



Leakage current under high electric fields and magnetic properties in Co and Mn co-substituted BiFeO₃ polycrystalline films



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ABSTRACT

Co and Mn co-substituted BiFeO₃ films were prepared on Pt/Ti/SiO₂/Si(100) substrates, and the effect of co-substitution on the structural, electric, and magnetic properties of the prepared films was systematically investigated. Cross-sectional transmission electron microscopy observations showed that the films were homogeneous; moreover, no magnetic secondary phases were observed in the films. Nano-beam energy-dispersive X-ray spectroscopy, carried out at various points in the films, revealed that Co and Mn were distributed in the films. Further, the average concentration of Bi, Co, Mn, and Fe was 59, 2, 2, and 37 at.%, respectively; these values were almost consistent with the nominal composition of the precursor solution used. X-ray diffraction profiles of the films showed that the (012)-*d*-spacing decreased and (104) and (110) peaks merged into a single peak with increasing co-substitution content. The leakage current in films under high electric fields drastically decreased upon co-substitution without any degradation of ferroelectricity; moreover, this effect was also observed for single Mn-substituted materials. Saturation magnetization of the films monotonically increased with the co-substitution content, and this increase was quantitatively identical to that in the case of single Co-substituted materials. These results indicate that Co and Mn play significant roles in determining the properties of co-substituted BiFeO₃ films.

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1. Introduction

Multiferroic materials have attracted significant attention for use in voltage driven magnetization devices that are based on the magneto-electric (ME) effect. BiFeO₃ is one such multiferroic material that is interesting from the industrial application viewpoint as it shows high temperatures for magnetic ordering ($T_N = 653$ K) and ferroelectric transition ($T_C = 1100$ K), which clearly results in the room temperature (RT) ME effect [1–3]. However, BiFeO₃ films show large leakage current densities at RT [4–7], and therefore suffer from electrical breakdown before the electric field required to induce magnetization by switching the ferroelectric polarization is attained. Mn substitution or addition to BiFeO₃ films is one of the approaches to reduce their leakage current density at RT [8,9]. However, because of its antiferromagnetism, BiFeO₃ used in voltage driven magnetic random access memories (V-MRAM), that are based on giant magnetoresistance (GMR) or tunnel magnetoresistance (TMR) effects, requires combination with ferromagnetic thin films for inducing the exchange coupling effect. For spin filter devices operated by voltage, magnetic ordering is required. Recently, it was

reported that the substitution of *A*- or *B*-sites in BiFeO₃ with La [10], Gd [11], Co [12–17], and Mn [18] increases its magnetization at RT. In addition, we found a noticeable enhancement of magnetization in BiFeO₃ upon increasing the substitution of Fe by Co up to concentrations of around 20 at.% [14]. Moreover, Co substitution increased magnetization while avoiding the degradation of ferroelectric polarization. Although the mechanism underlying the enhancement of magnetization by Co substitution is still a matter of debate, this approach opens the door for future industrial applications. Thus, Co substitution engineers the magnetic structure and Mn substitution reduces the leakage current density of BiFeO₃; thus Co and Mn are expected to have a positive co-substitution effect on BiFeO₃. Although there are some reports on the co-substitution of Co and *M* (*M* = Eu, Ca) [19,20] as well as other pairs [21,22] in BiFeO₃ films, the co-substitution of the important pair of Co and Mn in these films has not been reported yet. In this study, we systematically investigated the effect of Co and Mn co-substitution on the structural, electric, and magnetic properties of BiFeO₃ polycrystalline films.

2. Experimental methods

By employing the chemical solution deposition (CSD) method, Co and Mn co-substituted BiFeO₃ films ($t = 167$ nm) were fabricated onto (111)-textured Pt (140 nm)/Ti (5 nm)/SiO₂/Si(100) substrates.

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This deposition was followed by post-deposition annealing at 923 K for 10 min in air. The nominal compositions of the precursor solutions were adjusted to obtain films with the formula $\text{Bi}(\text{Fe}_{1-2x}\text{Co}_x\text{Mn}_x)\text{O}_3$ [$0 \leq x \leq 0.05$], while the concentration of the solutions was fixed at 0.2 M. The film structure was confirmed by conventional $\theta/2\theta$ X-ray diffraction (XRD, PANalytical X'pert PRO MPD) and transmission electron microscopy (TEM, FEI Tecnai). The ferroelectric properties of the films were evaluated using ferroelectric testers (FCE-1A and aixACCT, TF-2000, TOYO Corporation). The leakage current in the films was estimated using positive-up–negative-down (PUND) measurements [12]. The magnetic properties of the films were measured using a vibrating sample magnetometer (VSM; Tamakawa) at RT.

