Results in Physics 6 (2016) 534–535

Contents lists available at ScienceDirect

Results in Physics

journal homepage: www.journals.elsevier.com/results-in-physics

Microarticle

Electrostatic tuning of oxygen octahedral rotations in ferroelectric perovskites

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ARTICLE INFO

Article history:
Received 28 July 2016
Accepted 4 August 2016
Available online 8 August 2016

Keywords:
Oxide perovskites
Superlattices
Density functional theory

ABSTRACT

Using first-principles methods, we investigate the joint effects of epitaxial strain and electrostatic coupling on the appearance of oxygen octahedral rotations, O_6, in ferroelectric perovskites. We find that by varying the relative content of ferroelectric and paraelectric layers in epitaxially strained superlattices the size of O_6 can be efficiently tuned.

Introduction

Oxygen octahedral rotations, O_6, can influence profoundly the electronic, dielectric, ferroelectric, and magnetic properties of oxide perovskites, ABO_3. For instance, in some materials like $SrTiO_3$ they compete with ferroelectricity and can actually suppress it. Also, O_6 can couple with the magnetic spin moments and alter their interactions by changing the metal–oxygen–metal bond angles. For these reasons, oxygen octahedral rotations offer promising avenues to the discovering and design of materials with enhanced functionality. Cases of special interest are those in which both ferroelectricity and oxygen octahedral rotations coexist [1]. However, practical ways of controlling O_6 in ferroelectric materials thus far appear to be limited to epitaxial strain engineering, which is exploited in the synthesis of thin films [2].

In this work, we use first-principles methods and simple energy models to investigate the influence of epitaxial strain and electrostatic coupling on the appearance of O_6 in ferroelectric perovskites. Electrostatic coupling states that the normal component of the electric displacement field, D, must be preserved at the boundary between two insulating layers; this is one of the most valuable principles in the design of superlattices. We focus our analysis on two archetypal ferroelectrics, namely, $PbTiO_3$ (PTO) and $BiFeO_3$ (BFO). Our results show that by combining layers of ferroelectric and paraelectric materials in epitaxially strained superlattices, the behaviour of O_6 can be precisely adjusted.

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Methods

The ground-state energy of a monodomain two-colour superlattice can be expressed as:

$$U_{\mathrm{tot}}(D,\lambda,a) = \lambda \cdot U_{\mathrm{A}}(D,a) + (1-\lambda)\cdot U_{\mathrm{B}}(D,a),$$

where a represents the lattice parameter, U_{A} and U_{B} the internal energies of the individual constituents, and λ the relative content of material A [$\lambda \equiv m/(n+m)$, where m and n are the thickness of layers A and B]. By construction, D-continuity along the out-of-plane stacking direction is enforced in the equation above, which is appropriate for analysing superlattices with nominally uncharged interfaces. Once functions U_{A} and U_{B} are known, one can predict the ground-state of any hypothetical A/B superlattice by finding the global minimum of U_{tot} with fixed values λ and a (possible interface effects are neglected) [3]. We calculated the energy and structural properties of PTO and BFO over wide (D,a) intervals by using constrained-D density functional theory methods (for technical details, see Ref. [4]).

Results

At moderate and large compressive strains, $\eta < 0$, PTO stabilises in a tetragonal *P4mm* phase with a large out-of-plane ferroelectric polarisation and null O_6. Meanwhile, BFO adopts a monoclinic *Cc*-II phase in which the ferroelectric polarisation is mostly out-of-plane and small out-of-phase oxygen octahedral rotations are contained in the epitaxial plane, $(a^-a^-a^0)$ in Glazer's notation (the so-called supertetragonal "T" phase [5]). In a recent work [4], we have predicted the existence of a metastable *I4cm* phase in compressive

http://dx.doi.org/10.1016/j.rinp.2016.08.004
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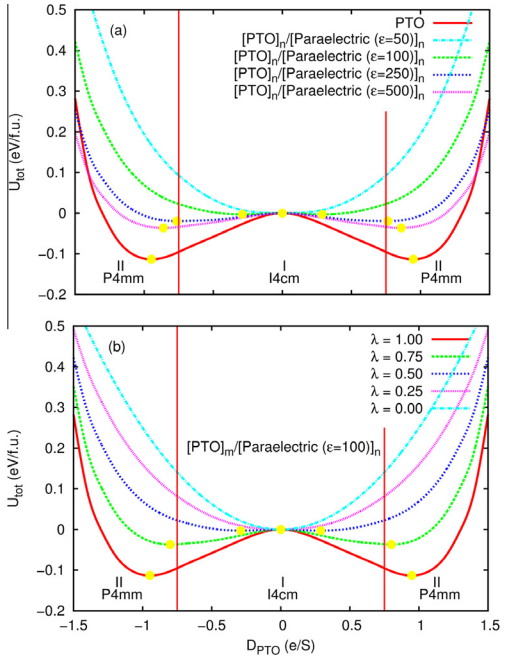

Fig. 1. (a) Ground-state energy of PTO/Paraelectric superlattices ($\lambda = 0.5$ and $a = 3.76$ Å) considering different paraelectric materials. (b) Ground-state energy of PTO/Paraelectric superlattices ($a = 3.76$ Å) with a paraelectric dielectric constant of $\epsilon = 100$. Equilibrium states (phase boundaries) are indicated with yellow dots (red lines). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

