

Effect of Mg doping on dielectric properties of sol-gel derived $(\text{Pb}_{0.7}\text{Sr}_{0.3})\text{Mg}_x\text{Ti}_{1-x}\text{O}_{3-x}$ thin film

X. T. Li · W. L. Huo · W. J. Weng · G. R. Han · P. Y. Du

Published online: 23 March 2007
© Springer Science + Business Media, LLC 2007

Abstract $(\text{Pb}_{0.7}\text{Sr}_{0.3})\text{Mg}_x\text{Ti}_{1-x}\text{O}_{3-x}$ ($x=0\sim 0.3$) thin films were successfully prepared on ITO/glass substrate by sol-gel technique. The crystalline phase structures were measured through X-ray diffraction (XRD). The dielectric properties were measured by a precision impedance analyzer. Results show that the perovskite phase was stable in $(\text{Pb}_{0.7}\text{Sr}_{0.3})\text{Mg}_x\text{Ti}_{1-x}\text{O}_{3-x}$ thin film. Its lattice constant was found to decrease with the increase of x when $x<0.1$ and increase when $x>0.1$. The crystalline phase formation and the dielectric properties of the $(\text{Pb}_{0.7}\text{Sr}_{0.3})\text{Mg}_x\text{Ti}_{1-x}\text{O}_{3-x}$ thin film depend on Mg doping content. The phase formation ability was decreased below $x=0.1$ and then increased above $x=0.1$ with the increase in x . The dielectric constant of the thin film is correspondingly changed. The tunabilities of about 35%~63% were obtained at 10 kHz. The highest tunability and the lowest dielectric loss of the thin films appeared at $x=0.2$. The FOM of the thin film with Mg doping of $x=0.2$ is about three times higher than that of $x=0.1$ under applied frequency of 10 kHz.

Keywords Sol-gel processes · PST · Thin films · Mg doping · Dielectric properties

1 Introduction

Thin film ferroelectric materials are being investigated for integrations as charge storage dielectrics [1, 2] and electric-field tunable elements for high frequency devices such as varactors, oscillators and voltage tunable phase shifters [3–6]. Most of the applications mentioned above exploit properties of the nonlinearity of its dielectric properties with respect to applied direct current (DC) voltage [7]. Recently, Lead strontium titanate ($\text{Pb}_x\text{Sr}_{1-x}$) TiO_3 (PST) has been investigated as a promising candidate for the applications mentioned above due to the large-scale variations of its dielectric constant by direct current biasing fields [8]. Therefore, it is possible to expect that PST thin films will show the properties of dielectric materials with a low dielectric loss.

The investigations of PST thin films have been reported recently. The dielectric properties of PST depend on the composition and the structural properties of the thin films. Heat treatment and doping are often used as the effective methods to modify the dielectric properties of ferroelectric films [9–11]. The PST system compounded with an addition of a non-ferroelectric oxide such as MgO has low dielectric loss below 0.3%, which is just above the transition temperature [12]. However, limited attempt has so far been made to understand PST thin film with a heavy doping of Mg especially by sol-gel technique. In this paper, the main aim of our work includes the fabrication of heavy Mg-doped $(\text{Pb}_{0.7}\text{Sr}_{0.3})\text{Mg}_x\text{Ti}_{1-x}\text{O}_{3-x}$ thin films using sol-gel method and the investigation of the influence of Mg doping on structure and dielectric properties of the thin films.

X. T. Li · W. L. Huo · W. J. Weng · G. R. Han · P. Y. Du
State Key Laboratory of Silicon Materials,
Zhejiang University, Hangzhou 310027, China

P. Y. Du (✉)
Department of Material Science and Engineering,
Zhejiang University, Hangzhou 310027, China
e-mail: dupy@zju.edu.cn

2 Experimental

The multi-component $Pb_{0.7}Sr_{0.3}Mg_xTi_{1-x}O_{3-x}$ precursor solution was synthesized using lead acetate trihydrate, strontium carbonate, basic magnesium carbonate and titanium isopropoxide as starting materials and acetic acid and 2-methoxyethanol as the solvent. The precursor solutions were dip-coated on the ITO/glass substrates and then rapidly heat treated on a muffle stove at 600°C to remove the organics and finally annealed at 600°C for 1 h in oxygen atmosphere for crystallization. The rapid heat treatment process was repeated for eight times and kept 5 min for each time.