3. Results and discussion

Fig. 1 shows the $\theta/2\theta$ XRD profiles for $\text{Bi}(\text{Fe}_{1-2x}\text{Co}_x\text{Mn}_x)\text{O}_3$ [$0 \leq x \leq 0.05$] films grown on Pt/Ti/SiO₂/Si(100) substrates. At $x = 0$, the formed BiFeO₃ polycrystalline film did not have any secondary phase and the Pt electrode did not affect BiFeO₃ growth. The intensity of the (012) peak increased and the d -spacing of (012) decreased with increasing co-substitution content [Fig. 1(b)]. These results are consistent with those in our previous report dealing with Co substituted BiFeO₃ polycrystalline films [23]. The ionic radius of high-spin-state six-coordinate Co^{3+} (0.061 nm) is smaller than that of Fe^{3+} (0.0645 nm) with the same state. Thus, the decrease in d -spacing might be attributed

to Co substitution. The magnified XRD profiles [Fig. 1(c)] for pure BiFeO₃ films ($x = 0$) at around 32° showed a (104) and (110) BiFeO₃ peak split, indicating that it possesses a rhombohedral structure within the R3c space group. These two peaks became integrated as the substitution content increased and finally merged at a substitution content of $x = 0.03$. At this point, the crystal structure changed to one with a lower symmetry, such as a monoclinic or tetragonal structure. Singh et al. [8] reported a similar behavior for a Mn substitution content higher than 5 at.%. Thus, it can be considered that the co-substitution of Co and Mn in BiFeO₃ resulted in structural changes qualitatively similar to those in the case of single Co or Mn substitution.

Fig. 2 shows the surface morphology images of pure BiFeO₃ and $\text{Bi}(\text{Fe}_{0.94}\text{Co}_{0.03}\text{Mn}_{0.03})\text{O}_3$ films as obtained using atomic force microscopy. In pure BiFeO₃ films, a few nano-sized small grains were formed around a few micron-sized larger grains. The smaller grains appeared to have agglomerated by the co-substitution of Co and Mn in BiFeO₃ films, which might have suppressed the crystal orientation distribution. This is roughly consistent with the growth of the (012) peak observed in the XRD pattern. The grooves between grains became larger upon Co and Mn substitution, and a valley with a width of approximately 100 nm was formed in the $\text{Bi}(\text{Fe}_{0.94}\text{Co}_{0.03}\text{Mn}_{0.03})\text{O}_3$ film.

Fig. 3 shows the leakage current density at RT for $\text{Bi}(\text{Fe}_{1-2x}\text{Co}_x\text{Mn}_x)\text{O}_3$ [$0 \leq x \leq 0.05$] films. The leakage current density was estimated via PUND measurements carried out using short pulses in order to evaluate the leakage current under high electric fields and without electrical

