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Effect of biphasic on dielectric properties of Bi-doped lead strontium titanate thin films

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ABSTRACT

$\text{Pb}_{0.4}\text{Sr}_{0.6}\text{TiO}_3$ (PST) thin films doped with various concentration of Bi were prepared by a sol–gel method. The phase status, surface morphology and dielectric properties of these thin films were measured by X-ray diffraction (XRD), scanning electron microscopy (SEM) and impedance analyzer, respectively. Results showed that the thin films with the maximum dielectric constant and minimum dielectric loss were obtained for $x=0.15$. For $x < 0.15$, only pure PST perovskite phase were in the thin films. For $0.2 < x < 0.4$, the $\text{PST}/\text{Bi}_2\text{Ti}_2\text{O}_7$ biphasic were obtained. The thin films with pure $\text{Bi}_2\text{Ti}_2\text{O}_7$ pyrochlore phase were obtained for $x=0.67$. The biphasic thin films had high tunability and high figure of merit (FOM). The FOM of $\text{PST}/\text{Bi}_2\text{Ti}_2\text{O}_7$ biphasic thin film was about 6 times higher than that thin films formed with pure perovskite phase or pure pyrochlore phase.

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1. Introduction

The dielectric constant of ferroelectric materials will be varied by an applied direct current electric field, which led to their use in tunable microwave devices. Such as dynamic random-access memory (DRAM) resonators, phase shifters in antenna, and so on [1–3].

Ferroelectric material PST thin films have small ferroelectric critical size, low crystallization temperature and good dielectric properties [4–6]. It is compatible with fabrication of Si-based integrated circuit (IC) and is a promising candidate for voltage-tunable devices. To optimize the relative dielectric properties, more and more attention has been paid towards the PST system [7,8]. As it is known that increase of tunability and decrease of dielectric loss are both helpful for improving the figure of merit (FOM), which is the most important role to evaluate the quality of tunable device. In fact, doping in matrix system is an important way to improve the tunability and to decrease the loss of the thin film. The dopant of Al ion into $(\text{Ba,Sr})\text{TiO}_3$ (BST) makes the unit cell smaller, resulting in a short distance between the Ti^{4+} and the neighboring O^{2-} , and induce the structure more compact [9,10]. The vibration amplitude of central ions is softened easily by its nearest neighbors. This enhances the anharmonic effect and increases the anharmonic coefficient. Hence, a larger tunability is yielded. The dopant of Mg ion into the BST system

makes two phases formed, the domain-wall movements of the composite thin films were constrained and thus the dielectric loss decreased [11].

In this paper, PST thin films compounded with $\text{Bi}_2\text{Ti}_2\text{O}_7$, which has low permittivity and low dielectric loss, were investigated. Results showed that the biphasic in the thin films could contribute to the high tunability and FOM of the PST thin films, and made the thin films a good candidate for tunable devices use.

2. Experimental

The sol precursor used for preparation of $(\text{Pb}_{0.4}\text{Sr}_{0.6})_{1-3x/2}\text{Bi}_x\text{TiO}_3$ thin film was initially synthesized with Pb $(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$ (Wenzhou, 99.5%), SrCO_3 (Zhenxin, 99.0%), $\text{Bi}(\text{NO}_3)_3$ (Hengxin, 99.0%) and $\text{Ti}(\text{OC}_4\text{H}_9)_4$ (Meixing, 98.0%) as starting materials and glacial acetic acid (Hangzhou, 99.5%), $\text{H}_2\text{NCH}_2\text{CH}_2\text{OH}$ (Hangzhou, 99.0%) and $\text{C}_2\text{H}_5\text{OC}_2\text{H}_4\text{OH}$ (Yalian, 99.0%) as solvents. The precursor concentration was 0.35 mol/L. Wet thin films were then dip-coated on the ITO/glass substrate with the as-synthesized sol precursor. After they were air-dried and rapidly heat-treated at 500 °C for 5 min, initial mono-layer thin films were obtained. To control the thickness, multi-layered thin films were prepared after several repeating dip-coating and heat-treating process and then post annealing at 600 °C for 1 h. The total thickness of the thin films was about 400 nm.

