

# In situ formation of sol-gel derived $\text{PbTiO}_3/\text{NiFe}_2\text{O}_4$ biphasic thin film

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**Abstract** In this article, magnetoelectric (ME) biphasic composite thin films consisted of  $\text{PbTiO}_3$  as ferroelectric phase and  $\text{NiFe}_2\text{O}_4$  as ferromagnetic phase which were successfully formed in situ by sol-gel process. The phase structure, morphology and dielectric properties of the films were measured by X-ray diffraction (XRD), scanning electron microscope (SEM) and LCR precision impedance analyzer. It is concluded that the thin films were capable of being controlled to form the biphasic composite of  $\text{PbTiO}_3$  and  $\text{NiFe}_2\text{O}_4$  at the heat-treatment temperature between 600 and 850 °C. The phases coexisting in the composite thin film are in forms of solid solutions doped with  $\text{Ni}^{2+}$  and  $\text{Fe}^{3+}$  and with  $\text{Ti}^{4+}$ , respectively. Their lattice constants vary with their doping contents. The capacitance of the composite thin film depends on the content of perovskite phase and the doping addition of  $\text{Ni}^{2+}$  and  $\text{Fe}^{3+}$  in crystalline phase of  $\text{PbTiO}_3$ .

**Keywords** Ferroelectric/ferromagnetic composites ·  $\text{PbTiO}_3/\text{NiFe}_2\text{O}_4$  · In situ · Sol-gel

## 1 Introduction

Ferromagnetic/ferroelectric composites are a kind of new composite materials which show both ferroelectric and ferromagnetic properties together. The magnetoelectric (ME) composites can provide both inductance and capacitance. They are used as sensors, wave guides, etc [4]. Moreover, they have the ME effect [2]. Therefore, these

materials can be used to design and produce EMI filters [8], which can reduce the occupied space on the circuit board and realize integration and miniaturization.

The ME composites are usually compounded into bulks or films using ferromagnetic phase and ferroelectric phase which are prepared separately by ceramic sintering [1–6] or sol-gel method [7–10]. Compared with the conventional method, in situ combination of the ME composites makes the two phases contact on a molecule scale level, leading to high ME coefficient [2, 5]. Sol-gel method, thus, will get widely used in recent years with the devices tending to be miniaturized, lightened and integrated.

In this work, in situ combined  $\text{PbTiO}_3/\text{NiFe}_2\text{O}_4$  biphasic thin film composites were prepared. The structure, formation mechanism and dielectric properties of the biphasic composites were investigated in detail.

## 2 Experimental

Lead acetate ( $\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$ ), tetrabutyl titanate ( $\text{Ti}(\text{OC}_4\text{H}_9)_4$ ), nickel acetate ( $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 5\text{H}_2\text{O}$ ) and ferric nitrate ( $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ) as raw materials whose composition is 1:1:1:2 and acetic acid ( $\text{CH}_3\text{COOH}$ ) and ethylene glycol monomethyl ether ( $\text{CH}_3\text{OCH}_2\text{CH}_2\text{OH}$ ) as solution were initially used to prepare a sol precursor with concentration of 0.1% [11]. The thin films were then prepared using the sol precursor by dip-coating method on silicon substrates. After taken out of the sol precursor, the samples were sintered by rapid heat-treatment at 550 °C for 8 min in an oven in air. And the process was repeated up to eight times (layers) in order to control the thickness about 1.5  $\mu\text{m}$  for all the thin films in this paper. The samples were finally post heat-treated for 1 h between 550 and 900 °C for promoting and controlling phase formation. The phase

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structure and morphology of the thin films were measured by X-ray Diffraction (RIGAKUD/MAX-C) and Scanning Electron Microscopy (XL30E), respectively. Their dielectric properties were analyzed by Precision Impedance Analyzer (HP4294A-LRC).

