



Lead-free BLTO/NMFO magnetoelectric composite films prepared by the sol-gel method

Min Shi*, Guannan Qiu, Ruzhong Zuo, Yudong Xu, Lei Wang, Yafeng Shi, Xiaofeng Zhang

School of Materials Science and Engineering, Hefei University of Technology, 230069 Hefei, China

ARTICLE INFO

Keywords:

Sol-gel method
Magnetoelectric coupling
Lead-free composite film

ABSTRACT

The lead-free ferroelectric films of $\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$ (BLTO) and ferromagnetic films of $\text{Ni}_{1-x}\text{Mn}_x\text{Fe}_2\text{O}_4$ (NMFO) were prepared on Pt/Ti/SiO₂/Si substrate by means of the sol-gel and spin-coating method. The lead-free magnetoelectric composite films with the structure of $\text{Bi}_{3.4}\text{La}_{0.6}\text{Ti}_3\text{O}_{12}/\text{Ni}_{0.7}\text{Mn}_{0.3}\text{Fe}_2\text{O}_4/\text{substrate}$ (BN) and $\text{Ni}_{0.7}\text{Mn}_{0.3}\text{Fe}_2\text{O}_4/\text{Bi}_{3.4}\text{La}_{0.6}\text{Ti}_3\text{O}_{12}/\text{substrate}$ (NB) were also deposited on Pt/Ti/SiO₂/Si substrate. The X-ray diffraction results show that two composite films possess BLTO and NMFO phases without any intermediate phase. The SEM images show that two composite films exhibit layered structure, clear interface and no transition layer between BLTO and NMFO films. Two composite films exhibit both good ferromagnetic and ferroelectric properties, as well as magnetoelectric coupling effect. The deposition sequence of ferroelectric and ferromagnetic films in the composite films has significant influence on the ferroelectric, ferromagnetic and magnetoelectric coupling properties of the composite films. The values of magnetoelectric voltage coefficient of the BN composite films are higher than those of the NB composite films at any fixed H_{bias} .

1. Introduction

Generally, the magnetoelectric materials exhibit ferroelectric properties and ferromagnetic properties, as well as magnetoelectric coupling effect, which is a spontaneous electric polarization induced by an external magnetic field [1–3]. Nowadays, the magnetoelectric materials have attracted growing interest due to their potential application in novel multi-functional devices, such as spintronics, transducers, sensors, and four-state logic memories [1,2,4]. However, it is known that single-phase materials, e.g., BiFeO_3 , possess very poor magnetoelectric coupling effect at room temperature and thus their applications are limited [5–8]. As a consequence, more and more researchers focused on the composite materials to acquire large magnetoelectric effect [5]. Compared with the single-phase materials, the magnetoelectric composite films possess some unique advantages [9]. Firstly, different phases could combine at atom-level in the composite films, which makes it easy to understand the mechanism of magnetoelectric coupling effect at atomic scale. Secondly, the phase composition and connectivity can be controlled at nanometer scale. Nowadays, it is well known that the magnetoelectric coupling effect in composite films arises from coupling between the magnetostrictive effect in ferromagnetic films and piezoelectric effects in ferroelectric films [10]. The magnetoelectric coupling effect is a coupled electrical and magnetic phenomenon via elastic interaction. That is, when a magnetic field is

applied to a composite film, strain was generated in the magnetic film due to magnetostriction. The strain is then passed to the ferroelectric film through the interface between the ferromagnetic and ferroelectric phases, resulting in an electric polarization [11]. Thus, the magnetoelectric coupling effect in composite films depends on the ferromagnetic and ferroelectric properties of the composite films and coupling interaction across the interfaces [12]. In order to enhance magnetoelectric coupling effect, ferromagnetic phases with large magnetostrictive effect and ferroelectric phases with large piezoelectric effect were commonly adopted [10]. For instance, predominant ferromagnetic phases in magnetoelectric composite films are referred to as CoFe_2O_4 (CFO) or NiFe_2O_4 (NFO) for their high magnetostrictive coefficients. As NFO materials have small magnetic anisotropy in comparison with CFO materials, NFO materials have thus been considered to be the promising ferromagnetic phase in the magnetoelectric composite films. What's more, transition metals, such as Ni and Mn, were doped to prepare $\text{Ni}_{1-x}\text{Mn}_x\text{Fe}_2\text{O}_4$ (NMFO) with enhanced ferromagnetic properties in the magnetoelectric composite films. On the other hand, it is known that $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$ (PZT) materials have been widely used as the main ferroelectric constituent in a magnetoelectric composite film for their excellent piezoelectric properties [13], nevertheless, as a main constituent element in PZT, lead (Pb) have brought about pollution to environment and exert serious damage to human's brain and nervous system [14,15]. Therefore, in view of environmental protection and human health, it is

* Corresponding author.

E-mail address: mrshimin@hotmail.com (M. Shi).

<http://dx.doi.org/10.1016/j.ceramint.2017.09.192>

Received 30 May 2017; Received in revised form 23 September 2017; Accepted 23 September 2017

Available online 25 September 2017

0272-8842/ © 2017 Elsevier Ltd and Techna Group S.r.l. All rights reserved.

rather urgent to develop lead-free ferroelectric based composite films. Recently, what is noticeable is that lead-free ferroelectric $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ (BTO) materials are expected to be used in the next-generation magnetoelectric composite films. As ferroelectric property of BTO materials are poor, La was usually doped to BTO ($\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$ (BLTO)) to enhance the ferroelectric properties. However, up to date, the relevant researches mostly focused on $\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$ ceramics and there are rather few researches on preparing $\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$ films in the magnetoelectric composite system. And few reports on the relationship between the structures and magnetoelectric properties of the composite films are available now. Therefore, we aim to investigate the relationship between the structures and magnetoelectric properties of the composite films by modifying the deposition sequence in the composite films in order to acquire the composite films with enhanced magnetoelectric coupling effect.

Based on the above discussion, the ferroelectric BLTO films and ferromagnetic NMFO films were prepared on Pt/Ti/SiO₂/Si substrate by using the sol-gel and spin-coating method firstly. Then, the layered composite films were prepared by spin-coating the BLTO and NMFO precursor solutions alternately on the Pt/Ti/SiO₂/Si substrate. By changing the deposition sequence of BLTO and NMFO precursor solutions, we obtain the composite films with the structure of BLTO/NMFO/substrate (BN) and NMFO/BLTO/substrate (NB). The impact of deposition sequence on the phase compositions, microstructures and properties of the magnetoelectric composite films was investigated in detail.

