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2006 J. Phys.: Condens. Matter 18 L97

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LETTER TO THE EDITOR

A mechanism for the $150 \mu\text{C cm}^{-2}$ polarization of BiFeO_3 films based on first-principles calculations and new structural data

Dan Ricinski, Kwi-Young Yun and Masanori Okuyama

Graduate School of Engineering Science, Osaka University, 1-3 Machikaneyama-cho, Toyonaka, 560-8531 Osaka, Japan

E-mail: ricinski@semi.ee.osaka-u.ac.jp

Received 31 August 2005

Published 27 January 2006

Online at stacks.iop.org/JPhysCM/18/L97

Abstract

Following our experimental report of a giant ferroelectric polarization in the region of $150 \mu\text{C cm}^{-2}$ in BiFeO_3 (BFO) films, we have performed first-principles calculations based on the local density approximation to density functional theory, aiming to clarify its mechanism. Upon optimization of lattice constants we have shown that the natural tetragonal structure of BFO has a giant tetragonality ratio of 1.26 and large ionic off-centring. Experimentally this structure has been detected in BFO films deposited on La-doped SrTiO_3 substrates. The spontaneous polarization calculated *ab initio* for this structure is $143.5 \mu\text{C cm}^{-2}$, in agreement with the remanent polarization of hysteresis loops measured at 90 K. These results suggest that the giant polarization of our BFO films may occur upon stabilization of the optimal tetragonal phase with giant tetragonality. Future experimental effort aiming to routinely obtain such values of spontaneous polarization should concentrate on how to isolate this phase without compromising the insulating and switching properties of BFO.

1. Introduction

A research topic of materials science that is expanding with a high rate due to its potential importance for novel applications refers to the so-called *multiferroics*, materials that exhibit both ferroelectric and ferromagnetic order. The recent progress follows theoretical advances extending the knowledge of the material properties required for robust magnetoelectricity, and after modern preparation methods allowed better control of these properties. Among several topical reviews currently available, a recent one named ‘Revival of the magnetoelectric effect’ [1] provides a useful outline of the field in view of historical and contemporary data.

Among the several classes of multiferroics, BiFeO_3 (BFO) has attracted attention due to its large Curie temperature (expected to bring about a large spontaneous polarization) and

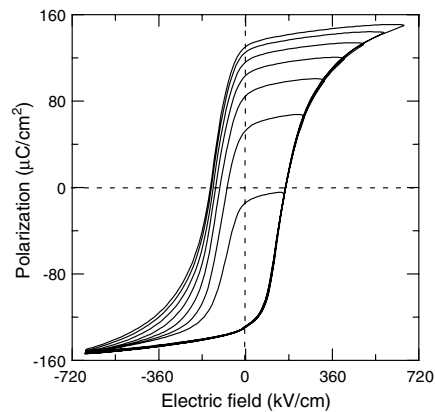


Figure 1. Hysteresis loops with giant polarization measured at 90 K for BFO films grown on Pt/TiO₂/SiO₂/Si by PLD.

its complex magnetic symmetry: antiferromagnetic with weak ferromagnetism due to spin canting. Controversially, the experimental remanent polarization has been in the region of $6 \mu\text{C cm}^{-2}$ until recently, when values an order of magnitude larger started to be measured in samples with sufficient resistivity [2], followed by our recent report of a giant polarization beyond $150 \mu\text{C cm}^{-2}$ (the largest ever measured to date for any ferroelectric material) [3]. In this paper we examine in more detail the possibility of such giant spontaneous polarization in BFO using first-principles calculations (FPC) and comparison with new experimental data. Recent experiments reporting values of remanent polarization in the region of $100 \mu\text{C cm}^{-2}$ and more in BFO thin films [3, 4] and FPC on rhombohedral BFO [5] are useful background for this work.

2. Measurements of giant polarization in BFO thin films

In this section we show the results of hysteresis loop measurements on BFO thin films prepared by pulsed laser deposition (PLD) on Pt/TiO₂/SiO₂/Si substrates under the conditions specified in [3]. The polycrystalline BFO films (containing mostly (001)-oriented tetragonal grains) have 300 nm thickness and 240 μm Pt circular electrodes deposited by rf-sputtering. Upon cooling down to 90 K, electrical measurements were made with a Toyotechnica FCE tester. This is a commercially available virtual ground system for automated measurement of ferroelectric properties, similar to those of Radiant Technologies and aixACCT. Using triangular waveforms, we have acquired the major hysteresis loop corresponding to complete polarization reversal and asymmetrical minor loops. The latter have been measured by driving the ferroelectric capacitor from a saturation state induced by a strong electric field to partial switched levels of opposite polarization.

