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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

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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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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 0.68$Pb(Mg_{1/3}Nb_{2/3})O_3$–0.32$PbTiO_3$. 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.

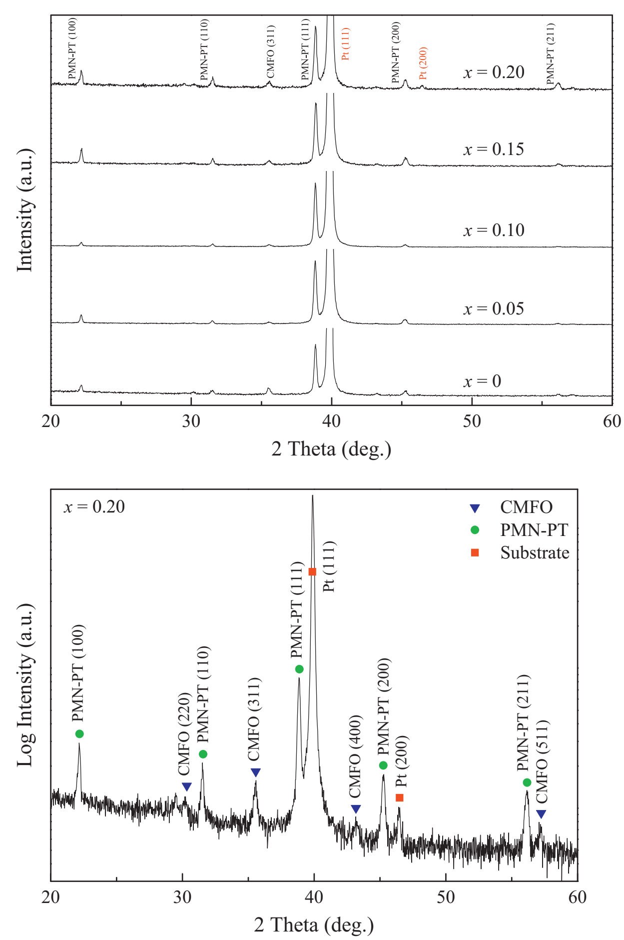

Fig. 1. XRD patterns of the $Co_{1-x}Mg_xFe_2O_4$/PMN–PT bilayered thin films with different Mg contents in CMFO layer. As an example, the bottom pattern was plotted with the log scale for clear illustration of all peaks in the sample with x=0.20.