Available online at www.sciencedirect.com

Journal of the European Ceramic Society 26 (2006) 2147–2150

www.elsevier.com/locate/jeurceramsoc

Effect of La doping on tunable behavior of sol–gel-derived PST thin film

Piyi Du*, Xiaoting Li, Yuanliang Liu, Gaorong Han, Wenjian Weng

State Key Laboratory of Silicon Materials, Zhejiang University, Hangzhou 310027, China

Abstract

$Pb_xSr_{1-x}TiO_3$ and $(Pb_{0.4}Sr_{0.6})_{1-x}La_{2x/3}TiO_3$ thin films were prepared on ITO/glass substrate by sol–gel technique. The crystalline phase structures of thin films were investigated by XRD. The dielectric properties were measured by LCZ meter. Results show that the perovskite phase was stable in $Pb_xSr_{1-x}TiO_3$ thin film. Its lattice constant was found to increase with the increase of x. When Pb/Sr ratio was about 50/50, the transformation of the perovskite phase between cubic and tetragonal took place at room temperature. To ensure better tunability, $Pb_{0.4}Sr_{0.6}TiO_3$ thin film was selected in both paraelectric state (cubic structure) and near the phase transformation point between cubic and tetragonal. The tunability of more than 80% and figure of merit (FOM) of 14.17 were obtained. $(Pb_{0.4}Sr_{0.6})_{1-x}La_{2x/3}TiO_3$ was also prepared as La-doped thin film. Its dielectric constant was decreased below $x = 0.4$ and then increased above $x = 0.4$ with the increase in x. The inharmonic coefficient depicting ability of tunability of $(Pb_{0.4}Sr_{0.6})_{1-x}La_{2x/3}TiO_3$ thin film kept constant due to the changeable shape of the crystal cell under electric field at a fixed temperature below $x = 0.4$, which is in good agreement with Johnson's theory. And the coefficient reveals a distinctive variable because of easily changeable shape under different bias above $x = 0.4$. The tunability of about 70% and FOM of about 7 were obtained in the $(Pb_{0.4}Sr_{0.6})_{1-x}La_{2x/3}TiO_3$ thin film.

Keywords: Sol–gel processes; PST; Dielectric properties; Films

1. Introduction

Over the past decades, there has been a great interest in the application of ferroelectric and paraelectric thin films for tunable microwave device such as electrically tunable mixers, delay line, filters, capacitor, oscillators, resonators and phase shifters. Ferroelectric materials are selected due to their sufficient advantages including adjustable dielectric constant by applied electric field. To ensure a better tunability, the materials need to be designed to ensure its paraelectric state (cubic structure) and its phase transformation point between cubic and tetragonal[4] is just below room temperature. Barium strontium titanate $(Ba,Sr)TiO_3$ (BST),[1] lead strontium titanate $Pb_xSr_{1-x}TiO_3$ (PST)[2] and similar titanates, whose compositions satisfy the above conditions have been well studied for tunable microwave applications.

Barium strontium titanate and the series doped with some minors have been investigated intensively. They have tunability of about 50%, dielectric loss of 10^{-2} and FOM of ≤ 300. Lead strontium titanate with higher tunability and lower loss was suggested for tunable microwave applications recently by Cross and co-workers.[3] The performence of PST is better than that of BST in tunable microwave application. The investigations of PST thin films have therefore been reported recently. As it is known that the doping is significant to improve electrical properties of ferroelectric thin films. However, limited attempt has been made so far to understand PST thin film with a doped content especially by sol–gel technique.

In this paper, the sol–gel-derived PST and La-doped PST thin films were prepared and the influence of La content on tunable behavior of the thin film was investigated in detail.

2. Experimental

Sol precursor of $Pb_xSr_{1-x}TiO_3$ ($x = 0.2$–0.8) and $(Pb_{0.4}Sr_{0.6})_{1-x}La_{2x/3}TiO_3$ were prepared using lead acetate trihydrate, strontium carbonate, lanthanum nitrate and titanium iso-propoxide as starting materials and acetic acid and 2-methoxyethanol as the solvent. PST thin films were deposited by dip-coating the sol precursor on a conductive ITO/glass substrate and then rapidly heat-treated on a muffle stove at 450 °C or 600 °C initially. After that, the PST thin films were annealed at 600 °C for 1 h in oxygen atmosphere for complete crystallization. The rapid heat treatment process was repeated for eight times and kept 5 min for each time. The thickness of PST thin film obtained was approximately 200–400 nm.