We observe in figure 1 that the maximum value of polarization measured on the major hysteresis loop under a 20 V amplitude waveform of 1 kHz frequency is $151 \mu\text{C cm}^{-2}$, while the remanent polarization is $131 \mu\text{C cm}^{-2}$. The minor loops show an almost flat relaxation at the field turning points with saturation visible at high fields, all loops being closed. Had a conductive component artificially inflated hysteresis loops, changing the measuring frequency would significantly distort them, particularly not preserving their closed-loop appearance. In the case of our samples, on varying the measuring frequency from 10 kHz to 100 Hz, the hysteresis loop shapes are preserved and the change in polarization (containing the contribution

Table 1. Structural parameters of Rr BFO ($R3c$ space group).

Lattice constants	Calculated			Experimental [7]		
	a_{rh} (Å)	α_{rh} (deg)		a_{rh} (Å)	α_{rh} (deg)	
	5.50	60.18		5.63	59.35	
Ionic coordinates	x	y	z	x	y	z
Bi (2a)	0	0	0	0	0	0
Fe (2a)	0.231	0.231	0.231	0.221	0.221	0.221
O (6b)	0.399	0.541	0.946	0.395	0.528	0.933

of any conduction/relaxation charges activated in this time domain) is less than $20 \mu\text{C cm}^{-2}$. Under these circumstances one can estimate that the real spontaneous polarization for this BFO sample is close to $140 \mu\text{C cm}^{-2}$, reproducing well our results measured previously [3]. In order to confirm whether or not such giant spontaneous polarization measured in our BFO films can be certified from a fundamental viewpoint, we have employed first-principles calculations for the study of structure and properties of this material. These results are given in the next sections.

3. First-principles calculations of BFO structures

All FPC have been done using the ABINIT code, a common project of the Université Catholique de Louvain, Corning Incorporated, the Université de Liège and other contributors [6] (URL <http://www.abinit.org>), based on the density functional theory (DFT), under the local density approximation (LDA). The used pseudopotentials included valence and semicore electrons ($5d^{10}6s^26p^3$ for Bi, $3s^23p^63d^64s^2$ for Fe and $2s^22p^4$ for O) which are allowed to spin polarize in order to account for the antiferromagnetic ordering (collinear magnetism has been assumed). The Brillouin zone integrations have been performed using $4 \times 4 \times 4$ Monkhorst–Pack meshes and a 950 eV cutoff energy for plane waves. These parameters have been tested for consistency and were found appropriate for all structural calculations, while for evaluating the spontaneous polarization a denser k -space sampling has been used. The structural relaxations have been done until the interatomic forces are smaller than $1 \text{ meV } \text{Å}^{-1}$.

It is known that the ground state of single-crystal BFO is rhombohedral (space group $R3c$), as a result of a phase transition from the centrosymmetric cubic phase. The cubic phase is unstable against Bi^{3+} and Fe^{3+} ionic displacements along [111] and counter-rotations of oxygen octahedra about [111]. The angles between unit cell vectors are slightly distorted from the ideal value of 60° in the cubic phase. In order to validate the calculation method on the basis of these known facts [7], we have performed structural optimizations of lattice constants and ionic coordinates in the rhombohedral (Rr) BFO unit cell. We note in table 1 that the calculated ionic coordinates in the unit cell are in reasonable agreement with experimental ones, while, typically for DFT/LDA implementations, there is a 2% underestimation of the Rr lattice constant. Our results are consistent with the FPC on Rr BFO made under DFT/LDA using a different calculation code [5]. The agreement of ionic coordinates with experimental values can be further improved if the former are calculated by first-principles methods at the experimental lattice constants, which is a standard workaround in the present stage of simplified implementation of the quantum-mechanical formalism needed for calculations. On the other hand, it will shown in the next section that the predicted values of the spontaneous polarization in Rr BFO are already rather precise (no more than 7% difference from recent experimental results) even if one works with the lattice constants determined *ab initio*. Therefore it is