Crystallinity and phase status of the Bi-doped PST thin films were measured by the X-ray diffraction (Rigaku, D/Max) using Cu $K\alpha$ radiation of 0.15405 nm; under 0.02° sampling interval and

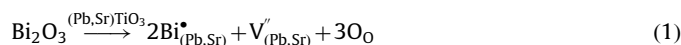
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4°/min scan speed. Surface morphologies of the thin films were observed by the scanning electron microscopy (SEM). The dielectric properties were measured with the impedance analyzer (kthley 3330).

3. Results and discussion

Fig. 1 shows the XRD patterns of $(\text{Pb}_{0.4}\text{Sr}_{0.6})_{1-3x/2}\text{Bi}_x\text{TiO}_3$ thin films with various Bi contents (x). The typical perovskite structure with six main peaks is observed when x is below 0.15. When the Bi contents reach 0.2, a new pyrochlore phase of $\text{Bi}_2\text{Ti}_2\text{O}_7$ has appeared. For $0.2 < x < 0.4$, the content of perovskite phase in the thin film is decreased and the pyrochlore phase is increased. Therefore the thin film is consisted of PST/ $\text{Bi}_2\text{Ti}_2\text{O}_7$ biphas. At $x=0.67$, only pyrochlore phase $\text{Bi}_2\text{Ti}_2\text{O}_7$ can be obtained.

The change of the biphas in PST thin film is due to the A-site vacancy induced by Bi dopant. As is known, the Bi dopant can bring A-site vacancy in the perovskite phase PST system due to the substitution of high valence Bi^{3+} ion for low valence Pb^{2+} and Sr^{2+} ions [12];



The intrinsic oxygen vacancies can be neutralized by A-site vacancies due to their opposite charges as follows [13]:



Furthermore, the concentration of A-site vacancy increases with increasing Bi dopant. The intrinsic oxygen vacancies in the thin films will be gradually neutralized by the increasing A-site vacancies, which are induced by Bi dopant. That is to say, when the charges induced by the two vacancies are the same, they will neutralize each other completely.

In this study, two kinds of vacancies seem to be neutralized completely at about $x=0.15$. For $x < 0.15$, the concentration of A-site vacancy is less than the intrinsic oxygen vacancy. When the Bi dopant is added into the thin film, the intrinsic oxygen vacancies in the thin films will be gradually neutralized by the increasing A-site vacancies. Thus the lattice distortion caused by intrinsic oxygen vacancy is minished. Thus the stability of crystal

and the formation ability of PST thin films are improved as seen in the XRD patterns. For $x > 0.15$, the concentration of A-site vacancy is more than the intrinsic oxygen vacancy. For the sake of charge balance, the excessive A-site vacancies induce the excessive oxygen vacancies. The stability of the perovskite phase is therefore decreased with increasing Bi content. With the decreasing of perovskite phase, the stable pyrochlore phase of $\text{Bi}_2\text{Ti}_2\text{O}_7$ appears and increases with increasing Bi dopant, as seen from the XRD patterns.

The morphologies of these $(\text{Pb}_{0.4}\text{Sr}_{0.6})_{1-3x/2}\text{Bi}_x\text{TiO}_3$ thin films are shown in Fig. 2. The thin film with pure perovskite phase, such as $x=0.1$ in Fig. 2(a), shows that the grain-like particles aggregate in a layer. The “aggregate” is exactly the perovskite phase in the film. It is also seen that the morphologies of aggregated particles change into the uniformly stacked crystalline grain, as is shown in Fig. 2(b) and (c). It indicates that the content of the perovskite aggregates decrease and the pyrochlore phase appears with increasing Bi content. Moreover, the thin film with the stable pyrochlore phase, such as $x=0.67$ in Fig. 2(d), shows a continuous and fine grained microstructure without obvious cracks. The particle of the crystalline phase is clear and no “aggregate” is seen in the picture, indicating that the thin film is mainly formed by the stable pyrochlore phase $\text{Bi}_2\text{Ti}_2\text{O}_7$.