The phase structure of the thin film was analyzed by X-ray diffraction (Rigaku, D/Max) using Cu K α radiation of 0.15405 nm; under 0.02° sampling interval and 4°/min scan speed. The dielectric constant (ϵ_r) and dissipation factor ($\tan\delta$) of the samples were measured at different frequencies via using an Agilent 4294A precision impedance analyzer. The FOM (figure of merit) was identified as tunability/ $\tan\delta$ (%).

3 Results and discussion

Figure 1 shows the XRD patterns of the $(Pb_{0.7}Sr_{0.3})Mg_xTi_{1-x}O_{3-x}$ ($x=0\sim 0.3$) thin films. Each layer of the thin films is heat treated at 600°C for 5 min respectively. All of the films possess a typical polycrystalline cubic perovskite structure without any evidence of secondary phase formation. The XRD results indicate that the diffraction peak intensities of the thin films change with different Mg

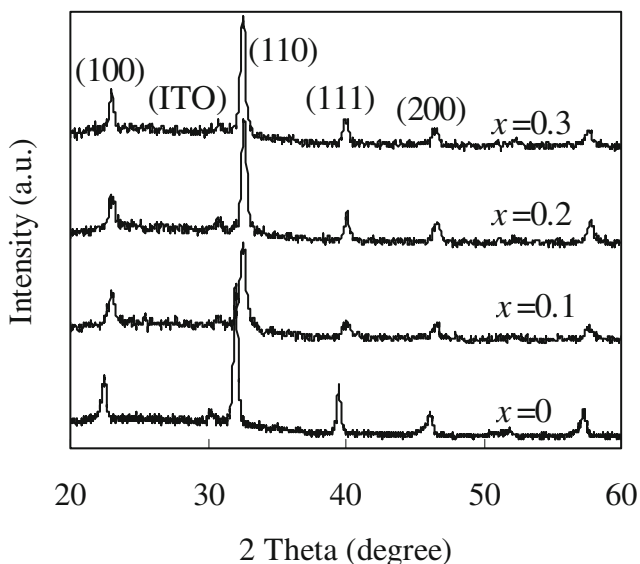


Fig. 1 XRD patterns of the $Pb_{0.7}Sr_{0.3}Mg_xTi_{1-x}O_{3-x}$ thin films annealed at 600°C with different Mg contents

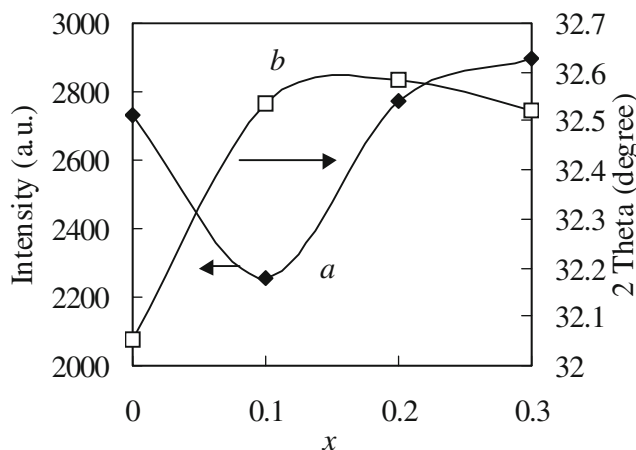
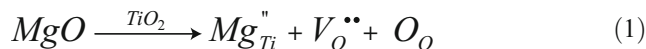


Fig. 2 XRD (110) peak positions in 2θ and intensity of $Pb_{0.7}Sr_{0.3}Mg_xTi_{1-x}O_{3-x}$ thin film with different Mg doping x

doping content. They are decreased with doping small amounts of Mg ($x < 0.1$) and increased with doping heavy amounts of Mg from $x \geq 0.1$ to $x = 0.3$ as shown in curve a in Fig. 2. The lowest diffraction peak intensity in the thin films is obtained at $x = 0.1$.

