

Materials for Smart Systems II
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SURFACE RELAXATION IN FERROELECTRIC PEROVSKITES: AN ATOMISTIC STUDY

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ABSTRACT

The effect of the [001] surface relaxation on the polarization of the paraelectric BaTiO₃ is simulated in the framework of the shell model. Our atomistic simulations show a large polarization of ions in the first several layers nearby the surface and confirm the possibility of co-existence of Ti- and Ba-terminated [001] BaTiO₃ surfaces which have very close surface energies.

INTRODUCTION

Although there exist several theoretical studies of defects in technologically important perovskites [1, 2, 3], they were devoted mainly to the investigation of point defects. However, any crystalline surface, even perfect, is nothing but 2D defect which may lead to unusual behavior of perovskite films and nanocrystals, including the changes of the thermodynamic and the kinetic properties of first-order phase transitions. The relaxation of the surface atoms may turn out to be large enough for affecting the thermodynamic parameters characterizing the phase transitions, as compared with their bulk values. In particular, the atomic relaxation nearby the surface of paraelectric SrTiO₃ may result in its *ferroelectric* reconstruction at the finite temperatures, as suggested in ref. [4].

The aim of this communication is to study in details the surface relaxation of a large (up to ten planes) near-surface region and, on its basis, to demonstrate creation of a considerable *polarization* induced by a surface in perovskites. We use cubic BaTiO₃ as a prototype. Although *ab initio* calculations are known to be efficient in the study of the oxide properties [5], their use is essentially restricted by a relatively small number of surface layers which could be realistically handled. This is why in this paper a simpler, the so-called *shell-model* technique is used [6]. This approach was previously successfully applied to the investigation of defects in numerous ionic crystals including perovskites [1, 2, 3]. Its advantage is that the shell model is very-well suited for the treatment of the polarization effects which are a central issue of our study.

SIMULATION TECHNIQUE

In the present simulations we have studied a periodic two-dimensional slab of BaTiO₃.

Table 1: Short-range potential parameters for BaTiO₃ used in our simulations.

| Interaction | A(eV) | $\rho(\text{\AA})$ | C(eV/\text{\AA}^6) |
|------------------------------------|---------|--------------------|--------------------|
| Ba ²⁺ - O ²⁻ | 1214.4 | 0.35220 | 8.0 |
| Ti ⁴⁺ - O ²⁻ | 877.2 | 0.38096 | 9.0 |
| O ²⁻ - O ²⁻ | 22764.0 | -0.1490 | 43.0 |
| Ion | Y(e) | k(eV/\text{\AA}^2) | |
| Ba ²⁺ | 1.848 | 29.1 | |
| Ti ⁴⁺ | -35.863 | 65974.0 | |
| O ²⁻ | -2.389 | 18.41 | |

To study the surface relaxation, we have optimized the atomic positions in several (varied from one to ten) [001] surface planes placed into the electrostatic field of the remainder of the crystal (simulated by six additional planes whose atoms were fixed in their perfect lattice sites). The number of these additional planes was chosen to reach a convergence of the crystalline field in the surface planes.

The interatomic interactions are described, as usual, by the core-core, core-shell and shell-shell pair potentials, representing the shell-model (Table 1). In this approach each ion has a charged core and electronic shell. The sum of the core and shell charges is equal to the charge of the corresponding ideal ion. The spring constant k connects the core and the shell of the same ion. The value of this spring coefficient and the shell charge Y are chosen to describe correctly the polarizability α of the ion in the crystal:

$$\alpha = Y^2/k. \quad (1)$$

The interactions between the cores and between cores and shells of different ions are of entirely Coulombic nature. At the same time, the interactions between the shells of different ions besides the Coulombic part contain also the short-range potentials accounting for the effects of the exchange repulsion as well as van-der-Waals attraction between them. The short-range potential is

$$W_{sh} = A \cdot \exp(-r/\rho) - C/r^6. \quad (2)$$

Parameters A , ρ , and C depend on the nature of the interacting ions and on the crystalline environment. The use of integer ionic charges does not imply restrictions to ionic materials: the short-range potential in Eq.(2) takes into account the covalency and charge-transfer effects. The detailed description of the shell model can be found in [6]. The relevant shell model parameters were earlier carefully fitted to lattice constant of the cubic bulk BaTiO₃, its elastic properties (C_{11} , C_{12} , C_{14}), and low/high frequency dielectric constants [1]. Our calculations are done by means of the MARVINS computer code [7]. This code effectively realizes the shell-model technique for simulations of the surface structures. In our slab calculations we simulated both Ti- and Ba-terminated [001] surfaces.

CALCULATIONS AND MAIN RESULTS

Our calculations show that Ti⁴⁺, Ba²⁺ and O²⁻ ions are displaced from their crystal sites quite differently. This leads to creation of a dipole moment at the surface. The induced

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dipole moment in both possible cases (Ti- or Ba-terminated surface) is directed perpendicularly to the surface. This is because all ions move only along the z axis perpendicular to the surface thus retaining the unrelaxed surface symmetry.