The lattice constant of the perovskite phase PST thin film with different Bi dopant is shown in Fig. 3. It is seen that the lattice constant of the perovskite phase PST thin film increases when the smidgen of Bi ($0.1 < x < 0.2$) is doped into the thin film. When the content of Bi is more ($0.2 < x < 0.4$), the lattice constant of the perovskite phase PST thin film decreases quickly with the increasing pyrochlore phase $\text{Bi}_2\text{Ti}_2\text{O}_7$, which is seen in Fig. 3. The increase of the lattice constant in perovskite phase PST thin film is due to the A-site vacancy induced by Bi dopant. As mentioned above, the Bi dopant can take the place of $\text{Pb}^{2+}/\text{Sr}^{2+}$ and bring A-site vacancies in the PST system, which make the PST unit cell loose. Therefore, the lattice constant of the perovskite phase PST is increased with increasing Bi dopant for $0.1 < x < 0.2$. After that the Bi dopant forms a new pyrochlore phase $\text{Bi}_2\text{Ti}_2\text{O}_7$ and the content of Bi in the perovskite phase PST is reduced. So the lattice constant of PST decreases at about $x=0.2$. For $0.2 < x < 0.4$, the Bi dopant is mainly in the pyrochlore phase $\text{Bi}_2\text{Ti}_2\text{O}_7$ and only a little Bi exists in the perovskite phase PST. Therefore the lattice constant of PST reduces to 3.93 Å as seen in Fig. 3.

Fig. 4 shows both the capacitance and the loss factor of the Bi-doped PST thin films with various Bi contents. In this study, the effect of Bi dopant on the dielectric constant of the PST thin films is investigated through the change of capacitance because the thicknesses of those thin films are the same. From Fig. 4 we can see that the dielectric constant of $(\text{Pb}_{0.4}\text{Sr}_{0.6})_{1-3x/2}\text{Bi}_x\text{TiO}_3$ thin films increases with increasing Bi doping content from $x=0.1$ to 0.15, and then decreases when x reaches to 0.4. The change of dielectric loss is just on the contrary. The thin films exhibit the maximum dielectric constant and minimum loss at $x=0.15$.

As discussed above, proper Bi addition ($x=0.15$) in the PST thin films can bring enough A-site vacancy with negative charge, which can be used to balance the intrinsic oxygen vacancy with positive charge. According to the thermodynamic theory, the phase formation ability of the films is therefore increased with increasing Bi doping content up to $x=0.15$. At the same time, more polarization path may be provided when the crystalline phase content in the films increased. So the dielectric constant of the thin films is correspondingly increased and the dielectric loss is reduced. However with further Bi doping, the $\text{Bi}_2\text{Ti}_2\text{O}_7$ appears and the Bi content in the perovskite phase PST decreases when the two phases exist together. Therefore, the dielectric constant of the thin films decreases and the dielectric loss of the thin films increases when Bi content is more than 0.15 in the thin film as

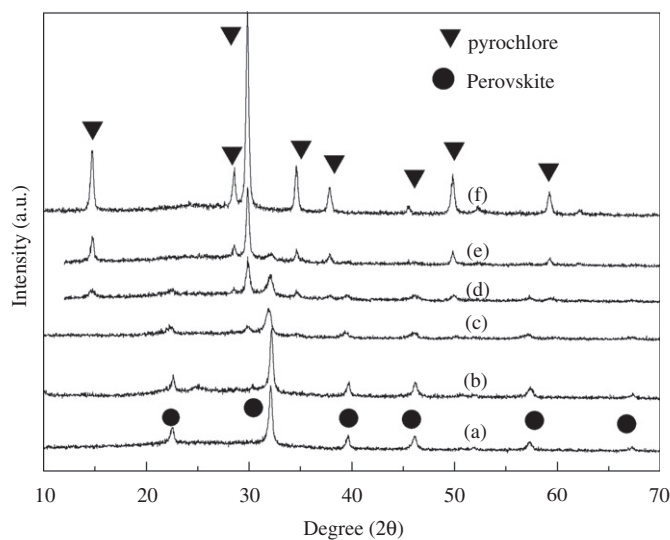


Fig. 1. XRD patterns of $(\text{Pb}_{0.4}\text{Sr}_{0.6})_{1-3x/2}\text{Bi}_x\text{TiO}_3$ thin films with (a) $x=0.1$, (b) $x=0.15$, (c) $x=0.2$, (d) $x=0.3$, (e) $x=0.4$ and (f) $x=0.67$.

