

Multiferroic and magnetoelectric properties of lead-free $\text{Ba}_{0.8}\text{Sr}_{0.2}\text{Ti}_{0.9}\text{Zr}_{0.1}\text{O}_3\text{-Ni}_{0.8}\text{Zn}_{0.2}\text{Fe}_2\text{O}_4$ composite films with different deposition sequence

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ABSTRACT

$\text{Ba}_{0.8}\text{Sr}_{0.2}\text{Ti}_{0.9}\text{Zr}_{0.1}\text{O}_3/\text{Ni}_{0.8}\text{Zn}_{0.2}\text{Fe}_2\text{O}_4(\text{BN})$ and $\text{Ni}_{0.8}\text{Zn}_{0.2}\text{Fe}_2\text{O}_4/\text{Ba}_{0.8}\text{Sr}_{0.2}\text{Ti}_{0.9}\text{Zr}_{0.1}\text{O}_3$ (NB) composite film were deposited on Pt/Ti/SiO₂/Si substrates by the sol-gel method and spin-coating method. The results show that the deposition sequences of the composite films have significant influence on the ferroelectric, ferromagnetic and magnetoelectric properties of the composite films. Two composite films possess not only good ferroelectric and ferromagnetic properties but good magnetoelectric properties as well. The NB composite film has clear interface between the ferroelectric film and ferromagnetic film and possesses greater magnetoelectric coupling effect than the BN composite film under the same H_{bias} . The maximum value of α_E is $70.14 \text{ mV cm}^{-1} \text{ Oe}^{-1}$ was obtained in the NB composite film when H_{bias} is 638 Oe.

1. Introduction

Magnetoelectric materials possess both ferromagnetic properties and ferroelectric properties [1,2]. Coexistence of ferromagnetism and ferroelectricity may result in the magnetoelectric effect [2,3]. Magnetoelectric materials have recently attracted scientific and technological interest because of their potential applications in novel multi-functional devices, such as spintronics, actuators, sensors, multiple state memory elements [4–7]. The magnetoelectric effect is a spontaneous electric polarization induced by an external magnetic field [8–11], which is characterized by magnetoelectric voltage coefficient, $\alpha_E = \delta E / \delta H$ (where E is the induced electric field and H is the applied magnetic field) [12]. Magnetoelectric effect can occur either in single phase materials or composite films in which ferroelectric and ferromagnetic phases are mechanically coupled [13,14]. However, at room temperature, magnetoelectric effect of single phase materials is too weak for practical devices [2,3,8]. Therefore, researchers focus on the magnetoelectric composite films to acquire large magnetoelectric effect. Compared with single phase materials, the composite films have some unique advantages. For example, the composite films have much lower interface loss and higher magnetoelectric coupling effect and the artificial film can thus be achieved to modify the magnetoelectric behavior, such as lattice strain or inter-layer interaction. Furthermore, the magnetoelectric effect can be controlled in nanoscale and enhanced magnetoelectric effect can be obtained [11,15,16].

Generally speaking, the magnetoelectric composite films have three different structures including 0-3, 1-3 or 2-2 type [1,10,17]. It is found that great magnetoelectric effect can be obtained in 0-3 and 1-3 structured films owing to a leakage problem, which results from the low resistance of the ferromagnetic phase in the ferroelectric matrix [17]. In addition, it is not easy to control growth of the composite films with 0-3 or 1-3 type structures [1,8,15]. Noticeably, the leakage currents of magnetoelectric composite films with 2-2 type or layered structures can be reduced significantly by isolating the low resistive ferromagnetic phases with insulating ferroelectric phases [18]. As a consequence, great magnetoelectric effect can be obtained in 2-2 or layered composite films. In addition, it is easy to control growth of composite films with 2-2 type structures [13]. Therefore, the 2-2 type composite films have become potential candidates for magnetoelectric applications [14]. The magnetoelectric composite films with 2-2 type structure are composed of ferromagnetic films and ferroelectric films. Nowadays, it is well known that the magnetoelectric effect in these composite films arises from coupling between the magnetostrictive effect in ferromagnetic films and piezoelectric effect in ferroelectric films [1,2,5,8]. 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 phase, resulting in an electric polarization [5,12]. Thus, the

