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# Strained ultra-thin films of BaO: a molecular dynamics investigation.

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Abstract. A recent theoretical work by Bousquet and collaborators have predicted that ferroelectric ordering could be induced in the rocksalt oxides of alkaline earth metals (BaO, MgO, CaO and SrO) by strain. The expected functional properties present in these strained binary oxides, like polarization, dielectric constant and piezoelectric response, would be comparable to those of typical ferroelectric perovskites. Consequently, the strained binary oxides would be promising materials for fabrication of devices like ferroelectric memories and sensors.

One possible way to explore the potential underlying these theoretical predictions is to grow thin and ultra-thin films of these binary oxides under epitaxial strain by choosing an adequate substrate. In such systems the interplay between epitaxial strain and the lack of translational symmetry (limited film thickness) may lead to the formation of interesting (anti)ferroelectric phases.

Our goal in this work is to explore the potential structural and functional phase diagram of BaO ultra-thin films (thickness of only 8 BaO layers,  $\approx 20$  nm) obtained for different values of compressive epitaxial strain and temperature by performing a molecular dynamics investigation. A polarized phase (antipolar) is observed at a compressive strain of -9.0%, wich resists till a melting temperature around 1500 K, which is indeed high for such an ultra-thin film.

#### 1. Introduction

The rocksalt structured alkaline earth binary oxides (AO) constitute an interesting group of compounds due to many factors like their large presence in our planet's mantle [1], their role of precursors in chemical industry and their potential use for fabrication of electronic devices [2]. MgO, CaO, SrO and BaO are examples of these referred alkaline earth binary oxides. These materials have been subjects of a considerable number of studies [3] in which their electronic, elastic, and thermal properties were investigated [4, 5].

Some interest in AO oxides has recently aroused due to their possible application as gate dielectrics to replace  $SiO_2$  in MOSFET devices [2]. This interest is motivated especifically by their wide band gaps as well as their compatibility with silicon. Due to this compatibility alkaline earth oxides have also played a key role as buffer layers in the epitaxial growth of multifunctional perovskite oxides directly on silicon [6]. As a result of these properties, a large number of recent studies have focused on the study of AO oxide thin films on silicon substrates [2, 6, 7].

The practical applications of AO oxides remain very limited if compared to the "multifunctional" perovskite oxides [8], which present several interesting properties like

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ferroelectricity, ferromagnetism, metal-insulator transitions, among others. However, the possible emergence of ferroelectricity in these simple binary oxides, as suggested by a recent theoretical work [9], may indeed be a game changer and attract more attention to the AO oxides. Bousquet *et.al.* have performed density functional calculations having as main subject the BaO binary oxide and obtained results that suggest the induction of ferroelectricity by the use of an appropriate epitaxial strain. Yet according to the theoretical predictions, the functional properties like polarization, dielectric constant and piezoelectric response would be comparable to those of typical ferroelectric perovskite oxides. As a consequence, AO oxides grown under epitaxial strain would be promising candidates for future technological applications like sensors, ferroelectric memories, power storage devices and others.

Since the beginning of the investigation of ferroelectricity phenomena, the role and effects of discontinuities of polarization at surfaces and interfaces have been well known. These discontinuities create a bound charge as a consequence of fundamental electrostatics. Uncompensated surface charges are created by the discontinuity of the normal polarization component,  $\sigma = \vec{P}.\vec{n}$ , which result in non-local depolarization fields (opposite to the polarization direction) that suppress polarization. This effect strongly affects the stability of polarization in ultra-thin ferroelectric films. [10, 11] . Stability of ferroelectricity in ultra-thin films can only be achieved by a balance between bulk thermodynamics and screening mechanisms for polarization. This may occur by several mechanisms like formation of stripe domains, [12, 13] inplane closure domains, domain branching, toroidal structures, [14] surface charge compensation due to band bending, [15, 16] oxygen vacancy formation [17] or chemisorption of charge species from environment [18, 19]. A thorough discussion of surface-screening mechanisms in ferroelectric thin films can be found in a review by Kalinin *et. al.* [20].