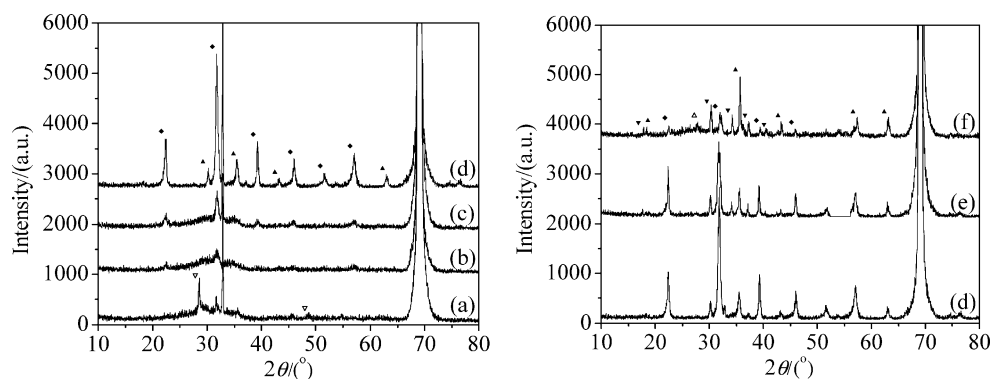
### 3 Results and discussion

Figure 1 shows the XRD patterns of the Pb–Ti–Ni–Fe–O thin film composites heat-treated initially at 550 °C for 8 min  $\times$  8 layers. Then most of the films were post heat-treated between 550 and 900 °C for 1 h. When the sample was just rapidly heat-treated at 550 °C for 8 min,  $\text{Pb}_{0.94}\text{Ti}_{0.06}\text{O}_{1.06}$  was formed (see  $\nabla$  in Fig. 1). When the sample was post heat-treated at 550 °C for 1 h,  $\text{PbTiO}_3$  and  $\text{NiFe}_2\text{O}_4$  began to form (see  $\blacklozenge$  and  $\blacktriangle$  in Fig. 1) in the system.  $\text{PbTiO}_3$ ,  $\text{NiFe}_2\text{O}_4$  and  $\text{Pb}_{0.94}\text{Ti}_{0.06}\text{O}_{1.06}$  thus coexisted in the thin film. When post heat-treatment temperature increased up to 600 °C, both  $\text{PbTiO}_3$  and  $\text{NiFe}_2\text{O}_4$  phases were formed in the thin film. However above 900 °C, two new phases, hexagonal  $\text{PbFe}_{12}\text{O}_{19}$  (see  $\blacktriangledown$  in Fig. 1) and rutile phase of  $\text{TiO}_2$  (see  $\blacktriangle$  in Fig. 1) began to form in the thin film. The tetra-phase composite thin film consisting of  $\text{PbTiO}_3$ ,  $\text{NiFe}_2\text{O}_4$ ,  $\text{PbFe}_{12}\text{O}_{19}$  and  $\text{TiO}_2$  formed in this case. The formation of the thin film composites mentioned above is directly connected with the heat-treatment temperature. In the thin film rapidly heat-treated at 550 °C for 8 min, a lot of active ions were formed while volatilizing organic ingredients. Because of the relatively low calcination temperature of 550 °C, the energy of the atoms in the system keeps actually not so high. Only the oxide of comparable simple composition, for example  $\text{PbO}$ , was formed by combining ions with those nearby through simply adjustment. At the same time, a few of  $\text{Pb}^{2+}$  is in fact substituted by  $\text{Ti}^{4+}$  to form a more thermally stable phase,  $\text{Pb}_{0.94}\text{Ti}_{0.06}\text{O}_{1.06}$ , in the complex system in this case. However, the calcinations temperature of 550 °C is very near to the formation temperature of the crystalline phases of  $\text{PbTiO}_3$  and  $\text{NiFe}_2\text{O}_4$ . Therefore, when the thin film was post heat-treated at 550 °C for 1 h, there is enough time for

