Atomic displacements at a Σ3(111) grain boundary in BaTiO₃: A first-principles determination

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Barium titanate (BaTiO₃) based ceramics are extensively used in the production of many electro-ceramic components such as capacitors and positive temperature coefficient thermistors. The electrical properties displayed by these devices are known to be grain-boundary (GB) phenomena, and the difference between the atomic structure near the GB and of the bulk is one of the key factors in understanding the limited reproducibility of the properties of these materials.

BaTiO₃ is tetragonal at room temperature, and undergoes a phase transition to a cubic structure at about 400 K. Upon cooling, observations suggested that at 90 K, it becomes again cubic. The Σ3(111) twin GB in cubic BaTiO₃ has recently attracted much attention of experimentalists. With quantitative high-resolution transmission electron microscopy (HRTEM) and spatially resolved electron-energy-loss spectroscopy (EELS), the boundary plane of the Σ3(111) GB in bulk BaTiO₃ was identified as a (111) Ba-O plane. Oxygen atoms located at the GB form a Ti₂O₉ group, and this group is a building block of hexagonal BaTiO₃ which is stable at temperatures above 1598 K. An expansion of the Ti-Ti spacing was observed in hexagonal BaTiO₃, caused by the repulsion between Ti atoms. Eibl et al. suggested a similar expansion of the Ti-Ti spacing across the Σ3(111) GB; this was not yet confirmed by the HRTEM study, as single HRTEM images often suffer from nonlinear contrast artifacts, transfer gaps, and severe optical distortions introduced by the objective lens of the electron microscope.

Very recently, Jia and Thust attempted to give a more precise determination of the spacing between atomic planes at a BaTiO₃ Σ3(111) twin boundary, with a focal-series reconstruction technique in HRTEM. A value of 2.67 Å (vs 2.32 Å for the ideal GB) for the Ti-Ti spacing across the boundary was observed in their study. They also found an additional contraction of the nearest BaO-BaO spacing. The fact that this issue remains an open question is due to the difficulty and uncertainty in the precise determination of the spacing in experiment.

In this work, we applied the first-principles band-structure DMol³ method to investigate the detailed atomic and electronic structure at a Σ3(111) grain boundary in BaTiO₃. An inherent advantage of the first-principles electronic structure theory is that it is independent of any adjustable parameters, and so its numerical results provide a solid basis for an electronic level understanding of the driving force for these atomic displacements. Our focus in the present work is on the treatment of the GB. As we did in the GB study for Fe (Ref. 10) and Ni, we used a slab model to simulate the boundary interface in BaTiO₃. The calculations were performed for a finite thickness slab which is infinitely periodic in the plane parallel to the surface. The features of this model have been discussed at length by Appelbaum and Hamann. Dmol³ i.e., Density functional for Molecules and 3-dimensional periodic solids, uses fast convergent three-dimensional numerical integrations to calculate the matrix elements occurring in the Ritz variational method. The basic description of Dmol method for molecules can be found in Ref. 13. The localized numerical linear combination of atomic orbital (LCAO) used as basis sets are designed to give a maximum of accuracy for a given basis set size. The atomic response to the molecular or solid environment can be handled robustly to an excellent approximation by a relatively small number of additional numerical functions. Updated from the well-known Dmol approach, Dmol³ is now capable of dealing with three-dimensional (3D) periodic solids. The step from finite molecules and clusters to solids, is done as usual, by employing perfect translation symmetry with respect to a unit cell. The molecular sum over orbitals generalizes into an integration over the first Brillouin zone. The Dmol method and its predecessors have been successfully applied to calculating various systems such as molecular clusters, chemisorption, surface reconstruction, and the ground state of highly correlated transition metal clusters. Dmol³ has also been successfully applied to band-structure calculations of several insulating and metallic solids. As a different approach, it is necessary to determine its validity in a variety of applications to a number of systems. Thus, one purpose of the present work is to apply Dmol³ to the complex structure of the grain boundary of an oxide, BaTiO₃, in order to assess its applicability and reliability.

