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Effects of Mg doping on multiferroic properties of bilayered $Co_{1-x}Mg_xFe_2O_4$/PMN–PT composite thin films

J.M. Li[a,b], G.Z. Li[a], Z.H. Bai[b], L.L. Wang[c], M. Feng[a,*], H.B. Li[a,*]

[a] Key Laboratory of Functional Materials Physics and Chemistry of the Ministry of Education, Jilin Normal University, Siping 136000, PR China
[b] School of Materials Science and Engineering, Changchun University of Science and Technology, Changchun 130022, PR China
[c] College of Science, Changchun University, Changchun 130022, PR China

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Abstract

Multiferroic $Co_{1-x}Mg_xFe_2O_4$/0.68Pb$(Mg_{1/3}Nb_{2/3})O_3$–0.32PbTiO$_3$ (CMFO/PMN–PT) bilayered thin films were prepared on Pt/Ti/SiO$_2$/Si substrates by a simple sol–gel spin-coating technique. The effects of the Mg content on the electrical, magnetic, and magnetoelectric (ME) properties of the CMFO/PMN–PT bilayered thin films were investigated. It was found that increasing the Mg concentration could obviously improve the ME properties of the bilayered thin films. The results indicated the Mg doping provides an effective way to obtain the high ME response in the CFO/piezoelectric bilayered thin films.

Keywords: A. Sol–gel processes; B. Nanocomposites; C. Magnetic properties; Magnetoelectric coupling

1. Introduction

Multiferroic materials have received considerable attention during the past decades due to their potential applications in multiple-state memories, actuators, sensors, microwave systems, and spintronic devices [1–4]. These materials not only exhibit ferroelectric and magnetic orders, but also have a magnetoelectric (ME) coupling effect between the electric and magnetic polarizations, that is, a spontaneous electric polarization induced by an external magnetic field or a magnetization induced by an applied electric field. In the single phase compounds, however, the electric polarization and magnetization interact weakly with each other or their ME response occurs at low temperatures for practical applications, which makes composite materials with combination of magnetic and ferroelectric phases become an alternate way to enhance the ME effect [5,6]. With much attention paid to composite multiferroic thin films in recent years due to that their phase composition and connectivity could be modified or controlled at the nanoscale, and the ME physical mechanism could be studied in nanoscale.

As known that the ME response in multiferroic composite is facilitated by an elastic interaction between ferroelectric and ferromagnetic components via piezoelectric effect and magnetostriction [3]. Thus, the high piezoelectric and magnetic sensitivities are essential to acquire a large ME signal. Cobalt ferrite $CoFe_2O_4$ (CFO) is well known for its largest magnetostriction in all the spinel ferrites along with a moderate value of saturation magnetization. However, the ME voltage coefficient was far smaller than the predicted value due to the poor ME coupling between the ferroelectric and CFO phase. This feature was attributed to the large magnetic anisotropy and coercivity of CFO which restricted the domain wall motion process [7]. Substitution of Mg for Co at the tetrahedral site in CFO was considered to reduce magnetic anisotropy and coercivity while the value of magnetostriction coefficients kept a constant [8,9]. The substitution of Mg for Co in CFO is a good choice for the magnetostrictive phase due to its higher magnetostrictive response. $(1-x)Pb(Mg_{1/3}Nb_{2/3})O_3-xPbTiO_3$ (PMN–PT) with a larger piezoelectric response than $Pb(Zr_{0.52}Ti_{0.48})O_3$ (PZT) has become a better candidate for the ferroelectric phase [10]. Accordingly, it is of considerable interest to investigate $Co_{1-x}Mg_xFe_2O_4$/0.68Pb$(Mg_{1/3}Nb_{2/3})$

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*Corresponding authors. Tel.: +86 434 3292210; fax: +86 434 3292233.
E-mail addresses: mingfeng@jlnu.edu.cn (M. Feng), lihaibo@jlnu.edu.cn (H.B. Li).

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O_3–0.32$PbTiO_3$ (CMFO/PMN–PT) composite thin films with an optimized composition with varying x from 0 to 0.20. Up to now, to the best of our knowledge, the experimental research on $Co_{1-x}Mg_xFe_2O_4$/PMN–PT composite thin films has not been reported yet. In this work, we report the fabrication of CMFO/PMN–PT bilayered thin films was fabricated on Pt/Ti/SiO_2/Si substrates via a simple sol–gel process. The influence of the Mg content of CMFO layer on electrical, magnetic, and ME coupling properties of these bilayered films is systematically investigated.

