Effect of Doping for Epitaxial $(\text{Ba}_{1-x}\text{Yb}_x)(\text{Fe}_{0.2}\text{Zr}_{0.8})\text{O}_{3-\delta}$ Thin Films with Yb

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We fabricated epitaxial $(\text{Ba}_{1-x}\text{Yb}_x)(\text{Fe}_{0.2}\text{Zr}_{0.8})\text{O}_{3-\delta}$ (BYFZO) thin films and studied their structural and dielectric properties using synchrotron X-ray photoelectron spectroscopy. The 10%-Yb-substituted BYFZO samples had almost the same good insulation properties as the non-doped BFZO samples. Saturation magnetization occurred at $0.242 \mu\text{B}/\text{f.u.}$ It is believed that a large amount of Yb^{3+} substitution produced carrier electrons, leading to recombination of the charge balance. This resulted in an increase in the leakage current and a decrease in the saturation magnetization. The ferromagnetic nature of the $x = 0.0$ and $x = 0.1$ samples was believed to have super-exchange interactions because the samples showed good dielectric properties. Additionally, for the $x = 0.1$ samples, the magnetic moments of the Yb^{3+} ions added to the magnetization. Therefore, the maximum saturation magnetization occurred when the amount of Yb-substitution was $x = 0.1$.

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1. Introduction

Multi-functional magneto-dielectric materials have been studied over the last couple of decades. Especially, the elemental substitution of the main components with other components is one of the most successful methods to improve their original properties.¹⁻⁵⁾

We have intensively studied Zr-substituted $\text{BaFeO}_{3-\delta}$ single crystalline films on SrTiO_3 (STO) substrates that exhibited ferromagnetic and dielectric properties, even at room temperature. The magneto-dielectric properties of $\text{BaFeO}_{3-\delta}$ were optimized when 80% of the Fe ions were substituted by Zr ions. The origin of the ferromagnetism was thought to be ascribed to the 180° super-exchange coupling of $\text{Fe}^{4+}-\text{O}^{2-}-\text{Fe}^{4+}$ ($d^4-\text{O}^{2-}-d^4$), which is quite unique and rarely observed in this class of materials.⁶⁻¹⁰⁾

In recent years, the substitution of A-site ions with rare earth elements in ABO_3 -type perovskite oxides has been reported to either add to their function or improve the original function of the materials.¹¹⁻¹⁴⁾ Hence, it is useful to replace the A-site ions in BFZO thin films with other elements for such purposes. Based on this, we focused on Ytterbium (Yb), which is a rare earth element that forms di- and tri-valent ions in its ordinary state. Considering the number of 4f electrons in Yb, the di- and tri-valent Yb ions have closed and non-closed 4f-shells, respectively. Thus, it is of interest to determine the correlation between the valence states of the Fe and Yb ions as well as the structural, magnetic and electric properties of Yb-substituted BFZO thin films.

In this study, we fabricated epitaxial $(\text{Ba}_{1-x}\text{Yb}_x)(\text{Fe}_{0.2}\text{Zr}_{0.8})\text{O}_{3-\delta}$ (BYFZO) thin films and discuss their structural, magnetic and dielectric properties.

2. Experimental Procedure

$(\text{Ba}_{1-x}\text{Yb}_x)(\text{Fe}_{0.2}\text{Zr}_{0.8})\text{O}_{3-\delta}$ (BYFZO) ($x = 0.0-0.3$) thin

films with a thickness of 120 nm were synthesized on (001) STO and (001) Nb-doped STO (Nb-STO) single crystal substrates by pulsed laser beam deposition with a KrF excimer laser ($\lambda = 248 \text{ nm}$, 2 Hz). Samples were synthesized on Nb-STO substrates to measure their electric properties. BYFZO bulk targets were prepared by a conventional ceramic process from a stoichiometric mixture of BaCO_3 , Yb_2O_3 , $\alpha\text{-Fe}_2\text{O}_3$ and ZrO_2 powders. The substrate temperature was 973K, and the oxygen partial pressure during deposition and subsequent cooling was maintained at 0.67 Pa.

Structural characterizations of the films were performed by X-ray diffraction (XRD). The leakage properties were measured with a 2-probe technique at room temperature. To measure the electric properties, Pt upper electrodes were deposited on the BYFZO/Nb-STO samples by ion beam sputtering at room-temperature. The leakage properties were then measured via a two-probe technique at room-temperature. The magnetization loops were measured using a superconducting interference device magnetometer at 300 K. To evaluate the valence state of the Yb and Fe ions, X-ray photoelectron spectroscopy (XPS) with synchrotron X-ray radiation was performed on the BL27A beamline at the High Energy Accelerator Research Organization (KEK). The XPS measurements were performed at room temperature with an incident energy of $h\nu = 3.1 \text{ keV}$.