As a test of employing the Dmol³ method to attack the GB properties in BaTiO₃, we first calculated some bulk...
properties, such as lattice constant, bulk modulus, and ferroelectricity. In our calculations, an unshifted $k$ points mesh which contains the $G$ point are used, as well as a double set of numerical valence functions with the local basis cutoff $R_c$ of 11.0 a.u. $\approx 5.82 \text{Å}$. Since Ba is a heavy element, a relativistic treatment of BaTiO$_3$ is necessary. The relativistic effect is considered in the pseudopotential scheme in DMol. The commonly used Ceperley and Alder exchange energy and a simple analytic representation of the electron-gas correlation energy are employed in solving the local density equations.

Three kinds of basis, namely, (I) nonrelativistic all electron, (II) scalar relativistic pseudopotential, and (III) averaged relativistic pseudopotential basis, were utilized for the total energy-lattice constant calculations. The equilibrium lattice constant is 3.95 Å $\approx 7.47$ a.u., 3.96 Å $\approx 7.48$ a.u., and 3.97 Å $\approx 7.51$ a.u., with basis I, II, and III, respectively. The agreement between calculation with basis III and experiment $\approx 4.01$ Å is within the usual 1% error in LDA. We found that different basis sets give a very similar bulk modulus ($\pm 2$ GPa) and the number given by basis III is 180 GPa. The bulk modulus calculated from recently measured elastic constants of BaTiO$_3$ is 142 GPa. This agreement is as good as that in a LMTO study of KNbO$_3$ and KTaO$_3$. We note that the overestimate of bulk modulus is a well-known feature of LDA.

To investigate the ferroelectricity of BaTiO$_3$, we studied its tetragonal perovskite phase for convenience of comparison with experiment. The experimentally measured lattice constant of the tetragonal phase, $a_0 = 3.9945$ Å and $c_0 = 4.0335$ Å (Ref. 30) were used along with basis sets, I, II, and III. The Brillouin zone integration is performed using 18 special $k$ points. It turns out that the different basis give very similar results. The calculated atomic displacements are listed in Table I, in comparison with the experimental value. It is seen that the theoretical values are slightly larger than experiment. Cohen and Krakauer addressed this issue with the full-potential linearized augmented plane-wave (FLAPW) method; the relative displacements of Ba:Ti:O(1) they obtained are 0.53:1:−0.29, with the displacement of O(2) set to zero. Our DMol results, 0.56:1:−0.35, are in quite good agreement with those from the highly precise FLAPW method. It can therefore be expected that DMol gives a reasonable description of the ferroelectric features of BaTiO$_3$.

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TABLE I. Atomic displacements (in Å) along the $c$ direction in the ferroelectric tetragonal phase of BaTiO$_3$, relative to their ideal positions, (0, 0, 0) for Ba, (0.5, 0.5, 0.5) for Ti, (0.5, 0.5, 0) for O(1), and (0.5, 0, 0.5) for O(2).

<table>
<thead>
<tr>
<th></th>
<th>Ba</th>
<th>Ti</th>
<th>O(1)</th>
<th>O(2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMol</td>
<td>0</td>
<td>0.066</td>
<td>−0.137</td>
<td>−0.085</td>
</tr>
<tr>
<td>Exp.</td>
<td>0</td>
<td>0.053</td>
<td>−0.101</td>
<td>−0.048</td>
</tr>
</tbody>
</table>

FIG. 1. Computational model of an ideal $\Sigma 3(111)$ GB in BaTiO$_3$, shown in top and side views. Black circles represent Ti atoms, and white and gray ones for Ba and O atoms, respectively.