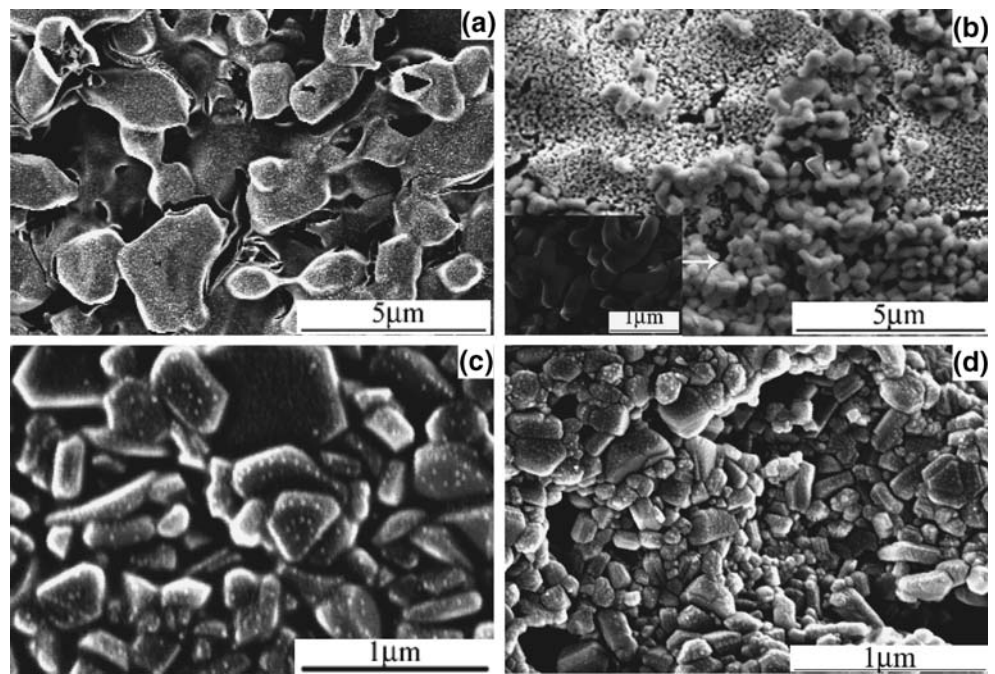
the atoms to transfer and adjust.  $\text{PbTiO}_3$  and  $\text{NiFe}_2\text{O}_4$ , which are of comparable complex structure, were formed although they need in fact higher formation energy than that of  $\text{Pb}_{0.94}\text{Ti}_{0.06}\text{O}_{1.06}$ . Hence there are three phases coexisting in the thin film after post heat-treated at 550 °C for 1 h. When post calcination temperature increases to 600 °C and above, the atoms possesses enough energy to form  $\text{PbTiO}_3$  and  $\text{NiFe}_2\text{O}_4$ . And  $\text{Pb}_{0.94}\text{Ti}_{0.06}\text{O}_{1.06}$  can't be stable any longer. The biphasic composite thin film keeps stable and  $\text{PbTiO}_3$  and  $\text{NiFe}_2\text{O}_4$  coexist in the thin film system. When increasing post heat-treatment temperature to about 900 °C,  $\text{PbFe}_{12}\text{O}_{19}$  of more complex structure began to come into being due to the high enough temperature. On the other hand, because lots of  $\text{Pb}^{2+}$  and  $\text{Fe}^{3+}$  are consumed to form  $\text{PbFe}_{12}\text{O}_{19}$ , at the same time,  $\text{Fe}^{3+}$  and  $\text{Ni}^{2+}$  are consumed to form  $\text{NiFe}_2\text{O}_4$ . Rutile phase  $\text{TiO}_2$  is formed simultaneously because excessive  $\text{Ti}^{4+}$  ion remains in the system with a suitable high formation temperature. Thus, tetra-phase composite thin film containing  $\text{PbTiO}_3$ ,  $\text{NiFe}_2\text{O}_4$ ,  $\text{PbFe}_{12}\text{O}_{19}$  and  $\text{TiO}_2$  is formed above 900 °C. Hence,  $\text{PbTiO}_3/\text{NiFe}_2\text{O}_4$  two phase composite thin films exhibiting the ferromagnetic/ferroelectric behavior can be obtained by controlling post heat-treatment temperatures between 600 and 850 °C.

Affected by the multiphase system, the phases coexisted in the thin film are mostly in forms of solid solutions. The peak of  $\text{Pb}_{0.94}\text{Ti}_{0.06}\text{O}_{1.06}$  increased in  $2\theta$  with the increase in post sintering temperature, as shown in Fig. 1. It means that the lattice constant decreases with increasing sintering temperature. In fact,  $\text{Pb}_{0.94}\text{Ti}_{0.06}\text{O}_{1.06}$  stabilizes at low temperature. With increasing temperature, deficiencies such as lead or oxygen vacancies easily occur and increase gradually. On the other hand,  $\text{Ni}^{2+}$  and  $\text{Fe}^{3+}$  which are smaller than  $\text{Pb}^{2+}$  in size may dissolve in the crystal structure of  $\text{Pb}_{0.94}\text{Ti}_{0.06}\text{O}_{1.06}$  to substitute for  $\text{Pb}^{2+}$ . And the substitution content increases with increasing temperature. Therefore,  $\text{Pb}_{0.94}\text{Ti}_{0.06}\text{O}_{1.06}$  exists in the form of solid solution with  $\text{Pb}^{2+}$  being substituted by  $\text{Ni}^{2+}$  and  $\text{Fe}^{3+}$ . The peak of perovskite phase decreased in  $2\theta$  with the increase in temperature from 550 to 650 °C and kept constant between 650 and 900 °C and increases above 900 °C, as