2. Experimental

Multiferroic CMFO/PMN–PT bilayer films with different Mg contents were grown on (111)Pt/Ti/SiO_2/Si substrates via a simple sol–gel spin-coating method. The PMN–PT precursor solution was obtained as before [11]. $Pb(CH_3COO)_2 \cdot 3H_2O$, $Mg(CH_3COO)_2 \cdot 4H_2O$, $Nb(OC_2H_5)_5$, and $Ti(OC_4H_9)_4$ were dissolved in 2-methoxyethanol to obtain the precursor solution of $0.68Pb(Mg_{1/3}Nb_{2/3})O_3$–$0.32PbTiO_3$. The $Co(NO_3)_2 \cdot 6H_2O$, $Mg(NO_3)_2 \cdot 6H_2O$ and $Fe(NO_3)_3 \cdot 9H_2O$ of AR grade were dissolved in 2-methaoxyethanol to get a precursor solution of Mg substituted cobalt ferrite $Co_{1-x}Mg_xFe_2O_4$ ($x=0.0$, 0.05, 0.10, 0.15, and 0.20). The final concentration of the PMN–PT and CMFO precursor solution was diluted to 0.4 M and 0.2 M, respectively. Firstly, the PMN–PT precursor solutions were spin coated on a Pt (111)/Ti/SiO_2/Si substrate at 4000 rpm for 30 s and pyrolyzed on a hot plate at 450 °C for 5 min. The pyrolyzed thin films were performed by repeating above processes to obtain a desired thickness, and finally annealed at 650 °C for 10 min by rapid thermal annealing (RTA). Secondly, the CMFO precursor solutions were spin coated repeatedly on the PMN–PT layer until the CMFO layer with a desired thickness was achieved via the same process with that of CFO films as reported previously [12]. The second step of the annealing process was performed to crystallize the top CMFO layer at 750 °C for 10 min by RTA. Five bilayered CMFO/PMN–PT thin films with different Mg content were fabricated on Pt(111)/Ti/SiO_2/Si substrates through the sol–gel method.

The phase of the bilayered thin films and its orientation was analyzed by X-ray diffraction (XRD, Rigaku, D/max-2500/PC). The morphology and thickness of the films were observed using field emission scanning electron microscopy (FE-SEM, Hitachi, S-4800). The ferroelectric hysteresis loops of the bilayered thin films were measured by ferroelectric tester (Precision Multiferroic, Radiant Technologies). The magnetic measurements were performed with vibrating sample magnetometer (VSM, Lake Shore, M-7407). The dielectric properties of the composite thin films at room temperature were analyzed by precision impedance analyzer (Agilent, 4294A). The ME coupling properties were measured by the applied alternating magnetic field (H) of 10 Oe over a prescribed frequency of 1 kHz under various dc bias magnetic field (H_{dc}) of up to 7 kOe. The voltage signal generated from the films induced by the in-plane magnetic field was measured through a lock-in amplifier (SRS Inc., SR850, Sunnyvale, CA). All measurements were performed at room temperature.

3. Results and discussion

Fig. 1 shows the XRD patterns of the CMFO/PMN–PT bilayered thin films deposited on Pt(111)/Ti/SiO_2/Si substrates. As can be seen, the perovskite PMN–PT peaks are quite obvious, but the spinel CMFO peaks are much weak (see the bottom pattern for a clear illustration of the CMFO peaks). This is because that the PMN–PT layer has a higher average atomic number than that of the CMFO layer, and the CMFO layer is not well-crystallized at the low annealing temperature applied. It is found that all the peaks correspond to CMFO and PMN–PT compositional phases without any impurity phase. The PMN–PT layer is crystalline with highly (111) preferred orientation through the two-step annealing process, which the orientation controlling is the same as the single phase PMN–PT films. The PMN–PT films on the (111)-oriented Pt tend to take the (111) orientation due to the lattice matching effect. The CMFO phase exhibits polycrystalline structures not having evident preferential crystallographic orientations.