2. Experimental

BLTO, NMFO films and BLTO-NMFO composite films were deposited on Pt(100)/Ti/SiO₂/Si substrate via the sol-gel and spin-coating method. For the preparation of the BLTO precursor solution, bismuth nitrate pentahydrate ($\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$) (5 wt% excess Bi to compensate for the volatilization of Bi), lanthanum nitrate hydrate ($\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$) were dissolved in glacial acetic acid ($\text{C}_2\text{H}_4\text{O}_2$) to obtain one solution. Tetrabutyl titanate ($\text{Ti}(\text{C}_4\text{H}_9\text{O})_4$) were dissolved in ethylene glycol monomethyl ether ($\text{C}_3\text{H}_8\text{O}_2$) to obtain another solution. Then the above two solutions were mixed while adding acetylacetone ($\text{C}_5\text{H}_8\text{O}_2$) as stabilizer and stirred at 60 °C to obtain a sol precursor solution of BLTO (0.3 mol L^{-1}). The BLTO precursor solution was then spin-coated on the Pt/Ti/SiO₂/Si substrate to form one-layered BLTO precursor films at a spinning rate of 3500 rpm for 30 s. The BLTO precursor films were dried at 120 °C for 10 min to evaporate water and organic solvent, then pre-annealed at 400 °C for 15 min to decompose organic components and annealed at 700 °C for 20 min to obtain BLTO films. Finally, three-layered BLTO films were prepared by repeating the spin-coating, pre-annealing and annealing process twice.

For the preparation of the NMFO precursor solution, nickel acetate ($\text{C}_4\text{H}_6\text{NiO}_4 \cdot 4\text{H}_2\text{O}$) and manganese acetate ($\text{C}_4\text{H}_6\text{MnO}_4 \cdot 4\text{H}_2\text{O}$) were dissolved in glacial acetic acid ($\text{C}_2\text{H}_4\text{O}_2$) to obtain the first solution. Ferric nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) were dissolved in ethylene glycol monomethyl ether ($\text{C}_3\text{H}_8\text{O}_2$) to obtain another solution. Then the above solutions were mixed while adding polyvinylpyrrolidone ($\text{C}_6\text{H}_9\text{NO}$)_n as stabilizer and stirred at 60 °C to form a sol NMFO precursor solution (0.1 mol L^{-1}). The NMFO precursor solution was then spin-coated on the Pt/Ti/SiO₂/Si substrate to form one-layered NMFO precursor films at a spinning rate of 3500 rpm for 30 s. The NMFO precursor films were dried at 120 °C for 10 min to evaporate water and organic solvent, pre-annealed at 500 °C for 15 min to decompose organic components and annealed at 700 °C for 20 min to obtain pure NMFO films. Finally, two-layered NMFO films were prepared by repeating the spin-coating, pre-annealing and annealing process once.

The layered composite films of BLTO/NMFO were prepared by spin-coating the BLTO and NMFO precursor solutions alternately on the substrate. By changing deposition sequence of precursor films of BLTO and NMFO, we prepared the composite films with two different layered

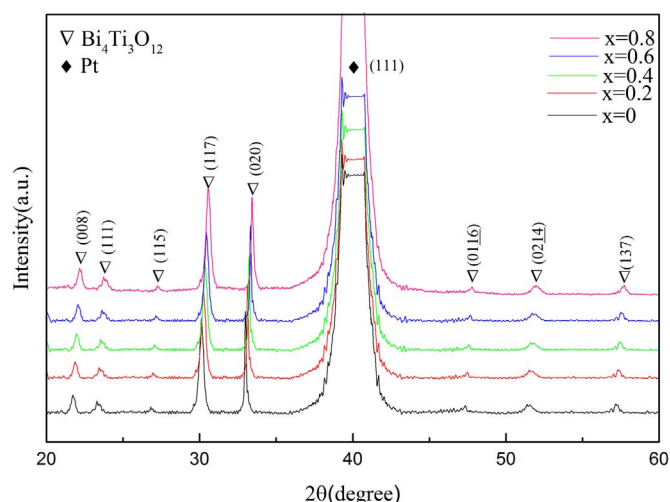


Fig. 1. XRD patterns of the BLTO films under different x, mole fraction of doping La.

structures: BLTO/NMFO/substrate (BN) and NMFO/BLTO /substrate (NB).

The phase compositions of the films were determined by X-ray diffractometer (X'Pert PRO MPD, PANalytical B.V., Holland) with CuKα radiation. The morphology of the surfaces and cross-sections of the films was observed with a field emission scanning electron microscope (SU8020, Hitachi, Japan). The ferromagnetic behavior of the films was detected by a vibration sample magnetometer (S-VSM, Quantum Design, USA). The polarization versus electric field (P-E) hysteresis loops of films were characterized by a ferroelectric test system (Precision LC, Radiant Technologies Inc, USA). Magnetoelectric effect of the composite films was measured via a measuring device designed by superconducting and magnetism laboratory, University of Science and Technology of China. Ag electrodes with a diameter of 150 μm were deposited through a shadow mask on the BLTO and composite films before testing the ferroelectric and magnetoelectric coupling property.

3. Results and discussion

The XRD patterns of $\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$ (BLTO) films and pure $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ (BTO) films were presented in Fig. 1. It reveals that both the BTO film and BLTO films are evidently polycrystalline structure without any preferred orientation. On the other hand, the XRD peaks from BLTO films are all composed of those from the main phase ($\text{Bi}_4\text{Ti}_3\text{O}_{12}$) and Pt from the substrate, which is in good agreement with pure BTO films. This implies that, for BLTO films, La has dissolved into the lattice of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$.