Simulations show that the values of the surface dipole moment *oscillate* as a function of the number of layers allowed to relax (Fig. 1). These oscillations practically vanish when the number of relaxed layers reached six. Note that the same six layers is necessary to reach convergence in the crystalline field in the surface region. This clearly shows that the surface affects 5-6 near-surface planes of a BaTiO_3 crystal. The value of the surface dipole moment converges to $0.271 e \cdot \text{\AA}$ for the Ba termination and to $-0.755 e \cdot \text{\AA}$ for the Ti-termination.

Calculations also demonstrate the dependence of the very *sign* of the dipole moment on the terminating atom type: for the Ba ions the induced dipole moment is positive whereas for the Ti-terminated surface it is negative. This is true irrespective of the number of the relaxed surface layers.

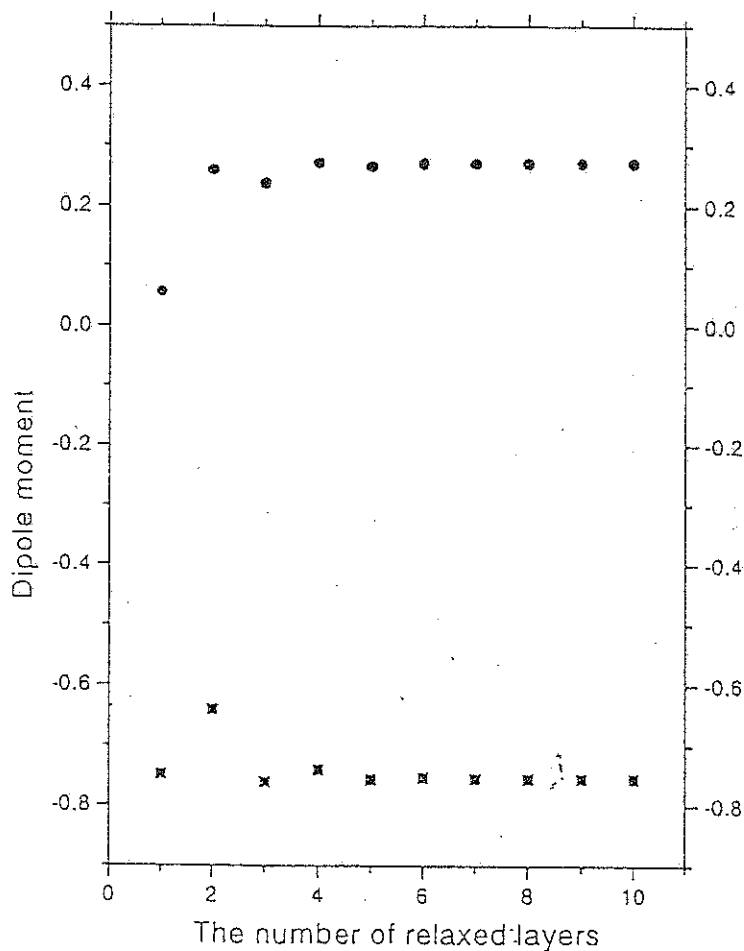


Fig. 1. Calculated surface dipole moments in the cubic BaTiO_3 as a function of a number of planes allowed to relax on the Ti-terminated (filled squares) and Ba-terminated surface (filled circles). The dipole moments are in units of $e \cdot \text{\AA}$.

In Table 2 we listed the displacements of ion cores and shells for 6 top layers for Ba-terminated surface. One can see that displacements of ions in the top layer are directed inwards whereas those in the second layer are pointed outwards. The same results were obtained for Ba- and Ti-terminated surfaces.

For the Ba-terminated case the surface Ba ions move inwards, approximately by 3.5% of the lattice constant (a_0), in the third layer their displacements are reduced to 0.5%. Ti ions move outwards the crystal by $\sim 1.3\%$ in the 2nd layer and 5 times less in the 4th layer. O^{2-} ions move inwards on Ba-terminated surface but outwards on the Ti-terminated one. Magnitudes of O^{2-} displacements fall down in an order from the first to the fourth layers. These displacements in the third and the fourth layers are very small.

The total positive sign of the surface dipole moment appears because of large displacements of negative O^{2-} ions in the top layer inwards, and positive Ti^{4+} ions in the second layer outwards the crystal. Ba^{2+} ions have twice smaller charges and thus their movement inwards the crystal cannot compensate the dipole moment created by the movement of both Ti^{4+} and the surface O^{2-} ions. The very similar trends in ion displacements takes place for the Ti-terminated surface. The displacement of the surface Ti ions is $\sim 2.7\%$ inwards the crystal, and the displacement of Ba ions in the second layer is $\sim 2.1\%$ outwards. O^{2-} ions move inwards in the surface layer but slightly outwards in the second one. Displacements of ions in the deeper layers fall down approximately by an order of magnitude and practically vanish in the 5th-6th layers. The negative sign of the surface dipole moment is determined by inward displacement of the strongly charged Ti ions on the surface.

