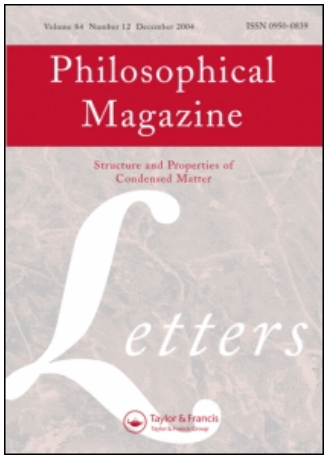

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Growth and structural properties of $Bi(Fe_xSc_{1-x})O_3$ thin films

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Epitaxial $Bi(Fe_xSc_{1-x})O_3$ thin films with a range of compositions were fabricated by pulsed laser deposition on $SrTiO_3$ (001) substrates with a $BiFeO_3$ buffer layer. X-ray diffraction and transmission electron microscopy reveal that this composition series forms a solid solution in the thin film form. Second harmonic generation measurements showed a maximum at $x = 0.7$, which may be associated with a phase transition. The present $BiScO_3$ films did not exhibit ferroelectric or antiferroelectric behaviour at the field levels which could be probed.

Recently, Bi-based perovskites such as $BiFeO_3$ [1] and $SrBi_2Ta_2O_9$ [2] have attracted much interest as ferroelectric/piezoelectric materials. Bi is highly polarizable when it occupies the A position in the ABO_3 perovskite structure. These materials have a wide range of potential applications, from sensors and actuators to information storage devices [3].

$BiFeO_3$ is especially interesting since ferroelectric and magnetic properties coexist. Epitaxially grown $BiFeO_3$ thin films have a rhombohedrally distorted perovskite structure [4]. In order to enhance the ferroic properties of $BiFeO_3$, one might consider alloying it with another ferroelectric and/or ferromagnetic material with a similar structure. It is of particular interest to find a morphotropic phase boundary [5], where the polarizability is enhanced.

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One strategy to systematically search for novel compositions with enhanced properties is to explore new solid solutions and monitor variations in the ferroelectric and magnetic properties. Previously, it was demonstrated that $(BiScO_3)_{0.43}$–$(PbTiO_3)_{0.57}$ (bulk ceramics, single crystals and thin films) have good piezoelectric properties [6–8], comparable to those found in $Pb(Zr_{0.53}Ti_{0.47})O_3$ (PZT) but with substantially higher transition temperatures [9]. However, pure bulk $BiScO_3$ has only been synthesized under very high pressure (7 GPa) [10]. We have succeeded in growing epitaxial $BiScO_3$ films on $SrTiO_3$ (001) substrates. We have also combined $BiFeO_3$ and $BiScO_3$ to map the structural properties of $Bi(Fe_xSc_{1-x})O_3$ using the composition spread technique [11, 12].

Pulsed laser deposition was used to fabricate the thin films. Sintered ceramic targets with nominal composition of $BiScO_x$ and $BiFeO_y$ were ablated with an excimer laser (KrF with $\lambda = 248$ nm) for deposition. The deposition temperature was 600°C, and the oxygen partial pressure was 10 mTorr. The ablation energy was 1.5–2 J cm^{-2}, and the thickness of the films was 70–500 nm. After deposition, films were annealed *in situ* at 500°C in 1–2 Torr of oxygen for 1 hour, and then cooled by turning the heater off. The technique for depositing composition spreads is described in detail elsewhere [11, 12].

A scanning X-ray microdiffractometer (D8 DISCOVER with GADDS for combinatorial screening by Bruker-AXS) was used to characterize the out-of-plane lattice constant of the films. The diffraction pattern was taken with the ω-scan mode using, and at each 2θ, the intensities were subsequently integrated in χ over the range of $\sim\pm13°$, so that plots equivalent to θ–2θ XRD are obtained. High resolution transmission electron microscopy (HRTEM) was used to study the microstructure of the films.

Second harmonic generation (SHG) was used to investigate the local symmetry in a setup described previously [13] with a coherent Ti:sapphire pulsed fs laser. The wavelength of the incident light was 760 nm, and the average power was about 300 mW. The light was chopped at a frequency of 2 kHz and focused to a spot size of about 50 microns. Measurements were made in reflection, and the incident *s*-polarized light was at nearly normal incidence ($\sim3°$ away from the surface normal). The intensity of both the *s*- and *p*-polarized SHG was measured with a photomultiplier tube and lock-in detection after filtering by both broadband and narrowband filters. Measurements were made at room temperature with an applied magnetic field of up to 3 kOe. The films were aligned so that the light is *s*-polarized along the [100] direction of the substrate. Separate measurements showed that SHG from the substrate alone was negligible.

