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Coherent Growth of $\alpha$-Fe$_2$O$_3$ in Ti and Nd Co-doped BiFeO$_3$ Thin Films

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Coherent dendritic $\alpha$-Fe$_2$O$_3$ precipitates were observed to form at the surface of epitaxial films of (Bi$_{0.75}$Nd$_{0.25}$)(Fe$_{0.97}$Ti$_{0.03}$)O$_3$ (BNFO) grown by pulsed laser deposition. The Fe$_2$O$_3$ dendrites are assemblages of nanosized particles with an approximate length of 500 nm. Through the use of atomic resolution scanning transmission electron microscopy, a transition zone at the BNFO/$\alpha$-Fe$_2$O$_3$ interface, $\sim$2 unit-cells wide, was observed to be Fe$_2$O$_3$-rich with the perovskite structure. It is proposed that the formation of the Fe$_2$O$_3$-rich perovskite structure encourages epitaxial growth of the $\alpha$-Fe$_2$O$_3$ rather than the formation of the incoherent Fe$_2$O$_3$ particulate second phase frequently reported in BiFeO$_3$-based thin films.

Keywords: Fe$_2$O$_3$ Precipitate, BiFeO$_3$ Thin Film, Aberration-Corrected Scanning Transmission Electron Microscopy, High-Angle Annular Dark Field Imaging

Impact Statement The discovery of the new structure may explain the abnormally high ferromagnetic response observed in the BiFeO$_3$-based single-phase epitaxial films, and will benefit the communities of materials science.
(∼2 pseudocubic unit cells) of coherent Fe₂O₃-rich perovskite structure was observed to promote the epitaxial growth of the α-Fe₂O₃ rather than incoherent Fe₂O₃ particulate second phase. The new structure may exist in many BiFeO₃-based single-phase films reported before in which the crystal structures of the films were characterized solely using XRD, and may in part, explain the ferromagnetic response observed at room temperature.

A BNFO ceramic PLD target was prepared according to the process described in [7,8]. Films were deposited on (001) SrTiO₃ (STO) substrates using a home-built PLD system with a 248 nm KrF excimer laser. The detailed film growth process is described in [16]. Cross-sectional and plan-view transmission electron microscopy (TEM) samples were prepared with a dual beam FIB/SEM FEI Quanta 3D 200. Plan-view TEM samples were prepared by thinning the substrate side. Samples were finished in low-angle and low-voltage conditions to reduce ion-beam damage. A double aberration-corrected microscope JEM-Z3100F-R005 STEM/TEM operated at 300 keV was used to perform STEM analysis.

Figure 1(a) shows an annular bright field (ABF) STEM image of a cross-sectional sample which reveals some bright needle-shaped precipitates in the upper relaxed region of the BNFO film. The precipitates are dark in the corresponding high-angle annular dark field (HAADF) STEM image (Figure 1(b)). The contrasts in HAADF-STEM and ABF-STEM images suggest that the precipitates have a lower average atomic number than the surrounding BNFO matrix. The precipitates grow obliquely upwards inside the BNFO film, rather than the growth of the Fe₂O₃-rich perovskite nanophase perpendicular to the substrate found in a previous work.[16] Figure 1(c) shows an enlarged HAADF-STEM image containing a precipitate, in which a white line illustrates the position for an X-ray energy-dispersive spectroscopy (EDS) line-scan analysis performed to check the chemical distribution in the BNFO matrix and the dark precipitate. Figure 1(d) shows the profiles of the relative composition (in atomic percentage at%) of the Fe, Nd and Bi cations (Ti was omitted due to the very weak Ti peaks which were barely above noise levels). The chemical profiles show that the cation composition of the BNFO matrix is close to the stoichiometry of the BNFO ceramic target. In contrast the precipitate is rich in Fe and deficient in Nd and Bi. In the center of the precipitate, the Fe content is as high as 96 at%, which suggests that the precipitate is an iron-oxide.

Plan-view samples were further prepared by thinning the substrate side to study the distribution of the iron-oxide precipitate in the BNFO film. Figure 2(a) shows a HAADF-STEM image of a plan-view sample, which reveals dark nanoprecipitates (∼10 nm) in the
surface of the BNFO film. The nanoprecipitates assemble into dendrites with an approximate length of 500 nm. The precipitates are bright in the corresponding ABF-STEM image (Figure 2(b)). The shape and contrast as well as the electron energy-loss spectroscopy (EELS) analysis of the precipitates in the surface of the BNFO film suggest that they are the needle-shaped precipitates in the cross-sectional sample viewed end-on. The iron-oxide composition of the precipitate was confirmed by the EELS analysis. Figure 2(c) shows the EELS spectra acquired from the BNFO matrix and precipitate, respectively. A reference spectrum of Fe$_2$O$_3$ from Gatan EELS Atlas is also plotted in Figure 2(c) for comparison.