In both cases of surface termination we observe a large *electronic* polarization of ions in the first two layers of the surface. It exhibits itself in large core-shell relative displacement of ions. This reaches, for example, $\sim 3\%$ for O^{2-} ions in the surface layer at the Ba-terminated surface. Although the differences between core and shell displacements of Ti ions look sometimes very small, one has to remember that the charge of Ti shell is quite large in the employed shell-model parameters (Table 1). This leads to the large dipole moment of Ti ions, even with a relatively small relative shift of its shell from the core position. A large polarization of ions in a $BaTiO_3$ crystal is an evidence of a large electric field created in surface layers.

The surface energy for the Ba-terminated surface (16.588 J/m^2) is only slightly larger than that for the Ti-terminated one (16.538 J/m^2). The total energy of relaxed surface *per surface unit cell* with the same number of relaxed layers is only by 0.05 eV lower for the Ti-terminated surface. This difference appears only due to different relaxation energies of the surfaces in both cases.

CONCLUSIONS

Our simulations have clearly demonstrated that polarization of the surface in the $BaTiO_3$ crystal is determined by three main factors:

- Large electric field appears at the perovskite surface because of destroyed force balance for the surface atoms (short-range vs long-range, Coulomb forces). It pushes ions of the surface layer inwards and the second layer ions outwards the surface.
- Quite different ionic radii lead to their different displacements.

Table 2: Relaxation of 6 layers for the Ba-terminated surface. Totally 10 layers were relaxed. Coordinates and displacements are given in the lattice parameter units of the unrelaxed lattice.

| No. of layer | Ion | Type | Coordinates of site | | | Displacement along z axis |
|--------------|------------------|-------|---------------------|-----|------|---------------------------|
| 1 | Ba ²⁺ | core | 0.5 | 0.5 | -0.5 | -0.0372 |
| | | shell | 0.5 | 0.5 | -0.5 | -0.0343 |
| 2 | O ²⁻ | core | 0.0 | 0.0 | -0.5 | 0.0099 |
| | | shell | 0.0 | 0.0 | -0.5 | -0.0276 |
| | Ti ⁴⁺ | core | 0.0 | 0.0 | -1.0 | 0.0125 |
| | | shell | 0.0 | 0.0 | -1.0 | 0.0123 |
| 3 | O ²⁻ | core | 0.0 | 0.5 | -1.0 | 0.0076 |
| | | shell | 0.0 | 0.5 | -1.0 | 0.0103 |
| | O ²⁻ | core | 0.5 | 0.0 | -1.0 | 0.0076 |
| | | shell | 0.5 | 0.0 | -1.0 | 0.0103 |
| 4 | Ba ²⁺ | core | 0.5 | 0.5 | -1.5 | -0.0051 |
| | | shell | 0.5 | 0.5 | -1.5 | -0.0048 |
| | O ²⁻ | core | 0.0 | 0.0 | -1.5 | 0.0016 |
| | | shell | 0.0 | 0.0 | -1.5 | -0.0026 |
| 5 | Ti ⁴⁺ | core | 0.0 | 0.0 | -2.0 | 0.0020 |
| | | shell | 0.0 | 0.0 | -2.0 | 0.0019 |
| | O ²⁻ | core | 0.0 | 0.5 | -2.0 | 0.0011 |
| | | shell | 0.0 | 0.5 | -2.0 | 0.0015 |
| 6 | O ²⁻ | core | 0.5 | 0.0 | -2.0 | 0.0011 |
| | | shell | 0.5 | 0.0 | -2.0 | 0.0015 |
| | Ba ²⁺ | core | 0.5 | 0.5 | -2.5 | -0.0003 |
| | | shell | 0.5 | 0.5 | -2.5 | -0.0002 |
| 7 | O ²⁻ | core | 0.0 | 0.0 | -2.5 | 0.0007 |
| | | shell | 0.0 | 0.0 | -2.5 | 0.0002 |
| | Ti ⁴⁺ | core | 0.0 | 0.0 | -3.0 | 0.0006 |
| | | shell | 0.0 | 0.0 | -3.0 | 0.0006 |
| 8 | O ²⁻ | core | 0.0 | 0.5 | -3.0 | 0.0005 |
| | | shell | 0.0 | 0.5 | -3.0 | 0.0005 |
| 9 | O ²⁻ | core | 0.5 | 0.0 | -3.0 | 0.0005 |
| | | shell | 0.5 | 0.0 | -3.0 | 0.0005 |

- The large difference in cation charges (Ti^{4+} and Ba^{2+}) does not allow to compensate a dipole moment created by Ti^{4+} displacements. There is no complete cancellation possible also because of the opposite displacements of ions of both types.

We would like to stress that the Ti-terminated surface is only slightly more stable than the Ba-terminated one. However, this energy difference is very small and herefore both types of surfaces should co-exist in the reality. Note that macroscopic depolarization fields were not accounted for in our calculations focusing on microscopic effects for a finite number of near-surface planes.

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