In this study, we report some preliminary results of a molecular dynamics (MD) simulation of structural and physical properties of BaO ultra-thin films and their variation with temperature and epitaxial compressive strain  $[\eta(\%)]$ , based on an effective two-body interaction potential of the Vashishta type[21, 22]. We have been able to discover five distinct structural regions, as a function of applied compressive strain. An stable and interesting antipolar phase is present from compressive strain values from -3.0 to -10.0% in multi and single domains scenarios. This structure is stable and presents no structural phase transition up to around 1500 K, point at each it melts down.

# 2. Methodology

As previously discussed our simulations have adopted the interaction potential proposed by Vashishta et al. [21, 22], which has been previously applied succesfully to the BaO bulk system. [22] The Vashishta potential employed in our investigation, in order to mimic the ionic interactions in BaO (BaBa, BaO, OO), is given by

$$\Phi = \sum_{i < j} \left( \frac{H_{\alpha\beta}}{r_{ij}^{\eta_{\alpha\beta}}} + \frac{Z_{\alpha\beta}e^{\frac{-r_{ij}}{\lambda}}}{r_{ij}} - \frac{D_{\alpha\beta}e^{\frac{-r_{ij}}{\xi}}}{2r_{ij}^4} - \frac{W_{\alpha\beta}}{r_{ij}^6} \right)$$
(1)

with the following contribuctions:

i) the first term represents the steric repulsion described by parameters  $H_{\alpha\beta}$  and  $\eta_{\alpha\beta}$ ; *ii*) the second term corresponds to Coulomb interactions due to charge transfer; *iii*) the third contribution is due to the induced charge-dipole interaction consequend of the large electronic polarizability of the ions; *iv*) the last and fourth term takes into account the van der Waals dipole-dipole interaction. Screening is included in both Coulomb and charge-dipole interactions in order to avoid long-range calculations. Screening parameters employed were  $\lambda = 0.65$  nm and  $\eta = 0.325$  nm, with the two-body potential being truncated at  $r_c = 0.9$  nm.

	Ba-Ba	Ba-O	O-0
$H_{lphaeta}$	$3.092 \times 10^{-7}$	$4.204 \times 10^{-9}$	$5.555 \times 10^{-9}$
$Z_{\alpha\beta}^{\alpha\beta}$	$1.227e^{2}$	$1.227e^{2}$	$1.227e^{2}$
$D_{lphaeta}$	$6.387e^{2}$	$7.025e^{2}$	$7.664 \ e^2$
$W_{lphaeta}$	0	$0.568 \times 10^{-10}$	0
$\eta_{lphaeta}$	11	9	7
$\lambda$ =0.65 nm	$\eta{=}0.325~\mathrm{nm}$	$r_{cut}=0.9~\mathrm{nm}$	e = e e e e e e e e e e e e e e e e e e

Table 1. Vashishta potential parameters for BaO [22] (energy in ergs and distances in nanometers).

The interaction potential for  $r < r_c$  was shifted in the usual way [23, 24] in order to ensure continuity of both the potential and its first derivative at the cutoff length. The exponents  $\eta_{BaBa}$ ,  $\eta_{BaO}$ , and  $\eta_{OO}$  were assigned values of 11, 9, and 7 respectively, based on previous performed simulations [22]. All remaining constants were optimized from the elastic constant, bulk modulus, and melting-decomposition temperature and lattice stability in room conditions for bulk BaO [22]. A summary of all adopted constants values are presented in table 1.

