Structural and magnetic properties of pulsed laser deposited (x)$CoFe_2O_4$ + (1-x)$Ba_{0.8}Sr_{0.2}TiO_3$ nanocomposite thin films

C. M. KANAMADI, H. K. YANG, B. K. MOON, B. C. CHOI, J. H. JEONG*, KWANG HO KIM[a]
Department of Physics, Pukyong National University, Busan 608-737, Korea
[a]*School of Materials Science and Engineering, Busan National University, Busan 609-735, Republic of Korea*

Magnetoelectric (ME) thin films viz. (x) $CoFe_2O_4$ + (1-x) $Ba_{0.8}Sr_{0.2}TiO_3$ where x = 0.15 and 0.45 have been synthesized on Pt(111)/Ti/SiO_2/Si substrate using pulsed laser deposition (PLD) method. These films were grown by using single target containing both ferromagnetic and ferroelectric phases. The presence of constituent phases in the composites were confirmed by X – ray diffraction and EDAX studies. The surface morphology and thickness were studied by field emission scanning electron microscope (FE-SEM) and atomic force microscope (AFM). The magnetic hysteresis behaviour was studied with the help of vibrating sample magnetometer (VSM). Our results show that it is possible to grow biphasic ME nanocomposite by using single target containing both ferromagnetic and ferroelectric phases.

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1. Introduction

Composite materials which exhibit simultaneous ferromagnetic and ferroelectric properties have been the focus of scientists due to their unique coupling between different fields such as magnetic, electric and stress. They possess great potential for applications in devices such as energy converters, sensors and actuators [1-4]. Magnetoelectric (ME) composite is a kind of multiferroic material in which ferromagnetic and ferroelectric phases exist. The figure of merit for ME materials is the magnetoelectric voltage coefficient (dE/dH) which represents the amount of polarization induced under an applied magnetic field. That is, when a magnetic field is applied to a composite, the magnetic phase changes its shape magnetostrictively. The strain is then passed along to the polarization phase, resulting in an electric polarization [5, 6]. Thus, ME effect results from the cross interaction between different ordering of the two phases in the composite. The ME output in composites depending on the composite microstructure and coupling interaction across magnetic – piezoelectric interfaces. Neither the ferromagnetic phase nor the ferroelectric phase has the ME effect, but the composite of these two phases have remarkable ME effect [7, 8].

In these days research interest is attracted towards nanocomposite than bulk materials due to the significant possibility of microstructure – controllable ME effect and drives the magnetoelectric devices towards technological applications in miniaturization and integration. In comparison to bulk ME composites, the nanostructure thin film provide more degrees of freedom such as lattice strain or interlayer interaction, to modify the ME behavior. It also offers a way to investigate the physical mechanism of ME effect in nanoscale. Up to now, some relative investigations have been done on several composite nanofilms developed by various physical and chemical methods. Recently, the work has been reported on magnetoelectric effect in multiferroic $BaTiO_3$ – $CoFe_2O_4$ nanostructures [9].

In this work, we successfully synthesized magnetoelectric nanocomposite thin films of (x) $CoFe_2O_3$ + (1-x) $Ba_{0.8}Sr_{0.2}TiO_3$ where x = 0.15 and 0.45 by pulsed laser deposition method. It is well known that $(Ba,Sr)TiO_3$ exhibits excellent dielectric properties and $CoFe_2O_4$ is a best magnetostrictive material with the largest magnetostriction coefficient. The work on such type of nanocomposite synthesized by pulsed laser deposition, using separate targets of ferromagnetic and ferroelectric was published [10, 11]. But in the present work, we made single target of two phases and used it for preparation of thin films.

2. Experimental

In order to prepare composite target, the individual phases were synthesized by solid state reaction method. AR grade CoO and Fe_2O_3 were used to synthesize $CoFe_2O_4$ and $BaCO_3$, $SrCO_3$ and TiO_2 were used to synthesize $Ba_{0.8}Sr_{0.2}TiO_3$. The precursor powders were mixed thoroughly and ground into fine powder by using planetary mill. The grounded powders of $CoFe_2O_4$ and $Ba_{0.8}Sr_{0.2}TiO_3$ were sintered at 1000 ^oC and 1100 ^oC for 4 hours respectively. The composite of these two phases (x) $CoFe_2O_4$ + (1-x) $Ba_{0.8}Sr_{0.2}TiO_3$ where x = 0.15 and 0.45 were mixed by using planetary mill. These composites were pressed by applying pressure of 70 MPa in a hydraulic press and finally sintered at 1200 °C for 4 hours. These sintered targets of 25 mm diameter and 5mm thickness were used as a target to synthesize thin films.