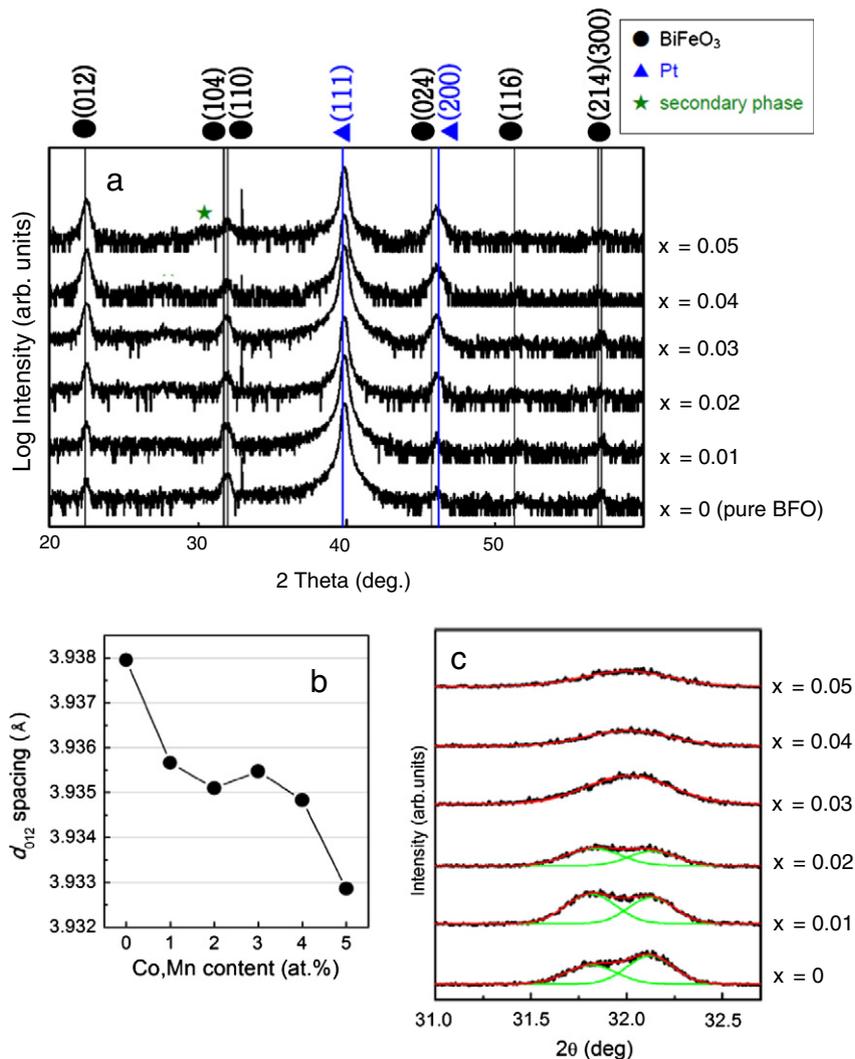


Fig. 1. (a) $\theta/2\theta$ XRD profiles for $\text{Bi}(\text{Fe}_{1-2x}\text{Co}_x\text{Mn}_x)\text{O}_3$ [$0 \leq x \leq 0.05$] films on Pt/Ti/SiO₂/Si(100) substrates; (b) d -spacing estimated from (012) peak; (c) magnified XRD profiles.

