Orthorhombic strontium titanate in $BaTiO_3$ –$SrTiO_3$ superlattices

LETTER TO THE EDITOR

Orthorhombic strontium titanate in BaTiO₃–SrTiO₃ superlattices

S Ríos[1], A Ruediger[1], A Q Jiang[1], J F Scott[1], H Lu[2] and Z Chen[2]

[1] Symetrix Centre for Ferroics, Department of Earth Sciences, University of Cambridge, Cambridge CB2 3EQ, UK
[2] Laboratory of Optical Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100086, People's Republic of China

E-mail: arue01@esc.cam.ac.uk

Abstract
It has been suggested by several authors that $SrTiO_3$ layers in $SrTiO_3$–$BaTiO_3$ superlattices should be tetragonal and ferroelectric at ambient temperatures, like the $BaTiO_3$ layers, rather than cubic, as in bulk $SrTiO_3$, and that free-energy minimization requires continuity of the polarization direction. A recent *ab initio* calculation constrained solutions to this structure. Surprisingly, our x-ray study shows that the $SrTiO_3$ layers are orthorhombic with 0.03% in-plane strain, with the $BaTiO_3$ c-axis matching the $SrTiO_3$ a- and b-axis better than the c-axis; strain energy overcomes the cost in electrostatic energy.

Strontium titanate in bulk changes from a simple cubic perovskite structure to a tetragonal antiferrodistortive structure near 105 K and retains that phase down to absolute zero [1]. However, in thin films on $YBa_2Cu_3O_{7-x}$ it is orthorhombic due to interfacial strain [2], and similar distortions occur with Ca doping [3, 4], doping with ^{18}O isotopes [5] or Ti isotopes [6], or deposition onto other thin-film devices [7]. It is thus clear that many kinds of small perturbation, e.g. optical illumination [8], substitutional impurities, or surface strain, can cause the tetragonal phase of strontium titanate to distort into an orthorhombic structure and/or produce related dielectric anomalies. The cause for this is well understood from the nature of the cubic–tetragonal phase transition near 105 K: the Γ_{25} soft mode responsible for this phase transition collapses at the R point ([111] corner) of the cubic Brillouin zone [9]. However, inelastic neutron studies show [10] that this mode is almost equally unstable all the way along the R–M[11ξ] line in reciprocal space from R to M, where M is the reciprocal-lattice point corresponding to the zone boundary along [110]. In the related perovskite $KMnF_3$, it is the M_3 soft mode at M which actually collapses first [11]. Thus instabilities at R and M are often very nearly equally unstable. Rather important for device applications is the fact that multilayer
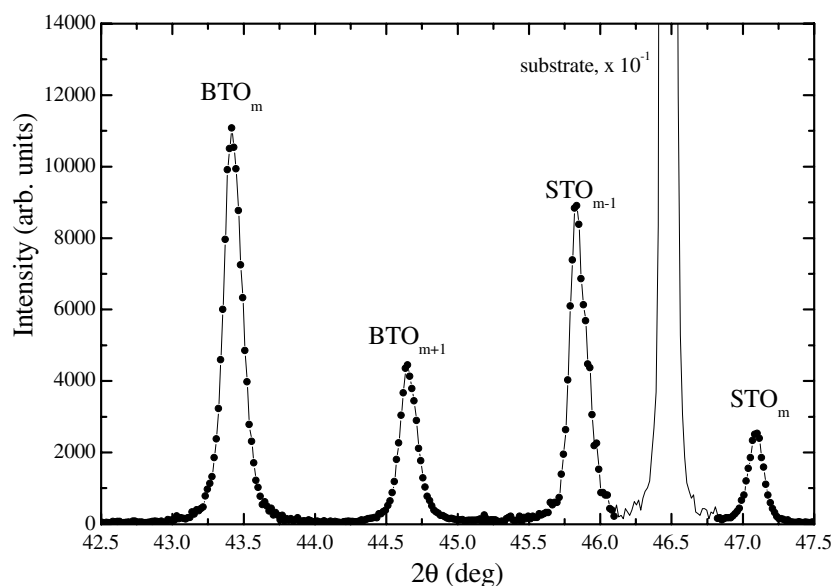
Figure 1. The XRD pattern around reflection (002) for the STO/BTO 10/10 superlattice. Main STO/BTO reflections are labelled as m, and superlattice reflections as $m \pm 1$.

superlattice structures of barium titanate/strontium titanate exhibit large permittivities, even at thicknesses <100 nm, whereas 50–50% barium–strontium titanate ceramics of the form $Ba_{1-x}Sr_xTiO_3$ do not [12]. This has motivated attempts to obtain a more detailed understanding of their structure and polarization properties.