The ferroelectric polarization-electric field (P-E) hysteresis loops of the BLTO films doped with different mole fraction of doping La were displayed in Fig. 2. The variation of the saturation polarization (P_s) and coercive field (E_c) of the BLTO films with different mole fraction of doping La was shown in the inset of Fig. 2. It is observed that P-E hysteresis loops for the BLTO films and pure BTO film exhibit well-saturated shape. It can be seen that four BLTO films possess greater values of P_s , and smaller values of E_c than those of the pure BTO film ($x = 0$), implying that the doping of La is helpful to improving the ferroelectric properties. From the inset of Fig. 2, it is clear that, with the increase of mole fraction of doping La, the values of P_s of BLTO films increase firstly, reach the maximum (when $x = 0.6$), then decrease. However, with the increase of mole fraction of doping La, the values of E_c of BLTO films decrease firstly, reach the minimum (when $x = 0.6$), then increase. It is clear that, when mole fraction of doping La is 0.6, the BLTO films possess greatest value of P_s and smallest value of E_c , which is corresponding to the best ferroelectric properties. So, in this

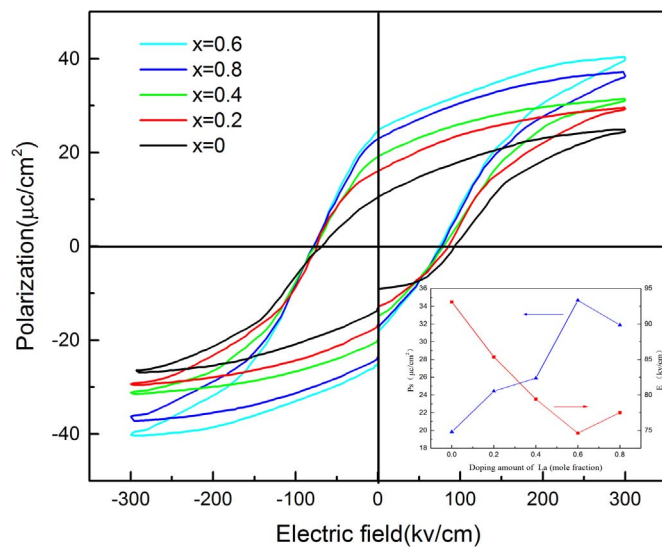


Fig. 2. The ferroelectric hysteresis loops of BLTO films under different x , mole fraction of doping La. The inset shows P_s and E_c of the BLTO film.

work, the chemical formula of BLTO films in the composite films we chose is $\text{Bi}_{3.4}\text{La}_{0.6}\text{Ti}_3\text{O}_{12}$.

The SEM images of the surface and cross-section of $\text{Bi}_{3.4}\text{La}_{0.6}\text{Ti}_3\text{O}_{12}$ film were shown in Fig. 3(a) and (b), respectively. From Fig. 3(a), it is clear that $\text{Bi}_{3.4}\text{La}_{0.6}\text{Ti}_3\text{O}_{12}$ film exhibits high density and uniform microstructure. Moreover, the polygonal particles can be observed. It can also be seen from Fig. 3(b) that interface between the $\text{Bi}_{3.4}\text{La}_{0.6}\text{Ti}_3\text{O}_{12}$ film and substrate is distinct and flat. The thickness of $\text{Bi}_{3.4}\text{La}_{0.6}\text{Ti}_3\text{O}_{12}$ film is uniform and the average thickness of $\text{Bi}_{3.4}\text{La}_{0.6}\text{Ti}_3\text{O}_{12}$ film is about 108 nm.

The XRD patterns of $\text{Ni}_{1-x}\text{Mn}_x\text{Fe}_2\text{O}_4$ (NMFO) films and pure NiFe_2O_4 (NFO) films were presented in Fig. 4. It clearly demonstrates that both the NMFO films and pure NFO film have evidently polycrystalline structure without any preferred orientation. In NMFO films, the main phase (NFO) and Pt from the substrate are presented, which is accordance with the pure NFO film. This indicates that, in NMFO films, Mn has dissolved into the lattice of NiFe_2O_4 .

The typical magnetic hysteresis loops of NMFO films with different mole fraction of doping Mn were displayed in Fig. 5. The saturation magnetization (M_s) and coercive force (H_c) of the NMFO films were shown in the inset of Fig. 5. It is clear that magnetic hysteresis loops of all of the NMFO films and pure NFO film exhibit good symmetry and well-saturated shape, indicating better ferromagnetic properties. It can be observed that the NMFO films possess greater values of M_s and smaller value of H_c than those of the pure NFO film, implying the

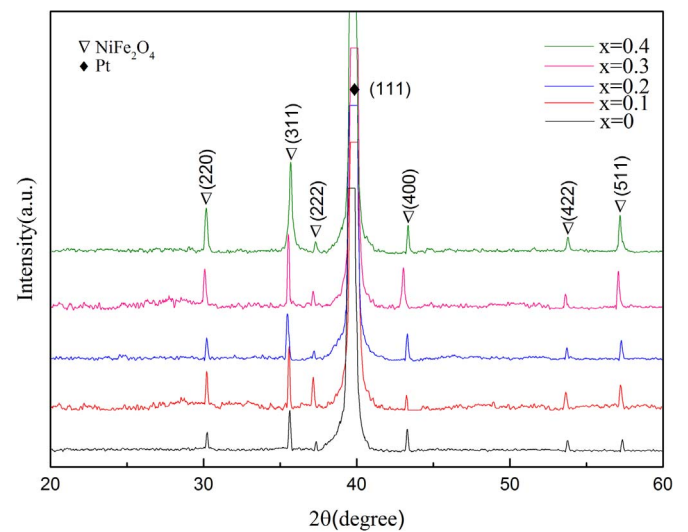


Fig. 4. XRD patterns of NMFO films under different x , mole fraction of doping Mn.

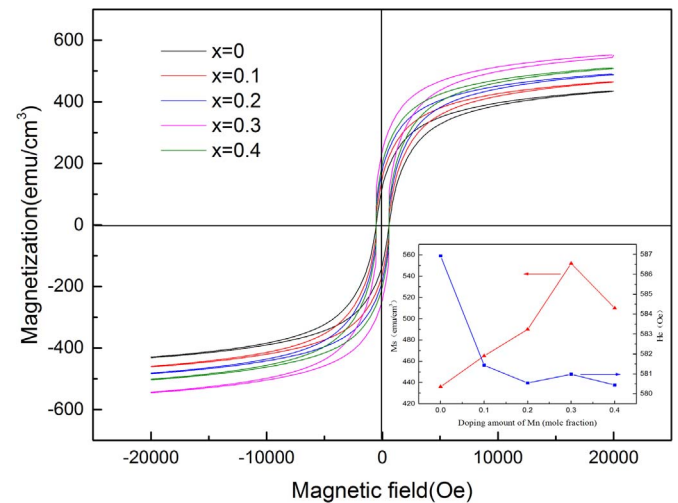


Fig. 5. Magnetic hysteresis loops of NMFO films doped with different x , mole fraction of doping Mn. The inset shows M_s and H_c of the NMFO film.