---

* Corresponding author.
E-mail address: mse-dupy@dial.zju.edu.cn (P. Du).

0955-2219/$ – see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jeurceramsoc.2005.09.074

The crystallinity and phase structure of the PST and La-doped PST thin films were analyzed by X-ray diffraction (XRD). Dielectric properties (capacitance as well as dielectric loss) of the thin films were measured by Keithley 3330 impedance analyzer under different applied voltages. The dielectric tunability of the thin film was defined as $(\varepsilon_{\max} - \varepsilon_{\min})/\varepsilon_{\max}$ figure of merit (FOM), a frequently used parameter to characterize correlations between tunability and dielectric loss, was defined as FOMs = (tunability/tan δ(%)).

3. Results and discussion

Fig. 1 shows XRD patterns of the PST thin films with the ratio of Pb/Sr from 10/90 to 80/20. All the PST thin films with different compositions are found non-textured polycrystalline perovskite phase without any evident secondary phase. The peaks of the perovskite phase shifts slightly towards low 2θ angle while the ratio of Pb/Sr is increased in PST, and peak between $45^\circ < 2\theta < 47^\circ$ split into two peaks at the ratio of 50/50 and above.

As it is known, the lattice constant of a perovskite phase can be decreased when Pb^{2+} is substituted by Sr^{2+} due to smaller radii of Sr^{2+}(1.12 A). For the $Pb_xSr_{1-x}TiO_3$ thin films of this study, the lattice constant of the perovskite phase increases with the increase in Pb content as shown in Fig. 1, which is in agreement with the above argument. The distortion of the perovskite phase structure appears and becomes serious with increasing Pb/Sr ratio. Actually the nature of the perovskite phases of PST with low Pb addition would be different from that with high Pb. The lattice system will change probably from original cubic to a new tetragonal, while the lattice constant and the structure distortion of the perovskite phase is increased with adding Pb to certain content at a certain temperature. Fig. 2 shows the lattice constant of the perovskite phase as a function of Pb content in the thin film. It exhibits evidently that, when the ratio of Pb/Sr is about 50/50, the phase transformation from cubic to tetragonal occurs at room temperature. The sol–gel-derived $Pb_{0.4}Sr_{0.6}TiO_3$ thin film is therefore paraelectric state with cubic perovskite structure and has a phase transformation point near room temperature. The $Pb_{0.4}Sr_{0.6}TiO_3$ thin film is actable to be used in microwave devices for its tunability since the perovskite phase usually possess low loss in its paraelectric state and high tunability near the phase transformation point.[4] Therefore, it would play an important role in the device with high FOM. Fig. 3 shows the plots of normalized-dielectric-constant of $Pb_{0.4}Sr_{0.6}TiO_3$ thin film as functions of electric bias under different frequencies of 1, 10 and 100 kHz. The dielectric tunabilities of the thin films are greater than 80%, which is much higher than that ever reported in literatures.[5–7] It further exhibits a tendency of increase from 80.8% to 85.0% with the frequency from 1 to 100 kHz although the dielectric constants without bias show a trend of decrease.