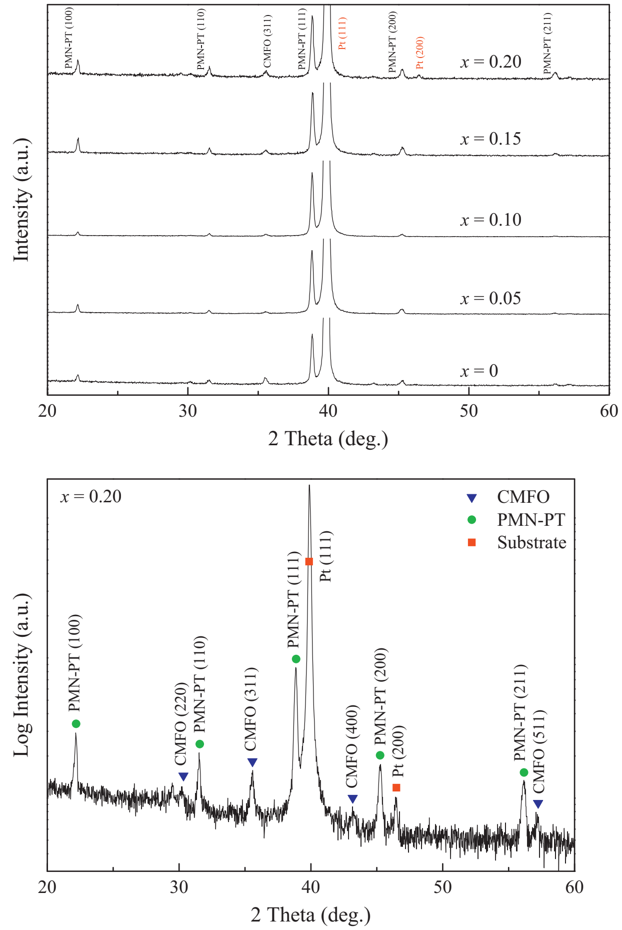

Fig. 1. XRD patterns of the $Co_{1-x}Mg_xFe_2O_4$/PMN–PT bilayered thin films with different Mg contents in CMFO layer. As an example, the bottom pattern was plotted with the log scale for clear illustration of all peaks in the sample with $x=0.20$.

As shown in Fig. 2, the cross-sectional scanning electron microscopy images of CMFO/PMN–PT bilayered thin films clearly illustrate the layered structures with clear interfaces, indicating that the CMFO/PMN–PT films are well grown on the Pt(111)/Ti/SiO_2/Si substrates. The thickness of the PMN–PT film is about 300 nm, in which the thicknesses of the PMN–PT layers in various samples are almost the same. The CMFO layer thicknesses were estimated to be about 320, 265, 270, 260, and 265 nm for $x=0$, 0.05, 0.10, 0.15, and 0.20, respectively. The polarization versus electric field (*P*–*E*) hysteresis loops for CMFO/PMN–PT bilayered thin films at maximum applied voltage of 10 V are shown in Fig. 3. The well-defined ferroelectric loops are observed in all the bilayered thin films. The remnant polarization P_r and coercive field E_c are 22.5 and 75.8 kV/cm at an applied voltage of 10 V, respectively, for the sample with $x=0.20$. The coercive field is much higher than that of reported pure PMN–PT films [11], because of the clamping effect resulted from between

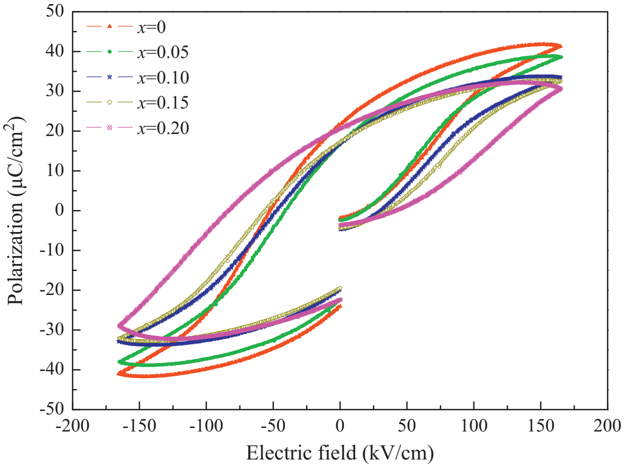

Fig. 3. Polarization vs. electric field (*P*–*E*) hysteresis loops for CMFO/PMN–PT bilayered thin films at maximum applied voltage of 10 V.

