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Enhancement of ferroelectric and magnetic properties in BiFeO₃ films by small amount of cobalt addition

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Both the ferroelectric and magnetic properties of polycrystalline BiFeO₃ films fabricated by chemical solution deposition were enhanced by adding small amounts of cobalt. Addition of 3 at. % cobalt to BiFeO₃ films increased the remanent polarization from 49 to 72 $\mu\text{C}/\text{cm}^2$ and decreased the electric coercive field from 0.54 to 0.44 MV/cm. The ferroelectricity degraded when the cobalt concentration exceeded 9 at. % due to the formation of the secondary phases of Bi₂Pt. The saturation magnetization was drastically enhanced by the addition of cobalt up to 12 at. %. This is because the magnetic moments are not canceled locally since the differences of magnetic moment between *B*-sites. The saturation magnetization decreased when the cobalt content exceeded 15 at. %, thereby attributing to the formation of a nonmagnetic secondary phase of Bi₂Pt. It is concluded that both ferroelectric and magnetic properties were enhanced, provided only small amount of cobalt were added to the films. © 2008 American Institute of Physics. [DOI: 10.1063/1.2836971]

I. INTRODUCTION

There is considerable interest in developing Bi-based multiferroic materials because of their magnetoelectric properties. BiFeO₃ is an example of a multiferroic material with a perovskite structure with rhombohedral distortion (space group: *R3c*) and it is expected to exhibit large spontaneous polarization values of $\sim 100 \mu\text{C}/\text{cm}^2$ (Ref. 1). In fact, relatively high remanent polarizations have been experimentally reported in BiFeO₃.²⁻⁴ However, due to their large electric coercive field, BiFeO₃ films require high electric field to produce large remanent polarizations, and this is not suitable for memory and/or piezoelectric application.²⁻⁴ On the other hand, although the magnetic ordering of BiFeO₃ is stable above room temperature ($T_N=653 \text{ K}$), large spontaneous magnetization could not be expected because the antiferromagnetic spin structure hinders the multiferroic property of BiFeO₃.⁵ By substituting iron atoms at the *B* sites with other 3*d* transition atoms, a local ferrimagnetic spin configuration can be expected to form because of the differences in magnetic moment between the *B*-sites. Indeed, the magnetic moment increased by adding a manganese atom to bulk BiFeO₃.⁶ Our aim in the present study is to enhance the ferroelectric and magnetic properties of polycrystalline

BiFeO₃ films by adding cobalt and to determine the concentrations of cobalt necessary to provide optimum enhancement.

II. EXPERIMENTS

Bi(Co_{*x*}Fe_{1-*x*})O₃ ($0 \leq x \leq 0.21$) films (thickness of 140–200 nm) were fabricated by chemical solution deposition (CSD) on the Pt/Ti/SiO₂/Si(100) substrates, followed by postdeposition annealing at 873 K in air. The crystal structure was determined by an x-ray diffraction measurement. The leakage current density at room temperature estimated from the pulse response form of a positive, up, negative, and down measurements using a trapezoidal wave. The ferroelectric hysteresis loops were measured at 90 K by a ferroelectric tester (aixACCT TF-2000, $f=1 \text{ kHz}$) using a single triangular wave. The magnetic properties were measured by a vibrating sample magnetometer at room temperature.

III. RESULTS AND DISCUSSION

A. Magnetic properties

Figures 1(a)–1(d) shows the magnetization curves for the Bi(Co_{*x*}Fe_{1-*x*})O₃ ($0 \leq x \leq 0.21$) films measured at room temperature. The saturation magnetizations (M_S) estimated from the magnetization curves is summarized in Fig. 1(e).

