Ferromagnetism in BiFe$_{1-x}$Co$_x$O$_3$ thin films and the correlation between ferroelectric and ferromagnetic domains

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BiFeO$_3$ (BFO) is the most widely studied multiferroic material that has attracted recent attention due to its giant electric polarization and room temperature multiferroic properties. It has a cycloidal space-modulated spin structure with a periodicity of 62 nm which generates a parasitic electric polarization superimposed on the G-type antiferromagnetic structure. Indeed, a sharp change in electric polarization is observed in a magnetic field of 18 T for a single-domain crystal of BFO due to the change in the spin structure to a collinear one [1]. On the other hand, the presence of cycloidal ordering prohibits the appearance of net ferromagnetic magnetization due to spin canting and a linear magnetoelectric effect. Modifying the spin structure is the key for realizing BFO-based ferromagnetic ferroelectrics.

We have recently observed a spin structure transition from low-temperature cycloidal one to high-temperature collinear one at ~120 K in rhombohedral BiFe$_{0.8}$Co$_{0.2}$O$_3$ using neutron powder diffraction [2]. Interestingly, magnetization measurements revealed that the collinear phase had a weakly ferromagnetic behavior with the saturation moments of 0.03 $\mu_B$/f.u. at 300 K, indicating that the spins were canted. Therefore, BiFe$_{0.8}$Co$_{0.2}$O$_3$ is expected to be a room temperature ferromagnetic ferroelectrics. In this study, we have fabricated epitaxial BiFe$_{1-x}$Co$_x$O$_3$ (BFCO) thin films using pulsed laser deposition and their crystal structures and electric/magnetic properties were examined. Since the spin structure of BFO is sensitive to structural distortion [3], two kinds of substrates, SrTiO$_3$ (STO) (111) and GdScO$_3$ (GSO) (110), were used to realize spin structure change in the BFCO thin films.

BFCO thin film ($x = 0, 0.05, 0.10, and 0.15$, thickness: 200 nm) were grown at a substrate temperature of 700 °C under an oxygen pressure of 15 Pa by focusing a KrF excimer laser pulse ($\lambda = 248$ nm/5 Hz/1.5 Jcm$^{-2}$/pulse$^{-1}$) onto a rotating target. Stoichiometric target at a cation ratio was used. The crystal structure of the BFCO films was studied by x-ray diffraction (XRD; Rigaku SmartLab). The magnetization was measured using a superconducting quantum interference device magnetometer (Quantum Design, MPMS XL). Piezoresponse force microscope (PFM) and magnetic force microscope (MFM) observations were performed using an atomic force microscope-based setup (Agilent 5420).

Figure 1 shows out-of-plane XRD patterns of BFCO thin films on STO (111) substrates, confirming that BFCO thin films grew along the [111] direction without detectable impurity phases. Together with reciprocal space mappings and $\varphi$–scans (not shown), it was confirmed that the crystal structure of the BFCO thin films are rhombohedral, as is generally reported for BFO thin films on STO (111).

Next, magnetic properties of the BFCO thin film were studied. In remnant magnetization ($M_r$) versus temperature plots, the same magnetic transitions could be observed for $x=0.10$ and 0.15 BFCO thin films at around 220 K and 130 K, respectively,
as was observed for bulk BiFe$_{0.8}$Co$_{0.2}$O$_3$ [2] while $M_r$ of $x=0$ and 0.05 BFCO thin films were almost zero [not shown]. In-plane magnetization curve of $x=0.15$ BFCO thin film at 300 K is shown in Fig. 2. Ferromagnetic hysteresis loop can be clearly seen. The value of $M_r$, ~0.04 µ$_B$/f.u. is comparable to that reported for bulk BFCO. Similar ferromagnetic hysteresis loop was observed for $x=0.10$ BFCO thin film. From these results, it can be safely concluded that $x=0.10$ and 0.15 BFCO films are weakly ferromagnetic at room temperature due to spin canting.

Finally, in order to determine whether a correlation between ferroelectric and magnetic orders is present, a combination of PFM and MFM observations was performed. Our attempts to observe the magnetic domains of BFCO thin films on STO (111) by MFM failed since the spontaneous magnetization is in the (111) plane and hard to detect by MFM. Therefore, BFCO thin films on GSO (110) substrates were used for these observations. Stripe contrast was visible in in-plane PFM image of BiFe$_{0.9}$Co$_{0.1}$O$_3$ thin film on GSO substrate (not shown), which is generally reported for BFO thin films on perovskite (001) substrates, and is characteristics of 71 ° ferroelectric domains. MFM observation was performed for the BiFe$_{0.9}$Co$_{0.1}$O$_3$ thin film at the identical area where PFM image was taken. We could clearly see the similar contrast that was observed in the PFM image. We confirmed that this contrast corresponds to magnetic domains by observing another MFM image using oppositely magnetized tip, which gave reversal of the contrast in the MFM image. From these results, we have confirmed that ferroelectric and magnetic domains are correlated in our BFCO thin films.

References