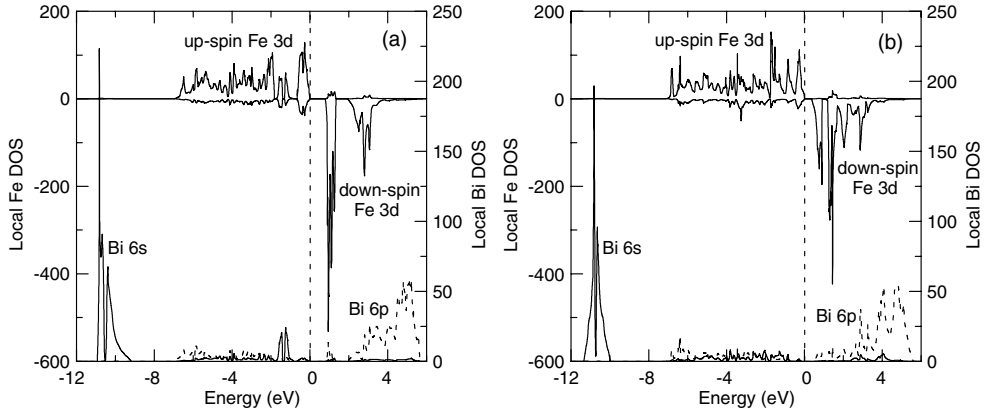


Figure 2. Local DOS for Rr (a) and Tt (b) optimized structure, for Fe and Bi, in the valence band of BFO. The down-spin (minority) DOS is shown as negative. The Bi 6p DOS is drawn with broken lines.

Table 2. Structural parameters of BFO optimized in the Tt phase ($P4mm$ space group).

Lattice constants	a_{tet} (Å)	c_{tet} (Å)	
	3.67	4.64	
Ionic coordinates	x	y	z
Bi (1a)	0	0	0
Fe (1b)	0.5	0.5	0.439
O (1b)	0.5	0.5	-0.164
O (2c)	0.5	0.0	0.308

worth employing the present method for more elaborate calculations and predictions of BFO properties.

As the crystal symmetry in the case of BFO thin films has been reported as tetragonal (Tt) with $P4mm$ space group [2, 3], we have subsequently concentrated on studying possible structures for this phase. As a first step, we have fully optimized the ionic coordinates and lattice constants for the Tt phase of BFO. The results shown in table 2 reveal a giant tetragonality ratio of 1.26 and large ionic displacements from the paraelectric phase.

It is instructive to compare the values of a and c in the optimized Tt structure of BFO with those of other ferroelectric perovskites described with the generic formula ABO_3 . Although the conventional ferroelectrics $BaTiO_3$ and $PbTiO_3$ are known to have rather small tetragonality ratios (1.01 and 1.06, respectively) due to the large ionic radius of the A-site cation, comparably larger tetragonality (≈ 1.2) has been calculated by FPC for $BiScO_3$ [8, 9]. The tolerance ratio of BFO as well as of $BiScO_3$ is relatively low (≈ 0.9), suggesting that one could also expect a very large c/a for tetragonal BFO, as our FPC have indeed shown. These values have been related to the geometrical frustration in the perovskite cell of these compounds, due to the small A-site cation that allows the formation of a layered structure by strongly compressing the in-plane lattice constant and loosening one of the B–O bonds [8, 9]. It will be seen in the next section that a tetragonal phase with a giant c/a can actually be detected experimentally for BFO films prepared under certain conditions.

Useful information relating to the chemical bonding in BFO with influence on the relative stability of its Rr and Tt phases can be obtained from an examination of the electronic band

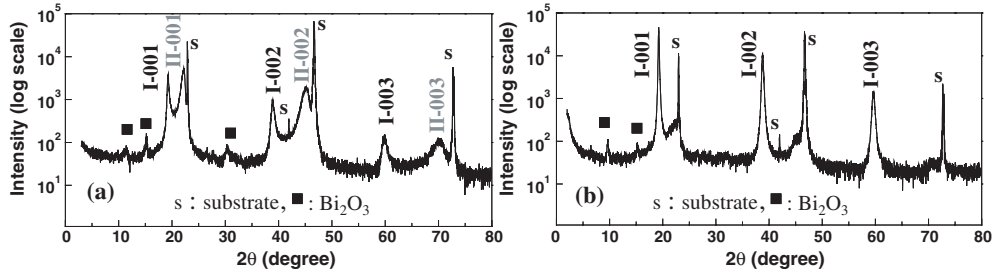


Figure 3. XRD patterns for BFO thin films grown on La-doped STO substrates by PLD using a laser frequency of 5 Hz (a) and 15 Hz (b). The black (grey) designators denote perovskite BFO with Tt phase I (phase II), respectively.