FIG. 2. Top and side views of the optimized structure of a relaxed $\Sigma 3(111)$ GB in BaTiO$_3$. Representation of the atoms as in Fig. 1.
of the $\Sigma 3(111)$ GB in BaTiO$_3$. A $1 \times 1$ unit cell in the (111) plane, and 13 layers in the (111) direction are included. One computational cell contains 34 atoms. A 3D relaxation is applied for the atoms at the GB, which ensures that our investigation of the interface includes ferroelectric effects. In order to simulate a bulk environment for the inner atoms, the interlayer distances for the outermost three layers are fixed during the relaxation. We employ the basis with an averaged relativistic pseudopotential, which gives a good description of the properties in pure BaTiO$_3$. When the number of special $k$ points employed in the self-consistency increases from 8 to 15, changes in atomic positions are within 0.001 Å.

The optimized geometry of the GB is indicated in Fig. 2 for the same top and side views. The numerical results of the distance between nearest Ti-Ti, Ba-Ba, and O-O layers across the GB are listed in Table II. The interlayer distance near the ideal GB is 2.317 Å. According to our DMol$^3$ calculations, the interlayer distance of the nearest Ti-Ti is expanded to 2.682 Å, while the Ba-Ba spacing is contracted to 2.164 Å. Our first-principles results strongly support the recent improved HRTEM experimental results, which gave the Ti-Ti and Ba-Ba spacing as 2.67 Å and 2.14 Å respectively. The expansion of the Ti-Ti spacing across the GB, from 2.317 Å to 2.682 Å, can be understood from the fact that the nearest-neighbor distance in the bulk of Ti is 2.89 Å. Interestingly, the nearest O-O interlayer distance does not experience a contraction together with Ba-Ba, but instead increases a little. Noticeable displacements of some oxygen atoms in the GB plane are shown in the top view of the optimized structure (cf. Fig. 2). These oxygen atoms are attracted closer to the nearest Ti-Ti atom pairs by 0.164 Å. This attraction is induced by the expansion of the Ti-Ti distance, as the O atoms try to keep the O-Ti bond length unchanged. The reconstruction also results in an increase of 0.095 Å in the total thickness of the slab across the GB, i.e., 4.1% of a unit cell, which is much smaller than that in, e.g., Fe $\Sigma 3$ cases due to its open structure.

The charge-density distribution near the optimized GB shown in Fig. 3(b) is compared with the charge density near the ideal GB shown in Fig. 3(a). It is clear that the charge density is very high between the nearest Ti atoms across the ideal GB, and reaches $4.5 \times 10^{-2} e$/a.u.$^3$. On the other hand, it is as low as $5.0 \times 10^{-3} e$/a.u.$^3$ between the nearest Ba atoms. The high accumulated charges between the Ti atoms push them away from each other. Similarly, the sparse charge density between nearest Ba atoms drag them closer to each other. After the relaxation, the lowest charge density increases to $9.0 \times 10^{-3} e$/a.u.$^3$ between Ba atoms, and decreases to $3.0 \times 10^{-2} e$/a.u.$^3$ between Ti atoms. Furthermore, the O atoms from the nearby Ba-O plane are strongly bonded with the expanding Ti atoms, which results in the O atoms’ expansion instead of contraction along with the Ba atoms. The charge-density distribution of the optimized GB structure gives a more stable electronic configuration.

In summary, we studied the geometric structure of a $\Sigma 3(111)$ GB of BaTiO$_3$ by local-density DMol$^3$ calculations. The experimentally observed expansion of the nearest Ti-Ti distance, and the contraction of the nearest Ba-Ba distance at the GB are confirmed by a theoretical study. The interlayer distances for Ti-Ti and Ba-Ba are found to be 2.68 and 2.16 Å, respectively, which are in very good agreement with recent experiments. It is also found that the expansion at the GB is only 0.095 Å along the direction vertical to the GB, i.e., 4.1% of a unit cell, which is very small due to its open structure. Our first-principles results indicate an attraction of the oxygen atoms, by 0.164 Å, to the nearest Ti pairs at the GB. The extraordinary high charge distribution between Ti atoms in the ideal GB pushes them away from each other, and similarly the low charge distribution between Ba atoms drags them closer to each other.

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22. We note that the all-electron scheme in DMol is nonrelativistic.