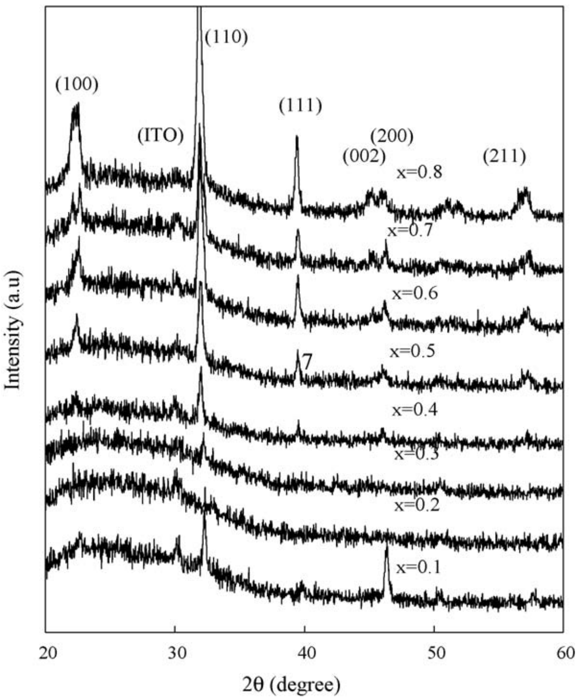

Fig. 1. XRD patterns of the $Pb_xSr_{1-x}TiO_3$ thin films annealed at 600 °C with different lead contents.

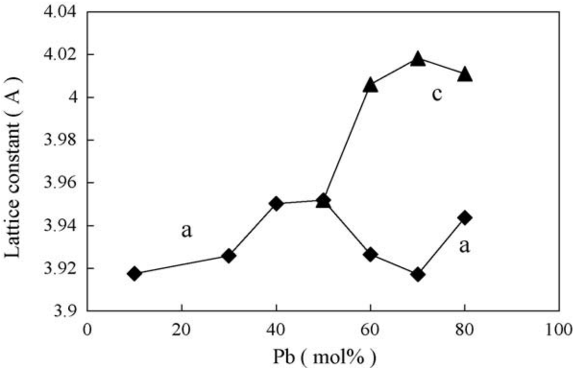

Fig. 2. Lattice constants as a function of the contents of Pb in the perovskite phase in $Pb_xSr_{1-x}TiO_3$ film.

La-doped PST, $(Pb_{0.4}Sr_{0.6})_{1-x}La_{2x/3}TiO_3$ was also selected for high tunability. Fig. 4 shows its X-ray diffraction patterns. It exhibits that the crystallinity of the perovskite phase decreases

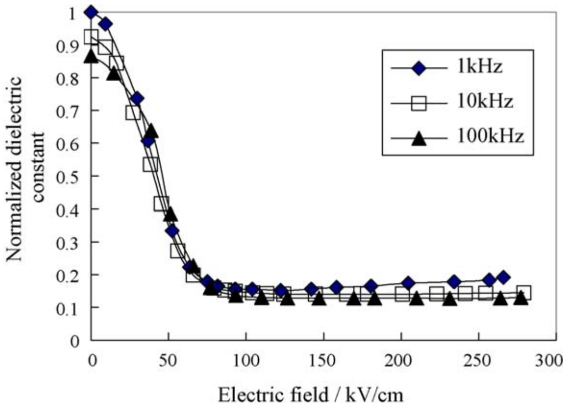

Fig. 3. Normalized-dielectric-constant–electric–voltage relationship of $Pb_{0.4}Sr_{0.6}TiO_3$ thin film under different applied frequencies at room temperature.

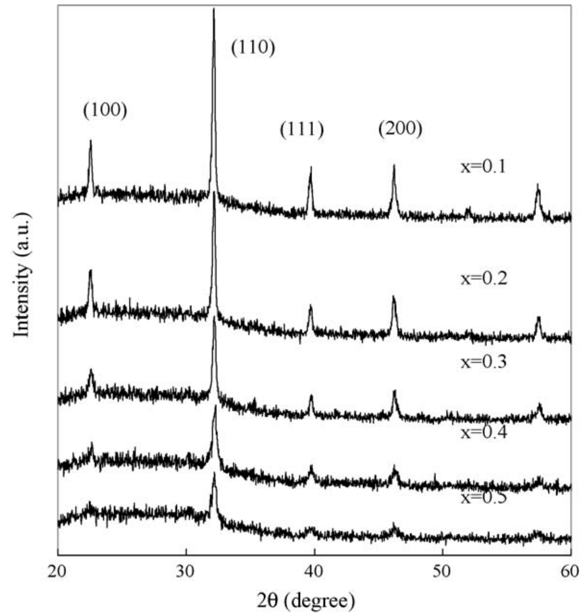

Fig. 4. X-ray diffraction patterns of $(Pb_{0.4}Sr_{0.6})_{1-x}La_{2x/3}TiO_3$ thin films.