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magnetoelectric coupling effect in composite films depends on the ferromagnetic and ferroelectric properties of the composite films and coupling interaction across the interfaces between ferroelectric and ferromagnetic films [8,13,14]. In order to enhance magnetoelectric coupling effect, ferromagnetic phases with large magnetostrictive effect and ferroelectric phases with large piezoelectric effect were commonly adopted [13,14,19]. For instance, predominant ferromagnetic phases in magnetoelectric composite films are CoFe_2O_4 or NiFe_2O_4 (NFO) for their high magnetostrictive coefficient [1]. As NiFe_2O_4 possess small magnetic anisotropy in comparison with CoFe_2O_4 , NiFe_2O_4 has thus been considered to be the promising ferromagnetic phase in the magnetoelectric composite films. What's more, transition metal, such as Zn and Mn, were doped to NiFe_2O_4 to improve ferromagnetic properties. Therefore, $\text{Ni}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ (NZFO) was used as ferromagnetic phase in this work. In this way, we intend to investigate the impact of doping of Zn^{2+} on the ferroelectricity and determine the optimized doping amount of Zn^{2+} . On the other hand, it is known that $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$ (PZT) have been widely used as main ferroelectric phases in the magnetoelectric composite films due to their excellent ferroelectric and piezoelectric properties [8]. However, as Pb as a main constituent element in PZT has brought about environment pollution and serious damage to human's health [8,20,21], it is necessary to investigate lead-free ferroelectric materials to replace PZT. Nevertheless, up to date, lead-free piezoelectric materials generally have inferior piezoelectricity and ferroelectricity compared with PZT. Liu and Ren [18] prepared Ca and Zr doped BaTiO_3 (BTO) which exhibits excellent piezoelectric behavior ($d_{33} = 620$ pC/N). Luo et al. [22,23] pointed out that doping of Ca^{2+} , Sr^{2+} or Zr^{4+} to BaTiO_3 will improve the piezoelectric properties [17]. Thus, $\text{Ba}_{1-x}\text{Sr}_x\text{Ti}_{0.9}\text{Zr}_{0.1}\text{O}_3$ (BSTZO) was used as ferroelectric phase in this work. We will investigate impact of doping of Sr^{2+} on the ferromagnetism and determine the optimized doping amount of Sr^{2+} . Besides, there has not been systematic investigation on the relationship between the deposition sequence in the composite films and magnetoelectric properties of the composite films. As magnetoelectric properties of the composite films depend not only on the intrinsic properties of ferroelectric and ferromagnetic films but also on the structures of the composite films which influence coupling interaction across the interfaces between ferroelectric and ferromagnetic films [21], therefore, it is necessary to investigate the relationship between 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 BSTZO films or NZFO 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 $\text{Ni}_{0.8}\text{Zn}_{0.2}\text{Fe}_2\text{O}_4$ and $\text{Ba}_{1-x}\text{Sr}_x\text{Ti}_{0.9}\text{Zr}_{0.1}\text{O}_3$ precursor solutions alternately on the substrate. By changing the deposition sequence of two precursor solutions, the composite films with the structure of $\text{Ba}_{1-x}\text{Sr}_x\text{Ti}_{0.9}\text{Zr}_{0.1}\text{O}_3$ - $\text{Ni}_{0.8}\text{Zn}_{0.2}\text{Fe}_2\text{O}_4$ -substrate (BN) and $\text{Ni}_{0.8}\text{Zn}_{0.2}\text{Fe}_2\text{O}_4$ - $\text{Ba}_{1-x}\text{Sr}_x\text{Ti}_{0.9}\text{Zr}_{0.1}\text{O}_3$ -substrate (NB) were prepared. The impact of deposition sequence on the phase compositions, microstructures and properties of the magnetoelectric composite films was investigated in detail.

2. Experimental

In order to prepare the $\text{Ba}_{1-x}\text{Sr}_x\text{Ti}_{0.9}\text{Zr}_{0.1}\text{O}_3$ ($x = 0, 0.1, 0.2, 0.3$) precursor solution, barium acetate and strontium acetate were dissolved in glacial acetic acid and then stirred at 55 °C until complete dissolution to obtain the first solution. The tetrabutyltitanate ($\text{Ti}(\text{C}_4\text{H}_9\text{O})_4$) and tetrabutylzirconate ($\text{Zr}(\text{C}_4\text{H}_9\text{O})_4$) were dissolved in ethylene glycol methyl ether ($\text{C}_3\text{H}_8\text{O}_2$) and stirred at room temperature to obtain the second 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 $\text{Ba}_{1-x}\text{Sr}_x\text{Ti}_{0.9}\text{Zr}_{0.1}\text{O}_3$ (BSTZO). The precursor solution was spin-coated on Pt/Ti/SiO₂/Si substrates at a spinning rate of 3200 rpm for 30 s to obtain one-layered precursor

films. The BSTZO precursor films were dried at 120 °C for 10 min, then pre-annealed at 450 °C for 10 min and annealed at 700 °C for 20 min to obtain BSTZO films. Finally, four-layered BSTZO films were prepared by repeating spin-coating, pre-annealing process and annealing process for three times.

In order to prepare $\text{Ni}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0, 0.1, 0.2, 0.3$) precursor solution, nickel acetate and zinc acetate were dissolved in glacial acetic acid and then stirred at 55 °C until the solution was completely dissolved to obtain solution A. The ferric nitrate was dissolved in ethylene glycol methyl ether to obtain solution B. The polyvinylpyrrolidone was dissolved in acetic acid and then stirred at room temperature to obtain solution C. Finally, solution A, B and C were mixed and stirred at 60 °C for 3 h to obtain a sol precursor solution of $\text{Ni}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ (NZFO). The NZFO precursor solution was spin-coated on Pt/Ti/SiO₂/Si substrates at a spinning rate of 3200 rpm for 30 s. The NZFO precursor films were dried at 120 °C for 10 min, then pre-annealed at 500 °C for 10 min and annealed at 650 °C for 20 min to obtain BSTZO films. Finally, three-layered NZFO films were prepared by repeating spin-coating, pre-annealing process and annealing process two times.

The composite films were prepared by spin-coating $\text{Ba}_{1-x}\text{Sr}_x\text{Ti}_{0.9}\text{Zr}_{0.1}\text{O}_3$ and $\text{Ni}_{0.8}\text{Zn}_{0.2}\text{Fe}_2\text{O}_4$ precursor solution alternately on the substrate. By changing deposition sequence of films of $\text{Ba}_{1-x}\text{Sr}_x\text{Ti}_{0.9}\text{Zr}_{0.1}\text{O}_3$ and $\text{Ni}_{0.8}\text{Zn}_{0.2}\text{Fe}_2\text{O}_4$, the BN and NB composite films were prepared.

The phase compositions and crystal structures of the films were performed by means of X-ray diffractometer (X'Pert, PRO, MPD, PANalytical, B.V., Holl) with $\text{CuK}\alpha$ radiation. The morphologies of surface and cross-section of films were observed by field-emission scanning electron microscopy (FESEM, SU8020, Hitachi, Japan). The ferromagnetic hysteresis loops of the films were studied by vibrating sample magnetometer (S-VSM, Quantum, Design, USA). The ferroelectric behavior of the films was characterized by a ferroelectric test system (Precision, LC, Radiant Technologies Inc, USA). The magnetoelectric effect of the composite films was measured by a measuring device designed by the superconducting magnetic laboratory of University of Science and Technology of China and manufactured by Quantum Design China (test accuracy of voltage, 1 μV).