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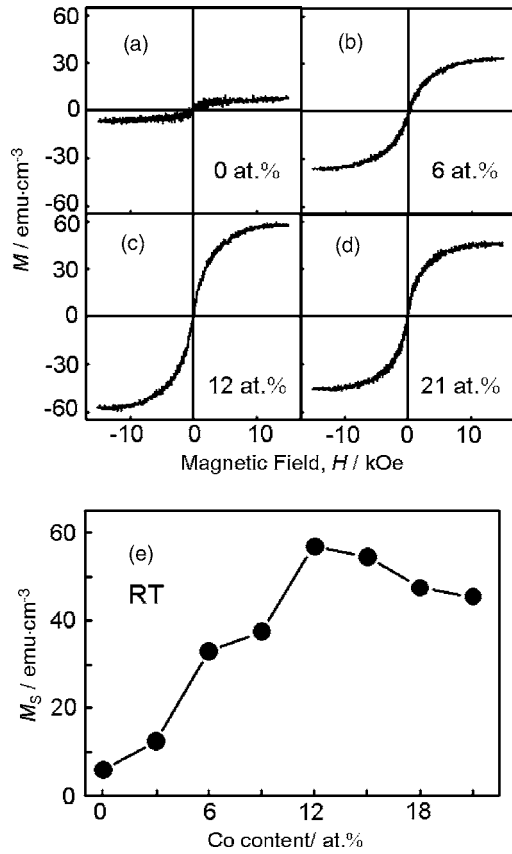
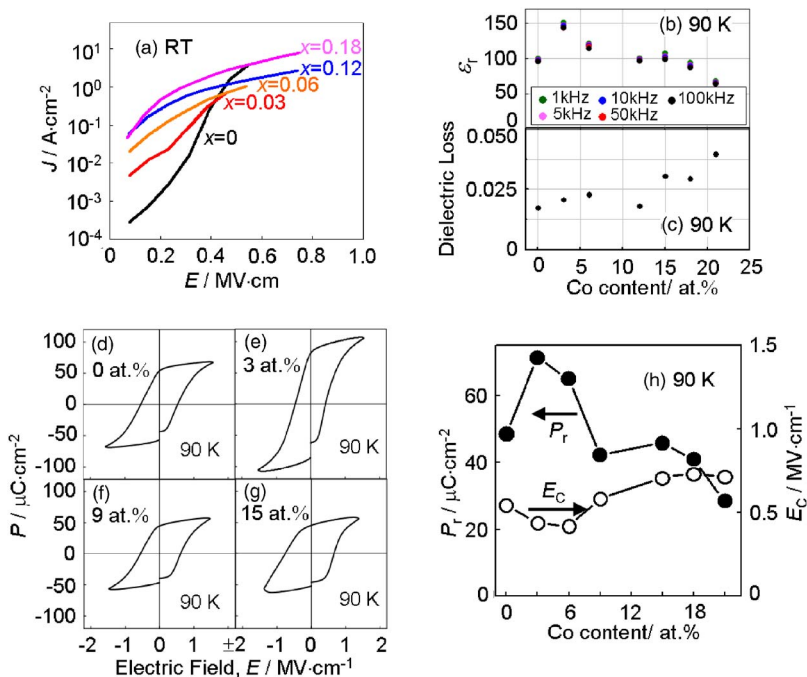


FIG. 1. Magnetization curves for the $\text{Bi}(\text{Co}_x\text{Fe}_{1-x})\text{O}_3$ ($0 \leq x \leq 0.21$) films measured at room temperature.

The saturation magnetization increased linearly with increasing cobalt content until its content reached 12 at.%, and decreased above 15 at.%.