with increasing La doping. Fig. 5 is the variation of (1 1 0) peak position against the dielectric constant of the La-doped thin film. The (1 1 0) peak position, which is related to the lattice constant, is linearly increased from $x = 0.1$ to $x = 0.4$ and then decreased until $x = 0.5$. Dielectric constant decreases from $x = 0.1$ to $x = 0.4$ and then increases from $x = 0.4$ to $x = 0.5$ with increasing La content. The maximum 2θ angle of (1 1 0) peak position (minimum of the lattice constant) and the minimum of the dielectric constant simultaneously appear in $x = 0.4$.

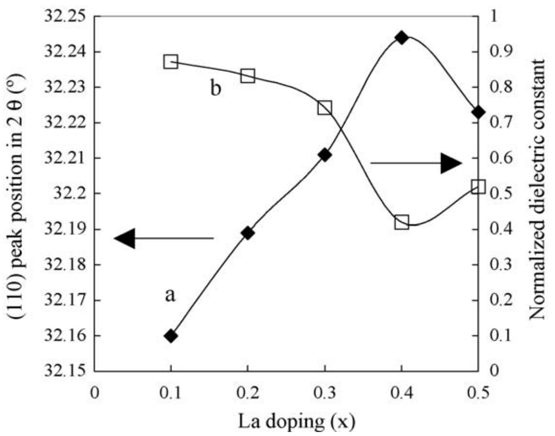

Fig. 5. XRD (1 1 0) peak position in 2θ and normalized dielectric constant of $(Pb_{0.4}Sr_{0.6})_{1-x}La_{2x/3}TiO_3$ thin film with different La doping x without bias.

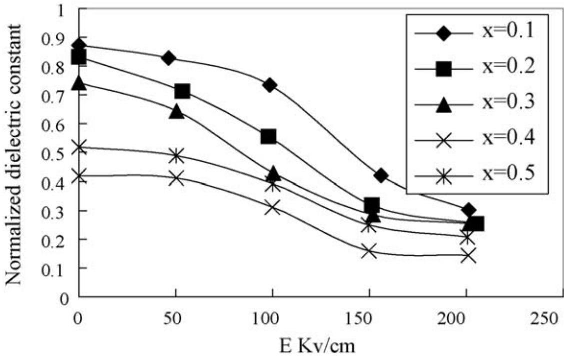

Fig. 6. Variation of normalized dielectric constant with changing electric field in $(Pb_{0.4}Sr_{0.6})_{1-x}La_{2x/3}TiO_3$.

In a strict sense, an electric dipole, which dominates the dielectric behavior, is normally dependent on lattice constant or distortion of the oxygen octahedron in the perovskite phase structure. When smaller size La^{3+} substitutes for larger size Pb^{2+} and Sr^{2+}, the vacancy defects of Pb and Sr appear. The crystal lattice will thus decrease when there is an increase in La addition. The lattice constant of the perovskite phase in $(Pb_{0.4}Sr_{0.6})_{1-x}La_{2x/3}TiO_3$ thin film will also decrease with increasing La as proved indirectly by Fig. 5(a) below $x = 0.4$. The dielectric constant is therefore decreased with increasing La^{3+} in the phase structure below $x = 0.4$ as shown in curve b in Fig. 5. In addition, as La^{3+} content is above $x = 0.4$, the dielectric constant is increased with increasing La doping in the thin film as shown in curve b in Fig. 5. This is because the high concentration of La ions promotes the disappearance of Pb and Sr while a lot of La ions substitute for Pb and Sr in the perovskite phase. Because Pb exhibits a high polarization itself and hence contributes a high bond force with surrounding atoms, the decrease in attractive force among atoms and the loosening of the crystal lattice will occur with decreasing Pb. Unlike shrinking the phase structure while generating the vacancy defects and decreasing ion size mainly below $x = 0.4$, the lattice size therefore increases when the Pb significantly decreases especially above $x = 0.4$. It means that the dielectric constant increases with decreasing Pb rather than decreasing with increasing La in this case. As confirmed in curve a in Fig. 5, the lattice constant is increased with the increase in La content ranging from $x = 0.4$ to $x = 0.5$. The dielectric constant is therefore increased with lattice constant, which is related to La doping within higher doping range. The lowest dielectric constant as well as the smallest lattice constant (i.e. largest peak position in 2θ) is at La content of $x = 0.4$ in $(Pb_{0.4}Sr_{0.6})_{1-x}La_{2x/3}TiO_3$ thin film.

