

Atomistic simulation of the [001] surface structure in BaTiO₃

Eugene Heifets^a, Simon Dorfman^b, David Fuks^c, Eugene Kotomin^d

^a Institute of Chemical Physics, University of Latvia, Rainis blvd. 19, Riga, LV-1586 Latvia

^b Department of Physics, Technion—Israel Institute of Technology, 32000 Haifa, Israel

^c Materials Engineering Department, Ben-Gurion University of the Negev, P.O.B. 653, 84105 Beer Sheva, Israel

^d Institute of Solid State Physics, University of Latvia, Kengara str. 8, Riga, LV-1063 Latvia

Abstract

We simulate the effect of the surface relaxation on the polarization of the layers of paraelectric phase in the vicinity of the [001] surface in BaTiO₃ in the framework of the shell-model potentials. We observe large polarization of ions in the first two layers of the surface. Our simulations confirm the possibility of existence of Ti- and Ba-containing top layers in [001] BaTiO₃ surfaces. © 1997 Elsevier Science S.A.

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1. Introduction

The size effect on phase transitions in ferroelectrics is the phenomenon which has been known from the middle of the 1950s [1]. It has recently attracted much attention because of the development of thin films and composite materials. Large capacity memory devices put this phenomenon into the group of hot topics in modern solid state physics [2]. The discrepancy of experimental results on the influence of the size of thin films or particles of ferroelectrics [3] may be affected by the surface preparation of the samples. Although there were some theoretical efforts to study the defects in ferroelectrics (see, for example, Refs. [4–7]) they were devoted mainly to the investigation of point defects, for example, doped or undoped bulk materials. At the same time surface represents the defect that may lead to unusual behavior of ferroelectrics, which may be realized in the changes of the thermodynamic and kinetic properties of paraelectric–ferroelectric phase transition. The relaxation of the surface may be sufficient in thin films as well as in small particles and may shift the thermodynamic parameters which are usually used in characterization of phase transitions in the film/particle-based devices. The aim of this paper is to demonstrate the effect of the surface relaxation on the polarization of the layers of paraelectric phase in the vicinity of the [001] surface in BaTiO₃. Although the ab initio calculations represent a more consistent procedure in the study of the properties of oxides [8] its application is restricted by a relatively small number of surface layers; for this reason we used the shell-model technique [9,10]. This technique was previously suc-

cessfully applied for the investigation of the defects in a lot of ionic crystals including ferroelectric perovskites [4–7].

2. Method

In the present simulation we kept cubic perovskite structure for the bulk of BaTiO₃ crystal. To study the surface relaxation we optimized the positions of several (from 1 to 10) surface layers situated into the field of the remainder of the crystal. Six additional layers modelled the remainder of the crystal. Ions in these layers were fixed in lattice sites. The number of additional layers was chosen to reach a convergency of the crystal field at the surface layers.

The interatomic interaction is chosen in the spirit of core–core, core–shell and shell–shell pair potentials, representing the shell-model. In this approach each ion is represented by charged core and shell. The sum of the core and the shell charges is equal to the charge of the corresponding ideal ion. A spring with elastic coefficient k connects the core and the shell of the same ion. The values of the elastic coefficient k and the shell charges Y have to be chosen to describe correct polarization of the ion in the crystal:

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

Interactions between the cores and between cores and shells of different ions include only Coulombic interaction. At the same time interactions between the shells of different ions besides of Coulombic part can contain the short-range potentials to account for the effects of exchange repulsion of

Table 1
Potential parameters for BaTiO₃, employed in the present simulations (taken from Ref. [4])

Interaction	A (eV)	ρ (Å)	C (eV Å ⁻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 Å ²)	
Ba ²⁺	1.848	29.1	
Ti ⁴⁺	-35.863	65974.0	
O ²⁻	-2.389	18.41	

the ions as well as Van-der-Waals attraction between them. The short-range interaction potential is given as

$$W_{\text{sh}} = A \exp(-r/\rho) - C/r^6$$

The detailed description of the shell model can be found in Refs. [9] and [10]. We employed parameters of the shell model fitted in Ref. [4] for BaTiO₃ to reproduce its lattice spacing, elastic properties and dielectric constants. Applied parameters are listed in Table 1. All simulations were made by MARVINS code [11]. This code realises the shell model technique for simulation of the surface structures.

3. Results and discussion

Our calculations show that Ti⁴⁺, Ba²⁺ and O²⁻ ions move differently from their crystal sites. This lead to the creation of a dipole moment at the surface. The induced dipole moment in both possible cases (Ti- or Ba-containing top layer) is perpendicular to the surface. This is because all ions move only along the surface perpendicularly and their movement during relaxation do not break the surface symmetry.

We plotted the values of the surface dipole moment for a different numbers of relaxed layers in Fig. 1. It can be seen from the plot that induced dipole moment oscillates during growth of the number of relaxed layers. These oscillations practically vanish when the number of relaxed layers reached six. The same number of layers was needed to reach convergence of the crystal field in the surface region. These data show that the influence of the surface extends on 5–6 ion layers inside a BaTiO₃ crystal. Finally, the value of the surface dipole moment converges to $0.271 e \text{ \AA}^{-1}$ for the Ba-containing top layer and to $-0.755 e \text{ \AA}^{-1}$ for the Ti-containing top layer.

