Improvement of dielectric tunability and loss tangent of (Ba,Sr)TiO_3 thin films with K doping*

Zhang Wei-Jie(张伟杰), Dai Jian-Ming(戴建明)†, Zhu Xue-Bin(朱雪斌), Chang Qing(常 青), Liu Qiang-Chun(刘强春), and Sun Yu-Ping(孙玉平)

Key Laboratory of Materials Physics, Institute of Solid State Physics, Chinese Academy of Sciences, Hefei 230031, *China*

(Received 24 February 2012; revised manuscript received 6 March 2012)

$Ba_{0.6}Sr_{0.4}TiO_3$ thin films doped with K were deposited on Pt/Ti/SiO_2/Si substrates by chemical solution deposition method. The structure, surface morphology, and dielectric and tunable properties of $Ba_{0.6}Sr_{0.4}TiO_3$ thin films have been studied in detail. The K content in $Ba_{0.6}Sr_{0.4}TiO_3$ thin films has a strong influence on the material's properties including surface morphology, dielectric and tunable properties. It is found that the Curie temperature of K-doped $Ba_{0.6}Sr_{0.4}TiO_3$ films shifts to higher values compared with that of undoped $Ba_{0.6}Sr_{0.4}TiO_3$ thin films, which leads to a dielectric enhancement of K-doped $Ba_{0.6}Sr_{0.4}TiO_3$ films at room temperature. At the optimized content of 0.02 mol, the dielectric loss tangent is reduced significantly from 0.057 to 0.020. Meanwhile, the tunability is enhanced obviously from 26% to 48% at the measured frequency of 1 MHz and the maximum value of the figure of merit is 23.8. This suggests that such films have potential applications for tunable devices.

Keywords: K-doped (Ba,Sr)TiO_3 thin films, chemical solution deposition, dielectric properties, tunability

PACS: 77.55.–g, 77.55.fe, 61.05.cp **DOI:** 10.1088/1674-1056/21/9/097702

1. Introduction

Dielectric thin films have recently been received considerable attention as promising candidates for applications in tunable microwave devices and in dynamic random access memories (DRAMs).[1] Specially, Barium strontium titanate ($Ba_{1-x}Sr_xTiO_3$, BST), has been investigated with considerable interest as a dielectric material for its large field-dependent permittivity, high dielectric constant, and relatively low loss tangent. At present, BST thin films have been prepared by a variety of techniques such as radio frequency magnetron sputtering,[2,3] pulsed laser deposition,[4] metal organic chemical vapor deposition,[5,6] and chemical solution deposition (CSD).[7,8] Among these methods, the CSD method has been used widely in processing the thin films because of its various advantages such as chemical homogeneity, low cost, accuracy of stoichiometry control, and especially convenience of large area deposition. However, the dielectric properties of BST thin films fabricated by CSD method are not satisfactory since its tunability is not high enough or the loss tangent is not low enough. In order to improve the microwave dielectric properties of BST thin films, much attention has been paid in the past few years. Doping is well known as a convenient and effective method to improve dielectric properties of BST thin films.[9] The induced electrons derived from the oxygen vacancies can hop between different titanium ions and provide a mechanism of dielectric loss. To compensate the oxygen vacancies, appropriate amount of acceptor dopants that occupy the B site (Ti^{4+} site) in the ABO_3 perovskite structure are doped to reduce the dielectric loss.[10,11] In previous investigations, Fe^{3+}, Co^{3+}, Cr^{3+}, Mn^{2+}, Mg^{2+}, and Al^{3+} ions have been employed to improve the dielectric and insulating properties of BST thin films. However, the tunability of BST thin films doped with Co^{3+}, Mn^{2+}, Mg^{2+}, and Al^{3+} by B site, respectively, is reduced simultaneously.[12–15] Sun *et al.*[16] pointed out that these acceptor ions occupying the Ti^{4+} ion sites result in oxygen vacancies and lead to a "break" of the cooperative vibration of the Ti–O chains. Therefore, the tunability of the doped BST system decreases owing to the decrease of Curie temperature (T_C). Thus, we expect that some ions can act as acceptors occu-

*Project supported by the National Natural Science Foundation of China (Grant Nos. 10874051 and 50802096) and the Innovation Project for Young Talents of Hefei Institutes of Physical Science, Chinese Academy of Sciences (Grant No. O84N391123).