doping of Mn to the NFO is beneficial to improving the magnetic properties. It can also be seen that, with the increase of mole fraction of doping Mn, the values of M_s of NMFO films increase firstly, reach the maximum (when x is 0.3), then decrease. Meanwhile, with the increase of mole fraction of doping Mn from 0 to 0.2, the values of H_c of the

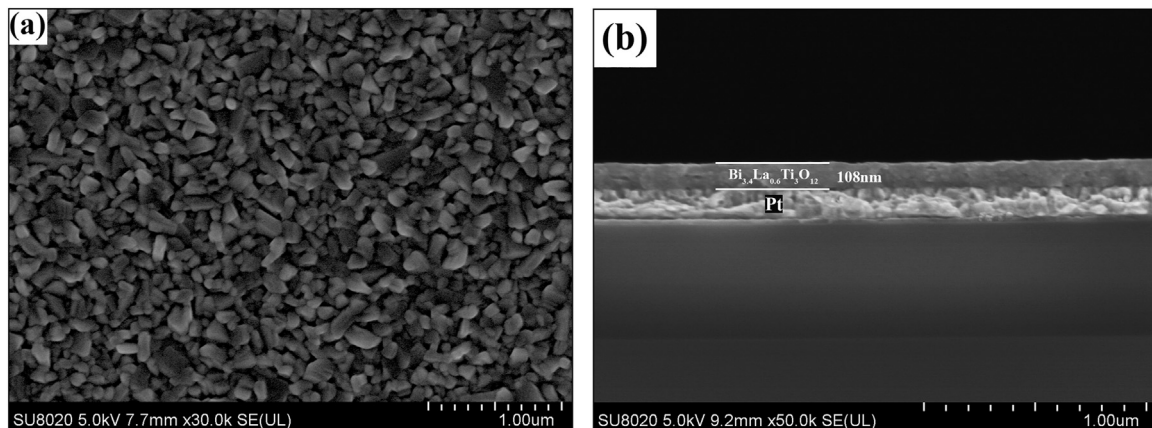


Fig. 3. The SEM micrographs of $\text{Bi}_{3.4}\text{La}_{0.6}\text{Ti}_3\text{O}_{12}$ film. (a) the surface; (b) the cross-section.

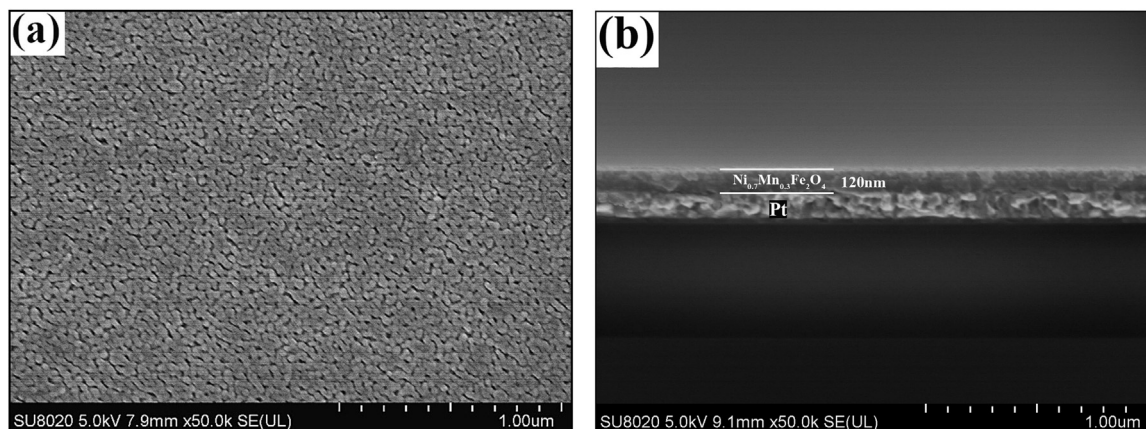


Fig. 6. The SEM micrographs of $\text{Ni}_{0.7}\text{Mn}_{0.3}\text{Fe}_2\text{O}_4$ film. (a) the surface; (b) the cross-section.

NMFO films decrease. Nevertheless, when mole fraction of doping Mn increase further, the values of H_c remain almost constant. It shows that, when mole fraction of doping Mn is 0.3, the NMFO films possess greatest value of M_s and relative smaller value of H_c , which is corresponding to good magnetoelectric properties. Comprehensive considering values of M_s and H_c , 0.3 is the best mole fraction of doping Mn for acquiring the best ferromagnetic properties. Consequently, in this work, the chemical formula of the ferromagnetic NMFO films in the composite films we chose is $\text{Ni}_{0.7}\text{Mn}_{0.3}\text{Fe}_2\text{O}_4$.

The SEM images of the surface and cross-section of $\text{Ni}_{0.7}\text{Mn}_{0.3}\text{Fe}_2\text{O}_4$ film were shown in Fig. 6(a) and (b), respectively. From Fig. 6(a), it is observed that the $\text{Ni}_{0.7}\text{Mn}_{0.3}\text{Fe}_2\text{O}_4$ film possesses uniform and crack-free microstructure. By comparing Fig. 6(a) with Fig. 3(a), it can be seen that the surface of $\text{Bi}_{3.4}\text{La}_{0.6}\text{Ti}_3\text{O}_{12}$ film is more compact than the $\text{Ni}_{0.7}\text{Mn}_{0.3}\text{Fe}_2\text{O}_4$ film. From Fig. 6(b), it is seen that the thickness of the $\text{Ni}_{0.7}\text{Mn}_{0.3}\text{Fe}_2\text{O}_4$ film is uniform. The average thickness of $\text{Ni}_{0.7}\text{Mn}_{0.3}\text{Fe}_2\text{O}_4$ film is about 120 nm. It can also be observed from Fig. 6(b) that there exist distinct and flat interfaces between the $\text{Ni}_{0.7}\text{Mn}_{0.3}\text{Fe}_2\text{O}_4$ film and the substrate.