**Fig. 1** XRD patterns of the film composites firstly heat-treated at 550 °C for 8 min and post heat-treated at different temperatures. (a) without second heat-treatment, (b) 550 °C, (c) 600 °C, (d) 850 °C, (e) 900 °C and (f) 950 °C. The phase structures are represented by the symbols of  $\blacklozenge$   $\text{PbTiO}_3$ ;  $\blacktriangle$   $\text{NiFe}_2\text{O}_4$ ;  $\nabla$   $\text{Pb}_{0.94}\text{Ti}_{0.06}\text{O}_{1.06}$ ;  $\blacktriangledown$   $\text{PbFe}_{12}\text{O}_{19}$  and  $\blacktriangle$   $\text{TiO}_2$



**Fig. 2** SEM photographs of the film composites firstly heat-treated at 550 °C for 8 min and post heat-treated at (a) RT (b) 850 °C (c) 900 °C (d) 950 °C for 1 h

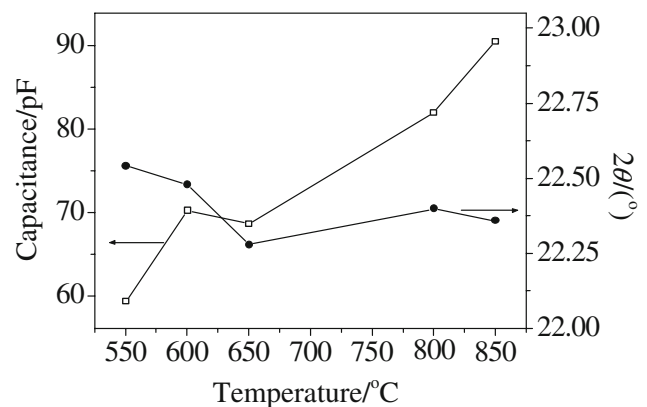


shown in Fig. 1. Its lattice constant in fact increases initially, then keeps constant and decreases finally.  $\text{PbTiO}_3$  is formed at higher temperature. With temperature increasing,  $\text{Ni}^{2+}$  or  $\text{Fe}^{3+}$  which are similar to  $\text{Ti}^{4+}$  in size may substitute for  $\text{Ti}^{4+}$ , causing the oxygen vacancies. The decrease of negative ions lessens the interaction between positive ions and negative ions, thus the lattice constants increase from 550 to 650 °C. With temperature increasing to 650 °C, the content of oxygen vacancies reaches the maximum, that is, the solubility of  $\text{Ni}^{2+}$  or  $\text{Fe}^{3+}$  gets to the maximum. And the lattice constant of  $\text{PbTiO}_3$  keeps constant above 650 °C as shown in Fig. 3 (b). Moreover, 900 °C is the temperature where  $\text{NiFe}_2\text{O}_4$  and  $\text{PbFe}_{12}\text{O}_{19}$  are formed rapidly (as shown in Fig. 1) by consuming so much  $\text{Ni}^{2+}$  and  $\text{Fe}^{3+}$  that the substitution of  $\text{Ni}^{2+}$  or  $\text{Fe}^{3+}$  for  $\text{Ti}^{4+}$  in  $\text{PbTiO}_3$  phase tends to drop above 900 °C. And the lattice constants of  $\text{PbTiO}_3$  decrease. Hence,  $\text{PbTiO}_3$  is in the form of solid solution with  $\text{Ti}^{4+}$  being substituted by  $\text{Ni}^{2+}$  or  $\text{Fe}^{3+}$ . For  $\text{NiFe}_2\text{O}_4$ , its peak position increases all along while decreasing lattice constant with increasing temperature. Similarly, in the complex system, other ions are easy to dissolve into the structure of  $\text{NiFe}_2\text{O}_4$ .  $\text{Ti}^{4+}$  in the system may substitute for  $\text{Ni}^{2+}$  or  $\text{Fe}^{3+}$  due to their close ionic radiuses, bringing some vacancies of positive ions, which may compress the lattice cell. The solubility increases with the increase in temperature, and the lattice constant of  $\text{NiFe}_2\text{O}_4$  decreases accordingly. However, the phase  $\text{PbFe}_{12}\text{O}_{19}$  keeps the lattice constant almost constant while increasing temperature. For  $\text{PbFe}_{12}\text{O}_{19}$ ,  $\text{Ti}^{4+}$  and  $\text{Ni}^{2+}$  may substitute for  $\text{Fe}^{3+}$  together to keep charge neutral. Therefore, the cell dimension doesn't have apparent changes, although the solubility may change with increasing temperature. Any

way,  $\text{PbFe}_{12}\text{O}_{19}$  is in the form of solid solution with  $\text{Fe}^{3+}$  being substituted by  $\text{Ni}^{2+}$  and  $\text{Ti}^{4+}$ .