3. Results and discussion

The XRD pattern of single BaTiO_3 film and $\text{Ba}_{1-x}\text{Sr}_x\text{Ti}_{0.9}\text{Zr}_{0.1}\text{O}_3$ (BSTZO) films with different x (mole fraction of doping Sr^{2+}) are displayed in Fig. 1. It can be seen that all of the three BSTZO films are composed of the main phase, BaTiO_3 and Pt from the substrate without any secondary phase or impurity phase, indicating that Sr^{2+} and Zr^{2+} have dissolved into the lattice of BaTiO_3 to form a solid solution. It is

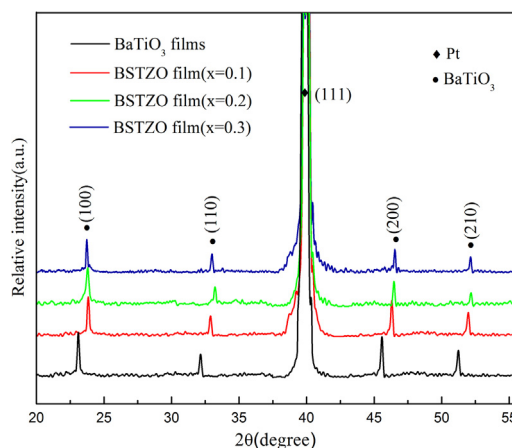


Fig. 1. XRD patterns of BaTiO_3 and BSTZO films with different x , mole fraction of doping Sr^{2+} ($x = 0.1, 0.2, 0.3$).

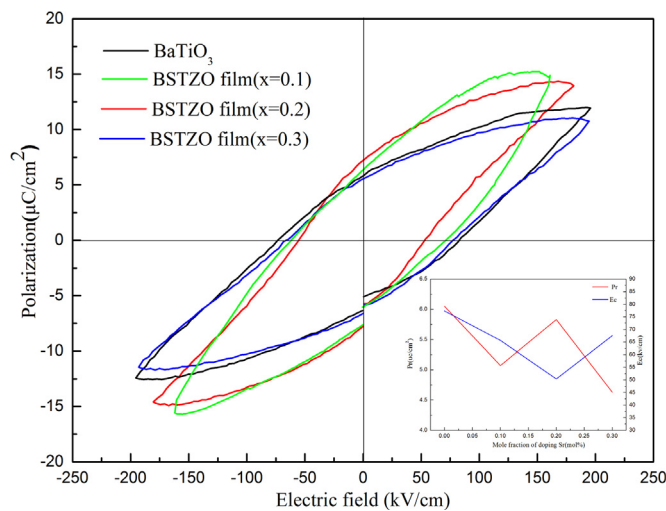


Fig. 2. The P-E hysteresis loops of BaTiO₃ and BSTZO films with different x, mole fraction of doping Sr²⁺ (x = 0.1, 0.2, 0.3). The inset shows the values of Pr and Ec of BaTiO₃ film and BSTZO films with different x.

clearly indicated that, compared with the BaTiO₃ film, the diffraction peaks of the BSTZO films shift towards higher 2θ, indicating that the doping of Sr²⁺ and Zr⁴⁺ to BaTiO₃ decrease the interplanar spacing of BaTiO₃ which leads the shift of the diffraction peaks of the BSTZO films towards higher 2θ.

The ferroelectric hysteresis loops of BaTiO₃ film and Ba_{1-x}Sr_xTi_{0.9}Zr_{0.1}O₃ films under different x (mole fraction of doping Sr²⁺) are presented in Fig. 2. It is observed that all of these films exhibit good ferroelectric properties. The remnant polarization (Pr) and the coercive field (Ec) for BaTiO₃ and Ba_{1-x}Sr_xTi_{0.9}Zr_{0.1}O₃ film are shown in the inset of Fig. 2. It is clear that the values of Pr decrease with the increase of doping mole fraction of Sr²⁺, reach a minimum value, then increase and finally decrease again after reaching a maximum value. Meanwhile, with the increase of doping mole fraction of Sr²⁺, the values of Ec decrease firstly, reach a minimum value and then increase for the higher mole fraction of Sr²⁺. It is worth to point out that, among the three BSTZO films, Ba_{0.8}Sr_{0.2}Ti_{0.9}Zr_{0.1}O₃ film possesses smallest value

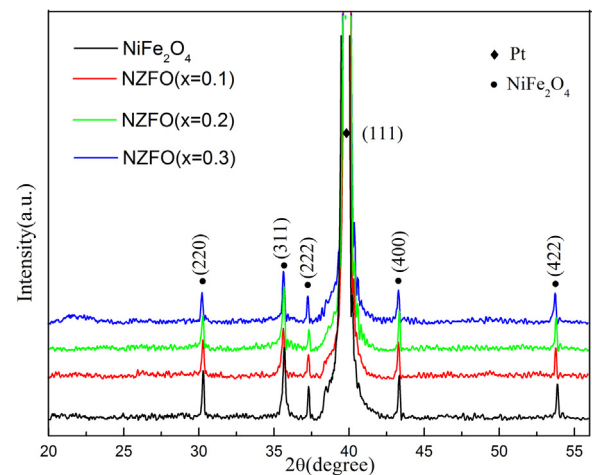


Fig. 4. XRD patterns of NiFe₂O₄ and NZFO films with different x, mole fraction of doping Zn²⁺ (x = 0.1, 0.2, 0.3).

of Ec, which is helpful to the movement and rotation of ferroelectric domain and beneficial to enhancing the magnetoelectric properties when it is used as a ferroelectric phase in the composite films. Ba_{0.8}Sr_{0.2}Ti_{0.9}Zr_{0.1}O₃ film possesses greater value of Pr, which is also beneficial to enhancing the magnetoelectric properties in the composite films. And the value of Pr of Ba_{0.8}Sr_{0.2}Ti_{0.9}Zr_{0.1}O₃ film in my work is 5.83 μC cm⁻² which is greater than 3 μC cm⁻² reported in Ref [24] for BaTiO₃ film. So in this work, the chemical formula of BSTZO film used in the composite film we chose is Ba_{0.8}Sr_{0.2}Ti_{0.9}Zr_{0.1}O₃.

