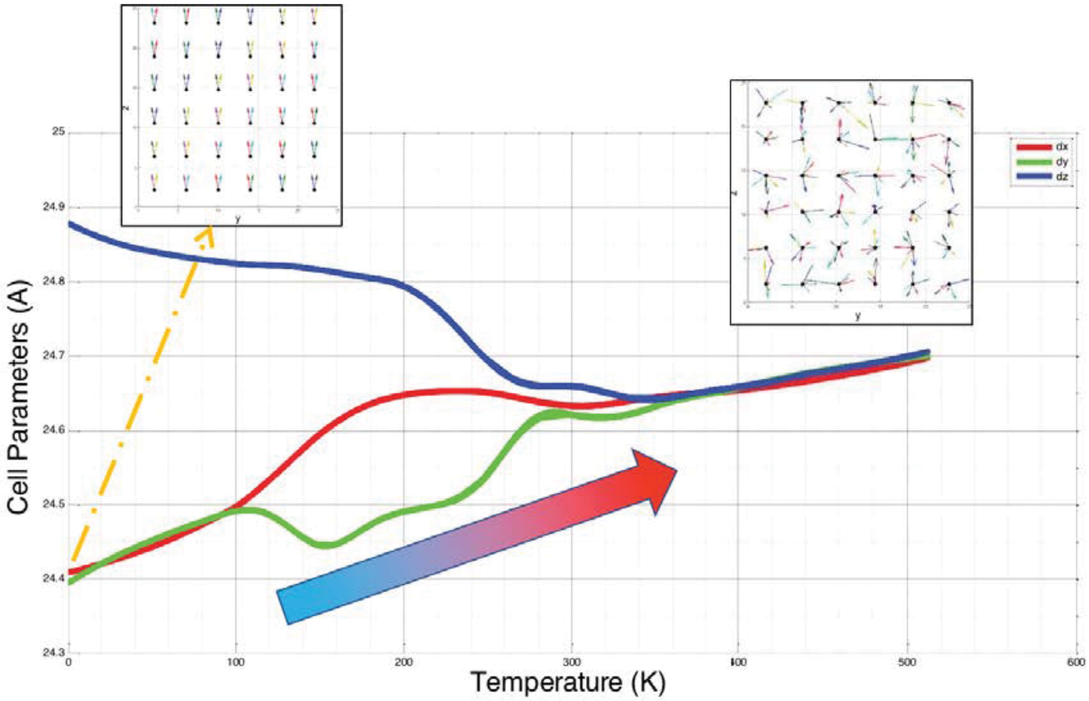

Figure 4 Cell Parameters for a BaTiO3 Supercell During a Heat-up Simulation Using the ReaxFF BaTiO3 Parameters

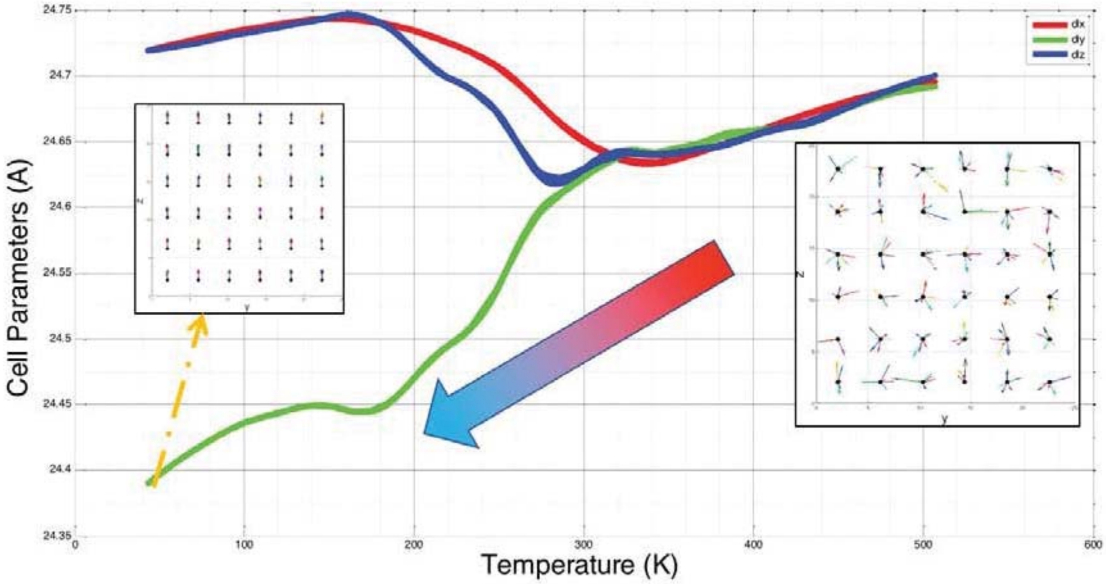

Figure 5 Cell Parameters for a BaTiO3 Supercell during a Cool-down Simulation Using the ReaxFF BaTiO3 Parameters