B. Electric properties

Figure 2(a) shows the leakage current (J) versus electric



field (E) characteristics measured at room temperature. The leakage current density of the pure BiFeO_3 films was small only at the low electric field region. At the high electric field region, the leakage current densities of the BiFeO_3 films with added cobalt were lower than those of the pure BiFeO_3 films, indicating that the addition of cobalt effectively suppresses the leakage current density. Although the leakage current density reduced by cobalt addition, it was still sufficiently high to allow the measurement of the ferroelectric properties, which were then measured at low temperature. Relative dielectric constants (ϵ_r) and the dielectric loss ($\tan \delta$) are shown in Figs. 2(b) and 2(c), respectively. The dielectric constant of the $\text{Bi}(\text{Co}_x\text{Fe}_{1-x})\text{O}_3$ films peaked at a cobalt content of 3 at.% and thereafter decreased monotonically until the cobalt content reached 21 at.%. The addition of cobalt tends to increase the dielectric loss. Figures 2(d)–2(g) show the ferroelectric hysteresis (P - E) loops measured at 90 K, and Fig. 3(h) shows the cobalt concentration dependence of the remanent polarization (P_r) and the electric coercive field (E_c). The P - E loops were measured at an applied electric field of 1.5 MV/cm. The remanent polarization apparently increased at a cobalt content of 3 at.% ($P_r=72 \mu\text{C}/\text{cm}^2$) compared to pure BiFeO_3 film ($P_r=49 \mu\text{C}/\text{cm}^2$). Moreover, the small amount of cobalt added to the BiFeO_3 film effectively reduced the electric coercive field. Above a cobalt content of 9 at.%, the remanent polarization was lower than that of a pure BiFeO_3 film, and the ferroelectric hysteresis loops expanded at cobalt contents above 15 at.%. Therefore, it can be concluded that the ferroelectricity of the BiFeO_3 films could be improved by adding small amount of cobalt.

C. Film structure

Figure 3 shows the $\theta/2\theta$ x-ray diffraction patterns for the $\text{Bi}(\text{Co}_x\text{Fe}_{1-x})\text{O}_3$ films. The diffraction peaks due to the BiFeO_3 structure (\bullet) were observed at cobalt contents between 0 and 9 at.% and no other secondary phase could be

FIG. 2. (Color online) Leakage current vs electric field characteristics measured at room temperature (a), cobalt contents dependence of relative dielectric constants (b), dielectric loss (c), P - E loops [(d)–(g)], and remanent polarization and electric coercive field (h) measured at 90 K.

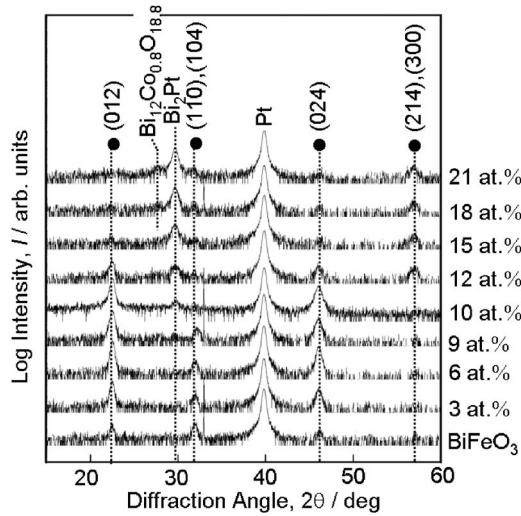


FIG. 3. $\theta/2\theta$ x-ray diffraction patterns for the $\text{Bi}(\text{Co}_x\text{Fe}_{1-x})\text{O}_3$ ($0 \leq x \leq 0.21$) films.

observed. The intensity of the diffraction peak of BiFeO_3 (012) became stronger as the cobalt contents increased up to 10 at.%. Above cobalt contents of 12 at.%, diffraction peaks due to the BiFeO_3 structure became weaker and a non-magnetic phase of Bi_2Pt began to appear. This reduced the saturation magnetization as well as the degradation of the ferroelectricity observed at cobalt contents above 12 at. %.

Figure 4 shows the x-ray reciprocal space mapping (XRSM) for cobalt contents of 0, 3, 6, and 12 at. % in the BiFeO_3 films. Without the cobalt addition ($x=0$), each diffraction line attributed to the BiFeO_3 structure was laid along the ψ direction, indicating a random orientation. The reflection line due to BiFeO_3 (012) became elliptical at cobalt contents of 3 and 6 at. %, indicating the formation of a 012-