structures and density of states (DOS). Figure 2 displays the orbitally resolved valence band DOS of Bi and Fe for the two phases. The valence band contains O 2p orbitals hybridized with Fe 3d, Bi 6s and Bi 6p. Both structures are insulating, with a bandgap of 0.77 eV in the Rr phase and 0.29 eV in the Tt phase. Although the bandgaps are known to be typically underestimated within the DFT/LDA (especially for the strongly correlated systems [5]), as conductivity is often a serious practical problem for BFO, a small bandgap is not entirely unexpected.

The spin polarization at the Fe site is clearly visible in both cases, and the total DOS (not shown here) is identical for the two spin channels, as antiferromagnetic symmetry has been enforced in our calculations. One important difference between the two structures is a larger contribution of Bi 6s to the total DOS just below the Fermi level of the Rr structure, suggesting an enhanced role of Bi in chemical bonding. This enhanced chemical activity of Bi (whose lone pair is known to be at the origin of the ferroelectric instability of BFO and other magnetic perovskites [10]) might be one of the important factors stabilizing the Rr structure for single-crystal BFO (see also section 5).

4. Experimental structural study and tetragonality ratio of BFO thin films compared to first-principles calculations

In what follows we describe some new results of a structural study in BFO thin films grown by PLD on conductive La-doped (001)-SrTiO₃ (STO) substrates. These films have been prepared under similar conditions as those in our previous publication [3] and their crystal structures have been analysed by conventional x-ray diffraction (XRD) θ - 2θ scans (shown in figure 3) as well as reciprocal space mapping (not shown here). The key parameter that was varied during deposition was the laser frequency, 5 and 15 Hz, respectively. In both cases figure 3 reveals the formation of (001)-oriented tetragonal BFO grown parallel to the (001)-STO plane, with out-of-plane lattice constant much larger (phase I) and slightly larger (phase II) than that of STO, respectively. There have been no secondary phases detected, except an insignificant fraction of Bi₂O₃.

The lattice constants have been determined from the relative position of the (103) BFO peaks with respect to the (103) STO substrate peak in the reciprocal space maps, allowing the calculation of BFO interplanar spacing in terms of the STO lattice constant [11]. The films deposited with a 5 Hz laser frequency consist of a mixture of two (001)-oriented Tt BFO phases: one with $a = 3.77$ Å, $c = 4.65$ Å (phase I) and the other with $a = 3.88$ Å, $c = 4.07$ Å (phase II), consistently with the θ - 2θ scans in figure 3. When the laser deposition frequency was changed to 15 Hz, virtually a single Tt phase having $a = 3.72$ Å, $c = 4.67$ Å was detected.

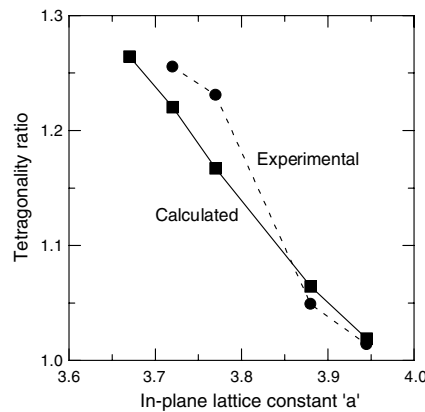


Figure 4. Experimental and calculated dependence of tetragonality in BFO on the in-plane lattice constant.

Knowing that the STO substrate has a lattice constant of about 3.89 \AA , the formation of a BFO phase with a much smaller in-plane lattice constant is surprising in the first instance. However, one should not overlook that a structure with a small in-plane lattice constant and large tetragonality has already been predicted by FPC in previous section.

To clarify matters further we have made a new series of FPC in which we have fixed a to several experimental values that we obtained for tetragonal BFO films (deposited under various conditions), and optimized in each case only the value of c . Figure 4 compares the tetragonality ratio calculated in this way with its experimental dependence. We have observed a reasonable agreement between theoretical predictions and experimental findings, attesting the capability of the FPC to account for the structure of BFO films obtained with a range of fabrication parameters.