Film growth was attempted on $LaAlO_3$ (001), $SrTiO_3$ (001), *c*- and *r*-plane Al_2O_3, and MgO (001) substrates. It was found that $BiScO_3$ does not grow as a single phase epitaxial film directly on any of these. Tomashpol'skii *et al.* [10] reported that the bulk perovskite $BiScO_3$ is triclinic, and its lattice parameters were: $a = c = 4.042$ Å, $b = 4.127$ Å, $\alpha = \gamma = 90.41°$, $\beta = 90.52°$. These lattice parameters are considerably larger than those of the substrates explored. Thus, the possibility of a buffer layer with a lattice constant intermediate between that of $BiScO_3$ and the substrate was explored.

$BiFeO_3$ on $SrTiO_3$ (001) was found to enable epitaxial growth of $BiScO_3$. In order to optimize the buffer layer thickness, $BiScO_3$ was deposited on a $BiFeO_3$

layer with a graded thickness (0–10 nm thick) across a chip. Figure 1 shows the three-dimensional microdiffraction intensity plot in the 2θ range from 19° to 37° as a function of the $BiFeO_3$ buffer layer thickness. $BiScO_3$ is polycrystalline when the $BiFeO_3$ buffer layer thickness is less than 3 nm. The epitaxial *b*-axis oriented $BiScO_3$ peak at $2\theta \approx 21.4°$ is visible for the $BiFeO_3$ buffer layer thickness greater than 3 nm. The out-of-plane lattice parameter of the $BiScO_3$ was 4.13 Å.

Figure 2 shows a cross-sectional dark-field HRTEM image of a $BiScO_3$ film on a 10 nm thick $BiFeO_3$ buffer. The $BiScO_3$ film shows a columnar feature. We speculate that the columnar growth of the film is due to the lattice mismatch with the substrate, even though we deposited a $BiFeO_3$ buffer to assist the $BiScO_3$ film growth. The electron diffraction pattern reveals that (010) and (001) reflections of

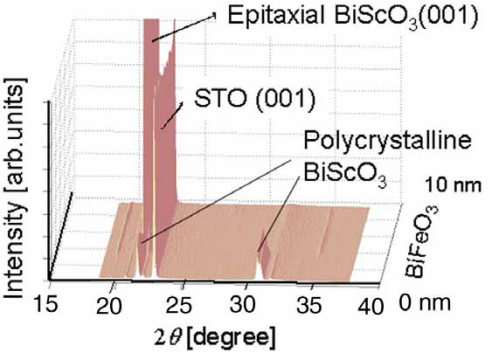

Figure 1. X-ray diffraction pattern of $BiScO_3$ films on a $SrTiO_3$ (100) substrate as the $BiFeO_3$ buffer layer varies from 0 to 10 nm. Second phases were observed for $BiFeO_3$ buffer thickness of 0–3 nm. For $BiFeO_3$ buffer thicknesses from 3 nm to 10 nm, only an epitaxial (010) $BiScO_3$ peak at $2\theta \approx 21.4°$ is observed.

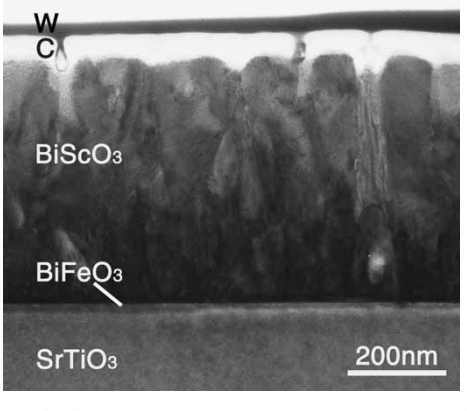

Figure 2. Cross-sectional high-resolution transmission electron microscopy image of the $BiScO_3$ films (~500 nm) on $BiFeO_3$ (~1 nm) buffered $SrTiO_3$ (100) substrate. The top of the film surface is covered with W (tungsten) and C (carbon) to observe the surface of the film clearly. (The electron beam is incident along ⟨100⟩ $SrTiO_3$.)

$BiScO_3$ have different spacing with a ratio of 1.021. The in-plane and the out-of-plane parameters were determined to be $a = c = 4.042$ Å and $b = 4.126$ Å, respectively. The crystal structure appeared to be pseudo-tetragonal with the long b axis normal to the substrate surface.