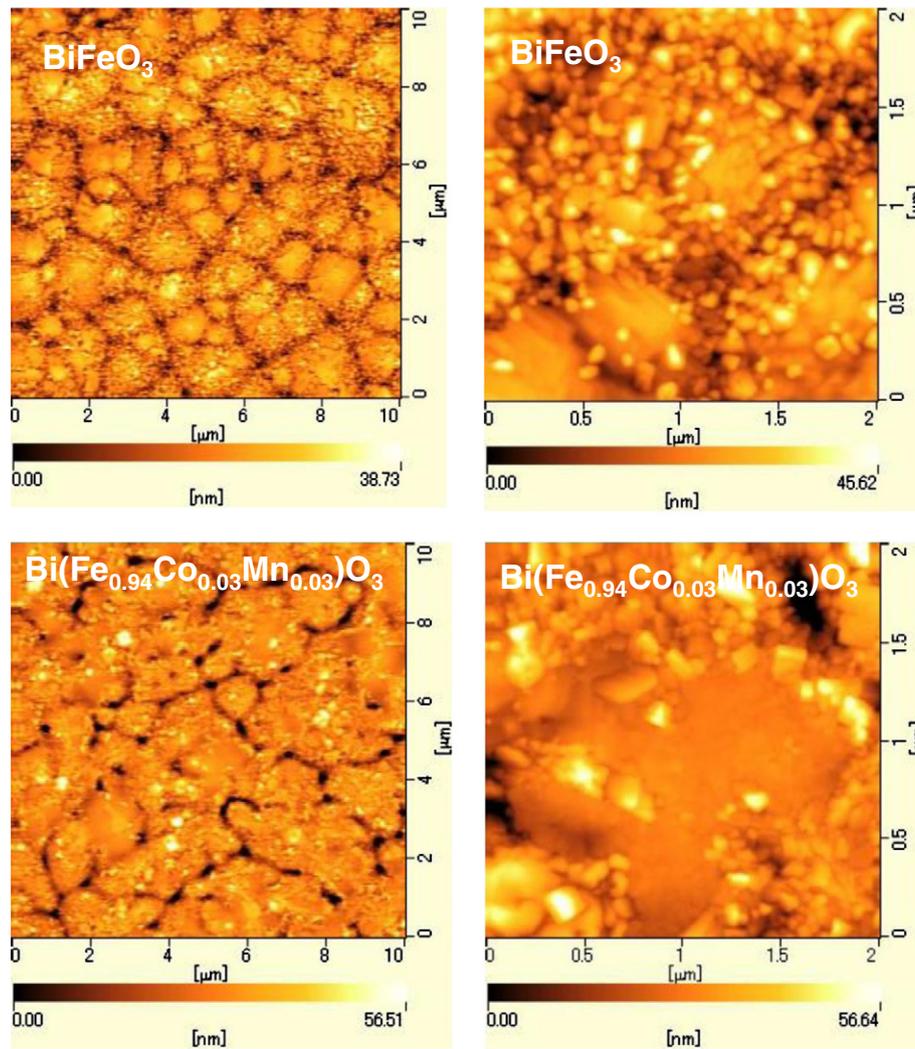


Fig. 2. Surface morphology of $\text{Bi}(\text{Fe}_{1-2x}\text{Co}_x\text{Mn}_x)\text{O}_3$ [$x = 0$ and 0.03] films. Small grains were formed around relatively larger grains in all samples and the sizes of both types of grains increased co-substitution content.

breakdown [12]. Below 0.1 MV/cm, the leakage current density of the co-substituted films was larger than that of the pure BiFeO_3 film. However, under high electric fields, the leakage current density drastically

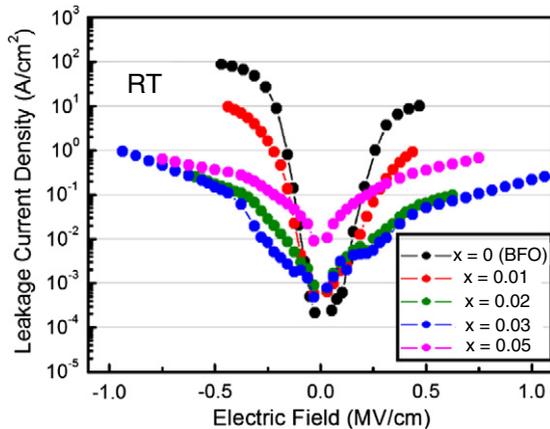


Fig. 3. Leakage current density at RT measured using the positive-up–negative-down (PUND) method for $\text{Bi}(\text{Fe}_{1-2x}\text{Co}_x\text{Mn}_x)\text{O}_3$ [$0 \leq x \leq 0.05$] films. By using the PUND method, the leakage current density under high electric fields was evaluated. The leakage current density under high electric fields effectively decreased upon substitution.

decreased with the co-substitution content, and the lowest leakage current density was observed at $x = 0.03$. The leakage current density was observed to increase at $x = 0.05$, although the current values at this composition were still smaller than those of pure BiFeO_3 ($x = 0$). Because an electric field was applied on all samples, it can be assumed that the grooves observed in the $\text{Bi}(\text{Fe}_{0.94}\text{Co}_{0.03}\text{Mn}_{0.03})\text{O}_3$ film did not reach the bottom electrode. In order to understand the leakage current mechanism, leakage current curves were fitted in accordance with various conduction mechanisms. The leakage current mechanism for the pure BiFeO_3 film was deduced to be the following: Ohmic conduction occurred when the electric field was low, and Poole–Frenkel trap limited conduction appeared as the electric field increased; thereafter, space charge limited conduction (SCLC) starts at a high electric field [7]. However, the leakage current mechanism for co-substituted film samples could not be simply fitted using a conventional leakage equation, indicating that the co-substituted films had complex leakage current conduction.