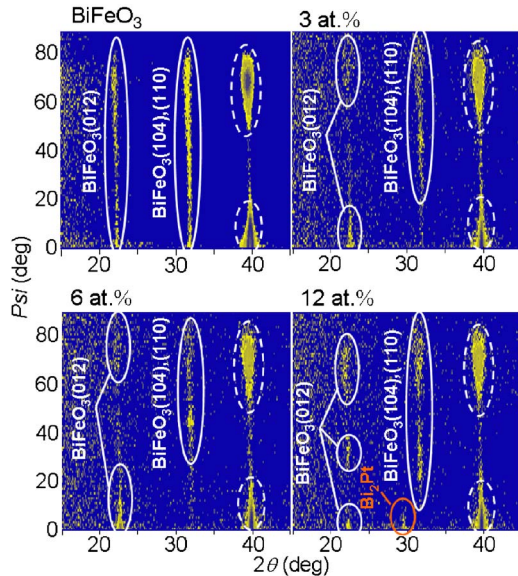


FIG. 4. (Color online) X-ray reciprocal space mapping (XRSM) at cobalt contents of 0, 3, 6, and 12 at. %.

texture structure. In these XRSMs, no secondary magnetic phases could be observed; therefore, it can be considered that the increment of the saturation magnetization might be attributed to cobalt addition. If the added cobalt substituted with B sites of iron of BiFeO_3 , the antiferromagnetic spin configuration of BiFeO_3 cannot persist locally due to the differences of the magnetic moment between Fe^{3+} ($5\mu_B$) and Co^{3+} ($4\mu_B$) at the B -site. A local collapse of the antiferromagnetic spin structure leads to an increase in the total spontaneous magnetization. It is therefore possible that local ferrimagnetic spin structures were formed around the B -site, where an iron atom was substituted by a cobalt atom, and that the total mass value of the magnetic moment increased by increasing the cobalt content. In fact, the saturation magnetization increased with increasing cobalt contents until the secondary phases were formed. However, further investigation using Raman spectroscopy to check the B -site substitution is necessary to confirm that this is, indeed, the mechanism behind the enhancement of the magnetic moment by addition of cobalt.

IV. CONCLUSION

We fabricated cobalt added BiFeO_3 polycrystalline films on the Pt (150 nm)/Ti(5 nm)/ SiO_2 (200 nm)/Si (100) substrates using CSD. The saturation magnetization was enhanced until cobalt contents reached 12 at. % and we attribute this to the formation of a local ferrimagnetic spin structure due to the substitution of an iron atom at the B -site by cobalt. The maximum remanent polarization was approximately $71 \mu\text{C}/\text{cm}^2$ ($49 \mu\text{C}/\text{cm}^2$ for pure BiFeO_3) at 1.5 MV/cm with a low electric coercive field of 0.44 MV/cm (0.53 MV/cm for pure BiFeO_3) at a cobalt content of 3 at. %. Finally, we conclude that both the ferroelectric and magnetic properties of the films were enhanced by adding small amounts of cobalt.

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¹J. B. Neaton, C. Ederer, U. V. Waghmare, N. Spaldin, and K. M. Rabe, *Phys. Rev. B* **71**, 014113 (2005).

²J. Wang, J. B. Neaton, H. Zheng, V. Nagarajan, S. B. Ogale, B. Liu, D. Viehland, V. Vaithyanathan, D. G. Schlom, U. V. Waghmare, N. A. Spaldin, K. M. Rabe, M. Wuttig, and R. Ramesh, *Science* **299**, 1719 (2003).

³K. Y. Yun, D. Ricinschi, T. Kanashima, M. Noda, and M. Okuyama, *Jpn. J. Appl. Phys., Part 2* **43**, L647 (2004).

⁴H. Naganuma, Y. Inoue, and S. Okamura, *IEEE Trans. Ultrason. Ferroelectr. Freq. Control* in press.

⁵C. Ederer and N. A. Spaldin, *Phys. Rev. B* **71**, 060401(R) (2005).

⁶M. Azuma, H. Kanda, A. A. Belik, Y. Shimakawa, and M. Takano, *J. Magn. Magn. Mater.* **310**, 1177 (2007).