The nanocomposite thin films of (x) $CoFe_2O_4$ + (1-x) $Ba_{0.8}Sr_{0.2}TiO_3$ were grown on Pt(111)/Ti/SiO_2/Si substrate by pulsed laser deposition using KrF excimer laser of 248 nm wavelength and 5 Hz in repetition rate. A laser fluency of 200 mJ with an energy density of 3 J/cm^2 was employed. The distance between target and substrate was maintained at 35mm. During deposition, the substrate temperature was kept constant at 650 °C in an oxygen pressure of 100 mTorr. The composite films were annealed in situ of same atmosphere and temperature for 10 minutes then cooled to room temperature.

The crystalline phase of the films was analyzed by X-ray diffraction (XRD) with CuKα radiation (λ = 1.5554 Å) and atomic force microscopy (AFM). The surface morphology was studied by using a field emission scanning electron microscope (FESEM). Magnetic hysteresis was carried out using a vibrating sample magnetometer (VSM) at room temperature with a maximum applied field of 20 kOe.

3. Results and discussion

Fig.1 shows the X-ray diffraction pattern of x = 0.45 nanocomposite thin film. From figure it is seen that two evident sets of peaks are observed corresponding to cubic spinel $CoFe_2O_4$ (JCPDS No.22-1086) and perovskite $Ba_{0.8}Sr_{0.2}TiO_3$ (JCPDS No.00-044-0093). All peaks are identified and they are compared with literature reports. The prominent peak of the ferrite phase is (311) and that of ferroelectric is (101). All the peaks have been identified corresponding to their parent phases and it is clear that there is no intermediate phase was formed in any of the composites. The lattice constant for the cubic cobalt ferrite was 8.3840 Å and a = 3.9849 Å, c = 3.9980 Å (c/a = 1.003) for the tetragonal $Ba_{0.8}Sr_{0.2}TiO_3$ phase. The intensity of ferrite peak increased with ferrite content in the composite.

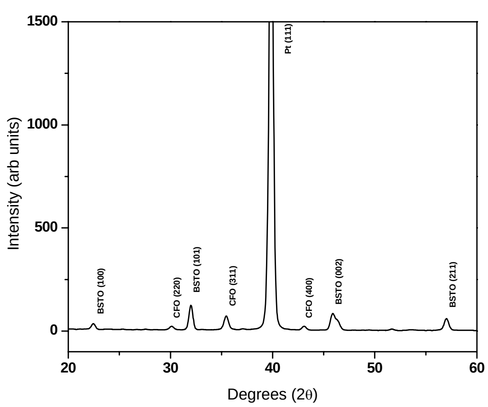

Fig. 1. XRD pattern of 45% $CoFe_2O_4$ + 55% $Ba_{0.8}Sr_{0.2}TiO_3$ composite.

The thickness and microstructure of the as-deposited films were determined by using FESEM. The surface morphology of the films was shown in Fig.2. The films were fractured into two equal halves and cross – sectional SEM micrographs were taken. The thickness of all the films measured to be about 200 nm. Figure 3 shows an atomic force microscopy surface image of CFO – BSTO film. The composite film clearly contains well defined CFO (light regions) and BSTO (dark regions) phases. The root mean square roughness is around 5.5 nm.