FESEM morphology of the cross-section of Ba_{0.8}Sr_{0.2}Ti_{0.9}Zr_{0.1}O₃ film is shown in Fig. 3. It can be seen that the interface between Ba_{0.8}Sr_{0.2}Ti_{0.9}Zr_{0.1}O₃ film and the substrate is clear and flat. As the lattice parameter of Ba_{0.8}Sr_{0.2}Ti_{0.9}Zr_{0.1}O₃ film (a = 0.39763, b = 0.39763, c = 0.39421) is close to that of cubic Pt (a = 0.3923 nm), it will be beneficial to obtaining the flat interface between the film and the substrate. And the thickness of Ba_{0.8}Sr_{0.2}Ti_{0.9}Zr_{0.1}O₃ film is estimated to about 148 nm.

The XRD pattern of the single NiFe₂O₄ film and Ni_{1-x}Zn_xFe₂O₄ (NZFO) films with different x (mole fraction of doping Zn²⁺) are

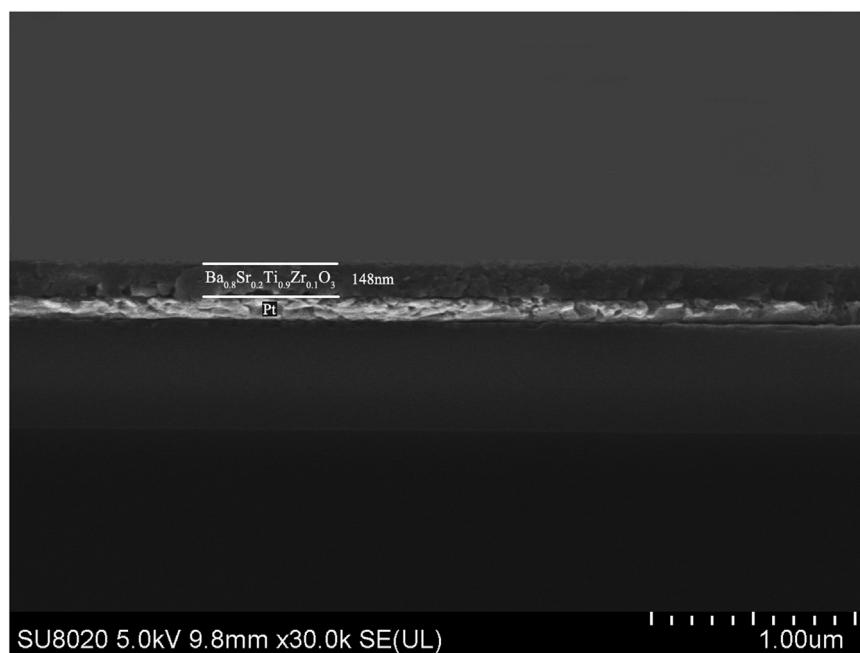


Fig. 3. The FESEM morphology of the cross-section of Ba_{0.8}Sr_{0.2}Ti_{0.9}Zr_{0.1}O₃ film.

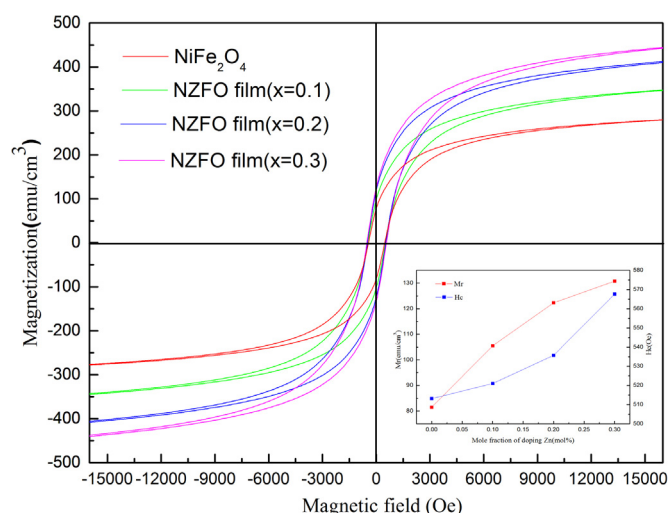


Fig. 5. The M-H hysteresis loops of NiFe₂O₄ and NZFO films with different x, mole fraction of doping Zn²⁺ (x = 0.1, 0.2, 0.3). The inset shows the values of Mr and Hc of NiFe₂O₄ film NZFO films with different x.

presented in Fig. 4. In the three NZFO films, the main phase, NiFe₂O₄ and Pt from the substrate are presented, which is accordance with the single NiFe₂O₄ film. And no secondary phase or impurity phase can be found, which indicates that Zn²⁺ has dissolved into the lattice of NiFe₂O₄ in the three NZFO films. Compared with the NiFe₂O₄ film, the diffraction peaks of the NZFO film have no apparent displacement, which is attributed to fact that the ionic radius of Zn²⁺ (0.074 nm) is close to that of Ni²⁺ (0.069 nm).