As it is known, the crystal content of a perovskite phase can sometimes be reduced when the oxygen vacancy increases due to the increase in the lattice distortion. [13] In this case, Mg is incorporated into $(Pb_{0.7}Sr_{0.3})TiO_3$ thin films as doping ion. On the basis of the similarity in ionic radii between Mg^{2+} ($r_{eff} = 0.72 \text{ \AA}$) and Ti^{4+} ($r_{eff} = 0.61 \text{ \AA}$) [14], it may be assumed that Mg replaces Ti in the $(Pb_{0.7}Sr_{0.3})TiO_3$ lattice and their defect reaction can be followed as the following:



where $V_O^{\bullet\bullet}$ is an extrinsic oxygen vacancy controlled by the Mg content. When the Mg^{2+} ion substitutes for Ti^{4+} ion in the perovskite phase thin film as $x < 0.1$, Mg doping brings out negative charge defects and thus brings out oxygen vacancies with positive charge. The lattice distortion of the perovskite phase will therefore increase and the formation ability thus decreases with the increase in Mg when $x < 0.1$. However, the activation energy to form the perovskite phase would be reduced when increasing Mg from about $x = 0.1$ to $x = 0.3$. [15] The formation ability of the perovskite phase will increase and keep almost constant finally when Mg is heavy doped.

Curve b in Fig. 2 shows (110) peak position of the Mg doped thin film, which shifts towards high in 2θ with increasing Mg doping as $x < 0.1$ and shifts towards low with doping heavy amounts of Mg from $x = 0.1$ to $x = 0.3$. As mentioned above, the oxygen vacancy would be increased when Mg content was doped in the PST thin film. The lattices will shrink and the lattice constant will therefore

decrease when Mg^{2+} ions are increased as shown in Fig. 2. However when $x > 0.1$, in this case, the Mg content seems to be excessive in respect of solubility limitation of the perovskite phase. The substitution of Mg for Ti ion in the perovskite phase will keep almost constant. On the other hand, the formation ability of the crystalline phase increases with increasing Mg. The formation of the oxygen vacancies in the perovskite phase may thus decrease. The lattice constant of the thin films has therefore a few increases with the decrease in oxygen vacancies induced by Mg^{2+} ions.

Curve *a* in Fig. 3 shows the dielectric constant of Mg doped $(\text{Pb}_{0.7}\text{Sr}_{0.3})\text{Mg}_x\text{Ti}_{1-x}\text{O}_{3-x}$ thin films. It is decreased with increasing Mg doping from $x=0$ to 0.1 and increased when $x > 0.1$. As mentioned above, the lattice distortion of the perovskite phase is increased when Mg was doped in PST thin films due to the increase in oxygen vacancies. The phase formation ability of the thin film is therefore decreased with increasing Mg doping from $x=0$ to $x=0.1$. And hence, the crystalline phase in the thin films is decreased. So the dielectric constant of the thin films is correspondingly decreased from $x=0$ to $x=0.1$. In addition, with the heavy Mg doping further from $x=0.1$ to $x=0.3$, the formation ability of the perovskite phase increase and thus the dielectric constant increase with increasing Mg doping.

The value of the dielectric loss of $(\text{Pb}_{0.7}\text{Sr}_{0.3})\text{Mg}_x\text{Ti}_{1-x}\text{O}_{3-x}$ thin film with different Mg content is illustrated as curve *b* in Fig. 3. It decreases with the increase in Mg content from $x=0.1$ to $x=0.2$ and then keep constant above $x=0.2$. As mentioned above, the formation ability of the perovskite phase would increase and keep almost constant finally when Mg is heavy doped. The lattice distortion of the perovskite phase will therefore decrease and the perfection of the crystalline phase thus improves with the increase in Mg when $x > 0.1$. The dielectric loss of the thin films is decreased accordingly.

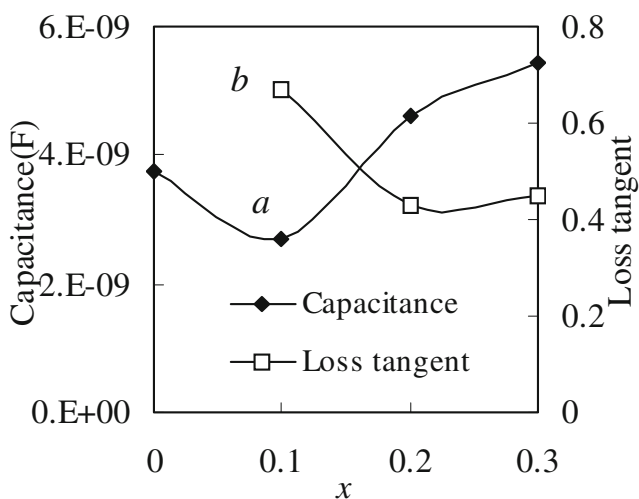


Fig. 3 The dielectric constant and loss tangent of $\text{Pb}_{0.7}\text{Sr}_{0.3}\text{Mg}_x\text{Ti}_{1-x}\text{O}_{3-x}$ thin films as a function of Mg doping content