In order to investigate impact of deposition sequence on the phase compositions, microstructures and properties of the magnetoelectric composite films, the composite films with the structure of $\text{Bi}_{3.4}\text{La}_{0.6}\text{Ti}_3\text{O}_{12}/\text{Ni}_{0.7}\text{Mn}_{0.3}\text{Fe}_2\text{O}_4$ /substrate (BN) and $\text{Ni}_{0.7}\text{Mn}_{0.3}\text{Fe}_2\text{O}_4/\text{Bi}_{3.4}\text{La}_{0.6}\text{Ti}_3\text{O}_{12}$ /substrate (NB) were prepared on the Pt/Ti/SiO₂/Si substrate. The XRD patterns of the BN and NB composite films were depicted in Fig. 7. It is clear that two composite films are all composed of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ and NiFe_2O_4 phases apart from Pt phase from the substrates. And the BN composite film

has stronger peaks from $\text{Bi}_4\text{Ti}_3\text{O}_{12}$. This can be attributed to the fact that $\text{Bi}_{3.4}\text{La}_{0.6}\text{Ti}_3\text{O}_{12}$ is the top layer in the BN composite film. The lattice parameters of the BLTO and NMFO film in the BN and NB composite film were calculated by Jade 6.5. The results were listed in Table 1. In order to compare those with bulks of BLTO and NMFO, standard lattice parameters of BLTO and NMFO from standard Powder Diffraction File were also listed in Table 1. It is clear that BLTO films in the BN and NB composite film possess tetragonal structures. The lattice parameters (a, b and c) of the BLTO films in the BN composite film are smaller than those of the standard BLTO phase, indicating that the BLTO film in the BN composite film is subjected to the three dimensional compressive stress. The lattice parameters (a and b) of the BLTO film in the NB composite film are small than those of the standard BLTO phase. Whereas, the lattice parameter (c) of the BLTO film in the NB composite film is great than that of the standard BLTO phase. This shows that the BLTO film in the NB composite film is subjected to the two dimensional compressive stress and one dimensional tensile stress. It can be observed that NMFO films in the BN and NB composite film have cubic structure. And the NMFO films in the NB and BN composite film are subjected to the three dimensional compressive stress.

The SEM images of the surfaces and cross-sections of the BN and NB composite film were shown in Fig. 8. From Fig. 8(a), it is observed that the BN composite film has obvious grain and dense microstructure without obvious pores. However, from Fig. 8(b), it can be seen that the NB composite film has obvious porosities and micro-cracks. By comparing Fig. 8(b) with Fig. 8(a), it can be concluded that the BN composite film has denser microstructure and fewer defects than the NB composite film. From Fig. 8(c) and (d), it is observed that the two composite films have obvious layered structure. The total thicknesses of two composite films were estimated to be ~ 230 nm, including ~ 110 nm $\text{Bi}_{3.4}\text{La}_{0.6}\text{Ti}_3\text{O}_{12}$ film and ~ 120 nm $\text{Ni}_{0.7}\text{Mn}_{0.3}\text{Fe}_2\text{O}_4$ film. It also indicates that, in these two composite films, there exist distinct and flat interfaces between $\text{Bi}_{3.4}\text{La}_{0.6}\text{Ti}_3\text{O}_{12}$ and $\text{Ni}_{0.7}\text{Mn}_{0.3}\text{Fe}_2\text{O}_4$ films without forming transition layer between $\text{Bi}_{3.4}\text{La}_{0.6}\text{Ti}_3\text{O}_{12}$ and $\text{Ni}_{0.7}\text{Mn}_{0.3}\text{Fe}_2\text{O}_4$ film.

The P-E hysteresis loops of the BN and NB composite films under different applied electric fields were illustrated in Fig. 9. The inset of Fig. 9 shows the P-E hysteresis loops of ferroelectric $\text{Bi}_{3.4}\text{La}_{0.6}\text{Ti}_3\text{O}_{12}$ film. In these two composite films, the saturated ferroelectric loops were observed, reflecting the ferroelectric nature. The ferroelectric parameters of the BN and NB composite film drawn from Fig. 9 were listed in Table 2. It is clear that two composite films possess smaller values of P_s and greater values of E_c than those of $\text{Bi}_{3.4}\text{La}_{0.6}\text{Ti}_3\text{O}_{12}$ film. The smaller values of P_s are due to the dilution effect of the ferromagnetic films in the composite films. Whereas, the greater values of E_c may be attributed to the interaction between ferroelectric and ferromagnetic phases. It should be noted that, compared with the BN

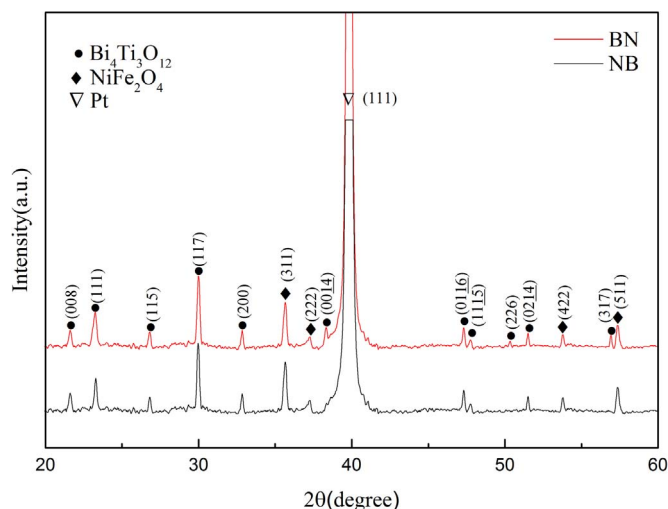


Fig. 7. XRD patterns of the BN and NB composite film.

Table 1

The calculated lattice parameters of the BLTO and NMFO film in the BN and NB composite film, the lattice parameters of bulks of BLTO and NMFO from standard Powder Diffraction File.

	a(nm)	b(nm)	c(nm)	α	β	γ
BLTO film in the BN composite film	0.5445 ± 0.0012	0.5445 ± 0.0012	3.2501 ± 0.0211	90	90	90
NMFO in the BN composite film	0.8336 ± 0.0008	0.8336 ± 0.0008	0.8336 ± 0.0008	90	90	90
BLTO film in the NB composite film	0.5451 ± 0.0006	0.5451 ± 0.0006	3.3051 ± 0.0109	90	90	90
NMFO film in the NB composite film	0.8340 ± 0.0008	0.8340 ± 0.0008	0.8340 ± 0.0008	90	90	90
BLTO(JCPDS No. 47-0398)	0.546	0.546	3.281	90	90	90
NMFO(JCPDS No. 03-0875)	0.834	0.834	0.834	90	90	90

composite film, the NB composite film possesses greater value of P_s and smaller value of E_c . This indicates that the deposition sequence of the composite films influences the ferroelectric properties of the composite films.