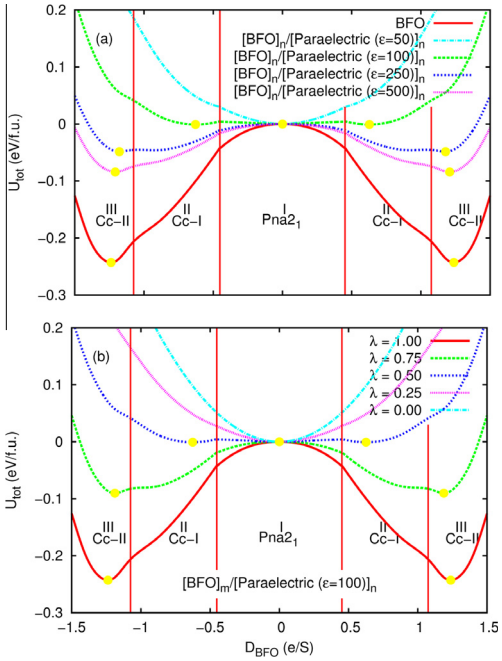

Fig. 2. (a) Ground-state energy of BFO/Paraelectric superlattices ($\lambda = 0.5$ and $a = 3.65$ Å) considering different paraelectric materials. (b) Ground-state energy of BFO/Paraelectric superlattices ($a = 3.65$ Å) with a paraelectric dielectric constant of $\epsilon = 100$. Equilibrium states (phase boundaries) are indicated with yellow dots (red lines). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

PTO thin films in which large out-of-phase O_6 appear along the z direction ($a^0a^0a^-$) and piezoelectricity is highly enhanced. Likewise, a metastable $Pna2_1$ phase has been found in compressive BFO thin films in which the O_6 pattern becomes ($a^-a^-b^+$) and the piezoelectric response of the system is dramatically increased [4]. Accessing such regions of intriguing functionality is of great relevance, both fundamentally and technologically. One could think of achieving that target by exploiting the built-in electrostatic coupling in ferroelectric PTO/BFO superlattices. However, we have realised that this is not possible, even when considering charge-mismatched interfaces [3], as the energy minimum of the resulting U_{tot} function always lies very close to the individual U_{PTO} and U_{BFO} minima, that is, too far from the regions of interest. A likely solution to overcome this design problem may consist in combining PTO and BFO with paraelectric materials since the equilibrium state in the latter compounds always lies at $D = 0$. The internal energy of a paralectric crystal depends quadratically on D hence it can be modelled as $U_P(D,a) = (\epsilon^{-1}a^3/8\pi)D^2$, where ϵ represents the corresponding dielectric constant and $c/a \approx 1$ is assumed [4].

In Fig. 1, we show our results obtained for PTO/Paraelectric superlattices at moderate compressive strain ($a = 3.76$ Å, $\eta \sim -3\%$) when considering two general situations: (a) a variety of paraelectric compounds, that is, different ϵs, while constraining the value of λ to 1/2, and (b) a variety of λs while constraining the value of ϵ to 100. We have found that PTO can be driven to the verge of an isostructural $P4mm \rightarrow I4cm$ phase transition by considering average dielectric materials ($\epsilon \leqslant 100$) and large relative PTO contents ($3/4 \leqslant \lambda \leqslant 1$). In the particular case of $\epsilon = 100$ and $\lambda = 1/2$, for instance, the out-of-phase oxygen octahedral rotations that appear along the z direction roughly amount to 8 degrees. In fact, this effect is achieved at the expense of reducing the out-of-plane electrical polarisation considerably (three fold), however, both polar and non-polar order parameters remain in coexistence. Such a promising O_6 tuning in PTO could be realised in practice by considering paraelectric materials similar to $LaAlO_3$ in strained superlattices.

In Fig. 2, we show our results obtained for BFO/Paraelectric superlattices at large compressive strain ($a = 3.65$ Å, $\eta \sim -6\%$). We have found that BFO undergoes a series of interesting phase transitions as a consequence of varying λ (or, equivalently, ϵ). In the particular case of $\epsilon = 100$, BFO transforms first into a monoclinic Cc-I phase ($1/2 < \lambda < 3/4$), which displays finite out-of-phase oxygen octahedral rotations along the z direction, and subsequently to the orthorhombic $Pna2_1$ phase ($1/4 < \lambda < 1/2$). The O_6 pattern changes first from ($a^-a^-a^0$) to ($a^-a^-b^-$) and then to ($a^-a^-b^+$), and the corresponding average rotation value dramatically increases from ~ 1 degree in the Cc-II phase to ~ 10 in the $Pna2_1$ phase; a change in antiferromagnetic spin order also occurs during these transformations. $LaFeO_3$, for instance, emerges as a promising paraelectric material for achieving such a desired O_6 control in strained BFO-based superlattices.

Summary

The presented analysis shows that a combination of epitaxial strain and electrostatic coupling can be used to control efficiently the size of oxygen octahedral rotations in ferroelectric perovskites.

Acknowledgement

This research was supported under the Australian Research Council's Future Fellowship funding scheme (Grant No. FT140100135).

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