Very recently, our laboratory has reported a critical periodicity for barium titanate/strontium titanate superlattices of about 30/30, below which the orthorhombic phase of $SrTiO_3$ exists [13]. We therefore use samples of alternating groups of ten layers of $BaTiO_3$ and ten layers of $SrTiO_3$ (10/10) on a $SrTiO_3$ substrate. During fabrication, the thickness of the multilayer structure was controlled at 80 nm. The samples were produced using a multi-target laser molecular-beam epitaxy (LBE) technique. $BaTiO_3$ and $SrTiO_3$ ceramic targets were alternately ablated onto the $SrTiO_3$ (001) substrate. The films were deposited at 900 K with an oxygen pressure of 10^{-4} Pa, and annealed at 820 K for 45 min in air after deposition.

In order to quantify the orthorhombic strain induced on the STO layer, an XRD investigation was performed on the superlattice with stacking periodicity 10/10. Measurements were carried out using Cu $K\alpha_1$ radiation and a one-dimensional position-sensitive detector [14]. The x-ray beam was parallel to the [010] direction. The diffraction angle was calibrated using the reflections from the $SrTiO_3$ substrate ($a = 0.3905$ nm [12]).

ω–2θ patterns around reflection (002) showed main STO/BTO peaks (labelled as m in figure 1) and corresponding satellite peaks, as published by Shimuta *et al* [15]. The lattice c-parameters were found to be 0.385 66(2) and 0.416 10(4) nm for STO and BTO respectively, in agreement with Tabata *et al* [12].

From the BTO + 1 satellite peak and the STO − 1 satellite peak the period of the superlattice was derived as 7.8(1) nm, in contrast to the theoretical 8.0 nm.

To evaluate the departure from tetragonal symmetry, a high-angle reflection, (033), was selected. Standard χ-scans (along the [100] direction) and ω-scans (within the diffraction plane) were performed; see figure 2.
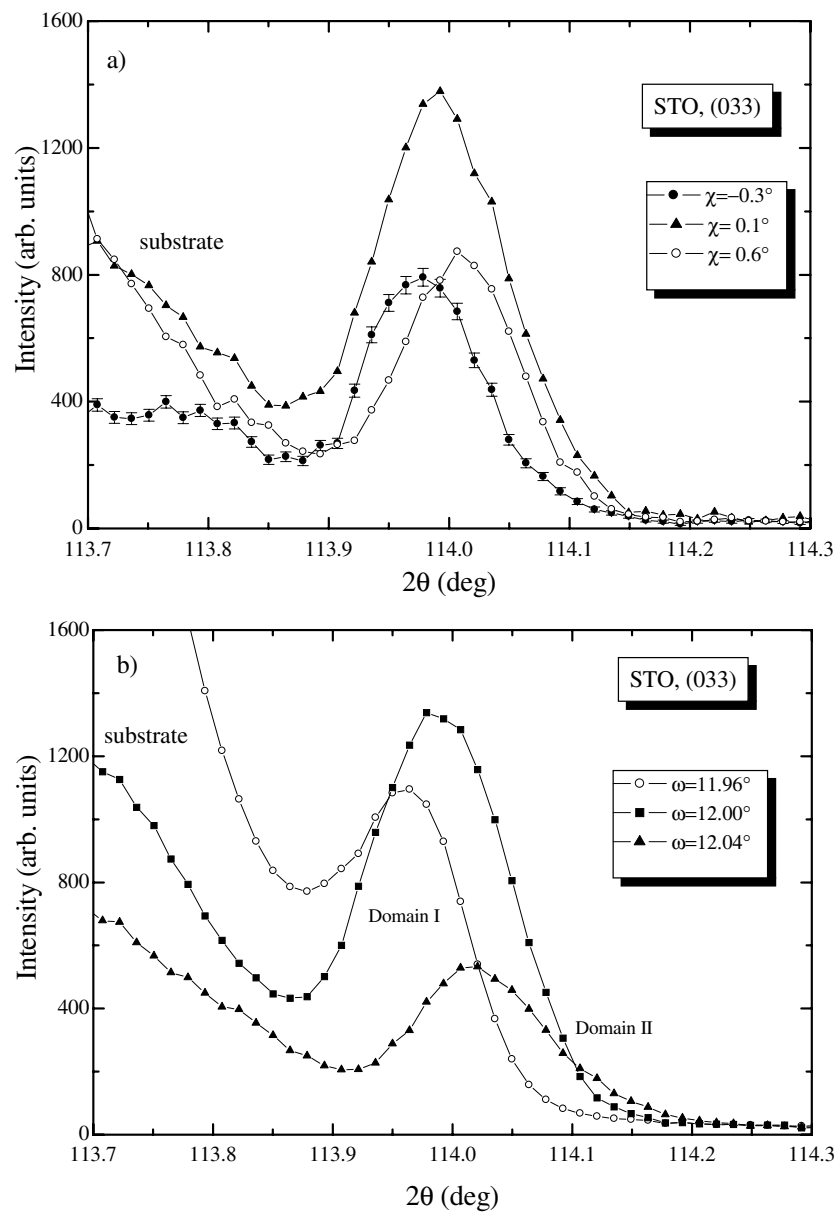
Figure 2. (a) χ-scans along the [100] direction and (b) ω-scans, around reflection (033) for the STO layer in the 10/10 superlattice.