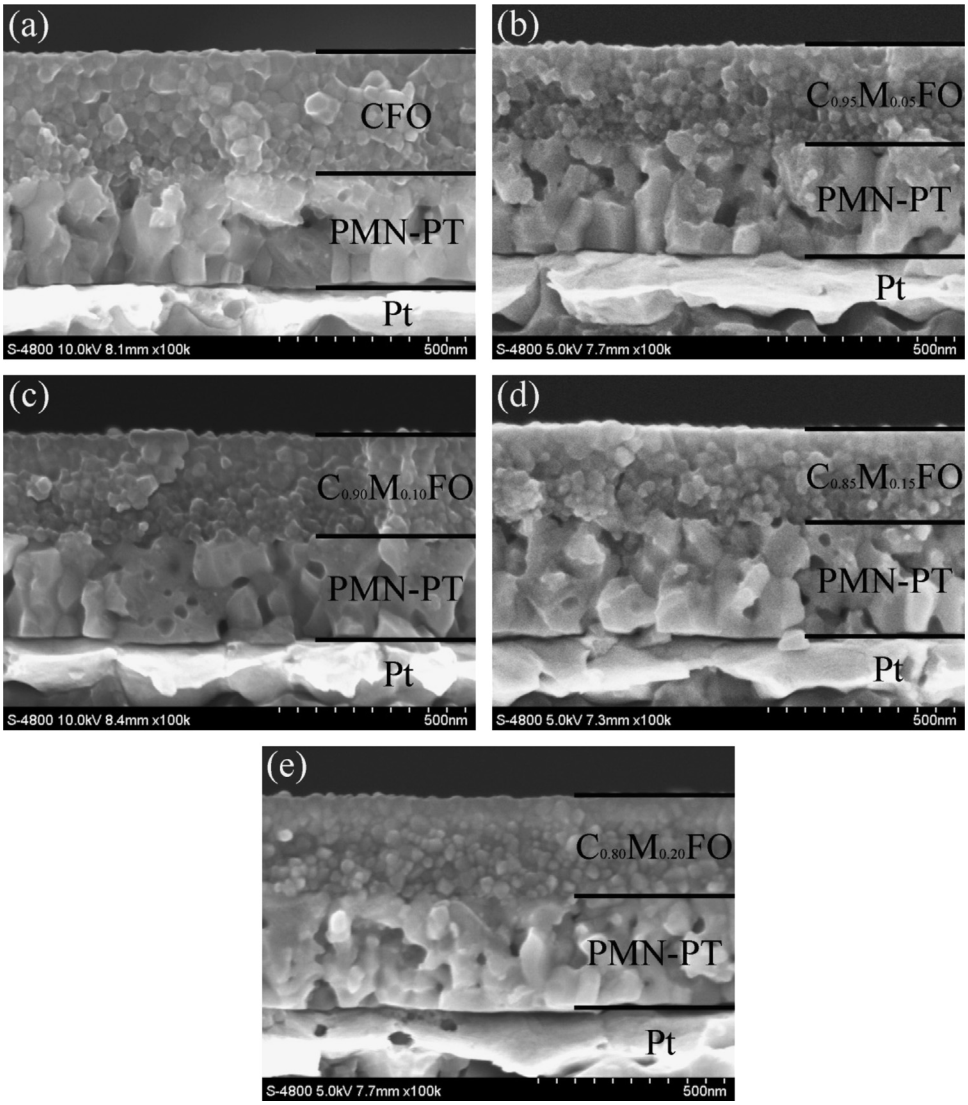

Fig. 2. Cross-sectional SEM images of $Co_{1-x}Mg_xFe_2O_4$/PMN–PT bilayered films with different compositions *x* (a) 0.0, (b) 0.05, (c) 0.10, (d) 0.15, and (e) 0.20, respectively, grown on the Pt/Ti/SiO_2/Si substrate.

the top CMFO layer and the substrate during the switching of ferroelectric domains, and the CMFO layer with low resistance also consumed some voltage [13].

Fig. 4 displays the frequency dependence of the dielectric constant of the CMFO/PMN–PT bilayered thin films. As can be seen, all the composite thin films exhibit a high dielectric constant. The dielectric constant decreases rapidly at lower frequencies and remains constant at higher frequencies. This result reported previously by many researchers can be explained on the basis of Maxwell–Wagner polarization theory [14,15]. In multiferroic composites, Maxwell–Wagner polarization at the interface of ferroelectric/ferromagnetic nanostructures would lead to the strong dependence of the dielectric constant especially at low frequency. It has been observed that the dielectric constant decreases as the Mg content increases from 0 to 0.20. This difference is attributed to space charge polarization due to inhomogeneous dielectric structure. The inhomogeneties presented in the structure may result from the porosity, stoichiometry and grain structure. Moreover, the samples sintered at 750 °C are highly dense as concluded by FE-SEM measurements. Hence, the stoichiometry and grain structure may be one of the reasons for lower dielectric constant of CMFO as compared to CFO.