The key result of the FPC that allows us to understand the formation mechanism of the two phases grown on La-STO is that the structure with giant c/a is actually the most natural one for BFO, when the Tt symmetry is enforced (by an external constraint such as the substrate). When film deposition with lower laser frequency is performed, due to the more gradual deposition process, it is possible for a fraction of the BFO film (phase II in figure 3(a)) to grow epitaxially on the STO substrate, with good matching between their in-plane lattice constants. Another fraction of the film (phase I), although still (001)-oriented, will not match the substrate period but will tend to acquire its own optimal lattice constants for the Tt phase (small a and giant tetragonality), as predicted by the FPC. When the laser frequency increases to 15 Hz and consequently the deposition process is accelerated, it appears no longer possible for the BFO film to match the STO substrate periodicity, but it will assume solely its natural lattice constants in the Tt phase (see figure 3(b)). However, the Tt BFO films with giant c/a grown on this particular substrate are likely to develop interface defects due to the significant tensile stresses induced by the much larger in-plane lattice constant of STO. This is expected to strongly impact on the ferroelectric properties of these films. Indeed, the remanent polarization was less than $5 \mu\text{C cm}^{-2}$ for the single-phase film (suggesting that the tensile stresses inhibit ferroelectric switching) and up to $50 \mu\text{C cm}^{-2}$ for the dual phase film (due to an averaging effect including phase II regions where the interface mismatch is smaller). We can therefore conclude that unless a substrate allowing better matching with the small in-plane lattice constant of ‘natural’ Tt BFO is used, it may be impossible to reverse the spontaneous polarization in a single-phase BFO film with giant c/a . Typical substrates such as

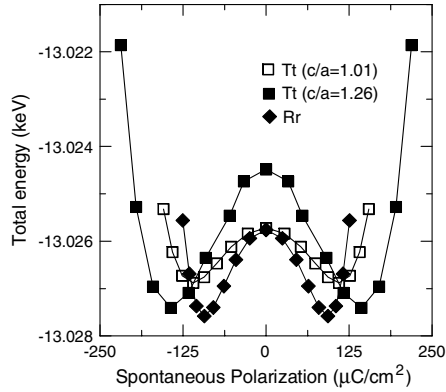


Figure 5. Double-well profiles of total energy as a function of polarization for increasing steps of ionic off-centring, in optimized Rr structure (rhombic symbols), optimized Tt structure (square symbols) and room-temperature Tt structure of BFO films with giant polarization at 90 K (empty square symbols). The polarization on the abscissa is along [111] for the Rr structure and along [001] for the Tt structure.

STO (that are suitable for enhancing the spontaneous polarization of conventional ferroelectrics such as BTO by in-plane compressive stresses) seem not good choices for BFO because its own optimal in-plane lattice constant becomes very small once the tetragonal symmetry is enforced.

5. Calculations of giant spontaneous polarization in BFO and discussion of its mechanism

For calculating *ab initio* the spontaneous polarization the Berry phase method [12], whose algorithm is directly available in ABINIT, has been used. The calculated values for the spontaneous polarization are $93.1 \mu\text{C cm}^{-2}$ along [111] in the optimized Rr phase and $143.5 \mu\text{C cm}^{-2}$ along [001] for the optimized Tt phase with giant c/a . The first value agrees with previous experimental results obtained on Rr (111)-oriented BFO films [4] and FPC on Rr BFO [5]. The giant spontaneous polarization calculated for the optimized Tt phase is in agreement with our experimental results on BFO films [3] at 90 K. However, the room-temperature structure of these films has been determined as polycrystalline, with preferentially (001)-oriented Tt grains having a modest tetragonality ratio of ≈ 1.01 [3] and a remanent polarization of $102 \mu\text{C cm}^{-2}$ for hysteresis loops measured with a 5 V amplitude waveform (not shown here).