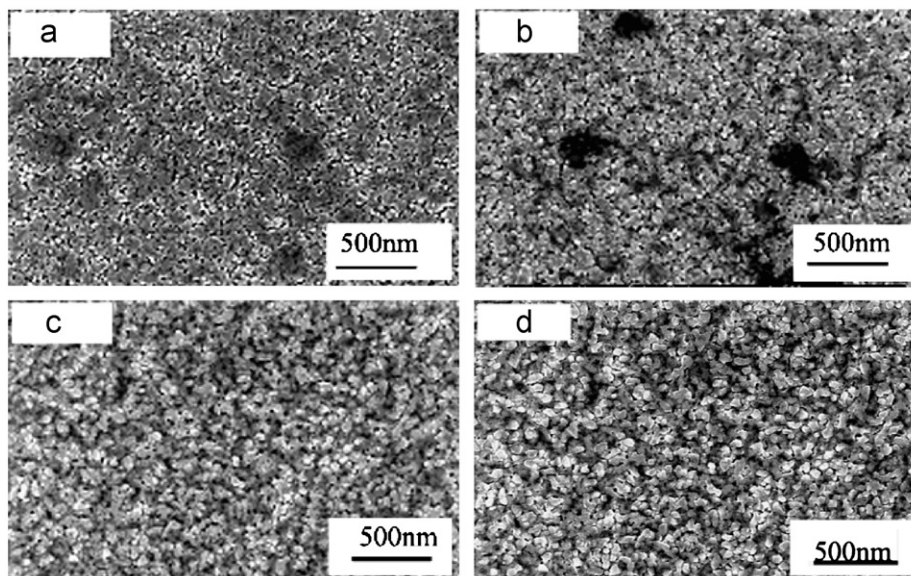


Fig. 2. SEM morphologies of $(\text{Pb}_{0.4}\text{Sr}_{0.6})_{1-3x/2}\text{Bi}_x\text{TiO}_3$ thin films with (a) $x=0.1$, (b) $x=0.2$, (c) $x=0.3$ and (d) $x=0.67$.

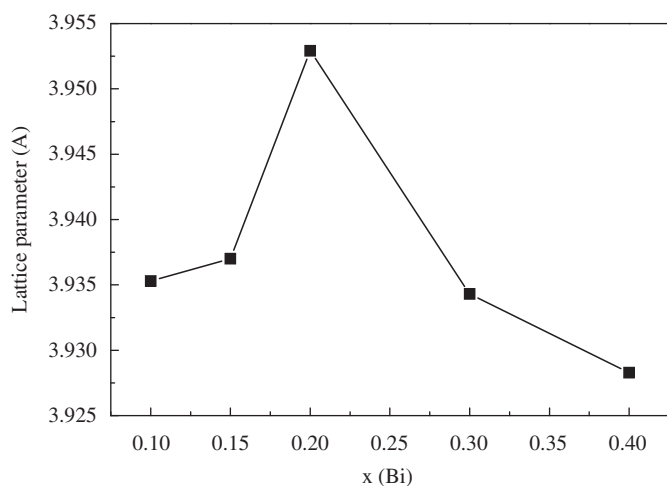


Fig. 3. A plot of lattice constant of perovskite phase films as a function of x .

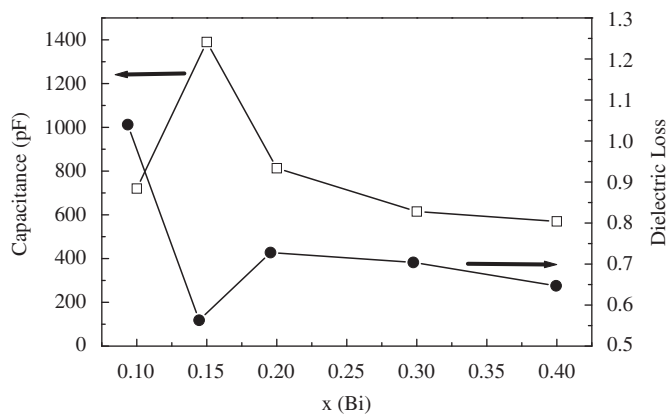


Fig. 4. Capacitance and dielectric loss of the $(\text{Pb}_{0.4}\text{Sr}_{0.6})_{1-3x/2}\text{Bi}_x\text{TiO}_3$ thin films under 100 kHz as a function of x .