Fig. 4 shows the ferroelectric hysteresis loops at RT for $\text{Bi}(\text{Fe}_{1-2x}\text{Co}_x\text{Mn}_x)\text{O}_3$ [$0 \leq x \leq 0.05$] films. The top Pt electrode (diameter: 100 μm) was prepared by radio frequency magnetron sputtering involving the use of a metal mask. Ferroelectric measurements were performed at a relatively low frequency of 2 kHz. The ferroelectric hysteresis loops for BiFeO_3 ($x = 0$) and low ($x = 0.01$) co-substituted BiFeO_3 films could not be obtained because of large leakage current. In contrast,

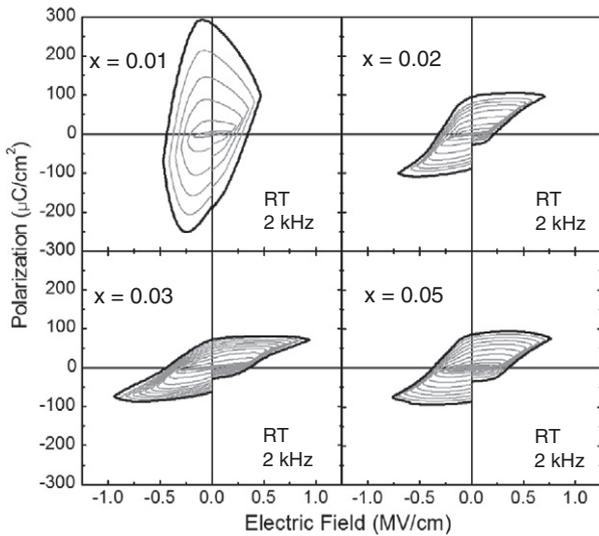


Fig. 4. RT ferroelectric hysteresis (P - E) loops at a frequency of 2 kHz for $\text{Bi}(\text{Fe}_{1-2x}\text{Co}_x\text{Mn}_x)\text{O}_3$ [$0 \leq x \leq 0.05$] films. P - E loops for $x = 0.01$ have an elliptical shape owing to large leakage current.

ferroelectric hysteresis loops for substitution values higher than $x = 0.02$ were obtained. A remanent polarization of around $\sim 80 \mu\text{C}/\text{cm}^2$ was obtained for co-substituted samples with $x = 0.03$.

Fig. 5 shows the (a) magnetization curves (M - H), (b) saturation magnetization (M_s) and magnetic coercivity (H_c) at RT versus the co-substitution content for $\text{Bi}(\text{Fe}_{1-2x}\text{Co}_x\text{Mn}_x)\text{O}_3$ [$0 \leq x \leq 0.05$] films. For the pure BiFeO_3 ($x = 0$) film, the magnetization was very small whereas M_s increased monotonically with the co-substitution content. Noticeable H_c was detected above $x = 0.03$, and this value increased with the co-substitution content. In our previous study, a $4\pi M_s$ value of around 0.042 mT at a Co content of 4 at.% was observed; this result is consistent with those presented herein. This quantitatively consistent result indicates that the enhancement in magnetization can be attributed exclusively to Co substitution. In this regard, we found that Mn substitution (via the CSD method) did not obviously increase the magnetization [12].

In order to clarify in detail the structure of Co and Mn substituted films, cross-sectional TEM observations were carried out. Fig. 6 shows (a) the cross-sectional TEM image, (b) the high-resolution TEM image of area A3 for the $\text{Bi}(\text{Fe}_{1-2x}\text{Co}_x\text{Mn}_x)\text{O}_3$ [$x = 0.05$] layer, and (c) area A4 for the Pt electrode layer. In Fig. 6(a), no apparent secondary phases such as magnetic particles can be clearly observed. The lattice contrast was roughly estimated from the lattice fringe of the high-resolution TEM images indicated as red arrows in Fig. 6(b) and (c). The lattice fringe was also measured from areas A1 and A2. The lattice constant for $\text{Bi}(\text{Fe}_{1-2x}\text{Co}_x\text{Mn}_x)\text{O}_3$ (0.400 nm) was almost consistent with XRD results, and the periodicity of the lattice fringe was almost equal for all positions. The Pt layer showed a (111)-texture structure and the lattice constant (0.22(7) nm) was almost consistent with the bulk value (0.226502 nm). The composition was confirmed by nano-beam EDX for which the beam diameter was around 30 nm. The measurement was carried out at several points. The typical observed areas are indicated as blue circles denoted by B1, B2, and B3. The average concentration of Bi, Co, Mn, and Fe was 59, 2, 2, and 37 at.%, respectively, as estimated from the various areas. These values are almost consistent with the nominal composition of the precursor used in the experiments. It can thus be concluded that Mn suppressed the leakage current density and Co increased the magnetization, even though Co and Mn were co-substituted in BiFeO_3 . This indicates that co-substitution can potentially be employed for independently tuning the characteristics of multiferroic BiFeO_3 .