Atomic-resolved HAADF-STEM and ABF-STEM analysis was further performed to identify the crystal structure of the dendritic precipitates. Figure 3(a) shows an atomic-resolution HAADF-STEM image of a coherently grown precipitate obtained along the pseudocubic ⟨001⟩ zone-axis of the BNFO matrix. The precipitate shows a darker contrast than the surrounding BNFO. The bright contrast of the atomic columns of the cations in Figure 3(a) is reversed in the corresponding ABF-STEM image in Figure 3(b). The BNFO matrix reveals distinct differences in intensity and size of the A- and B-site cations, but the precipitate generally shows identical contrast for all the cation columns. The uniform contrast is consistent with the above analysis of the precipitate having primarily an iron-oxide composition. The red dash-lines across the BNFO matrix and precipitate reveal the precipitate has a rhombic lattice (≈4° deviation from right angle) and the central cation approaches another...
Figure 3. (Colour online) (a) Atomic-resolved HAADF-STEM and (b) corresponding ABF-STEM plan-view images showing the coherent growth of $\alpha$-$\text{Fe}_2\text{O}_3$ and BNFO matrix. The red dash-lines are added as a guide to the eye to identify the change of the lattices across the BNFO matrix and precipitate. (c) The polyhedral model showing face and edge-sharing FeO$_6$ octahedra of a $\alpha$-$\text{Fe}_2\text{O}_3$ unit cell viewed along [241] zone-axis and (d) the corresponding projection of the unit cell. Oxygen anions are omitted and only Fe cations are shown for the sake of clarity. The black dash lines illustrate the dumbbell structure of the Fe–Fe cations in neighboring FeO$_6$ octahedra.

cation to form a dumbbell structure. Atomic resolution images of the precipitate are readily interpreted as the [241] zone-axis projection of rhombohedral $\alpha$-$\text{Fe}_2\text{O}_3$. Figure 3(c) shows a polyhedral model of the $\alpha$-$\text{Fe}_2\text{O}_3$ unit cell viewed along the [241] zone-axis, illustrating the neighboring FeO$_6$ octahedra with face and edge sharing, resulting in the Fe cations approaching each other in the [241] projection, as shown in Figure 3(d).

Atomic resolution HAADF-STEM imaging was used to study the mechanism of epitaxial growth at the $\alpha$-$\text{Fe}_2\text{O}_3$/BNFO interface. Figure 4 shows an enlarged HAADF-STEM image in the lower right portion of Figure 3(a). A structural model of the projection of the Fe cations of a $\alpha$-$\text{Fe}_2\text{O}_3$ unit cell viewed along the [241] zone-axis is overlaid on the image for comparison. The structural model matches well with the experimental image. Yellow dash-dot-dot lines are added as a guide to the eye to illustrate the interface. A transition zone (blue dashed lines) at the interface region between the BNFO matrix and $\alpha$-$\text{Fe}_2\text{O}_3$ precipitate is observed, $\sim$2 unit-cells wide, with a perovskite structure in which the intensity of the A-site columns is substantially reduced, suggesting Bi-deficiency. In a previous study, a Fe$_2$O$_3$-rich perovskite phase within BNFO films was reported which exhibits a high concentration of Fe$^{3+}$-ions on the A-site.[16] It is therefore reasonable to speculate that the BNFO perovskite/$\alpha$-$\text{Fe}_2\text{O}_3$ transition zone is composed of the newly discovered Fe$_2$O$_3$-rich perovskite phase which in turn is responsible for epitaxial growth of the Fe$_2$O$_3$ dendrites, due to the similar crystal chemistry of Fe$_2$O$_3$-rich perovskite phase and $\alpha$-$\text{Fe}_2\text{O}_3$. It should be noted that there are additional atomic columns superposed on the perovskite lattice in the Fe$_2$O$_3$-rich transition zone in a local area, as illustrated by the arrows in Figure 4.

The positions of these additional atomic columns are similar to Nd-rich nanoprecipitates recently observed by atomic resolution EELS spectrum-imaging analysis in Nd- and Ti-codoped BiFeO$_3$ films and ceramics.[21–23] The presence of some Nd-rich nanoprecipitates in the transition zone suggests that Nd was exsolved from the matrix and precipitated heterogeneously during the PLD process.

It should be noted that $\gamma$-$\text{Fe}_2\text{O}_3$ precipitate is favored to be formed in the BiFeO$_3$ films grown by PLD at low oxygen partial pressure, for example below 5
mTorr.[13–15] Recently, maghemite-like regions (γ-Fe$_2$O$_3$) were also evidenced at crossing of two antiphase boundaries in (Bi$_{0.85}$Nd$_{0.15}$)(Fe$_{0.9}$Ti$_{0.1}$)O$_3$ ceramics synthesized in air.[24] Although α-Fe$_2$O$_3$ is the favored precipitate with the oxygen partial pressure used in this work (40 mTorr) which is much higher than those for γ-Fe$_2$O$_3$ formation in the growth of BiFeO$_3$ films, whether there is the presence of γ-Fe$_2$O$_3$ precipitate in this Nd- and Ti-codoped BiFeO$_3$ film is still not clear.

In summary, coherent α-Fe$_2$O$_3$ forms at the surface of epitaxial films of Ti- and Nd-codoped BiFeO$_3$ grown by PLD. A Fe$_2$O$_3$-rich perovskite-structured transition zone of ~2 unit-cells wide at the BNFO/α-Fe$_2$O$_3$ interface promotes epitaxial growth of the α-Fe$_2$O$_3$ rather than the incoherent Fe$_2$O$_3$ particulate second phase. The new structure may exist in many BiFeO$_3$-based single-phase films reported before, and may in part, explain the ferromagnetic response observed at room temperature.

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References


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