3. Results and Discussion

Figure 1 shows the $\theta-2\theta$ XRD scans for the $(\text{Ba}_{1-x}\text{Yb}_x)(\text{Fe}_{0.2}\text{Zr}_{0.8})\text{O}_{3-\delta}$ (BYFZO) thin films, indicating that only (00L) peaks for perovskite BYFZO and (00L) peaks for the STO substrates were observed. Identical results were obtained for the films deposited on Nb-STO substrates. The lattice constant (c) and the full width half maximum (FWHM) estimated from the scans are indicated in Fig. 2. For the $x = 0.1$ BYFZO sample, c was larger than that of the $x = 0.0$ sample. In contrast, c values for the $x = 0.2$ and $x = 0.3$ samples were smaller than that for the $x = 0.1$

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Fig. 1 XRD θ - 2θ scans of BYFZO thin films on STO substrates.

Fig. 2 Lattice constant and FWHM for different amounts of Yb-substitution.

sample. Conversely, the FWHM for the (001) reflections had the opposite trend.

The I-V properties for the samples are shown in Fig. 3. Since the I-V properties were predominantly influenced by the crystallinity of the samples as well as the charge balance for the constituting ions, the crystallinities of the samples were roughly estimated by the FWHM of the XRD, as indicated in Fig. 2. The leakage current densities for the $x = 0.0$ and $x = 0.1$ samples exhibited almost the same values. With further Yb-substitution, the leakage current density and FWHM increased with an increasing amount of Yb. Finally, the $x = 0.3$ samples displayed semiconducting conduction behavior with an electric resistivity of $2.09 \Omega \text{ cm}$.

Fig. 4 shows the magnetization loops for the BYFZO film samples with Yb-substitution amounts of $x = 0.0$ – 0.3 . As can be seen, all the samples shown were ferromagnetic in nature, even at room temperature, regardless of the amount of substituted Yb. For the $x = 0.1$ samples, the saturation magnetization had a maximum value of $0.242 \mu_B/\text{f.u.}$ at 300 K. The relationship between the saturation magnetization and the amount of Yb-substitution is shown in Fig. 5. The change in the saturation magnetization exhibited a similar tendency to the change in c . With this, we obtained both maximum saturation magnetization and good dielectric properties for a Yb-substitution of $x = 0.1$.

In order to investigate the relationship between the structural, electrical and magnetic properties, the valence states of the Yb and Fe ions were evaluated using X-ray synchrotron XPS measurements. Synchrotron XPS is an

Fig. 3 I-V characteristics of the BYFZO thin films on (001) Nb-doped STO substrates at room temperature.

Fig. 4 Magnetization loops for the BYFZO thin films at room temperature.

Fig. 5 Relationship between the saturation magnetization and Yb-substitution level.

effective tool for measuring the valence states of the constituting ions in the deep region from the surface of the BYFZO thin films, because high energy X-rays with $h\nu = 3.1 \text{ keV}$ were employed as the incident beam. Figure 6 shows the XPS spectra of the $\text{Yb}3d_{5/2}$ core level. The intensity of the Yb spectra increased with an increasing amount of Yb-substitution. The relative amounts of di- and tri-valent ions were estimated by integrating the intensities of

Fig. 6 $\text{Yb}3d$ core level XPS spectra measured using synchrotron X-ray radiation with an energy of $h\nu = 3.1$ keV.

Fig. 8 $\text{Fe}2p$ core level XPS spectra measured using synchrotron X-ray radiation with an energy of $h\nu = 3.1$ keV.

Fig. 7 Relative amounts of di- and tri-valent Yb ions, estimated by integrating the intensities of the peaks separated by the two waves.

Fig. 9 Relative amounts of di-, tri- and tetra-valent states of the Fe ions, estimated by integrating the intensity of the peaks separated by the three waves.

the $\text{Yb}3d_{5/2}$ peaks separated by the two waves (see in Fig. 7). The relative amount of tri-valent Yb ions increased with an increasing amount of Yb-substitution. On the other hand, the XPS spectra of the $\text{Fe}2p$ core level are shown in Fig. 8. The relative amounts of di-, tri- and tetra-valent states for the Fe ions were also estimated by integrating the intensity of the $\text{Fe}2p_{3/2}$ peaks separated by the three waves (Fig. 9). Very few tetra-valent Fe ions existed in the $x = 0.1$ samples. The amounts of the di- and tri-valent Fe ions in the $x = 0.0$ and 0.1 samples exhibited almost the same values. The valence value of the Fe ions increased with an increase in the Yb-substitution level.