The M-H hysteresis loops of the BN and NB composite films were shown in Fig. 10. The inset of Fig. 10 shows M-H hysteresis loop of $\text{Ni}_{0.7}\text{Mn}_{0.3}\text{Fe}_2\text{O}_4$ film. It is clear that, for these two composite films, magnetic hysteresis loops exhibit good symmetry and well-saturated shape. The ferromagnetic parameters of the BN and NB composite film drawn from Fig. 10 were listed in Table 3. It is indicated that, two composite films have smaller value of M_s and greater value of H_c than those of $\text{Ni}_{0.7}\text{Mn}_{0.3}\text{Fe}_2\text{O}_4$ film. This may be attributed to the smaller volume contents of $\text{Ni}_{0.7}\text{Mn}_{0.3}\text{Fe}_2\text{O}_4$ phases in the composite films than those in the pure $\text{Ni}_{0.7}\text{Mn}_{0.3}\text{Fe}_2\text{O}_4$ film. However, the values of H_c of two composite films are greater than that of the pure $\text{Ni}_{0.7}\text{Mn}_{0.3}\text{Fe}_2\text{O}_4$ film, which may be due to the interaction between the ferroelectric and ferromagnetic phases [16]. This also indicates that the deposition sequence of the composite films influences the ferromagnetic properties of the composite films.

The co-existence of ferroelectric BNT0 and ferromagnetic CFO

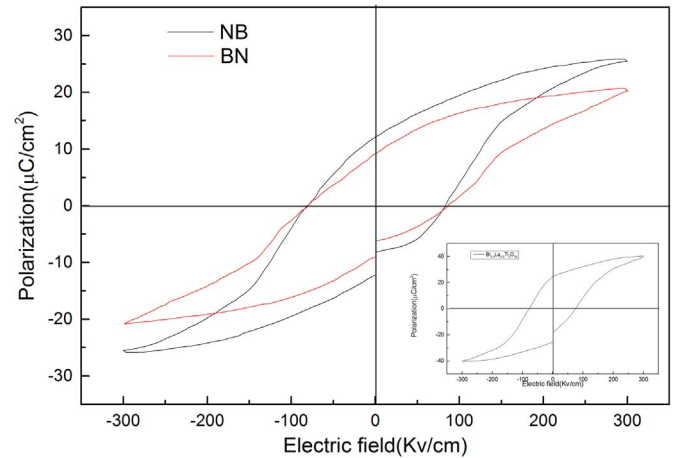


Fig. 9. The P-E hysteresis loops of the BN and NB composite film. The inset shows the P-E hysteresis loops of $\text{Bi}_{3.4}\text{La}_{0.6}\text{Ti}_3\text{O}_{12}$ film.

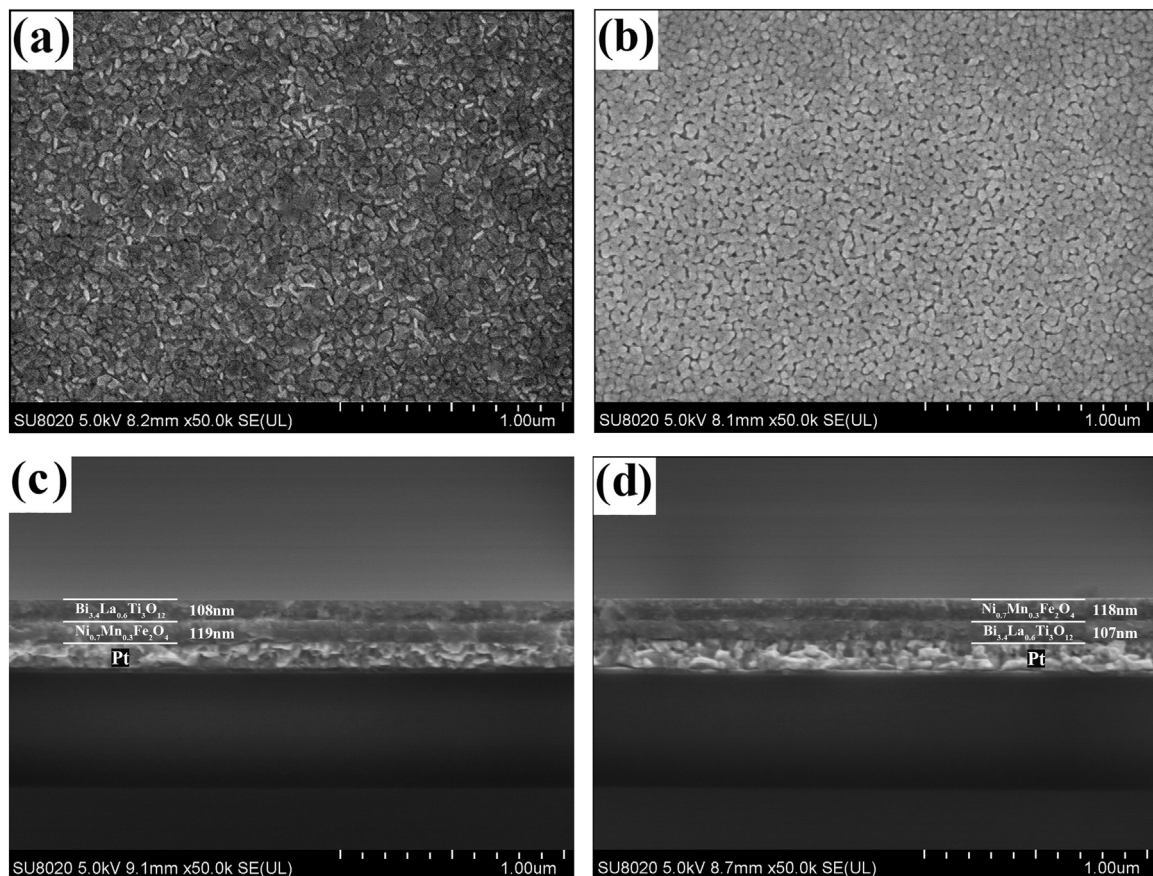
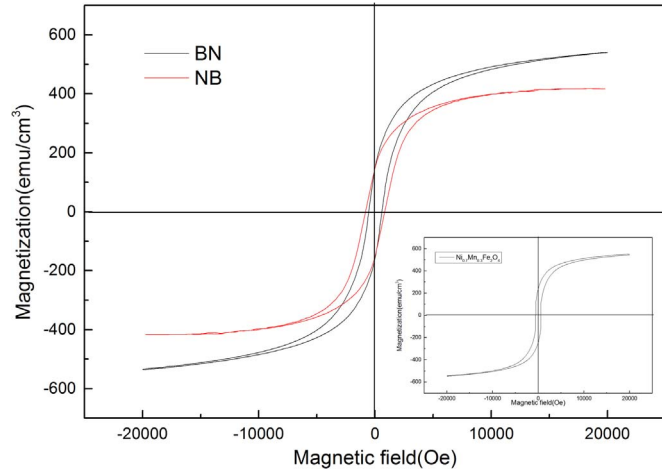


Fig. 8. The SEM micrographs of the surfaces and cross-sections of the BN and NB composite film. (a) the surface of the BN composite film; (b) the surface of the NB composite film; (c) the cross-section of the BN composite film; (d) the cross-section of the NB composite film.