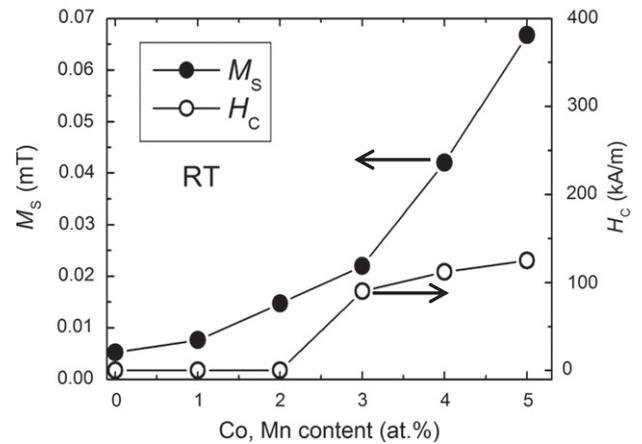
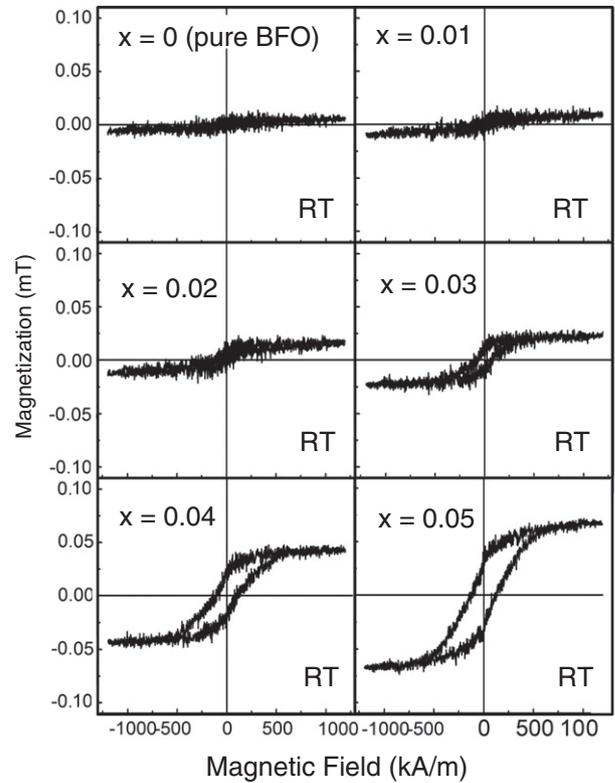


Fig. 5. Magnetic hysteresis (M - H) loops for $\text{Bi}(\text{Fe}_{1-2x}\text{Co}_x\text{Mn}_x)\text{O}_3$ [$0 \leq x \leq 0.05$] films. M - H loops were measured at RT. Saturation magnetization (M_s) and magnetic coercive fields (H_c) were evaluated from M - H loops.

4. Summary

Co and Mn co-substituted BiFeO_3 [$\text{Bi}(\text{Fe}_{1-2x}\text{Co}_x\text{Mn}_x)\text{O}_3$ ($0 \leq x \leq 0.05$)] polycrystalline films were fabricated on Pt/Ti/SiO₂/Si(100) substrates. The intensity of the (012) XRD peak increased and the peak shifted to higher angles (i.e. decrease in d_{012} -spacing) with increasing co-substitution content owing to the reduction in the ionic radius of B-sites in BiFeO_3 . The (104) and (110) XRD peaks, on the other hand, merged when the co-substitution content was higher than $x = 0.03$, indicating that the crystal structure became highly symmetrical. The co-substitution of Co and Mn in BiFeO_3 resulted in structural changes qualitatively similar to those resulting from single Co or Mn substitution. The leakage current density of the films under high electric fields decreased with the co-substitution content up to $x = 0.03$. Further, ferroelectric hysteresis loops for the films were measured at a relatively low frequency of 2 kHz at RT. The M_s value for the films increased with the co-substitution content, and a noticeable H_c value was observed at co-