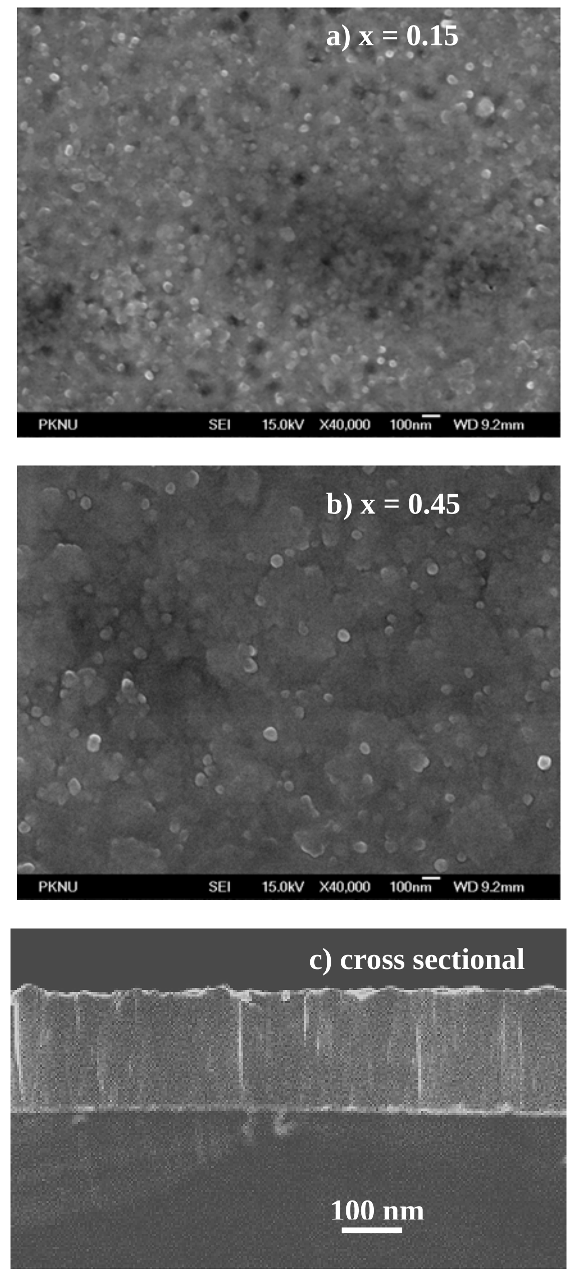

Fig. 2. FESEM image of a) 0.15 $CoFe_2O_4$ + 0.85 $Ba_{0.8}Sr_{0.2}TiO_3$ composite and b) 0.45 $CoFe_2O_4$ + 0.55 $Ba_{0.8}Sr_{0.2}TiO_3$ composite and c) cross – sectional.

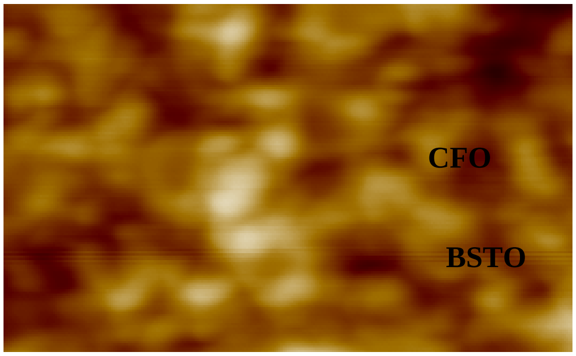

Fig. 3. Atomic force microscopy image of 0.45 $CoFe_2O_4$ + 0.55 $Ba_{0.8}Sr_{0.2}TiO_3$ composite

In literature, some researchers [10, 11] synthesized nanocomposite by using separate target of ferromagnetic and ferroelectric phase and nobody has tried to synthesize such nanocomposite by using single target. In this work, we used a target containing both phases, in required molar ratio and successfully synthesized films. The microscopical element analysis using the energy dispersive X – ray (EDAX) spectra confirmed both the phases in the composite (Fig. 4).

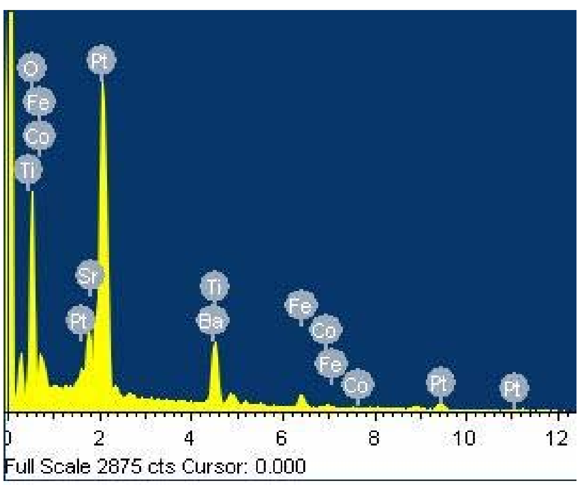

Fig.4 Area scan EDX pattern showing the presence of all elements.