Our MD simulations were performed in a canonical ensemble, where the amount of substance (N), volume (V) and temperature (T) were conserved, for a system consisting of 3200 particles (1600 Ba+1600 O). In our NVT simulations, the energy of endothermic and exothermic processes is exchanged with a Nosé-Hoover thermostat [25]. In every single simulation performed in this study the temperature was kept fixed by scaling the velocity of particles for every 500 time steps. Time steps of 1 fs were employed in our molecular dynamics calculations, which employed the LAMMPS code. [26, 27]

Our prototype system for the ultra-thin film consists on an eight BaO layers thick slab (1.9387 nm) stacked according to a NaCl-type structure (see figure 1-b) along the z direction, as it can be seen in figure 1-a. Periodic boundary conditions were assumed along x, y and z. In spite of the fact that periodic boundary conditions were employed along the z axis were, some extra empty space (without particles) was added, in order to mimic "vacuum" and consequently turning the  $1^{st}$  and  $8^{th}$  BaO layers (bottom and top) into surface layers. The empty space ("vacumm") was thick enough to ensure that there was no interaction between the referred bottom and top BaO layers. This decision took into account the cut-off radius of the potential that is 0.9 nm. The total volume of our system box was kept fixed during the simulations. Simulations have also been performed for larger systems (same thickness, but larger in plane (x,y) dimensions) typically employing 28800 and 204800 particles, in order to check for limited size effects in our results. No noticiable change was observed in these calculations.

Several molecular dynamics simulations were performed for this 8 BaO layers ultra-thin film prototype system varying both temperature and in-plane (x,y) strain. Here we define the strain  $\eta$  in the usual way,  $\eta(\%) = \left(\frac{a_{strained}-a_{bulk}}{a_{bulk}}\right) \times 100 \ (a_{bulk} = 0.55392 \text{ nm} [22])$ . The in-plane lattice constants  $a_{strained}$  and  $a_{bulk}$  are respectively the strained and bulk values. Only negative values of  $\eta$  were here explored, representing a compressive epitaxial strain scenario.

#### 3. Results and discussion

Our simulations aimed at reaching a phase diagram for our prototype ultra-thin films, by varying both compressive strain and temperature. Temperature was explored in the 100 to 500 K region while the compressive strain  $\eta$  was varied from 0 to -10 %. Our results are presented in figure

- 2 (a) and show the existence of five distinct regions, according to the compressive strain value.
- (i)  $\eta$  from 0 to -2.0%: In this compressive strain region the system keeps a bulk-like structure, with no change in the in-plane structure. However an expansion of around 3% along the z direction (normal to surface) is observed. See 3-(a).
- (ii)  $\eta$  from -2.0 to -3.0 %: Here the ultra-thin film presents a variation in its thickness of around 20% along one of the main in-plane directions (x or y), as schematically presented in the 3-(b). Only one domain was observed. This structure is not a finite size effect since it could also be observed in simulations of larger in-plane systems previously discussed.
- (iii)  $\eta$  from -3.0 to -4.0 %: Around an compressive strain value of -3.0% the zigzag BaO structure presented in figure 2-(b) appears. This structure presents an effective local electric dipole along the normal to surface direction (z) that can points up or down. Multiple domains of this structure are present and aligned along both x and y in-plane directions as schematically shown in figure 3-(c). However, even in this multiple domains situation, up and down polarized (electric dipoles) vertical layers are present.
- (iv)  $\eta$  from -4.0 to -7.5 %: In this region [figure 3-(d)] a large single domain of up and down polarized vertical layers is present along one of the main in-plane directions (x or y), but yet with a relatively high number of deffects.
- (v)  $\eta$  from -7.5 to -10 %: Finally a large single domain of up and down polarized vertical layers and almost deflect free, can be observed in the whole ultra-thin film. See figure 3-(e), which shows this antipolar phase.

The evolution of the ultra-thin film structure can be seen in figure 4 where the radial distribution function of Ba-O distance is presented for the five distinct regions. The system evolves from a bulk-like structure at -1% to the final vertical stacked up and down structure at -7.5%.

The most basic structural information information can be derived from a radial distribution function g(r). It can be given by  $g_{\alpha\beta}(r) = \frac{\delta n_{\alpha\beta}(r)}{4\pi r^2 \delta r \rho_{\alpha}}$ , for a binary system like BaO. The number of  $\beta$  particles around a radius r of a central  $\alpha$  particle is given by  $n_{\alpha\beta}$ , while  $\rho_{\alpha}$  denotes the density of  $\alpha$  particles. Basically this function give the density probability for an atom of the  $\alpha$  species to have a neighbor of the  $\beta$  species at a given distance r.