†Corresponding author. E-mail: jmdai@issp.ac.cn

© 2012 Chinese Physical Society and IOP Publishing Ltd

pying the A site of BST to reduce the dielectric loss tangent without decreasing the tunability. In fact, the ion radius of K^+ has almost the same value as Ba^{2+}, so it can replace Ba^{2+} or Sr^{2+} as an acceptor ion. The K-doped BST films fabricated by sol-gel method have shown good dielectric properties. However, Wang *et al.*[17] found that the dielectric loss of K-doped BST thin films prepared by radio frequency (RF) magnetron sputtering method increases simultaneously with tunability. Further studies on the effect and mechanism of K dopant on the dielectric properties of the BST thin films need to be carried out.

In this paper, $Ba_{0.6}Sr_{0.4-x}K_xTiO_3$ ($0 \leq x \leq 0.08$) thin films were prepared on $Pt/Ti/SiO_2/Si$ substrates using the CSD method. The crystal structures and surface morphologies of these films were studied and discussed. The influence of K dopant on the dielectric properties of BST thin films and its dielectric mechanism were also investigated.

2. Experiment

Thin films of $Ba_{0.6}Sr_{0.4-x}K_xTiO_3$ (x=0, 0.02, 0.05, 0.08) were prepared by the CSD method. The precursor solutions were synthesized using Barium acetate [$Ba(CH_3CO_2)_2$], strontium acetate [$Sr(CH_3COO)_2{\cdot}1/2H_2O$], potassium carbonate [$K_2CO_3$], and tetrabutyl titanate [$Ti(C_4H_9O)_4$] as initial materials. The $Ti(C_4H_9O)_4$ was mixed with acetylacetone in a molar ratio of 1:2 to form chelating complex for stabilization. $Ba(CH_3CO_2)_2$, $Sr(CH_3COO)_2{\cdot}1/2H_2O$, and K_2CO_3 were dissolved in acetic acid at 70 °C. The dissolved (Ba, Sr, and K) precursor solution was then dripped into titanium precursor solution and stirred. Finally, 2-methoxygethanol was added to adjust the solution concentration to 0.3 mol/L.

All the films were fabricated on $Pt/Ti/SiO_2/Si$ substrates by a spin-coating technique at 4000 rpm for 30 s and crystallized at 700 ° for 60 min in oxygen atmosphere. The final thickness of the film was about 400 nm.

The crystal structures of $Ba_{0.6}Sr_{0.4-x}K_xTiO_3$ films were examined by X-ray diffraction (XRD) (X' Pert Pro MPD) with CuK_α radiation. The surface morphologies were observed using a field emission scanning electron microscopy (FE-SEM) (Sirion 200 type). In order to study the dielectric properties, Au electrodes with the diameter of about 0.3 mm were deposited to form a metal–ferroelectric–metal configuration. The dielectric constants were measured via a computer-controlled system, including a LCR meter (TH2828S) and an environmental temperature box (MPMS-5).

3. Results and discussion

The XRD patters of $Ba_{0.6}Sr_{0.4-x}K_xTiO_3$ ($BSTK_x$) thin films at room temperature are shown in Fig. 1(a). It reveals that all the films show perovskite structure and no other phase is observed, which implies that the dopants enter the unit cell maintaining the perovskite structure of solid solution. The (110) diffraction peak of these films are shown in Fig. 1(b). From this figure, we can see that, compared with the undoped BST thin film, the (110) diffraction peaks of BST thin films doped with K shift slightly to lower angle when the K content increases from 0.02 mol to 0.08 mol. This means that the lattice parameters of BST films are enlarged when the content of K increases from 0.02 mol to 0.08 mol gradually.