Fig. 5 shows the magnetic hysteresis loops with the magnetic field parallel and perpendicular to the substrate surface at 300 K for x = 0.15, 0.45 and 1 respectively. It is found that all films possess coercivity of relatively high values, which are much higher than that of the reported values of bulk $CoFe_2O_4$ material (≈ 1.0 kOe) [12, 13]. It can be expected that the reduced size and dimensions of $CoFe_2O_4$ nanoparticles may change the magnetization and reversal mechanism, leading to an enhancement of coercivity. Both saturation magnetization (Ms) and coercivity (Hc) of the composite films increased with increasing in ferrite content because the magnetic contacts increase with ferrite content and result in increase of the net magnetization.

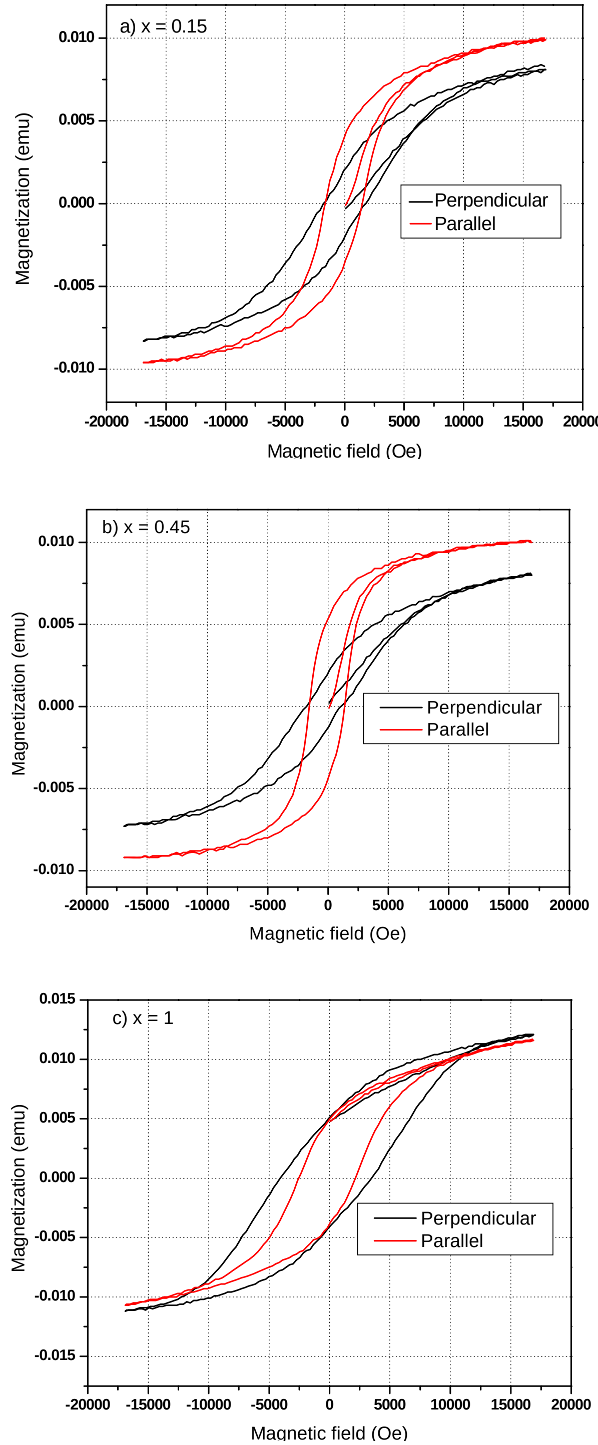

Fig. 5. Magnetic hysteresis loop of (x) $CoFe_2O_4$ + (1-x) $Ba_{0.8}Sr_{0.2}TiO_3$ composite with a) x = 0.15, b) x = 0.45 and c) x = 1 (pure ferrite).

Conclusions

In conclusion, we have successfully grown $CoFe_2O_4$ - $Ba_{0.8}Sr_{0.2}TiO_3$ magnetoelectric nanocomposite thin films by using single target containing both phases. These materials can be ideal candidates for the preparation of truly integrated passive filters due to the presence of both ferroelectric and ferromagnetic phases.

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*Corresponding author: jhjeong@pknu.ac.kr