Fig. 5(a) shows the typical magnetic hysteresis loops of the bilayered thin films measured with fields up to 15 kOe by applying magnetic fields parallel to the film plane (in plane). The saturation magnetization M_s and coercivity H_c as a function of Mg content for the CMFO/PMN–PT bilayered thin films are shown in Fig. 5(b). The H_c decreases with increasing the Mg content, while the M_s reaches a maximum value at $x=0.10$ and then decreases as $x>0.10$. The magnetic properties of the ferrite material mainly come from the super-exchange interaction between the tetrahedral (A) and octahedral (B) lattice sites [16]. In the spinel structure of $\mathrm{Co}_{1-x}\mathrm{Mg}_x\mathrm{Fe}_2\mathrm{O}_4$ ferrite, the non-magnetic Mg ions have a tendency to occupy the A-sites and Co ions occupy B-sites, while Fe ions exist at both A and B-sites [17]. As the Mg concentration increases with a corresponding decrease of the Fe ions at A-sites, which results in a decrease in the magnetic moment at A-sites. The coupling of the net magnetic moment is decided by $M=M_B-M_A$, which makes the net magnetic moment increase, leading to the increase of the magnetization. As the Mg content increases further, the magnetic Co ions decrease, leading to the weakening of the superexchange interaction between A and B sites. This causes a decrease in the magnetization. Consequently, the M_s increases firstly and then decreases with increasing the Mg content. The decrease of H_c can be attributed to that the decrease of the magnetocrystalline anisotropy caused by the non-magnetic Mg ions instead of Co ions [8,18].

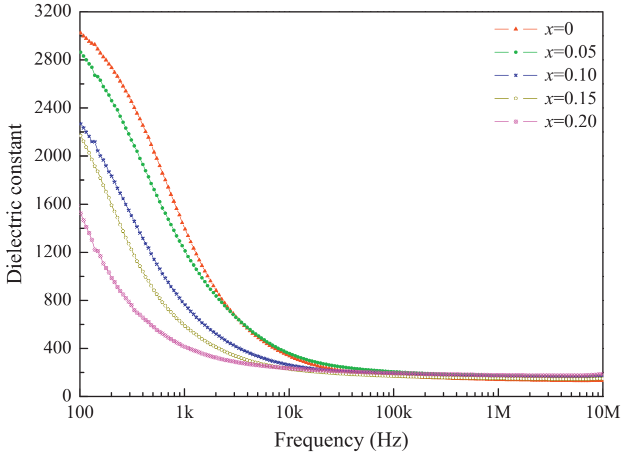

Fig. 4. The frequency dependence of the dielectric constant of the CMFO/PMN–PT bilayered thin films.

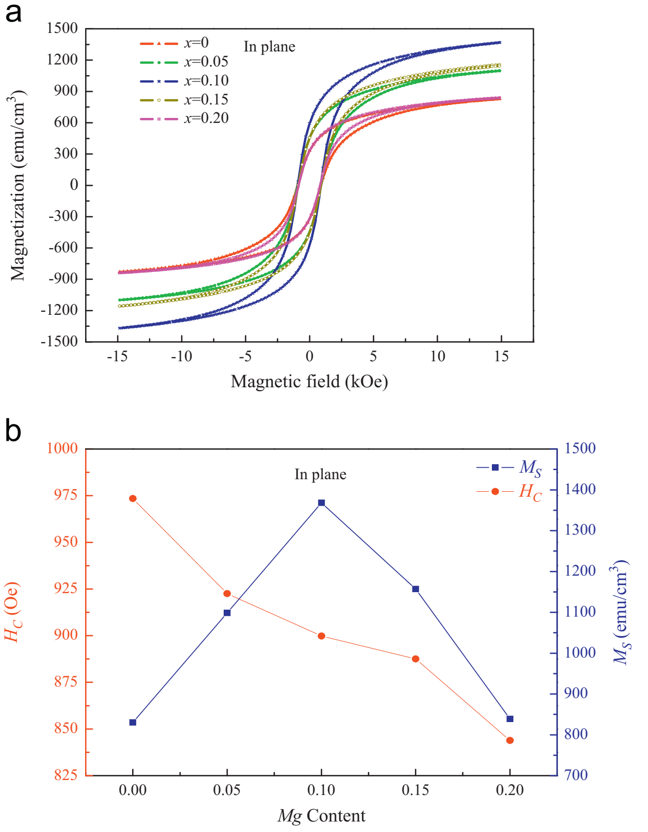

Fig. 5. (a) In-plane magnetic hysteresis loops and (b) saturation magnetization and coercivity as a function of Mg content for the CMFO/PMN–PT bilayered thin films.