Fig. 6 deals with the relationships between the dielectric constant and applied electric field for $(Pb_{0.4}Sr_{0.6})_{1-x}La_{2x/3}TiO_3$ thin film. When the electric field is applied to the $(Pb_{0.4}Sr_{0.6})_{1-x}La_{2x/3}TiO_3$ thin film, their dielectric constant changes with increasing La doping in almost the same rule under whole range of electric fields, which is similar to the fact shown in Fig. 5(b). In addition, the decrease in dielectric constants with increasing electric field due to the tunable nature of the thin films. But it is noticeable that their decreases are different with different La additions and under different bias. It implies that the dielectric constants almost keep the same degree of decrease (decrease percentage) for all thin films below $x = 0.4$ and distribution is of different extent of decrease above $x = 0.4$. Therefore, the dielectric tunabilities calculated from the values in Fig. 6 show little difference below $x = 0.4$, such as 65.37, 66.47, 65.57 and 65.46 at $x = 0.1$, $x = 0.2$, $x = 0.3$ and $x = 0.4$, respectively, but show the decrease finally above $x = 0.4$, such as 59.94 at $x = 0.5$. According to Johnson's expression with respect to dielectric constant depending on electric field,[8] inharmonic coefficient, the important factor which affects the tunability, is not a constant for $(Pb_{0.4}Sr_{0.6})_{1-x}La_{2x/3}TiO_3$ thin films below $x = 0.4$ at a fixed temperature. They are quite agreeable with his theory. In practice, as mentioned above, the effect of lattice size shrinkage mainly occur below $x = 0.4$. Evidently, the shrinkage of the crystalline phase could keep the phase dense although the vacancy defect content is increased with increasing La doping. It implies that the shape of dense crystalline phase is therefore difficult to be changed under electric field. The inharmonic coefficient is unchangeable under different bias since it would be much more related to the shape of crystal structure. However, in higher La doping above $x = 0.4$, considering the loosening of the crystal lattice due to amount plenty of Pb, it is confirmed that the inharmonic coefficient is decreased with increasing applied voltage. The tunability behavior of $(Pb_{0.4}Sr_{0.6})_{1-x}La_{2x/3}TiO_3$ thin film shows actually a special variable inharmonic coefficient under different bias. It is much more different from that with La doping below $x = 0.4$. As mentioned above, large distortion of octahedron of oxygen atoms and large crystal lattice of the perovskite phase would occur in high extent of La addition in $(Pb_{0.4}Sr_{0.6})_{1-x}La_{2x/3}TiO_3$ thin film. The crystal cell of the perovskite phase will probably be easily modified by electric bias. Unlike the inharmonic coefficient, which seems to be unchangeable under bias when La below $x = 0.4$, the crystal cell therefore changed with the changing electric field as x is above 0.4.

The tunabilities of about 60–70% and FOM of about 7 are obtained in this La-doped thin film system. The fact that the tunable feature of $(Pb_{0.4}Sr_{0.6})_{1-x}La_{2x/3}TiO_3$ is a little smaller than that without La doping. Considering Johnson's theory, the inharmonic coefficient of the $(Pb_{0.4}Sr_{0.6})_{1-x}La_{2x/3}TiO_3$ thin film must have been smaller than that of PST without La addition. It is attributed to the larger distortion and higher imperfection of the perovskite phase in $(Pb_{0.4}Sr_{0.6})_{1-x}La_{2x/3}TiO_3$ thin film than that in PST without La addition. Detail analysis will be discussed in a separate paper.