The same deposition conditions and substrate with a 10 nm thick $BiFeO_3$ buffer were used to deposit $Bi(Fe_xSc_{1-x})O_3$ composition spreads. The thickness of the composition spreads was 70–200 nm. Figure 3 shows the change in the out-of-plane lattice constant as a function of composition on a composition spread mapped using scanning X-ray microdiffraction. From $x = 0$ to 1, there is a continuous change in the lattice constant indicating that $Bi(Fe_xSc_{1-x})O_3$ is a solid-solution system in the epitaxial thin films. Additionally, the intensity of the film linearly decreases from the $BiScO_3$ film end to the $BiFeO_3$ end (not shown). This fact is also suggestive of the solid solution behaviour. However, between $x = 0.4$ and 0.8, there is a deviation in the lattice constant from the linear variation in x expected from Vegard's law. This may be an indication that there is a transition between slightly different structures.

To further investigate the structural properties, we performed SHG across the spread. The SHG signal arises from a lack of centrosymmetry, and the allowed SHG tensor elements are given by the point group of the local symmetry. The x dependence of the intensity of the two polarizations of SHG is shown in figure 4. In no measurement was any magnetic field dependence observed, suggesting that the electric dipole transitions can entirely account for the SHG [13]. Previously, it has been shown that $BiFeO_3$ grown on $SrTiO_3$ (001) is nearly tetragonal with a small monoclinic distortion and that the SHG signal came from the distortion and not from symmetry breaking at the surface [13]. It was observed that there is a non-monotonic dependence of the SHG signal on x. A small signal was observed for the $BiScO_3$ film; it is not known whether this is characteristic of the absence of a centre

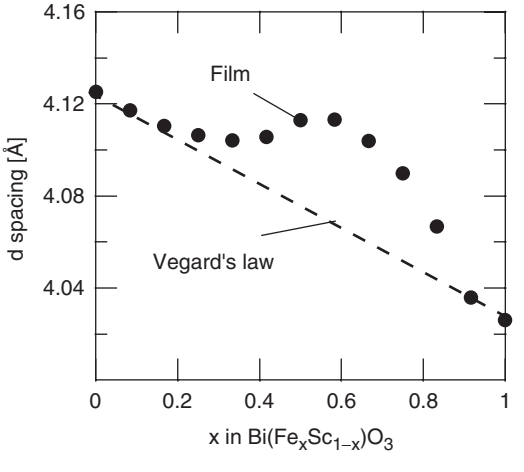

Figure 3. Change in the out-of-plane lattice constant around the (001) $SrTiO_3$ diffraction peak as a function of composition. The lattice constant changes linearly, in agreement with Vegard's law, near both the pure $BiScO_3$ and $BiFeO_3$ regions.

of symmetry in the $BiScO_3$ itself, or whether it arises from the $BiFeO_3$ buffer layer. A much larger signal develops in the $BiFeO_3$–$BiScO_3$ solid solutions. There was a local maximum near $x = 0.7$, corresponding to the region where deviation from Vegard's law (figure 3) was observed. This suggests local distortions in this region and could be another indication of a structural transition.

In order to perform capacitor measurements, $Bi(Fe_xSc_{1-x})O_3$ thin films with a 10 nm $BiFeO_3$ buffer layer were prepared on $SrTiO_3$ (001) with a 50 nm thick $SrRuO_3$ bottom electrode layer. We confirmed that $BiScO_3$ can grow epitaxially on $BiFeO_3$/$SrRuO_3$. Dielectric measurements were made in the parallel-plate geometry with an HP 4192 LF impedance analyzer and a probe station. All measurements were made at frequencies between 10 kHz and 1 MHz, and an oscillation level of 0.3 V. A Maxwell–Wagner relaxation was observed at lower frequencies; this is consistent with the $BiScO_3$/$BiFeO_3$ bilayer structure of the film. Figure 5 shows the plot of the dielectric constant and $\tan\delta$ (at 300 kHz, above the relaxation frequency) as a function of composition along the composition spread. With increasing x, the dielectric constant ε increased. $BiFeO_3$ and related compounds can be electrically leaky due to oxygen defects [14]. In the present sample, when x was larger than 0.6, the spread film was too conductive to perform accurate dielectric measurements. At around $x = 0.5$, we observed flattening of $\tan\delta$. This may be related with the film structure, as the lattice constant also flattens at the composition. In high electric field measurements, the $BiScO_3$-rich region did not show any anomalies consistent with ferroelectricity or antiferroelectricity over the probed electric field range (up to $\sim 1\,MV\,cm^{-1}$).

Recent theoretical calculations predict $BiScO_3$ to be ferroelectric [15]. It is possible that the apparent lack of ferroelectricity in epitaxial $BiScO_3$ films may be due to a high coercive field, or the existence of high field conduction, which would mask a switching polarization. However, the small SHG signal in the $BiScO_3$ films suggests that it is also possible that $BiScO_3$ is not ferroelectric.