The ferromagnetic hysteresis loops of the single NiFe₂O₄ film and NZFO films with different mole fraction of doping Zn²⁺ are displayed in Fig. 5. The saturation magnetization (Ms) and coercive force (Hc) of NiFe₂O₄ film and three NZFO films are shown in the inset of Fig. 5. It is indicated that magnetic hysteresis loops of the NiFe₂O₄ film and the three NZFO films exhibit good symmetry and well-saturated shape, implying good ferromagnetic properties. It is clear that NZFO films possess greater values of Ms and Hc than those of the NiFe₂O₄ film. It is clear that the values of Ms increase rapidly with the increase of mole

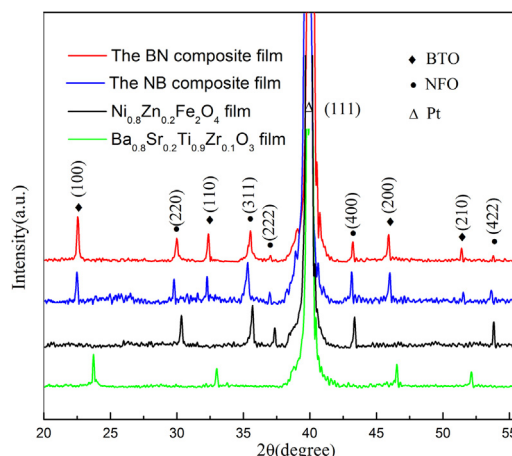


Fig. 7. The XRD patterns of the NB and BN composite films, Ni₀.₈Zn₀.₂Fe₂O₄ film and Ba₀.₈Sr₀.₂Ti₀.₉Zr₀.₁O₃ film.

fraction of doping Zn²⁺, and then increase slowly when x is greater than 0.2. Meanwhile, the values of Hc increase slowly at first, and then increase rapidly when x is greater than 0.2. As high values of Ms and low values of Hc are beneficial to enhancing the magnetoelectric properties in the composite films, therefore Ni₀.₈Zn₀.₂Fe₂O₄ was chosen as ferroelectric phases in the composite films.

The FESEM morphology of the cross-section of Ni₀.₈Zn₀.₂Fe₂O₄ film is shown in Fig. 6. It can be seen that there is no clear and flat interface between Ni₀.₈Zn₀.₂Fe₂O₄ film and the substrate. As the lattice parameter of Ni₀.₈Zn₀.₂Fe₂O₄ film (a = b = c = 0.83437 nm) is much greater than that of cubic Pt (a = 0.3923 nm), great lattice mismatch will make it difficult to acquire clear and flat interface between the film and the substrate.

In order to investigate impact the deposition sequence on the phase compositions, microstructures and properties of the magnetoelectric composite films, the NB and BN composite films were prepared on the Pt/Ti/SiO₂/Si substrate. The XRD patterns of the NB and BN composite films are shown in Fig. 7. It is indicated that, in the two composite films, there exist BTO, NFO and Pt from the substrate. Moreover, no peak of the secondary phase can be found, indicating the absence of any

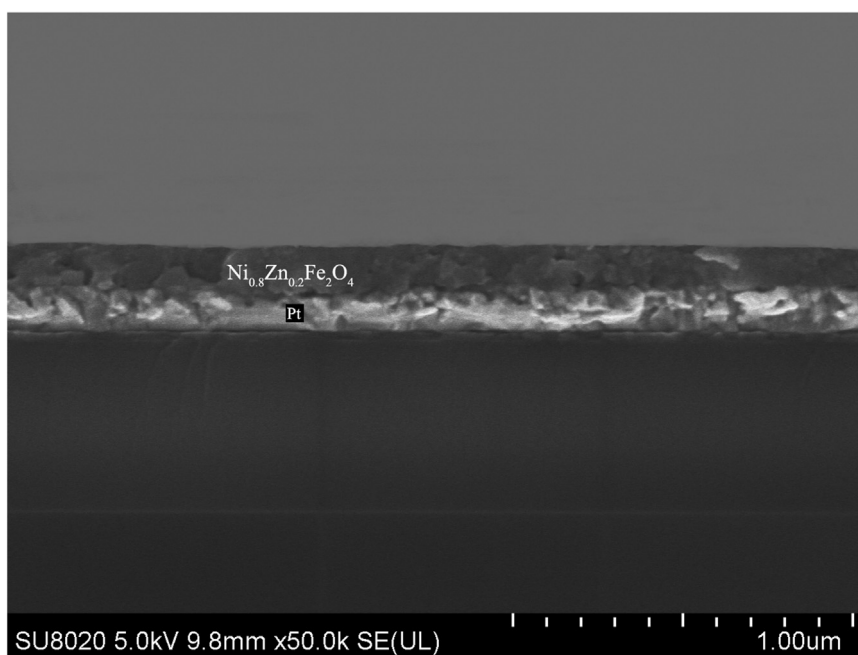


Fig. 6. The FESEM morphology of the cross-section of Ni₀.₈Zn₀.₂Fe₂O₃ film.

Table 1

The calculated lattice parameter and lattice mismatch of the BSTZO and NZFO film in the NB and BN composite film, the lattice parameter of BTO and NFO phase from standard power diffraction file.

Film	Lattice parameter			Lattice Mismatch		
	a(nm)	b(nm)	c(nm)	$\frac{\Delta a}{a_0}(\%)$	$\frac{\Delta b}{b_0}(\%)$	$\frac{\Delta c}{c_0}(\%)$
BSTZO film in the NB composite film	0.39835 ± 0.00045	0.39835 ± 0.00045	0.39638 ± 0.00073	0.29	0.29	0.15
NZFO film in the NB composite film	0.83578 ± 0.00137	0.83578 ± 0.00137	0.83578 ± 0.00137	0.22	0.22	0.22
BSTZO film in the BN composite film	0.39921 ± 0.00068	0.39921 ± 0.00068	0.39506 ± 0.00087	0.51	0.51	0.49
NZFO film in the BN composite film	0.83794 ± 0.00011	0.83794 ± 0.00011	0.83794 ± 0.00011	0.48	0.48	0.48
BTO(JCPDS NO.89-0274)	0.3972	0.3972	0.3970			
NFO(JCPDS NO.87-2337)	0.83393	0.83393	0.83393			