Here, we discuss the possible reasons for why the $x = 0.1$ BYFZO samples had a maximum saturation magnetization the good dielectric properties. The ion radii of the di-valent Ba ions are larger than those of the Yb ions with either valence state. In general, if an element with a small ionic radius is substituted for an element with a large ionic radius, the lattice constant tends to shrink. However, in the present case, the lattice constant became larger, even though the Yb ions had smaller ionic radii than the Ba ions that they were substituted for. As described above, the Fe state remained almost unchanged, irrespective of the amount of Yb-substitution. Hence, for the $x = 0.1$ samples, 22% tri-valent state Yb ions were introduced into the originally di-valent Ba

sites. Accordingly, it is thought that the increment of the lattice constant was produced by repulsions between the cations that modified the valence state to maintain the charge balance. The magnetic origin of the $x = 0.0$ BYFZO (BFZO) is believed to be from 180° super-exchange coupling of $\text{Fe}^{4+}-\text{O}^{2-}-\text{Fe}^{4+}$ ($d^4-\text{O}^{2-}-d^4$). If a ferromagnetic material has a dielectric nature, super-exchange interaction can dominantly determine their magnetic nature. However, if a ferromagnetic material has either semiconducting or conducting properties, another source, such as $s-d$ exchange, may produce the ferromagnetic nature. In the present case, the $x = 0.0$ and $x = 0.1$ samples had good dielectric properties. Thus, the ferromagnetic natures of the $x = 0.0$ and $x = 0.1$ samples were believed to be from super-exchange interactions. Additionally, for the $x = 0.1$ samples, the magnetic moments of the Yb^{3+} ions added to the magnetization. Therefore, the saturation magnetization increased for a Yb-substitution level of $x = 0.1$.

For the $x = 0.2$ and 0.3 BYFZO samples, it was expected that the lattice constant would increase with an increasing amount of Yb. Despite this, the experimental results showed that the lattice constant for those samples decreased. This suggests that the differences in the ionic radii for Yb and Ba ($\text{Yb} < \text{Ba}$) dominantly determined the lattice constant in the samples with high amounts of Yb. Moreover, the crystalline

structure was believed to have contained considerable amounts of disorder, because the FWHM of the BYFZO diffraction peak increased with an increasing amount of Yb. In addition to the lattice constant, it was expected that the saturation magnetization would increase with an increasing amount of Yb because the amount of tetra-valent Fe and tri-valent Yb increased. The saturation magnetization decreased when the Yb-substitution was greater than 0.2. In the I-V characteristics for the $x = 0.2$ and 0.3 samples, the leakage currents increased drastically. When the ferromagnetic materials displayed either semiconducting or conducting properties, some effects, such as the conduction of carriers, became magnetic. Therefore, it is believed that the super-exchange interactions were weakened.

As a result, the maximum saturation magnetization and good dielectric properties were obtained for the $x = 0.1$ samples. This suggests that a large amount of Yb^{3+} -substitution produced carrier electrons, leading to recombination of the charge balance. This resulted in an increase in the leakage current and a decrease in the saturation magnetization.

4. Summary

In this study, we fabricated epitaxial $(\text{Ba}_{1-x}\text{Yb}_x)\text{-(Fe}_{0.2}\text{Zr}_{0.8})\text{O}_{3-\delta}$ (BYFZO) thin films and evaluated their structural, dielectric and magnetic properties using synchrotron X-ray photoelectron spectroscopy. All of the samples were ferromagnetic in nature, even at room temperature, regardless of the amount of Yb-substitution. For the $x = 0.1$ samples, the saturation magnetization had a maximum value of $0.242 \mu_{\text{B}}/\text{f.u.}$ at 300 K. The leakage current density for the $x = 0.1$ samples had good insulating properties and almost the same value as the non-doped BFZO samples. The leakage current density and FWHM increased with an increasing amount of Yb-substitution. The $x = 0.3$ samples showed semiconducting properties with an electric resistivity of $2.09 \Omega \text{ cm}$. The ferromagnetic nature of the $x = 0.0$ and $x = 0.1$ samples were believed to be from super-exchange interactions because these samples showed good dielectric

properties. Additionally, for the $x = 0.1$ samples, the magnetic moments of the Yb^{3+} ions added to the magnetization. Therefore, the maximum saturation magnetization was obtained when the amount of Yb-substitution was $x = 0.1$.

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