4. Conclusion

$Pb_xSr_{1-x}TiO_3$ and $(Pb_{0.4}Sr_{0.6})_{1-x}La_{2x/3}TiO_3$ thin films which consisted of a perfect perovskite phase, are prepared on ITO/glass substrate by sol–gel technique. The lattice constant of the perovskite phase increases with the increase in Pb content in PST thin film. The lattice system changes from cubic to tetragonal when the Pb/Sr ratio is about 50/50 at room temperature. The tunability of the $Pb_{0.4}Sr_{0.6}TiO_3$ thin film is more than 80%. FOM of 14.17 is obtained in the film at the frequency of 100 kHz. In La-doped $(Pb_{0.4}Sr_{0.6})_{1-x}La_{2x/3}TiO_3$ thin film system, when La doping is below $x = 0.4$, the dielectric constant decreases since that La substitutes for Pb produces vacancy defects and decrease in atom size shrinks the lattice constant. The inharmonic coefficient keeps constant at a fixed temperature under different bias since the shape of the crystal cell is not modulated by electric field, which is quite agreeable with theoretical character. As La addition is above $x = 0.4$, the dielectric constant increases with increasing La doping since La^{3+} induces the significant disappearance of Pb^{2+} and Sr^{2+} and decreases attractive force between atoms to loosen the crystal lattice and then increase lattice constant. The inharmonic coefficient reveals a special variable under different bias at a fixed temperature due to the easily modified shape of the crystal cell under electric bias. The tunability of about 70% and FOM of about 7 are obtained in the $(Pb_{0.4}Sr_{0.6})_{1-x}La_{2x/3}TiO_3$ thin film.

Acknowledgements

This work is supported by NSFC (grants nos. 50372057, 50332030), and the National Key Scientific and Technological Project (grant no. 2002CB613302), respectively.

References

1. Kawahara, T., Yamamuka, M., Yuuki, A. and Ono, K., $(Ba,Sr)TiO_3$ films prepared by liquid source chemical vapor deposition on Ru electrodes. *Jpn. J. Appl. Phys.*, 1996, **35**, 4880–4885.
2. Chung, H. J. and Woo, S. I., Electrical characters of $(Pb, Sr) TiO_3$ thin films for untra-large-scale-integrated dynamic random access memory capacitors prepared by liquid-source missed chemical deposition. *J. Vac. Sci. Technol. B*, 2001, **19**, 275–280.
3. Somiya, Y., Bhalla, A. S. and Cross, L. E., Study of (Pb,Sr)TiO3 ceramics on dielectric and physical propties. *Int. J. Inorg. Mater.*, 2001, **3**, 709–714.
4. Cole, M. W., Nothwang, W. D., Hubbard, C., Ngo, E. and Ervin, M., Low dielectric loss and enhanced tenability of $Ba_{0.6}Sr_{0.4}TiO_3$ based thin films via material compositional design and optimized film processing method. *J. Appl. Phys.*, 2003, **93**, 9218–9225.
5. Jain, M., Majumder, S. B., Guo, R., Bhalla, A. S. and Katiyar, R. S., Synthesis and characterization of lead strontium titanate thin films by sol–gel technique. *Mater. Lett.*, 2002, **56**, 692–697.
6. Kim, K. T. and Kim, C. I., Structure and dielectrical properties of $(Pb,Sr)TiO_3$ thin films for tunable microwave device. *Thin Solid Films*, 2002, **420–421**, 544–547.
7. Chung, H. J., Chung, S. J., Kim, J. H. and woo, S. I., The effect of post-annealing on the electrical properties of $(Pb,Sr)TiO_3$ thin films prepared by liquid source misted chemical deposition for ultra large-scale integration (ULSI) dynamic random access memory (DRAM) capacitor. *Thin Solid Films*, 2001, **394**, 213–217.
8. Johnson, K. M., Variation of dielectric constant with voltage in ferroelectrics and its application to parametric devices. *J. Appl. Phys.*, 1962, **33**, 2826–2829.