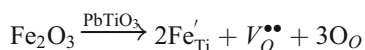
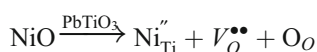
The SEM photographs of the thin film are shown in Fig. 2. For the thin film without post heat-treatment, there is no typical crystalline phase revealed. The thin film seems to be amorphous, which is consistent with the XRD results as shown in Fig. 1(a). When the films were post heat-treated above 550 °C, two special different crystalline phases  $\text{PbTiO}_3$  and  $\text{NiFe}_2\text{O}_4$  were formed whose grain size is about 100 nm for  $\text{PbTiO}_3$  and 500 nm for  $\text{NiFe}_2\text{O}_4$ , respectively at 850 °C. When post heat-treatment temperature increased to 900 °C and above 900 °C, the grains grow up to the typical crystalline phase and keep condensed thoroughly. The grain size is about 100–300 nm.

Figure 3 shows the capacitance of these films at 100 kHz and  $2\theta$  values of the peak (100) of the perovskite phase in



**Fig. 3** Plots of capacitance and  $2\theta$  (100) peak of the perovskite phase of the thin films post sintered at different temperatures

the thin films sintered at different temperatures. The capacitance of the films increases with post heat-treatment temperature before 600 °C, and decreases slightly from 600 to 650 °C then increases again above 650 °C. The  $2\theta$  value of  $\text{PbTiO}_3$  decreases from 550 to 650 °C and keeps almost constant above 650 °C. In the sample post heat-treated at 550 °C,  $\text{PbTiO}_3$ ,  $\text{NiFe}_2\text{O}_4$  and  $\text{Pb}_{0.94}\text{Ti}_{0.06}\text{O}_{1.06}$  coexist in the system and the major phase is  $\text{Pb}_{0.94}\text{Ti}_{0.06}\text{O}_{1.06}$  whose capacitance is very low. Thus the capacitance of the thin film is low. When increasing the temperature to 600 °C, the capacitance of the thin film increases with the disappearance of  $\text{Pb}_{0.94}\text{Ti}_{0.06}\text{O}_{1.06}$ . However, the dielectric constant of the composite thin film depends mainly on  $\text{PbTiO}_3$  phase because it is much higher than that of  $\text{NiFe}_2\text{O}_4$ . As mentioned above, oxygen vacancies are formed in  $\text{PbTiO}_3$  due to the substitution of  $\text{Ni}^{2+}$  or  $\text{Fe}^{3+}$  for  $\text{Ti}^{4+}$ . The defect equation is given as follow:



Therefore, the polarization may decrease and the capacitance of the thin film decreases slightly, although the content of  $\text{PbTiO}_3$  increases continually from 600 to 650 °C. The content of oxygen vacancies practically keeps constant when its solubility in  $\text{PbTiO}_3$  reaching the maximum at 650 °C. The capacitance of the thin film increases with increasing the content of  $\text{PbTiO}_3$  above 650 °C. Hence, the capacitance of the composite thin film depends on the content of  $\text{PbTiO}_3$  and the doping addition of  $\text{Ni}^{2+}$  and  $\text{Fe}^{3+}$  in crystalline  $\text{PbTiO}_3$  phase.

## 4 Conclusion

Biphase thin film composites of  $\text{PbTiO}_3$  of ferromagnetism and  $\text{NiFe}_2\text{O}_4$  of ferroelectricity were successfully prepared in situ by sol-gel method at the temperature between 600 and 850 °C.  $\text{PbTiO}_3$  phase in the composite system exists in the form of solid solution with  $\text{Pb}^{2+}$  substituted by  $\text{Ni}^{2+}$  or  $\text{Fe}^{3+}$ .  $\text{NiFe}_2\text{O}_4$  is in the form of solid solution with  $\text{Ni}^{2+}$  and  $\text{Fe}^{3+}$  substituted by  $\text{Ti}^{4+}$ . Two special different crystalline phases  $\text{PbTiO}_3$  and  $\text{NiFe}_2\text{O}_4$  were found in the SEM photographs. The capacitance of the films is affected by the content of the perovskite phase and the doping addition of  $\text{Ni}^{2+}$  and  $\text{Fe}^{3+}$  in crystalline  $\text{PbTiO}_3$ .

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