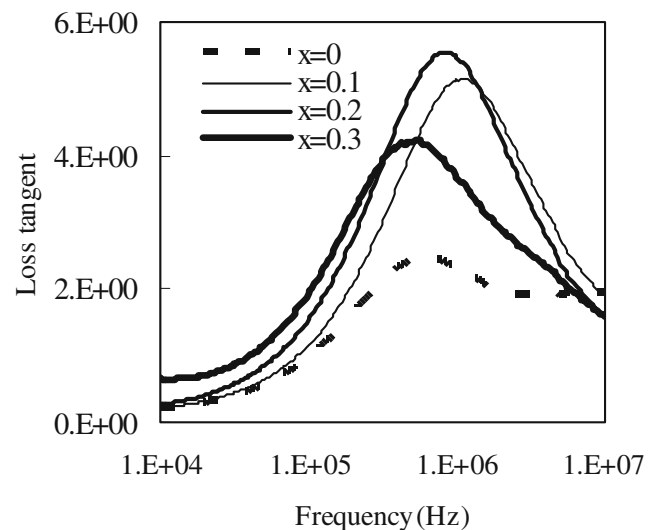
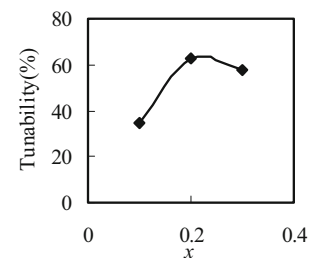


Fig. 4 The frequency dependence of the dielectric loss of $\text{Pb}_{0.7}\text{Sr}_{0.3}\text{Mg}_x\text{Ti}_{1-x}\text{O}_{3-x}$ thin films

Figure 4 shows the frequency dependence of dielectric loss of the $(\text{Pb}_{0.7}\text{Sr}_{0.3})\text{Mg}_x\text{Ti}_{1-x}\text{O}_{3-x}$ thin films. It shows the peaks of the polarized relaxation dielectric loss of $(\text{Pb}_{0.7}\text{Sr}_{0.3})\text{Mg}_x\text{Ti}_{1-x}\text{O}_{3-x}$ thin films with the different Mg addition under the frequency of 100 kHz. The peak position of the loss shifts to the high frequency with increasing Mg doping from $x=0$ to $x=0.1$ and then to low when $x > 0.1$. As indicated above, with Mg doping content increased from $x=0$ to $x=0.1$, the intrinsic oxygen vacancy induced by Mg would increase. In this case, the microstructure would be distorted, and thus the bonding energy among the ions in the system was weakened. Therefore, the activation energy of the dipoles was decreased. The polarized relaxation appears at a high frequency with increasing Mg. When x is from 0.1 to 0.3, the oxygen vacancies formed in the perovskite phase keep constant initially and have a little bit decrease finally. The perovskite phase hence becomes perfect with increasing Mg. The activation energy of the polarization is therefore increased and the dielectric relaxation appears at lower frequency with Mg doping increasing.

Consequently, Mg doped PST thin films reveal that both high crystalline content and low loss especially within the Mg addition range between $x=0.2$ and $x=0.3$. They are benefit to increase the Figure of Merit (FOM) of the tunable

Fig. 5 The dielectric tunability and loss tangent of $\text{Pb}_{0.7}\text{Sr}_{0.3}\text{Mg}_x\text{Ti}_{1-x}\text{O}_{3-x}$ thin film under 10 kHz



device if it is used for tunable devices and the tunability itself does not decrease between $x=0.2$ and $x=0.3$.

