Enhanced Piezoelectric Response due to Polarization Rotation in Co-substituted $BiFeO_3$ Epitaxial Thin Films

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Polarization rotation induced by an external electric field in piezoelectric materials such as $PbZr_{1-x}Ti_xO_3$ (PZT) is generally believed to be the origin of their large piezoelectric responses. However, this postulate has never been demonstrated experimentally because of lack of a model material with which to study the role of polarization rotation exclusively. We have discovered the same M_A-type monoclinic phase as the PZT at the MPB as a distinct phase in the solid solution between rhombohedral (Space group (SG); *R*3*c*) $BiFeO_3$ (BFO) and tetragonal (SG; *P*4*mm*) $BiCoO_3$, $BiFe_{1-x}Co_xO_3$ (BFCO)[1], at $x \sim 0.3$. Furthermore, the polarization rotation between $[001]_{pc}$ and $[111]_{pc}$ (Subscript pc denotes the pseudo-cubic notation) was observed as functions of temperature and composition[2] by synchrotron X-ray powder diffraction. The monoclinic BFCO is therefore an ideal material with which to study the role of the polarization rotation in piezoelectric materials.

In this study, we fabricated high-quality cobalt-substituted $BiFeO_3$ epitaxial thin films with a giant *c*/*a* ratio by pulsed laser deposition, and systematically studied the relationship between the crystal structure and the piezoelectric responses. BFCO (x= 0-0.50) thin films were prepared using pulsed laser deposition with a KrF excimer laser (λ = 248 nm). A $La_{0.5}Sr_{0.5}CoO_3$ (LSCO) layer with a thickness of 30 nm was deposited as a bottom electrode for piezoelectric measurements. The crystal structure of the thin films was investigated by XRD with Cu Kα radiation (Rigaku SmartLab) and by STEM (JEOL ARM-200F). Local piezoelectric strain versus electric field curves were measured by detecting the vertical motion of an AFM cantilever with a conducting tip connected to a ferroelectric test system (Toyo FCE-1E).

From crystal structure analysis, we found that all the BFCO thin films had a giant *c*/*a* ratio (1.2-1.3) same as the bulk phase and the crystal structure underwent successive transitions from M_C-type monoclinic phase (x= 0-0.15) to M_A-type monoclinic phase (x= 0.15-0.30), and finally to tetragonal phase (x= 0.50) with increasing Co content x (Fig. 1). The M_A phase is essentially the same as that found in the bulk BFCO where polarization rotation has been confirmed. From piezoelectric measurements, we found that the responses were enhanced in the M_A phase (Fig. 2). This indicates that polarization rotation does play a crucial role to realize improved piezoelectric responses in this material[3]. We will show the ferroelectric domain structures of the thin films measured by piezoelectric force microscopy(PFM) as well.

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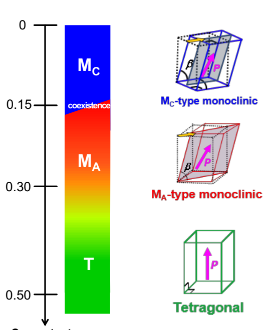

Figure 1. The phase diagrams for BFCO thin films and Schematic illustrations of the crystal structures

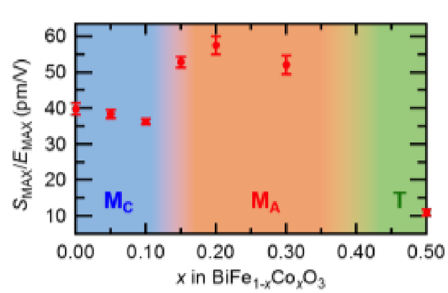

Figure 2. Effective piezoelectric constant S_{MAX}/E_{MAX} for BFCO thin