seen in Fig. 4. The dielectric constant of the composite thin films still decreases for $x > 0.2$ because the pyrochlore phase has lower dielectric constant than perovskite phase. Likewise the dielectric

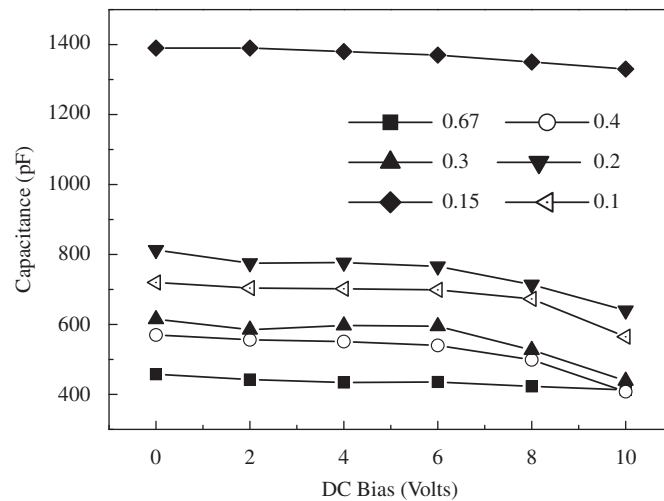


Fig. 5. The dielectric properties of the $(\text{Pb}_{0.4}\text{Sr}_{0.6})_{1-3x/2}\text{Bi}_x\text{TiO}_3$ thin films with changing electric field as a function of Bi doping content.

loss of composite films is decreased with increasing $\text{Bi}_2\text{Ti}_2\text{O}_7$ for $x > 0.2$ due to its low dielectric loss. $\text{PST}/\text{Bi}_2\text{Ti}_2\text{O}_7$ biphasic films provide both low permittivity and low loss especially with the Bi addition range from $x=0.3$ to $x=0.4$. At $x=0.67$, the pyrochlore phase become the only crystalline phase in the system. The most stabilized crystal structure is therefore formed as seen in Figs. 1 and 2, thus the lowest dielectric constant and dielectric loss appear as seen in Fig. 4.

The dielectric properties of the $(\text{Pb}_{0.4}\text{Sr}_{0.6})_{1-3x/2}\text{Bi}_x\text{TiO}_3$ films under DC bias are shown in Fig. 5. The dielectric tunabilities of those thin films, which are calculated from Fig. 5, are shown in Fig. 6. The tunability can be defined as

$$\text{Tunability} = (C_{\text{zero bias}} - C_{\text{DC bias}}) / C_{\text{zero bias}} \times 100\%. \quad (3)$$

For $x=0.15$, the film with single perovskite phase has almost no tunability due to its high dielectric constant. For $x=0.67$, the film with single pyrochlore phase has only low voltage-tunable behavior. However, for $0.3 < x < 0.4$, the $\text{PST}/\text{Bi}_2\text{Ti}_2\text{O}_7$ biphasic film shows significant voltage-tunable behavior. It is because the pyrochlore phase $\text{Bi}_2\text{Ti}_2\text{O}_7$ keeps the perovskite phases away from