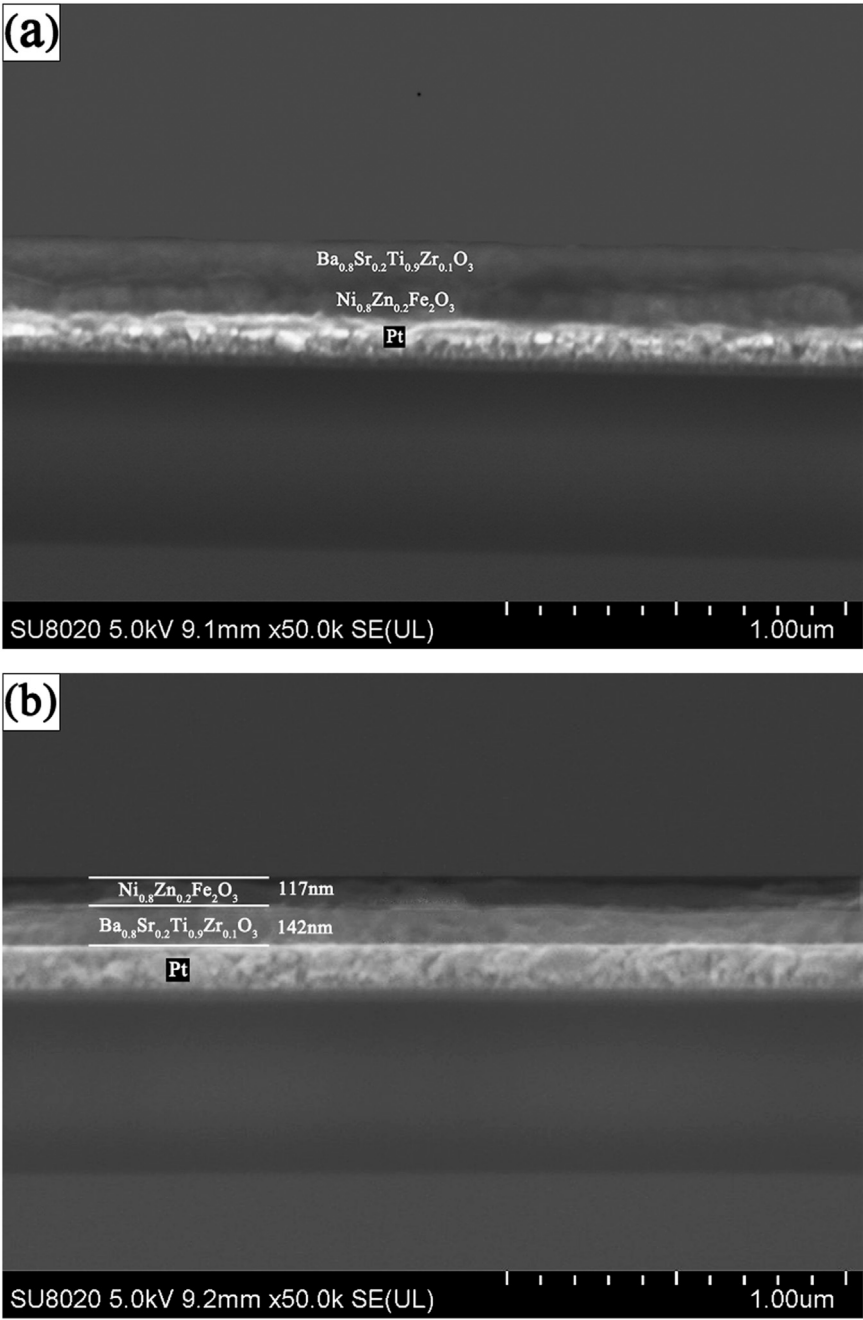


Fig. 8. The FESEM morphologies of cross-sections of (a)the BN composite film (b) the NB composite film.

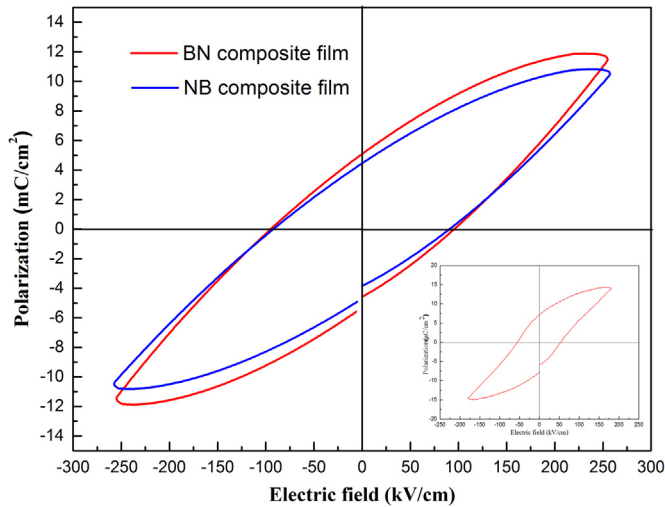


Fig. 9. The P-E hysteresis loops of the NB and BN composite film. The inset shows the P-E hysteresis loop of $\text{Ba}_{0.8}\text{Sr}_{0.2}\text{Ti}_{0.9}\text{Zr}_{0.1}\text{O}_3$ film.

Table 2

The values of P_r and E_c of the NB composite film, BN composite film and $\text{Ba}_{0.8}\text{Sr}_{0.2}\text{Ti}_{0.9}\text{Zr}_{0.1}\text{O}_3$ film.

