

Effect of Yb doping on magnetic properties of epitaxial $(\text{Ba}_{1-x}\text{Yb}_x)(\text{Fe}_{0.2}\text{Zr}_{0.8})\text{O}_{3-\delta}$ thin films

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1 Introduction

Zirconium substituted $\text{BaFeO}_{3-\delta}$ single crystalline films on SrTiO_3 (STO) substrates have been reported to exhibit ferromagnetic and dielectric properties even at room temperature. It was also revealed that the magneto-dielectric properties could be optimized, when 80% of the Fe ions were substituted by Zr ions. The origin of the observed 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 was quite unique and rarely observed in this class of materials [1,2].

In recent years, the substitution of A-site ions with rare earth material in ABO_3 type perovskite oxides has been considered to be one of effective methods to add their function and/or to improve the original natures of the materials. Hence, we think it useful to replace the A-site ions for of the 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-valent and tri-valent Yb ions have closed and non-closed $4f$ -shells, respectively. So it seems quite interesting to know the correlation between the valence states of the Fe and Yb ions as well as the magnetic properties of the Yb-substituted BFZO thin films. In this communication, we report the relation between the magnetic properties and the valence state of Fe ions of the $(\text{Ba}_{1-x}\text{Yb}_x)(\text{Fe}_{0.2}\text{Zr}_{0.8})\text{O}_{3-\delta}$ (BYFZO) thin films.

2 Experiment

Thin films of BYFZO ($x=0.0-0.3$) with a thickness of 120 nm were synthesized on (001) STO single crystal substrates by pulsed laser beam deposition with a KrF excimer laser ($\lambda=248$ nm, 2 Hz). 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 5 mTorr.

Structural characterizations of the films were performed by X-ray diffraction (XRD). The magnetization loops were measured using a superconducting interference device magnetometer at the temperature of 300K. In order to evaluate the valence state of the Yb and Fe ions, X-ray photoelectron spectroscopic (XPS) analysis using synchrotron soft X-ray radiation was performed at KEK BL-27A in High Energy Accelerator Research Organization. The

measurement of XPS was performed at room temperature, and the incident energy of X-ray was $h\nu=3.1$ keV.

3 Results and Discussion

According to the results of the structural characterization of the films, the epitaxially grown BYFZO films were successfully synthesized for $x=0.0-0.3$ samples. Figure 1 shows the magnetization loops for the BYFZO film samples with Yb substitution amount of $x=0.0-0.3$. As can be seen, all of the samples showed ferromagnetic nature even at room temperature regardless of the Yb substitution amount x . For the $x=0.1$ sample, the maximum saturation magnetization value of $0.242 \mu_B/\text{f.u.}$ was obtained at 300K. The change in the saturation magnetization is found to exhibit the similar tendency of the change in the lattice constant c . Consequently, we could obtain both the maximum saturation magnetization and the good dielectric property for the Yb substitution amount of $x=0.1$.

Here, we discuss the possible reasons for why the $x=0.1$ BYFZO samples indicated a maximum saturation magnetization and the good dielectric properties. The ion radius of the di-valent Ba ions is larger than that of the Yb ions with either valence state. In general, if elements with small ionic radius are substituted for others with large ionic radius, the lattice constant ordinary tend to shrink. However, in the present case, the lattice constant became larger even though the Yb ions with smaller ion radius had been substituted for the Ba ions with larger ion radius. As is already described above, the Fe state almost unchanged irrespective of the Yb substitution amount.

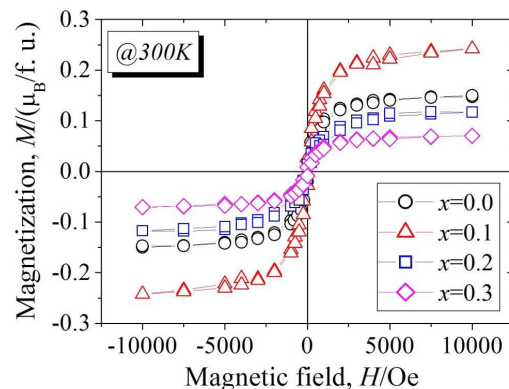


Fig. 1 Magnetization loops of the BYFZO thin films at room temperature

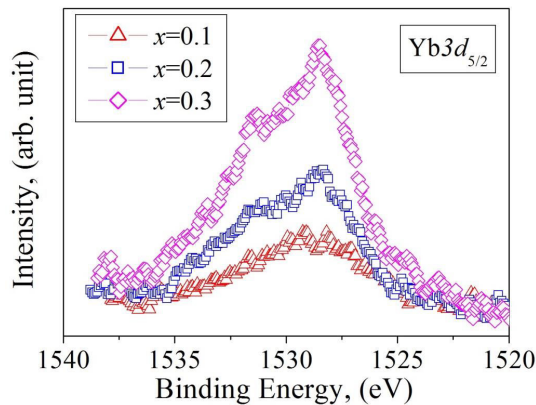


Fig. 2 Yb3d core level XPS spectra using synchrotron soft-x-ray radiation of $h\nu=3100$ eV.