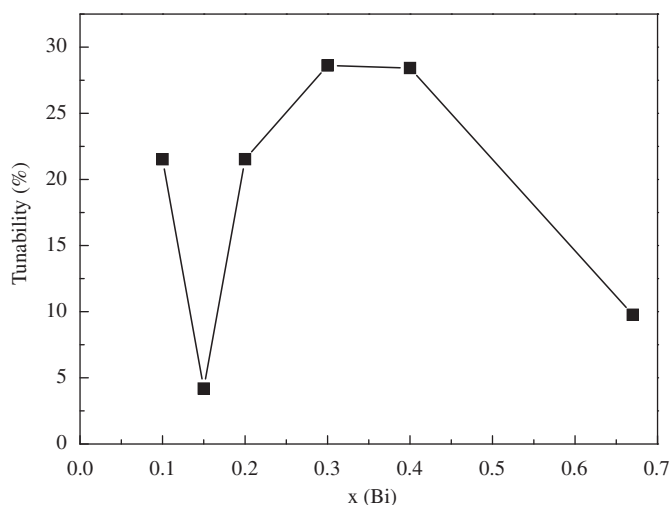


Fig. 6. Tunabilities of $(\text{Pb}_{0.4}\text{Sr}_{0.6})_{1-3x/2}\text{Bi}_x\text{TiO}_3$ thin films under 100 kHz as function of Bi addition.

each other, and the maximum tunability of about 30% is obtained for $0.3 < x < 0.4$ under 100 kHz. The figure of merit (FOM), which is defined as

$$\text{FOM} = [(\%)\text{tunability}/\tan \delta(\%)] \quad (4)$$

is also calculated. Due to the large tunability and low dielectric loss, the FOM of $(\text{Pb}_{0.4}\text{Sr}_{0.6})_{1-3x/2}\text{Bi}_x\text{TiO}_3$ films increase with increasing Bi from $x=0.15$ to $x=0.4$ as shown in Fig. 7. It is about 6 times higher for $x=0.4$ than $x=0.15$. Compared to the Ba-doped PST thin films [14], the Bi dopant can increase the FOM of PST thin films effectively. These results indicate that the Bi-doped PST thin films are good candidates for tunable applications.

4. Conclusion

In conclusion, $(\text{Pb}_{0.4}\text{Sr}_{0.6})_{1-3x/2}\text{Bi}_x\text{TiO}_3$ thin films were successfully prepared by the sol-gel method. Bi^{3+} in the perovskite phase thin film could induce the A-site vacancies to balance the intrinsic oxygen vacancies for $x < 0.15$. Thus the pure perovskite phase thin films were obtained. For $x > 0.15$, the formation ability of the perovskite phase decreased and pyrochlore phase of $\text{Bi}_2\text{Ti}_2\text{O}_7$ appeared with increasing Bi dopant. These two kinds of phases coexisted in the thin film for $0.2 < x < 0.4$. When x increased to about 0.67, the perovskite phase disappeared and the pyrochlore phase of $\text{Bi}_2\text{Ti}_2\text{O}_7$ was obtained in the thin film. The $\text{Bi}_2\text{Ti}_2\text{O}_7$, which has low dielectric constant and dielectric loss, kept the perovskite phase PST away from each other in the biphasic PST/ $\text{Bi}_2\text{Ti}_2\text{O}_7$ thin films. And these films with low dielectric

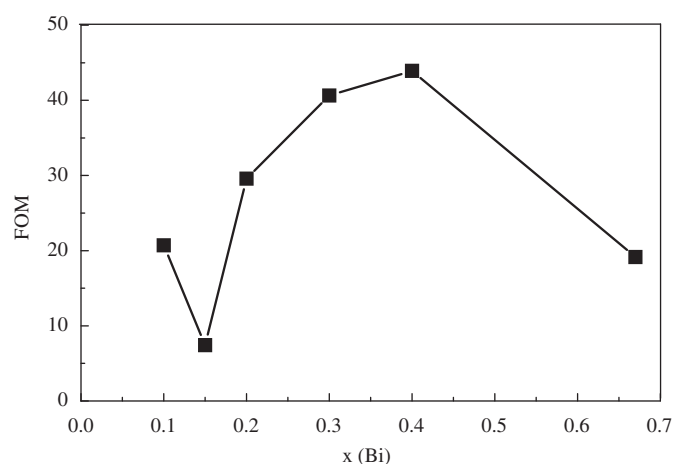


Fig. 7. FOM of the $(\text{Pb}_{0.4}\text{Sr}_{0.6})_{1-3x/2}\text{Bi}_x\text{TiO}_3$ thin films as a function of x .

constant as well as dielectric loss showed high tunability and FOM. The FOM of PST/ $\text{Bi}_2\text{Ti}_2\text{O}_7$ thin films was about 6 times higher than that with single phase.

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