Film	P_r ($\mu\text{C cm}^{-2}$)	E_c (kV cm^{-1})
NB composite film	4.37	87.55
BN composite film	5.06	96.62
$\text{Ba}_{0.8}\text{Sr}_{0.2}\text{Ti}_{0.9}\text{Zr}_{0.1}\text{O}_3$ film	5.83	50.37

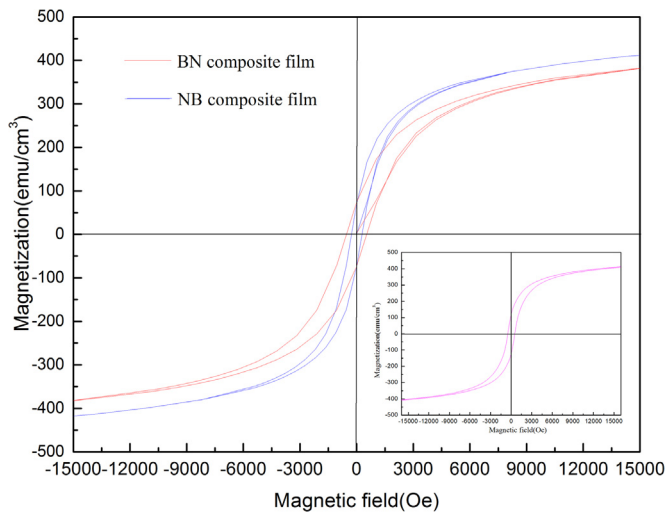


Fig. 10. The M-H hysteresis loops of the NB and BN composite films. The inset shows the M-H hysteresis loop of $\text{Ni}_{0.8}\text{Zn}_{0.2}\text{Fe}_2\text{O}_4$ film.

Table 3

The values of M_s and H_c of the NB composite film, BN composite film and $\text{Ni}_{0.8}\text{Zn}_{0.2}\text{Fe}_2\text{O}_4$ film.

Film	M_s (emu cm^{-3})	H_c (Oe)
NB composite film	386.06	449.56
BN composite film	364.72	543.78
$\text{Ni}_{0.8}\text{Zn}_{0.2}\text{Fe}_2\text{O}_4$ film	418.37	535.67

chemical reaction between ferroelectric and ferromagnetic phases during the annealing process. It is noted that, compared with the single BSTZO and NZFO films, XRD peaks of the BN and NB composite films shift to smaller angles, which may be due to residual tensile stress

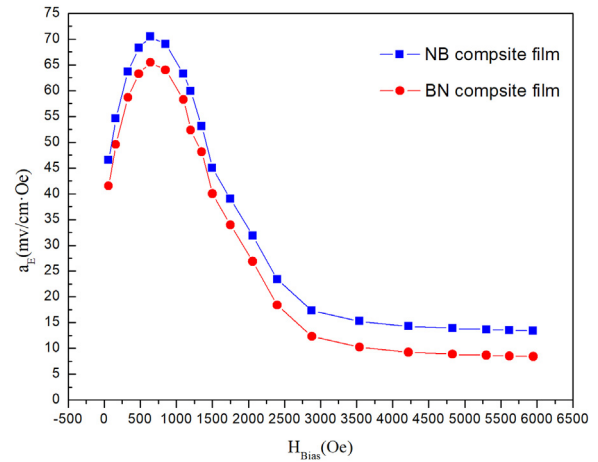


Fig. 11. The variation of α_E of the NB and BN composite film as a function of H_{bias} .

between BSTZO and NZFO films in the two composites. This will be discussed later. It can be also seen that the two composite films are well crystallized without preferred orientations. The lattice parameter of $\text{Ni}_{0.8}\text{Zn}_{0.2}\text{Fe}_2\text{O}_4$ and $\text{Ba}_{0.8}\text{Sr}_{0.2}\text{Ti}_{0.9}\text{Zr}_{0.1}\text{O}_3$ films in the BN and NB composite films are calculated by Jade 6.5. The lattice mismatch of ferroelectric and ferromagnetic phases in the composite films is determined by $\frac{\Delta a}{a_0}$, $\frac{\Delta b}{b_0}$ and $\frac{\Delta c}{c_0}$ (Where Δa , Δb and Δc are the difference between the lattice parameter of the corresponding single phase film in the composite film and that of the standard single phase). The results are listed in Table 1. It can be seen that BSTZO films in the NB and BN composite films possess tetragonal structure. The lattice parameter (a , b and c) of BSTZO and NZFO films in the NB and BN composite films are all greater than that of the standard BaTiO_3 phase, indicating the BSTZO and NZFO films in the two composite films are subjected to the three dimensional tensile stress. This can explain the reason why peaks of the BN and NB composite films have shifted to smaller angles. It is worthy to note that BSTZO film and NZFO film in the NB composite film possess smaller lattice mismatch than those in the BN composite film, which results in smaller residual stress in the composite film. This will help to enhance the magnetoelectric effect in the composite films.

The FESEM images of the cross-section of the BN and the NB composite films are shown in Fig. 8. From Fig. 8(a), it is seen that, in BN composite film, the interface between the ferroelectric film and ferromagnetic film and the interface between the composite film and the substrate is not clear and flat. As there is great difference between the lattice parameter of cubic Pt ($a = 0.3923 \text{ nm}$) and the lattice parameter of NZFO in the BN composite film shown in Table 1, it is different to acquire clear and flat interface between the composite film and the substrate. From Fig. 8(b), it is clear that the NB composite film possesses layered or 2-2 type structure. It is also indicated that, in the NB composite film, the interface between the ferroelectric film and ferromagnetic film and the interface between the composite film and the substrate are clear and flat. As the lattice parameter of BSTZO film shown in Table 1, is close to the lattice parameter of Pt, it will be beneficial to obtaining flat interface between the composite film and the substrate. It can be found that no intermediate layer is observed, which suggests that both NZFO and BSTZO phase can coexist without interface diffusion. Thus results are well agreement with those of XRD. As can be seen from the cross-sectional image, the thicknesses of NZFO and BSTZO film in the NB composite film are 117 nm and 142 nm, respectively.

The ferroelectric hysteresis loops of the NB and BN composite films are shown in Fig. 9. The ferroelectric hysteresis loop of single $\text{Ba}_{0.8}\text{Sr}_{0.2}\text{Ti}_{0.9}\text{Zr}_{0.1}\text{O}_3$ film is shown in the inset of Fig. 9. It is clear that both of these two composite films exhibit good ferroelectric properties.