In fact, the $(\text{Pb}_{0.7}\text{Sr}_{0.3})\text{Mg}_x\text{Ti}_{1-x}\text{O}_{3-x}$ thin films indeed have high tunability between $x=0.2$ and $x=0.3$. The dielectric tunability of $(\text{Pb}_{0.7}\text{Sr}_{0.3})\text{Mg}_x\text{Ti}_{1-x}\text{O}_{3-x}$ thin film defined as:

$$\text{Tunability} = (C_{\text{zero bias}} - C_{\text{DC bias}}) / C_{\text{zero bias}} \times 100\% \quad (2)$$

is shown in Fig. 5. The maximum of the DC field applied is about 100 kV/cm. The tunabilities of the $(\text{Pb}_{0.7}\text{Sr}_{0.3})\text{Mg}_x\text{Ti}_{1-x}\text{O}_{3-x}$ thin films under 10 kHz are about 35%~63%. It is increased with increasing Mg content from $x=0.1$ to $x=0.2$ and keep almost constant when $x>0.2$. It could be because the formation ability of the perovskite phase would increase and keep almost constant finally as mentioned above. The lattice distortion of the thin film is therefore decreased with the increasing Mg when $x>0.1$ and therefore the dipole moment will be suppressed under DC biasing. The tunability of the thin films becomes hence increased. The FOM of about 0.52, 1.46 and 1.28 are obtained respectively under the applied frequency of 10 kHz when Mg doping content is 0.1, 0.2, and 0.3. The FOM of the thin film with Mg doping of $x=0.2$ is about three times higher than that of $x=0.1$.

4 Conclusions

$(\text{Pb}_{0.7}\text{Sr}_{0.3})\text{Mg}_x\text{Ti}_{1-x}\text{O}_{3-x}$ ($x=0\sim 0.3$) thin films consisted of the perfect perovskite phase is prepared on ITO/glass substrate by sol-gel technique. The crystalline phase formation and the lattice constant of the thin film depend on Mg doping content. Both of them are decreased with increasing Mg up to 0.1 and then increased with increasing Mg up to 0.3. The dielectric constant of the thin film is

correspondingly changed. The lowest dielectric constant values of the thin films with Mg doping content appears at $x=0.1$. The tunabilities of about 35%~63% are obtained under 10 kHz with different Mg content. The FOM of about 0.52, 1.46 and 1.28 are obtained respectively at frequency of 10 kHz when Mg doping content is 0.1, 0.2, and 0.3. The FOM of the thin film with Mg doping of $x=0.2$ is about three times higher than that at $x=0.1$.

Acknowledgement This work is supported by NSFC (Grants Nos. 50372057, 50332030), and the National Key Scientific and Technological Project (Grant No. 2002CB613302), respectively.

References

1. S.R. Summerfelt, *Ferroelectric Thin Films* (Kluwer, The Netherlands, 1997), p. 1
2. D. Ueda, *J. Electroceram.* **3**, 105 (1999)
3. M.W. Cole, P.C. Joshi, M.H. Ervin, *Thin Solid Films* **374**, 34 (2000)
4. P.C. Joshi, M.W. Cole, *Appl. Phys. Lett.* **77**, 289 (2000)
5. H.J. Chung, S.I. Woo, *J. Vac. Sci. Technol.* **B19**, 27 (2001)
6. H.Y. Guo, J.B. Xu, I.H. Wilson, *Phys. Lett.*, **A294**, 217 (2002)
7. L.C. Sengupta, S. Sengupta, *IEEE. T. Ultrason., Ferr.* **44**, 792 (1997)
8. S. Yoshitaka, S.B. Amar, E.C. Leslie, *Int. J. Inorg. Mater.* **3**, 709 (2001)
9. M.W. Cole, W.D. Nothwang, C. Hubbard, *J. Appl. Phys.* **93**, 9218 (2003)
10. S.Y. Lee, T.Y. Tseng, *Appl. Phys. Lett.* **80**, 1797 (2002)
11. L. Wu, Y.C. Chen, C.L. Huang, *J. Am. Ceram. Soc.* **83**, 1713 (2000)
12. S. Yoshitaka, S.B. Amar, E.C. Leslie, *Ferroelectric Lett.* **30**, 81 (2003)
13. P.Y. Du, S. Sui, W.J. Weng, *Acta Phys. Sin.* **54**(11), 5411 (2005)
14. M.W. Cole, W.D. Nothwang, C. Hubbard, E. Ngo, M. Ervin, *J. Appl. Phys.* **93**, 9218 (2003)
15. P.Y. Du, L.W. Tang, X.H. Zhao, *Surf. Coat. Tech.* **198**(1–3), 395 (2005)