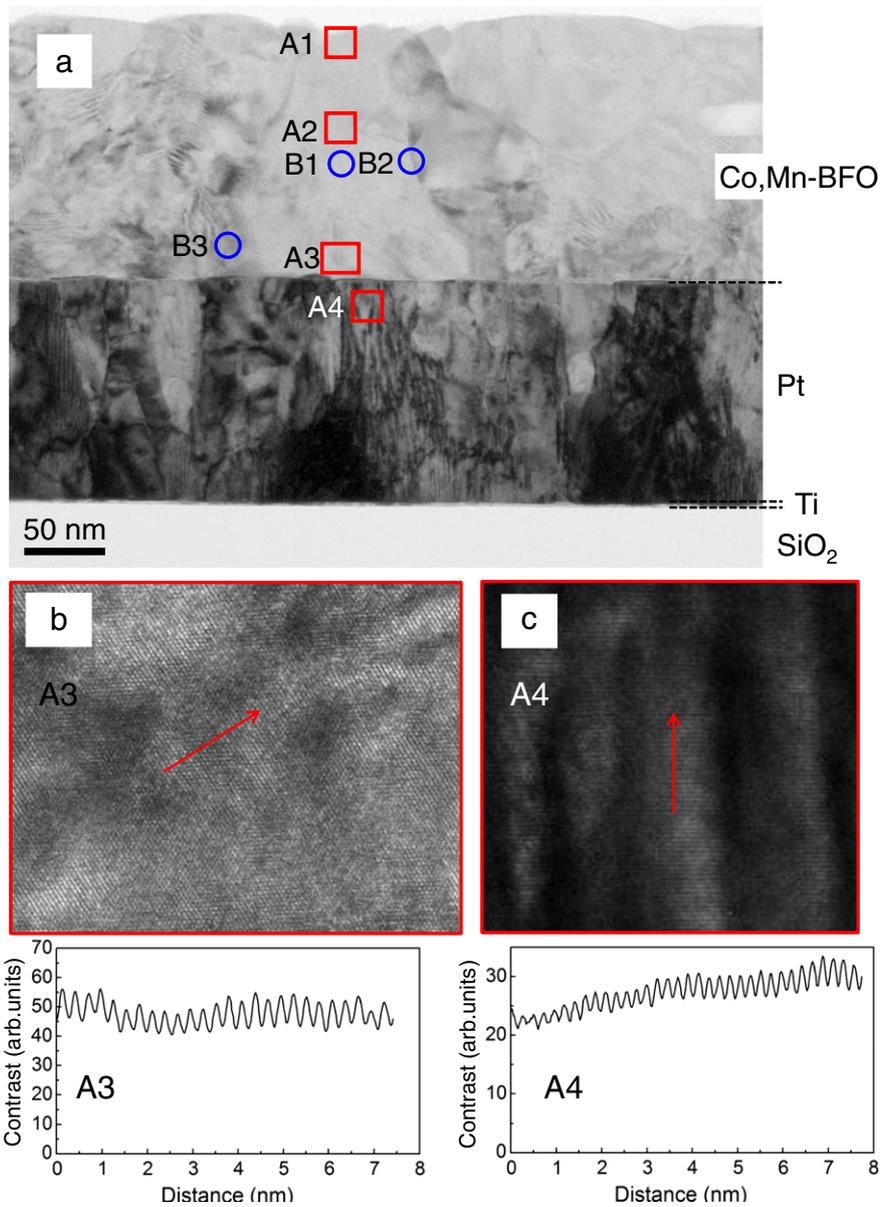


Fig. 6. Cross sectional transmission electron microscopy observations for $\text{Bi}(\text{Fe}_{0.9}\text{Co}_{0.05}\text{Mn}_{0.05})\text{O}_3$ films.

substitution content higher than $x = 0.03$. Cross-sectional TEM observations of the films revealed that they were homogeneous. Nano-beam EDX showed that Co and Mn were distributed in the films and the average concentration of Bi, Co, Mn, and Fe was 59, 2, 2, and 37 at.%, respectively. These values were almost consistent with the nominal composition of the precursor solution used. These results indicate that Co and Mn play significant roles in determining the properties of co-substituted BiFeO_3 films.

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