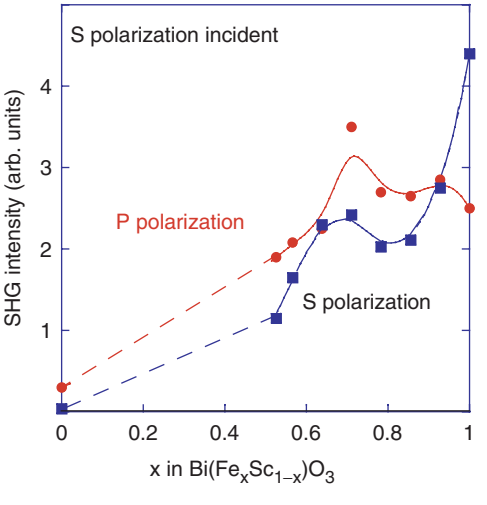

Figure 4. Second harmonic generation intensity of the two polarizations as a function of composition.

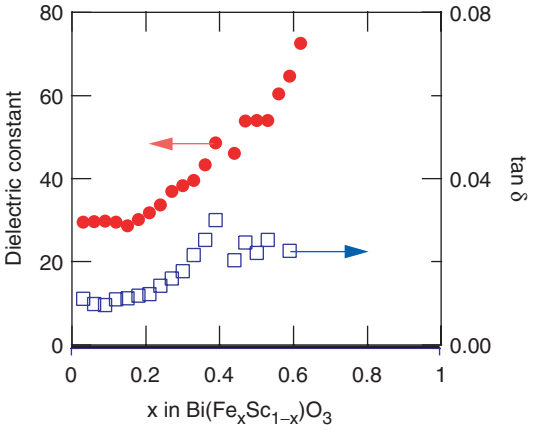

Figure 5. Dielectric constant and tan δ as a function of composition across the composition spread (300 kHz).

In conclusion, epitaxial $BiScO_3$ and $Bi(Fe_xSc_{1-x})O_3$ thin films with a range of compositions were successfully grown by pulsed laser deposition on $SrTiO_3$ (001) substrates with a $BiFeO_3$ buffer layer of thickness 5–10 nm. $Bi(Fe_xSc_{1-x})O_3$ was found to be a solid solution. There are indications that there is a structural phase transition near $x = 0.7$. Whereas the addition of $BiScO_3$ to $BiFeO_3$ decreased the conductivity, the insulating compositions, near $x = 0$, were neither measurably ferroelectric nor antiferroelectric.

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References

[1] G.A. Smolenskii and I. Chupis, Soviet Phys. Usp. **25** 475 (1982).
[2] A. Srinivas, D.-W. Kim and K.S. Hong, Appl. Phys. Lett. **83** 1602 (2003).
[3] W. Eerenstein, N.D. Mathur and J.F. Scott, Nature **442** 759 (2006).
[4] J. Li, J. Wang, M. Wuttig, R. Ramesh, *et al.*, Appl. Phys. Lett. **84** 5261 (2004).
[5] A.M. George, J. Inigues and L. Bellaiche, Phys. Rev. Lett. **91** 045504-1 (2003).
[6] S. Zhang, C.A. Randall and T.R. Shrout, Appl. Phys. Lett. **83** 3150 (2003).
[7] J.C. Nino and S. Trolier-McKinstry, J. Mater. Res. **19** 568 (2004).
[8] S.J. Zhang, C.A. Randall and T.R. Shrout, J. Appl. Phys. **95** 4291 (2004).
[9] T. Yoshimura and S. Trolier-McKinstry, Appl Phys. Lett. **81** 2065 (2003).
[10] Y.Y. Tomashpol'skii, E.V. Zubova, K.P. Burdina, *et al.*, Soviet Phys. Crystallogr. **13** 859 (1969).

[11] K.-S. Chang, O. Famodu, I. Takeuchi, *et al*., Appl. Phys. Lett. **79** 4411 (2001).
[12] M. Murakami, K.-S. Chang, M.A. Aronova, *et al*., Appl. Phys. Lett. **87** 112901 (2005).
[13] S.E. Lofland, K.F. McDonald, C.J. Metting, *et al*., Phys. Rev. B **73** 092408 (2006).
[14] J.K. Kim, S.S. Kim, W.-J. Kim, *et al*., Appl. Phys. Lett. **88** 132901 (2006).
[15] J. Íñiguez, D. Vanderbilt and L. Bellaiche, Phys. Rev. B **67** 224107 (2003).