In order to evaluate the capability of these ReaxFF parameters to evaluate surface effects on ferroelectric transitions, we subsequently performed a similar heatup/cooldown cycles for an 8192-atom $BaTiO_3$ slab, including various surface terminations. These terminations includes TiO and BaO surfaces – and we also tried TiO-surface with additional –OH groups and TiO-surfaces exposed to water molecules – which partially resulted in –OH terminated surfaces. Figure 6 and Figure 7 show the initial configuration of two bare TiO-terminated $BaTiO_3$ slab and its ferroelectric response during heating and cooling – while Figure 8 and Figure 9 show a similar simulation for a TiO-terminated slab where the bottom surface is covered with Ti-OH groups. As can be clearly observed when comparing Figure 7 and Figure 9, the surface termination has a distinct impact on the ferroelectric response – for the bare TiO-cases a domain wall is formed almost at the center of the slab, reducing the overall dipole moment to around 25% of its initial value. Such a domain wall was not observed for the Ti-OH covered surface, causing an almost complete recovery of the overall dipole moment after cooling.

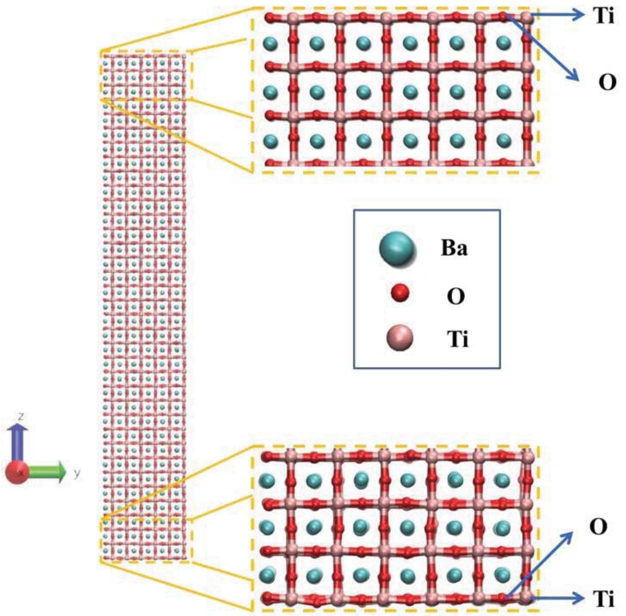

Figure 6 Structure for an 8192-atom BaTiO3 Slab with TiO-surfaces on Both Ends

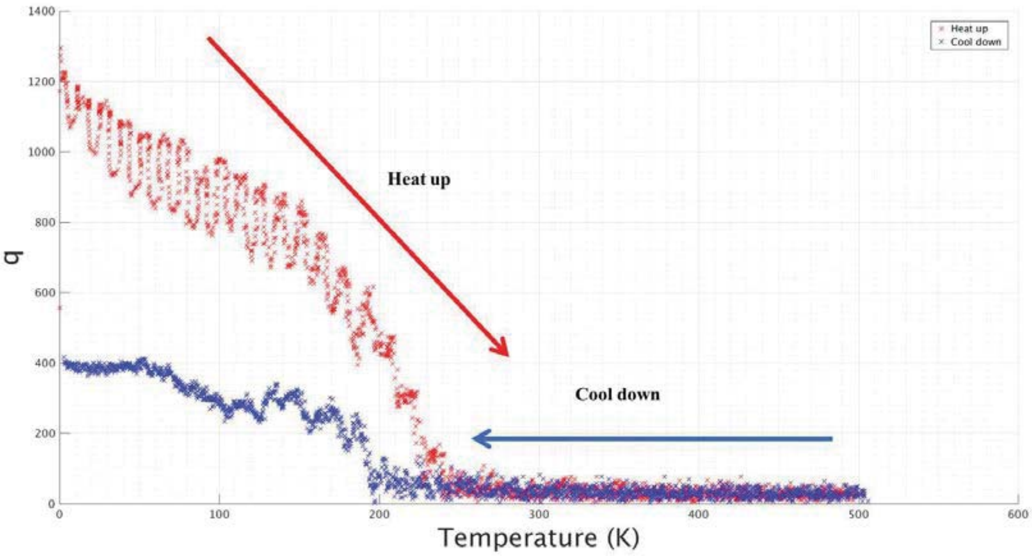

Figure 7 Overall Dipole Moment of the Bare-TiO Terminated BaTiO3 Slab (**Figure 6**) During a Heating/cooling Cycle