The ME voltage coefficient measurements were carried out by applying both constant (H_{dc}) and alternating (δ_H) magnetic fields parallel to the film plane. Fig. 6 depicts the change in the voltage increment δV induced by the in-plane dc bias magnetic field H_{dc} in the CMFO/PMN–PT bilayered films. It is seen clearly that the δV increases monotonically with increasing H_{dc} and does not reach the saturation at a high magnetic field due to the clamping effect in the films from the substrate. Fig. 6 shows an obvious difference among these CMFO/PMN–PT bilayer films. The δV increases as the Mg content increases to 0.10 and then decreases with the further increase of Mg content. The maximal in-plane ME coupling coefficient, defined as $\alpha_{E31}=\delta E/\delta H_{ac}=\delta V/\delta H_{ac}t$ (t being the total thickness of the bilayered thin films), is found to be 9.88, 11.42, 16.52, 15.19 and 13.06 mV/cm Oe when the Mg content increases from 0 to 0.20, respectively. The maximal ME

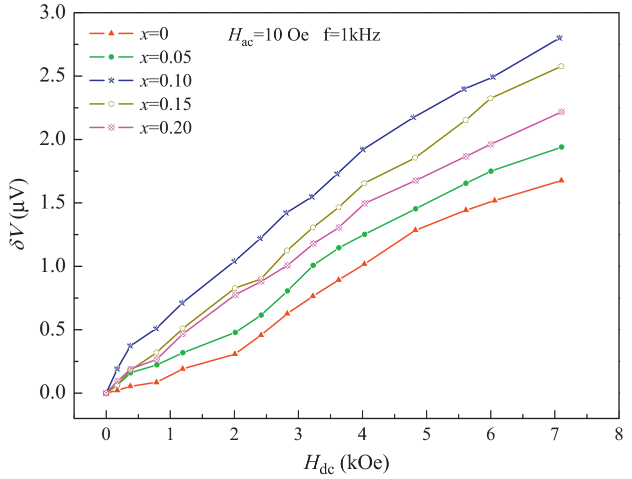

Fig. 6. Magnetically induced voltage increment δV as a function of dc bias magnetic field H_{dc} at 1 kHz for the CMFO/PMN–PT bilayered thin films.

coefficient of 16.52 mV/cm Oe for a sample with $x=0.10$, is about four times larger than that ($\alpha_{E31}=4$ mV/cm Oe) Ryu et al. reported in the NFO/PZT bilayered films [19]. This result indicates that the CMFO/PMN–PT bilayered film is a good candidate as a working material for ME random access memories and ME microsensors.

It is known that low magnetic anisotropy favors the magnetization mechanism in the crystal, such as domain wall movement and domain rotation that are the key factors for magneto-mechanical interaction to improves the ME coupling. Here, substitution of Mg for Co at the tetrahedral site in CFO is observed to improve the ME coupling of the CMFO/PMN–PT composite thin films. The Mg substitution can affect the structure of CFO, which can lead to the change of magnetization due to the coupling between the structure and magnetism. Therefore, it provides an effective way to obtain large direct ME effect in the CFO/piezoelectric bilayered thin films.

4. Conclusions

In summary, CMFO/PMN–PT bilayered thin films with different Mg contents have been grown on Pt/Ti/SiO_2/Si substrates. X-ray diffraction analysis showed that all the peaks corresponded to CMFO and PMN–PT compositional phases without any impurity phase. The bilayered thin films also exhibited good ferroelectric, piezoelectric and magnetic properties, as well as direct ME effect. The ME coupling coefficient increased firstly and then decreased with increasing the Mg content. Substitution of Mg for Co at the tetrahedral site in CFO is observed to improve the ME coupling of the CMFO/PMN–PT composite thin films. These results are interesting for technological applications on the next-generation multi-functional devices based on direct ME effect.

Acknowledgments

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