The peak width was observed to increase and subsequently decrease along the [100] direction from 0.118(2) to 0.135(2) and down to 0.118(2), indicating the presence of two peaks (the instrumental resolution was 0.0664(4)°). ω-scans also revealed the existence of two peaks as shown in figure 3.

The splitting of the peak is a consequence of the tetragonal symmetry changing into orthorhombic. The two peaks correspond to the existence of 90° and 270° rotation domains as observed by SHG measurements [13]. From the peak position of the two domains, the
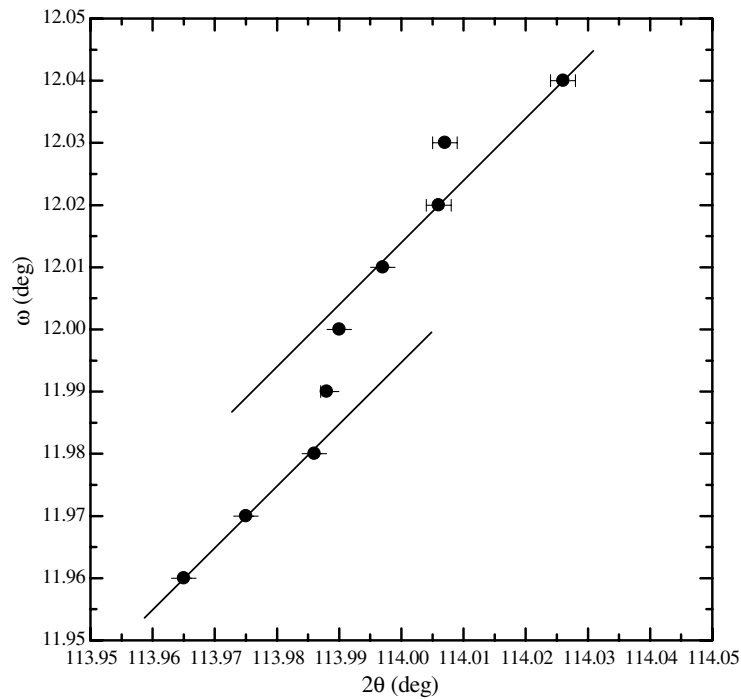
Figure 3. The peak position in 2θ as a function of the incident angle (ω) showing the two orthorhombic peaks for the STO layer in the 10/10 superlattice. Solid lines indicate the trend that a single peak should follow.

strain, $1 - b/a$, was estimated to be of the order of 3×10^{-4}, with $a = 0.393\,66(1)$ nm and $b = 0.393\,52(1)$ nm.