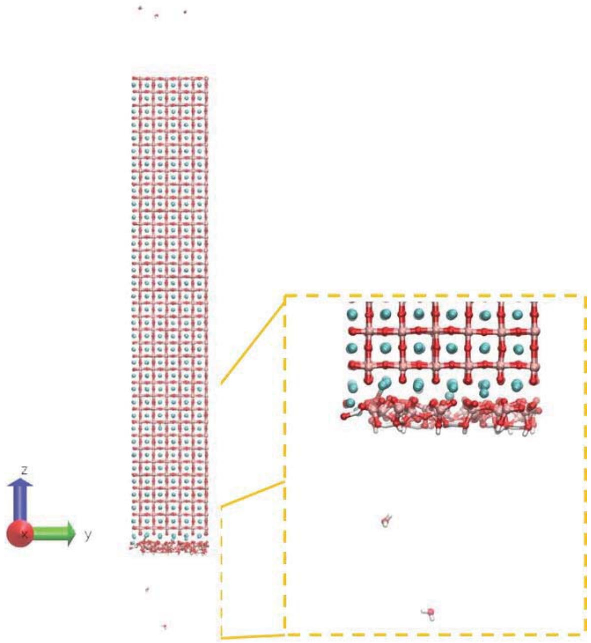

Figure 8 Structure for an 8192-atom BaTiO3 Slab with TiO-surfaces on the Top-end and a TiOH-covered Surface on the Bottom

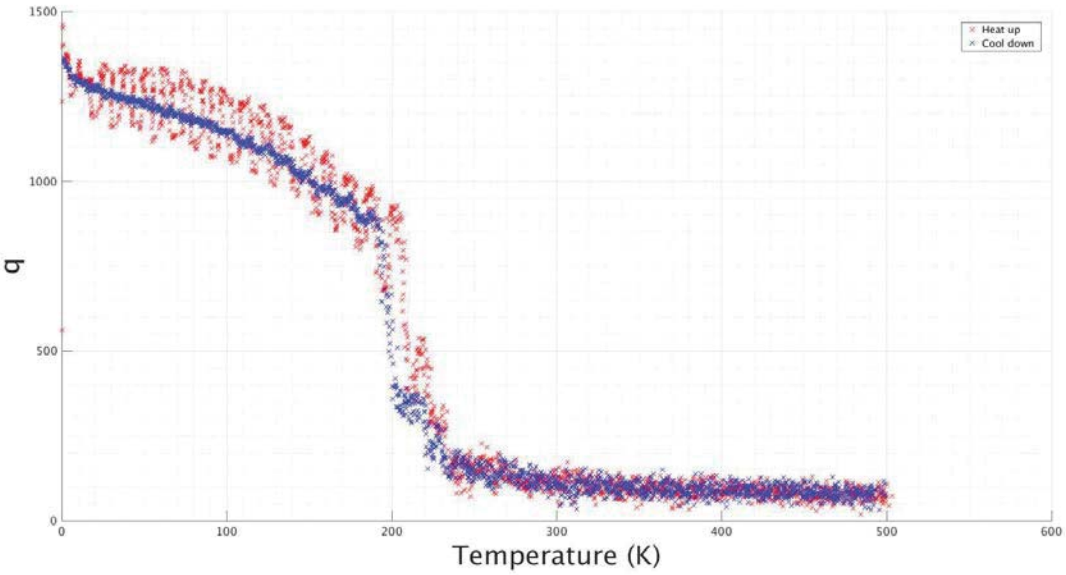

Figure 9 Overall Dipole Moment of the Ti-OH Terminated BaTiO3 slab (**Figure 8**) During a Heating/Cooling Cycle

The results in the previous figures serve as some highlights from the ReaxFF MD simulations – in addition to these MD cases we also simulated ferroelectric response in the presence of vacancies, external electric field and many different surface terminations. In all these cases we observe substantial interaction between the initial configuration and the overall ferroelectric response – indicating that this is a highly dynamic, environment-dependent property for which the ReaxFF parameter set, developed in this project, is highly suitable.

5.0 CONCLUSIONS

We have successfully extended the ReaxFF description to ferroelectric and non-ferroelectric phases for $BaTiO_3$. This extension was performed without any modification in the ReaxFF functional form – which means that this $BaTiO_3$ parameter set can be straightforwardly extended to a wide range of other materials and surfactant molecules –providing a unique and computationally inexpensive simulation tool for realistic ferroelectric materials. Oxygen vacancies – and their migration- were also considered in the force field development. Given that realistic $BaTiO_3$ materials have a significant concentrations of defects, this again extends the realism of the ReaxFF description.

We tested the ReaxFF $BaTiO_3$ parameter set in a series of molecular dynamics (MD) simulation, which reproduced a reversible ferroelectric/non-ferroelectric phase transition upon heating and cooling. We also performed MD simulations on a large $BaTiO_3$ slab and found that the surface termination and surface chemistry affects the ferroelectric response – changing the location and mobility of dipolar domain walls.

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LIST OF SYMBOLS, ABBREVIATIONS, AND ACRONYMS

AFRL	Air Force Research Laboratory
CDRL	Contract Data Requirements List
TR	Technical Report
MD	Molecular Dynamics
DFT	Density Functional Theory
RFF	Reactive Force Field
FF	Force Field
PBE	Perdew-Burke-Emzerhof exchange energy
TS	Transition State Structure
QM	Quantum Mechanical

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