It is good to observe that the peak around 2.5 Å remains basically unchanged with increasing strain, basically presenting a tiny shift in its position. This is due to the fact that the zigzag structure presented in figure 2-(b) keeps the first Ba-O distance unchanged.

Figure 5 shows a plot of system energy as a function of temperature (K) for an strain value of -7.5%. Figure 6 presents the radial distribution function of the ultra-thin film for five distinct temperatures. As it can be seen g(r) does not present any rearragement of peaks positions with increasing temperature. The peaks only present a normal thermal broadening, which certainly is a fingerprint of the system melting. The melting temperature, around 1500K, is indeed quite high for such an ultra-thin film.

The final structure obtained for compressive strain values from -7.5 to -10 % is said to be antipolar since it presents an spontaneous polarization. Indeed this structural phase is composed by vertical alternating layers presenting effective UP and DOWN electric polarization (dipole moments) along the z direction (normal to surface). However this phase does not belong to the class of antiferroelectric systems since we could not observe the existence of an associated ferroelectric phase [28].

### 4. Conclusions and Perspectives

Our simulational results indicate that a polar phase can be obtained only for in-plane compressive strain values from -3 to -10% and in a temperature range of 100 to 500K. However an ordered



**Figure 1.** (a) Structure of the ultra-thin films model used in this study. Periodic boundary conditions are present on (x,y) plane. Only 8 BaO layers are present along z direction, and the film presents two surfaces (bottom and top layers). (b) BaO rocksalt bulk structure for comparison.

single domain polar structure can be obtained only for a strain value around 9%. This value is too high to be experimentally obtained only by the choice of an adequate substrate. As a consequence, our simulational results present a very distinct scenario as the one expected by the theoretical predications by Bousquet *et.al.* [9]. The obtained antipolar phase can not be classified as antiferroelectric, since we were not able to observe any associated ferroelectric phase, condition that needs to be fulfiled according to the classical definition by Kittel [28].

As a next step we will try to investigate the thermal vibrations of our simulated strained 8 layers BaO ultra-thin films. Calculations will be performed to obtain the phonon total density of states for different values of compressive strain and temperatures. This investigation may be able to cast some light on the possible formation of polar or (anti)ferroelectric phases.

As previously discussed, the existence of polarization, defining possible ferroelectric phases, may be very difficult to obtain in ultra-thin films due to the very limited thickness. Our observed antipolar phase avoids the problems associated with uncompensated surface charges created by the discontinuity of the normal polarization component at the surface. However, we expect a very distinct scenario for thicker thin-films. Ou plan is to explore thicker thin films, with thickness from around 24 to 48 BaO layers, i.e., 6.3700 to 13.0171 nm.

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Figure 2. (a) Energy versus strain,  $\eta(\%)$ , for temperatures of 100, 200, 300, 400 and 500K. Five distinct regions are schematically presented, associated to energy minima located at different values of compressive strain. Each region presents a different structural configuration, as presented in the BaO ultra-thin filme images. (b) Schematic presentation of UP and DOWN polarized structures formed by the relative displacement of the Ba and O ions, generating electric dipoles. Arrows represent the local resultant dipole moment for UP and DOWN cases. This zigzag structure is responsible for forming three of the five distinct structural regions.



**Figure 3.** Schematic representation of the five distinct structural regions presented in figure 2-(a): (a)  $\eta$ : 0 ~ -2.0 (%); (b)  $\eta$ : -2.0 ~ -3.0 (%) (c)  $\eta$ :-3.0 ~ -4.0 (%); (d)  $\eta$ : -4.00 ~ -7.5 (%); (e)  $\eta$ : -7.5 ~ -10.0 (%);



**Figure 4.** Radial distribution function (g(r)) presenting the Ba-O distances for the ultra-thin for the five distinct structures at a temperature of 300K.



Figure 5. Energy versus temperature for  $\eta$  equal to -7.5 % compressive strain.



Figure 6. Radial distribution function (g(r)) for ultra-thin films of BaO with compressive  $\eta$  equal to -9.0 % at different temperatures.

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