A very high orthorhombic-to-tetragonal transition temperature for $SrTiO_3$ of 540 K is reported for the 10/10 superlattice [13], much larger than that of 23 K for the ferroelectric transition in bulk $SrTiO_3$ induced [5] by an almost complete isotope exchange of ^{16}O–^{18}O. However, the XRD set-up did not allow us to directly observe the transition in that temperature regime. The orientations of $\vec{P}_s$ in orthorhombic $SrTiO_3$ are along the pseudo-cubic [110], [1$\bar{1}$0] directions respectively [4].

The present results on orthorhombic structure of strontium titanate layers in a barium titanate/strontium titanate superlattice are surprising. Note that the $BaTiO_3$ layers remain tetragonal with polarization $\vec{P}$ along the superlattice direction. The orthorhombic strontium titanate, on the other hand, is also ferroelectric with $\vec{P}$ parallel to [110], as determined from the SHG experiments of Jiang *et al* (the present XRD data do not yield information on the direction of $\vec{P}$; they merely confirm the orthorhombic structure). This means that there is significant space charge accumulating at the $BaTiO_3$–$SrTiO_3$ interface, due to the Poisson term $\vec{\nabla} \cdot \vec{D}$. Hence the structure does *not* minimize the electrostatic terms in the free energy. Presumably this electrostatic energy is more than compensated by the interfacial strain energy.

The fact that neither of the two peaks that we observe coincides with the substrate peak allows us to discriminate against the interpretation of a contribution from strained and unstrained $SrTiO_3$.

We are aware that recent *ab initio* models of barium titanate/strontium titanate superlattices have constrained solutions to be tetragonal and to have $\vec{P}$ along [001] in $SrTiO_3$, in contradiction to our results and those of Jiang *et al* [16].

References

[1] Unoki H and Sakudo T 1967 *J. Phys. Soc. Japan* **23** 546
[2] Petrov P K, Ivanov Z G and Gevorgyan S S 2000 *Mater. Sci. Eng.* A **288** 231
[3] Bianchi U, Dec J, Kleemann W and Bednorz J G 1995 *Phys. Rev.* B **51** 8738
[4] Bednorz J G and Müller K A 1984 *Phys. Rev. Lett.* **52** 2289
[5] Itoh M, Wang R, Inaguma Y, Yamaguchi T, Shan Y and Nakamura T 1999 *Phys. Rev. Lett.* **82** 3540
[6] Itoh M *et al* 2002 *CIS-Japan Conf. on Ferroelectrics (St Petersburg, June 2002); Ferroelectrics* at press
[7] Xi X X, Clark A M, Hao J H and Si W 1999 *Integr. Ferroelectr.* **24** 239
[8] Hasegawa T, Mouri S, Yamada Y and Tanaka K 2003 *Phys. Rev. Lett.* at press
[9] Fleury P A, Scott J F and Worlock J M 1968 *Phys. Rev. Lett.* **21** 16
[10] Shirane G and Yamada Y 1969 *Phys. Rev.* **177** 858
[11] Minkiewicz V J *et al* 1969 *J. Phys. Soc. Japan* **26** 674
Minkiewicz V J *et al* 1970 *J. Phys. Soc. Japan* **28** 443
[12] Tabata H, Tanaka H and Kawai T 1994 *Appl. Phys. Lett.* B **65** 1970
[13] Jiang A Q, Scott J F, Lu H and Chen Z 2003 *J. Appl. Phys.* **93** 1180
[14] Locherer K R, Hayward S A, Hirst P J, Chrosch J, Yeadon M, Abell J S and Salje E K H 1996 *Phil. Trans. R. Soc.* A **354** 2815
[15] Shimuta T, Nakagawara O, Makino T, Arai S, Tabata H and Kawai T 2002 *J. Appl. Phys.* **91** 2290
[16] Rabe K private communication (Rutgers University)