As it is thus necessary to investigate the relationship between the giant spontaneous polarization measured at low temperature and the natural Tt structure of BFO with giant c/a , we have examined the relative stability of various possible BFO structures. Using the optimized ionic coordinates for the Rr and natural Tt structures, we divided the displacement of each ion (from its ideal position in a centrosymmetric cell) in small linear steps and calculated the Berry phase polarization along this path. We repeated this procedure for the Tt structure with the room-temperature lattice constants of the BFO film whose hysteresis loops exhibit giant polarization. The spontaneous polarization calculated *ab initio* in this case is $109.7 \mu\text{C cm}^{-2}$, reasonably close to the $102 \mu\text{C cm}^{-2}$ experimental value. As seen in figure 5, by plotting the total energy as function of polarization, we have obtained familiar double-well profiles similar with those derived from phenomenological theories of ferroelectricity. By this procedure, the minimum of total energy corresponds to the optimized ionic coordinates in each case.

We note that the optimized Rr structure is the most stable one, as it has the lowest total energy (possibly due to the enhanced chemical activity of the Bi lone pairs, as revealed by the DOS plots in figure 2). As in the case of thin films the substrate is likely to break the Rr single-crystal phase symmetry, a Tt BFO structure may become stabilized, as the experimental data have shown. Between the two Tt structures investigated, it is the optimized Tt phase with giant c/a that has its minimum energy closest to that of the Rr ground state (only 0.19 eV difference). Therefore, assuming that the BFO film initially takes on the Tt structure with low c/a in the as-deposited state, figure 5 suggests that this room-temperature structure is only metastable. Thus a Tt structure with giant c/a should ultimately form upon decreasing temperature (note that the optimal Tt structure determined by FPC actually corresponds to 0 K and that the giant polarization has been measured at 90 K). Furthermore, as the well depth increases for large c/a , a higher voltage than at room temperature may be required to obtain hysteresis loops with giant polarization. Indeed, we have measured hysteresis loops with giant polarization only when we applied a four times larger voltage than at room temperature. In addition, the high electric field applied during measurements is another factor that could contribute to the destabilization of the low c/a Tt structure. All these findings concur with the idea that the giant polarization of the BFO films grown on Pt/TiO₂/SiO₂/Si is in fact obtained after a transition to a Tt phase with giant tetragonality occurs in the measuring process.

Although direct evidence that such a change in lattice parameters occurs is yet to be found, the first-principles prediction of an optimal Tt structure with giant c/a (experimentally detected in BFO films grown on La-doped STO) suggests that values of spontaneous polarization in the region of 150 $\mu\text{C cm}^{-2}$ should no longer be considered surprising for this ferroelectric material. A foreseen difficulty in obtaining such giant polarization in BFO seems to be its complex total energy landscape, with several local minima, allowing metastable structures to be easily formed, leading to smaller than expected spontaneous polarization values measured in many experiments.

6. Final remarks and conclusions

In this paper we have employed first-principles calculations to examine possible BFO structures that may occur in thin film form, aiming to establish the origin of the giant polarization we have measured previously. In these calculations we have assumed perfect stoichiometry of the BFO films (neglecting contributions from vacancies or other point defects) and Rr and Tt symmetry, as two limiting cases found in experimental investigations. One should mention that a monoclinic phase with the polar axis slightly rotated from [111] has also been detected in some studies of BFO films [4]. The calculation results for the monoclinic phase will probably bridge those of Rr and Tt structures studied in the present article. It is the Tt structure that is the most likely to have the largest spontaneous polarization for two reasons. First, the ferroelectric instability is triggered by a single type of distortion for all ions, and therefore the off-centring is likely to be more efficient. And second, the fully optimized Tt structure has been found to intrinsically possess a giant tetragonality ratio in this material, so that an even larger ionic off-centring in the BFO unit cell should be expected. However, our study revealed that while this Tt structure can be obtained under certain preparation conditions for BFO films, it could remain difficult to isolate it in a defect-free sample.

The present results suggest that future experimental effort aiming at obtaining a giant spontaneous polarization in BFO should concentrate on how to stabilize its natural Tt structure without compromising the insulating and switching properties of the sample. A possibility for routinely obtaining a spontaneous polarization in the region of 150 $\mu\text{C cm}^{-2}$ for BFO may

be to continue with investigations of polycrystalline thin films, aiming at stabilizing the target phase with giant tetragonality gradually, inducing transformations between metastable states.

Financial support from Matsushita Corporation during the preparation of this paper is gratefully acknowledged. The first author would like to thank Dr M Veithen from the Université de Liège for his help with setting up the calculations in the initial stages of this work. Dr K Saito (Bruker AXS) is also thanked for his help with crystal structure analysis.

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