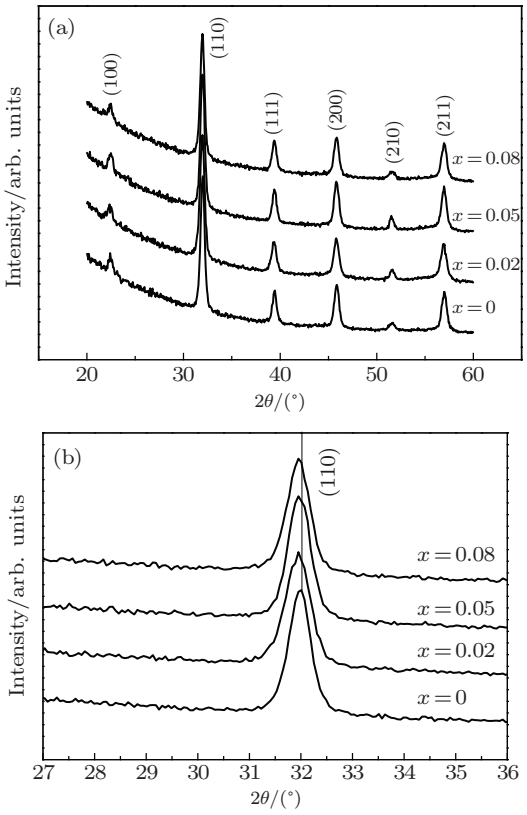


Fig. 1. (a) The XRD patterns and (b) (110) peaks of $Ba_{0.6}Sr_{0.4-x}K_xTiO_3$ thin films.

Considering the radius of Sr^{2+} and K^+ (1.13 Å and 1.33 Å) and the ratios of the react precursors, we

conclude that the K ions substitute for the Sr ions. Based on the Rietveld analysis, we also calculated the lattice parameters using fitting method. The lattice parameter of undoped BST thin films is 3.965 Å, while that for K-doped BST thin films are 3.967, 3.971, and 3.972 Å for 0.02, 0.05, and 0.08 mol, respectively. These results are in good agreement with the XRD measurements.

Figure 2 shows the surface morphology of the $BSTK_x$ thin films. The FE-SEM images show that all the samples are smooth and crack-free. Additionally, the average grain size of 0.02-mol K-doped BST film is the largest in this series of BST thin films. With increasing content of K, the average grain sizes decrease gradually, which indicates that appropriate amount of K doping can enhance the crystallization.

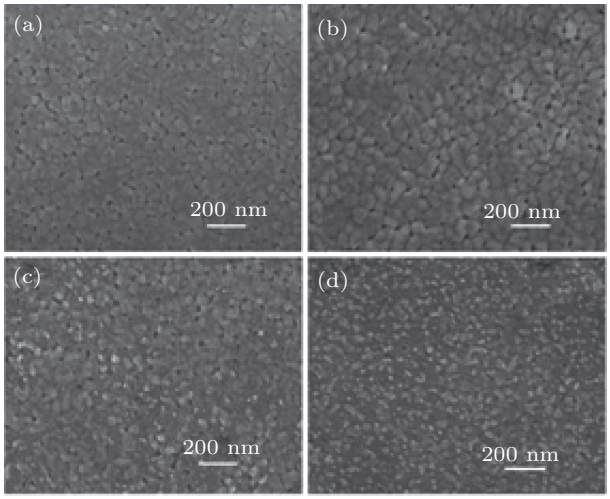


Fig. 2. FE-SEM images of $Ba_{0.6}Sr_{0.4-x}K_xTiO_3$ thin films. (a) $x = 0$, (b) $x = 0.02$, (c) $x = 0.05$, and (d) $x = 0.08$.

The dielectric constant of the $BSTK_x$ thin films at room temperature as a function of frequency is given in Fig. 3. The results were obtained at an oscillation voltage of 100 mV from 20 Hz to 1 MHz at room temperature. As shown in this figure, the dielectric constant is weakly frequency-dependent within the measured range. It can be also observed that the dielectric constant gradually increase with increasing K content from 0.02 mol to 0.08 mol, which is different from that the K-doped BST films fabricated by Sun *et al.*[16] In their studies, dielectric constant increases with increasing K content from 0.01 to 0.075 mol and then decreases with increasing K content from 0.075 to 0.2 mol in the BST thin films. The different change tendencies of dielectric constant are ascribed to the different grain sizes of BST films with different K contents. Moreover, larger grain size usually results in larger polarization,[18] and then leads to a higher value of dielectric constant. However, in our experiments, the grain size does not increase with increasing K content ranging from 0.02 to 0.08 mol. It could be concluded that the presence of oxygen vacancies causes the increase of the lattice parameter of oxide films[19] when the content of K increases from 0.02 to 0.08 mol, and enlarges the unit volume of polarization of BST structure, which finally results in a higher value of dielectric constant.[20]

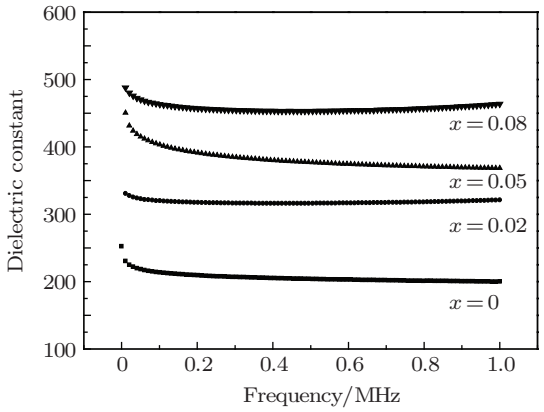


Fig. 3. Dielectric constant of the $Ba_{0.6}Sr_{0.4-x}K_xTiO_3$ thin films as a function of frequency.