We can see from Fig. 1 the dependence of the sign of the dipole moment on the type of atoms in the top layer. If the top layer contains Ba ions, then the dipole moment induced is positive. Contrary, for the Ti-containing top layer, the surface has the negative dipole moment. The same signs of the surface dipole moment were obtained for different numbers of the relaxed surface layers.

In Table 2 we listed the displacements of ions' cores and shells for 4 top layers. We can see displacements of ions in

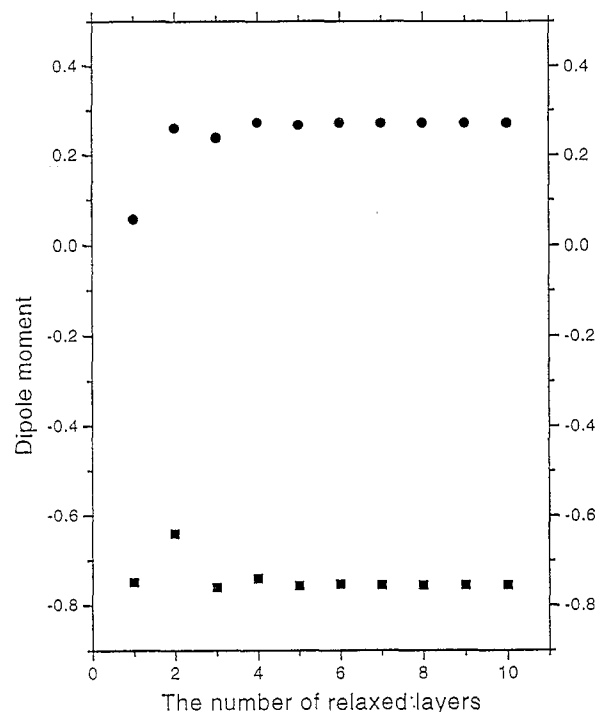


Fig. 1. The dependence of the surface dipole moment (in $e \text{ \AA}^{-1}$) in BaTiO₃ on the number of relaxed layers for Ti-containing (squares) and Ba-containing (circles) top layers.

the top layer inside the crystal, and the crystals and their displacements in the second layer outside the crystal. The same results were obtained for Ba- and Ti-containing surfaces.

The positive sign of the surface dipole moment appears because of large displacements of negative O²⁻ ions in the top layer inside and positive Ti⁴⁺ ions in the second layer outside the crystal. Ba²⁺ ions have twice less charges. Their movement inside the crystal cannot compensate the dipole moment, created by the movement of Ti⁴⁺ and the surface O²⁻ ions. The Ti-containing top layer shows very similar trends in ion displacement.

In both cases we can observe large polarization of ions in the first two layers of the surface. It shows large differences between displacements of cores and shells of ions. This difference reaches, for example, $\sim 3\%$ of a for O-ions in the top layer for the Ba-containing top layer. Although differences between cores and shells displacements of Ti ions occasionally look very small, we have to remember that the charge of Ti's shell is very large in the employed shell-model parameters (Table 1). This leads to the large dipole moment of Ti ions, even with a relatively small shift of its shell from the core position.

The surface energy for the Ba-containing top layer (16.588 J m^{-2}) is only slightly less than the surface energy for the Ti-containing top layer (16.538 J m^{-2}). The total energy of relaxed surface per a surface unit cell with the same number of relaxed layers is 0.05 eV lower for the Ti-containing top layer. This difference appears only owing to the difference in the relaxation energies of the surface in both cases.

Table 2

Relaxation of six layers for the Ba-containing top layer. In total, 10 layers were relaxed. Coordinates displacements are in 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
		core	0.0	0.0	-0.5	-0.0276
		core	0.0	0.0	-1.0	0.0125
		core	0.0	0.0	-1.0	0.0123
		core	0.0	0.5	-1.0	0.0076
		core	0.0	0.5	-1.0	0.0103
3	Ba ²⁺	core	0.5	0.5	-1.5	-0.0051
		core	0.5	0.5	-1.5	-0.0048
		core	0.0	0.0	-1.5	0.0016
		core	0.0	0.0	-1.5	-0.0026
4	Ti ⁴⁺	core	0.0	0.0	-2.0	0.0020
		core	0.0	0.0	-2.0	0.0019
		core	0.0	0.5	-2.0	0.0011
		core	0.0	0.5	-2.0	0.0015
		core	0.5	0.0	-2.0	0.0011
		core	0.5	0.0	-2.0	0.0015

4. Conclusion

Our simulations demonstrate that polarization of the surface in the BaTiO₃ crystal is determined by three main factors:

1. Large field appears at the surface because of destroyed force balance with the creation of the surface. It pushes ions of the top layer in toward the crystal and pulls them out toward the second layer.
2. Different ionic radii of ions lead to different displacements (different places, where ions will be stopped by neighbours).
3. A large difference in ionic charges of cations (Ti⁴⁺ and Ba²⁺) does not allow to compensate a dipole moment created by the Ti displacement. There is no complete compensation, even because of opposite displacements of both types of ions.

In summary, the Ti-containing top layer is slightly more stable than the Ba-containing one. However, the magnitude of this energy difference is very small. Therefore, both types of surfaces can appear in reality.

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