Table 2The ferroelectric parameters of the composite film of BN, NB and Bi_{3.4}La_{0.6}Ti₃O₁₂ film.

Film	P _s (μC/cm ²)	E _c (kV/cm)
The NB composite film	25.89	83.23
The BN composite film	20.75	85.51
Bi _{3.4} La _{0.6} Ti ₃ O ₁₂	40.41	74.61

**Fig. 10.** The magnetic hysteresis loops of the BN and NB composite film. The inset shows M-H hysteresis loops of Ni_{0.7}Mn_{0.3}Fe₂O₄ film.**Table 3**The ferromagnetic parameters of the composite films of BN, NB and Ni_{0.7}Mn_{0.3}Fe₂O₄ film.

Film	M _s (emu/cm ³)	H _c (Oe)
The BN composite film	540.35	590.29
The NB composite film	417.23	827.21
Ni _{0.7} Mn _{0.3} Fe ₂ O ₄	552.03	580.98

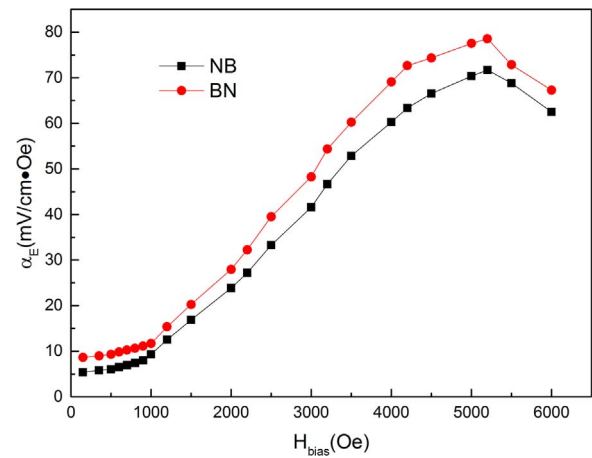
phases in the composite films may give rise to magnetoelectric coupling effect, which is characterized by magnetoelectric voltage coefficient, α_E . And α_E is given as follows [4]:

$$\alpha_E = \frac{\delta E}{\delta H} = \frac{\delta V}{t \delta H},$$

where t is the thicknesses of the composite films and V is the voltage induced by an applied AC magnetic field superimposed on a DC bias magnetic field (H_{bias}). AC magnetic field and DC bias magnetic field are parallel to surfaces of the composite films.

The variation of the values of α_E of the two composite films as a function of H_{bias} is shown in Fig. 11. It is clear that two composite films exhibit significant magnetoelectric coupling effect. When H_{bias} is smaller, two composite films exhibit initial low value of α_E . It can also be seen that, with the increase of H_{bias} , α_E increases firstly, after reaches maximum, then decrease. As α_E is dependent on H_{bias} , it is necessary to track the piezomagnetic coupling coefficient $q = dk/dH_{\text{bias}}$ [17,18] (where k is the magnetostriction). For the ferromagnetic phase, once the magnetostriction attains the saturation value, q decreases and the piezomagnetic coupling becomes gradually weak, resulting in the weakening of the magnetoelectric coupling effect [18]. When H_{bias} is near 5300 Oe, the greatest value of α_E can be obtained. This indicates that the magnetostriction of Ni_{0.7}Mn_{0.3}Fe₂O₄ phase in a composite film reaches a saturation value and produces a constant electric field in the piezoelectric phase.

It is worthy to note that the values of α_E of the BN composite films are greater than those of the NB composite films at any fixed H_{bias} , indicating that deposition sequence in the composite films influences the magnetoelectric coupling properties of the composite films. Now,

**Fig. 11.** The variation of α_E of the BN and NB composite film as a function of H_{bias} .

we will discuss the reason why the BN composite films have stronger magnetoelectric coupling effect. On the one hand, for magnetoelectric composite films, magnetoelectric coupling mainly arises from the magnetic-mechanical-electric transform through the stress-mediated transfer across the interface. The three dimensional compressive stress exerting on the BLTO films in the BN composite films may promote the magnetic-mechanical-electric transform in the BN composite films. Therefore, the BN composite film has greater value of α_E . On the other hand, the dynamic magnetoelastic coupling induced by the magnetostriction of ferromagnetic phase, due to the domain-wall motion and domain rotation, is involved in the magnetoelectric coupling effect [17,19]. As the BN composite films have lower value of H_c , which is very helpful to the motion of domain-wall or rotation of domain, resulting in larger magnetostriction, the BN composite films possess stronger magnetoelectric coupling effect.

It should be pointed out that the maximum of α_E for the BN composite film and the NB composite film are 80 and 70 mV cm⁻¹ Oe⁻¹, which are all greater than those reported in Ref [16] (45.38 mV cm⁻¹ Oe⁻¹) and Ref [20] (65.1 mV cm⁻¹ Oe⁻¹). The significant magnetoelectric coupling effect in my work may be attributed to the flat and clear interface between Bi_{3.4}La_{0.6}Ti₃O₁₂ and Ni_{0.7}Mn_{0.3}Fe₂O₄ film, which enhances the stress-mediated transfer across the interface.

4. Conclusions

The BLTO ferroelectric films, NMFO ferromagnetic films and the NB and BN composite films were prepared on Pt(100)/Ti/SiO₂/Si substrate via the sol-gel and spin-coating method. Two composite films have distinct interfaces between BLTO and NMFO films without forming transition layer between BLTO and NMFO films. Both these composite films exhibit not only good ferroelectric and ferromagnetic properties but also remarkable magnetoelectric coupling properties. The deposition sequence in the composite films has great impact on the ferroelectric, ferromagnetic and magnetoelectric coupling properties of the composite films. For these two composite films, with the increase of H_{bias} , α_E increases firstly, after reaches the highest value, then decreases. The BN composite films possess greater values of α_E than those of the NB composite films at any fixed H_{bias} .