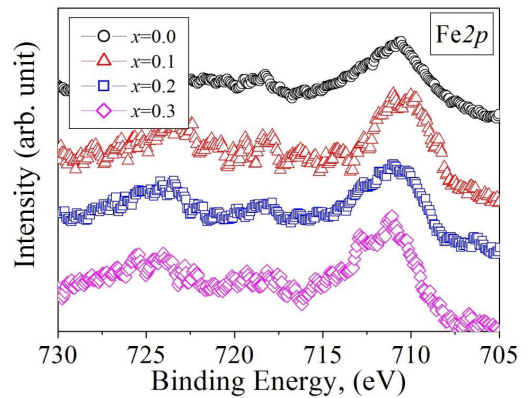


Fig. 4 Fe2p core level XPS spectra using synchrotron soft-x-ray radiation of $h\nu=3100$ eV.

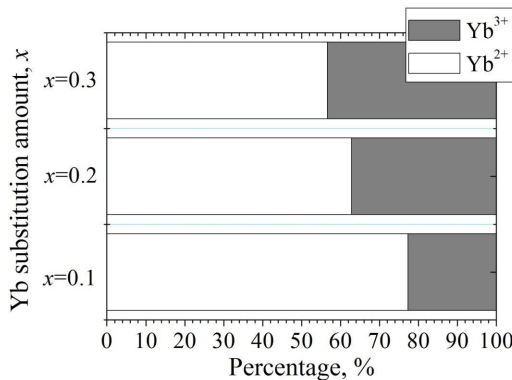


Fig. 3 Relative amount of di-valent and tri-valent Yb ions estimated from integrated intensities of the peaks.

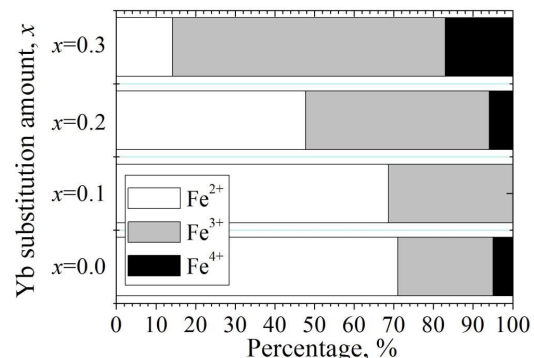


Fig. 5 Relative amount of di-valent, tri-valent and tetra-valent Fe ions estimated from integrated intensities of the peaks.

Hence, for the $x=0.1$ samples, 22% tri-valent state Yb ions were introduced into the originally di-valent Ba site. Accordingly, it is a reasonable speculation to consider that the increment of the lattice constant was produced by the repulsion between the cations that modified the valence state in order to maintain the charge balance. The magnetic origin of the $x=0.0$ BYFZO (i. e. BFZO) is considered to be the 180° super-exchange coupling of $Fe^{4+}-O^2--Fe^{4+}$ ($d^4-O^2-d^4$). If a ferromagnetic material has a dielectric nature, super-exchange interaction can dominantly determine their magnetic nature. But if the ferromagnetic materials show the semiconducting or conducting property, other source, such as $s-d$ exchange, may produce the ferromagnetic nature. In the present case, however, the $x=0.0$ and $x=0.1$ samples indicated good dielectric property. Thus, the ferromagnetic nature of the $x=0.0$ and $x=0.1$ samples were considered to be super-exchange interaction. In addition, in the $x=0.1$ samples, the magnetic moment of Yb^{3+} can be added to the magnetization. Therefore, the saturation magnetization increased when the substitution amount $x=0.1$. Regarding the $x=0.2$ and 0.3 BYFZO samples, it was expected that the saturation magnetization increases with increasing in the Yb substitution amount because the tetra-valent Fe and tri-valent state Yb increased, but the saturation magnetization also decreased when the Yb substitution amount x became larger than 0.2 . In the I-V properties of

the $x=0.2$ and 0.3 samples, the leakage current became drastically increased. When the ferromagnetic materials show the semiconducting or conducting property, some kinds of effects such as conducting carrier will become magnetic nature. Therefore, it is considered that the super-exchange interaction were weakened.

As a result, we could obtain the maximum saturation magnetization and good dielectric property when the Yb substitution amount was $x=0.1$. It is suggested that large amount substitution of Yb^{3+} produced carrier electron and led to the recombination of the charge balance, which resulted in the increase in the leakage current as well as the decrease in the the saturation magnetization.

References

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