Ferroelectric parameters of the two composite films drawn from Fig. 9 are listed in Table 2. The values of P_r of the NB and BN composite films in my work are 4.37 and 5.06 $\mu\text{C cm}^{-2}$ which are both greater than 2.5 $\mu\text{C cm}^{-2}$ reported in Ref [25] for $\text{BaTiO}_3/\text{SrTiO}_3$ composite film. From Table 2, it can be seen that the two composite films possess smaller values of P_r and greater values of E_c than single $\text{Ba}_{0.8}\text{Sr}_{0.2}\text{Ti}_{0.9}\text{Zr}_{0.1}\text{O}_3$ film. The smaller values of P_r are due to the dilution effect of the ferromagnetic phases in the two composite films. Whereas, the greater values of E_c are attributed to the interaction between ferroelectric and ferromagnetic phases in the two composite films [19]. It is clear that the NB composite film possess smaller values of P_r and E_c than the BN composite film, which indicates that the deposition sequence of the composite films influences the ferroelectric properties of the composite films.

The ferromagnetic hysteresis loops of the NB composite film and BN composite film are shown in Fig. 10. The ferromagnetic hysteresis loop of single $\text{Ni}_{0.8}\text{Zn}_{0.2}\text{Fe}_2\text{O}_4$ film is shown in the inset of Fig. 10. It can be seen that, for both of the two composite films, magnetic hysteresis loops exhibit good symmetry and well-saturated shape. The ferromagnetic parameter of the two composite films drawn from Fig. 10 is listed in Table 3. From Table 3, it can be seen that the two composite films possess smaller values of M_s than single $\text{Ni}_{0.8}\text{Zn}_{0.2}\text{Fe}_2\text{O}_4$ film, which may be due to the interaction between ferroelectric and ferromagnetic phases in two composite films [26]. It is clear that the NB composite film possesses greater values of M_s and smaller values of H_c than the BN composite films, which shows that the NB composite film possess better ferromagnetic properties. This indicates that the deposition sequence of the composite films influences the ferromagnetic properties of the composite films.

The coexistence of the ferromagnetic NZFO phase and ferroelectric BSTZO phase may give rise to magnetoelectric coupling effect, which is characterized by α_E , magnetoelectric voltage coefficient. And α_E is calculated according to Eq. (1) [27]:

$$\alpha_E = \frac{\delta V}{t \delta H} \quad (1)$$

Where t is the thickness of the composite film and V is the voltage induced by an applied AC magnetic field and DC bias magnetic field (H_{bias}). AC magnetic field and DC bias magnetic field are all parallel to the surfaces of the composite film.

The variation of the values of α_E of the two composite films with H_{bias} is shown in Fig. 11. It is seen that the two composite films exhibit significant magnetoelectric coupling effect, which depends on H_{bias} . It is also indicated that with the increase of H_{bias} , the values of α_E increase with the increase of H_{bias} , reach a maximum value, then decrease rapidly and remain almost invariable finally. As α_E is dependent on H_{bias} , it is necessary to track the piezomagnetic coupling coefficient $q = dk/dH_{\text{bias}}$ (where k is the magnetostriction) [11,19,28]. 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 [29].

It is clear that the NB composite film possesses greater values of α_E than the BN composite films at any fixed H_{bias} , implying that deposition sequence in the composite film influences the magnetoelectric coupling properties of the composite film. The reasons why the NB composite film has strong magnetoelectric coupling effect are as follows. On one hand, the dynamic magnetoelastic coupling induced by the magnetostriction of ferromagnetic phase and the piezoelectric effect of ferroelectric phase, which are related with the domain-wall motion and domain rotation, is involved in the magnetoelectric coupling effect [11,19,30]. As the NB composite film has lower values of H_c and E_c , which is very helpful to the motion of domain-wall or rotation of domain, resulting in larger magnetostriction or piezoelectricity, the NB composite film possesses stronger magnetoelectric coupling effect [11]. On the other hand, for magnetoelectric composite films, magnetoelectric effect mainly arises from the magnetic-mechanical-electric

transform through the stress-mediated transfer across the interface. The flat interface between ferroelectric phase and ferromagnetic phase in the NB composite film is beneficial to the magnetic-mechanical-electric transfer in the NB composite film. Therefore, the NB composite films possess greater value of α_E . It is worthwhile pointing out that the maximum of α_E for the NB composite film and the BN composite film are 70.48 and 65.48 $\text{mV cm}^{-1} \text{Oe}^{-1}$ when H_{bias} is about 638 Oe, which are all greater than those reported in Ref [19] (45.38 $\text{mV cm}^{-1} \text{Oe}^{-1}$) and Ref [30] (27.0 $\text{mV cm}^{-1} \text{Oe}^{-1}$). The significant magnetoelectric coupling effect in this work may be mainly attributed to the flat and clear interface between BSTZ and NZFO film in the NB composite film, which enhances the stress-mediated transfer across the interface.

4. Conclusions

The BN and NB composite films were prepared on Pt/Ti/SiO₂/Si substrates by sol-gel process and spin-coating technique. The results show that the deposition sequence for the composite films has significant impact on the structure, ferroelectric, ferromagnetic and magnetoelectric properties of the composite films. Both of these two composite films are composed of BaTiO_3 , NiFe_2O_4 and Pt from the substrate. Moreover, no secondary phases were found, indicating the absence of any chemical reaction between the two phases during the annealing process. The value of E_c and H_c of the NB composite film is smaller than that of the BN composite film. The maximum of α_E of the NB composite film (70.48 $\text{mV cm}^{-1} \text{Oe}^{-1}$) is greater than that of the BN composite film (65.48 $\text{mV cm}^{-1} \text{Oe}^{-1}$). The NB composite film has a larger α_E than the BN composite film, indicating that the NB composite film is more suitable for use as magnetoelectric composite materials.

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