Acknowledgments

The authors would like to acknowledge Prof. X. G. Li from University of Science and Technology of China for the measurement of the magnetoelectric coupling effect. This work was supported by National Natural Science Foundation of China (51272060, 51472069 and U1432113).

References

- [1] W. Eerenstein, N.D. Mathur, J.F. Scott, Multiferroic and magnetoelectric material, *Nature* 442 (2001) 759–765.
- [2] J.F. Scott, Applications of magnetoelectrics, *J. Mater. Chem.* 22 (2012) 4567–4574.
- [3] E.V. Ramana, J. Zavasnik, M.P.F. Graca, M.A. Valente, Magnetoelectric studies on $\text{CoFe}_2\text{O}_4/0.5(\text{BaTi}_{0.8}\text{Zr}_{0.2}\text{O}_3) - 0.5(\text{Ba}_{0.7}\text{Ca}_{0.3}\text{TiO}_3)$ lead-free bilayer thin films derived by the chemical solution deposition, *J. Appl. Phys.* 120 (2016) 074108–074110.
- [4] C.M. Zhu, L.G. Wang, Z.M. Tiana, H. Luo, D.L.G.C. Bao, C.Y. Yin, S. Huang, S.L. Yuan, Effect of annealing temperature on the multiferroic properties of $0.7\text{BiFeO}_3 - 0.3\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ solid solution prepared by sol–gel method, *Ceram. Int.* 42 (2016) 3930–3937.
- [5] F.W. Zhang, F. Yang, C.F. Dong, X.T. Liu, H.L. Nan, Y.Y. Wang, Z.H. Zong, M.H. Tang, Orientation-dependent properties of $\text{CoFe}_2\text{O}_4 - \text{Bi}_{3.15}\text{Nd}_{0.85}\text{Ti}_3\text{O}_{12}$ bilayer multiferroic films prepared by a sol-gel method, *J. Electron. Mater.* 44 (2015) 2348–2352.
- [6] G.A. Gehring, On the microscopic theory of the magnetoelectric effect, *Ferroelectrics* 161 (1994) 275–285.
- [7] M. Fiebig, Revival of the magnetoelectric effect, *J. Phys. D: Appl. Phys.* 38 (2005) R123–R152.
- [8] W. Prellier, M.P. Singh, P. Murugavel, The single-phase multiferroic oxides: from bulk to thin film, *J. Phys. D: Appl. Phys.* 17 (2005) R803–R832.
- [9] Y. Zhou, Y.X. Ye, J.F. Wang, J.J. Zhang, Z.W. Jiao, J.C. Zhang, Magnetoelectric effect in lead-free sandwich film composed of Co-ferrite and $(\text{K}_{0.5}\text{Na}_{0.5})\text{NbO}_3$ -based ferroelectric, *Mater. Lett.* 131 (2014) 158–160.
- [10] J. Rani, K.L. Yadav, S. Prakash, Enhanced magnetodielectric effect and optical property of lead-free multiferroic $(1-x)(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3/x\text{CoFe}_2\text{O}_4$ composites, *Mater. Chem. Phys.* 147 (2014) 1183–1190.
- [11] J. Ma, J.M. Hu, Z. Li, C.W. Nan, Recent progress in multiferroic magnetoelectric composites: from bulk to thin films, *Adv. Mater.* 23 (2011) 1062–1087.
- [12] C.W. Nan, M.I. Bichurin, S.X. Dong, D. Viehland, G. Srinivasan, Multiferroic magnetoelectric composites: historical perspective, status, and future directions, *J. Appl. Phys.* 103 (2008) 031101.
- [13] Y.X. Zhang, J.P. Zhou, Q. Liu, S.H. Zhang, C.Y. Deng, Dielectric, magnetic and magnetoelectric properties of $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4 + \text{Pb}(\text{Zr}_{0.48}\text{Ti}_{0.52})\text{O}_3$ composite ceramics, *Ceram. Inter* 40 (2014) 5853–5860.
- [14] T. Takenaka, H. Nagata, Y. Hiruma, Current developments and prospective of lead-free piezoelectric ceramics, *Jpn. J. Appl. Phys.* 47 (2008) 3787–3801.
- [15] J. Rodel, W. Jo, K.T.P. Seifert, E.M. Anton, T. Granzow, D. Damjanovic, Perspective on the development of lead-free piezoceramics, *J. Am. Ceram. Soc.* 92 (2009) 1153–1177.
- [16] J.Y. Chen, Z.H. Tang, Y.L. Bai, S.F. Zhao, Multiferroic and magnetoelectric properties of $\text{BiFeO}_3/\text{Bi}_4\text{Ti}_3\text{O}_{12}$ bilayer composite films, *J. Alloy. Compd.* 675 (2016) 257–265.
- [17] G. Srinivasan, E.T. Rasmussen, J. Gallegos, R. Srinivasan, Yu.I. Bokhan, V.M. Laletin, Magnetoelectric bilayer and multilayer structures of magnetostrictive and piezoelectric oxides, *Phys. Rev. B* 64 (2001) 214408-6.
- [18] M. Zeng, J.G. Wan, Y. Wang, H. Yu, J.M. Liu, X.P. Jiang, C.W. Nan, Resonance magnetoelectric effect in bulk composites of lead zirconate titanate and nickel ferrite, *J. Appl. Phys.* 95 (2004) 8069–8073.
- [19] J.G. Wan, X.W. Wang, Y.J. Wu, M. Zeng, Y. Wang, H. Jiang, W.Q. Zhou, G.H. Wang, J.M. Liu, Magnetoelectric $\text{CoFe}_2\text{O}_4 - \text{Pb}(\text{Zr,Ti})\text{O}_3$ composite thin films derived by a sol-gel process, *Appl. Phys. Lett.* 86 (2005) 122501–122503.
- [20] Y.L. Bai, H.L. Zhao, J.Y. Chen, Y.Z. Sun, S.F. Zhao, Strong magnetoelectric coupling effect of $\text{BiFeO}_3/\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$ bilayer composite films, *Ceram. Int.* 42 (2016) 10304–10309.