Additionally, it is well known that the T_C of BST system depends on the content of Sr.[21] Thus, with increasing Sr^{2+} is substituted by K^+, the T_C of BST films shift toward higher temperature, and therefore, its dielectric constant at room temperature increases. Figure 4 shows the dielectric constant of the $BSTK_x$ thin films as a function of temperature which was measured at 1 MHz. It indicates that the T_C of BST thin films shift toward higher temperature when the content of K increases.

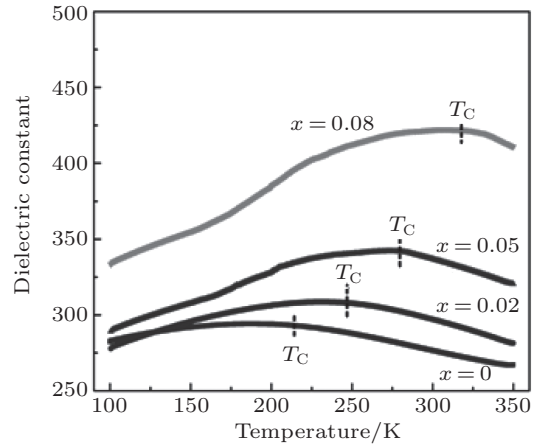


Fig. 4. Temperature dependence of the dielectric constant of the $Ba_{0.6}Sr_{0.4-x}K_xTiO_3$ thin films.

Figure 5 reveals the dielectric loss tangent of the $BSTK_x$ thin films as a function of frequency. It is obvious that the dielectric loss of the doped BST thin film is lower than that of the undoped film, which is 0.020 0.025, 0.044, and 0.057 at 1 MHz, respectively.

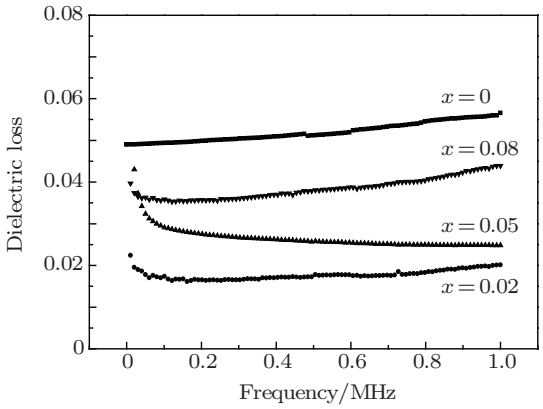


Fig. 5. Dielectric loss tangent of the $Ba_{0.6}Sr_{0.4-x}K_xTiO_3$ thin films as a function of frequency.

The significant decrease of dielectric loss can be ascribed to the fact that acceptor dopants induce oxygen vacancies, which neutralize the free electrons and restrain the transformation from Ti^{4+} to Ti^{3+} when the K content is 0.02 mol. The redundant oxygen vacancies with increasing content of K contribute to the increase of the dielectric loss which is still lower than that of the undoped BST thin films.

In the research field of BST materials, one of the most interesting physical properties is the dielectric tunability which can be calculated using the following formula:

$$\eta = [(\varepsilon_{\max} - \varepsilon_{\min})/\varepsilon_{\max}] \times 100\%,$$

where η is the tenability, and $\varepsilon_{\max}$ and $\varepsilon_{\min}$ are the maximal and minimal dielectric constants, respectively. Figure 6 shows the ε–V curves of the samples measured at a frequency of 1 MHz. The undoped BST film has a tunability of 26% when the electric field is 250 kV/cm, while the tunabilities of the K-doped BST films are all higher than 46%, and the highest tunability is 50% when the doped K content is 0.08 mol. The higher tunability of the K-doped BST film may be related to its larger dielectric constant and higher T_C. The increase in T_C will lead to more polar clusters in the paraelectric phase, resulting in the increase of tunability.[22]

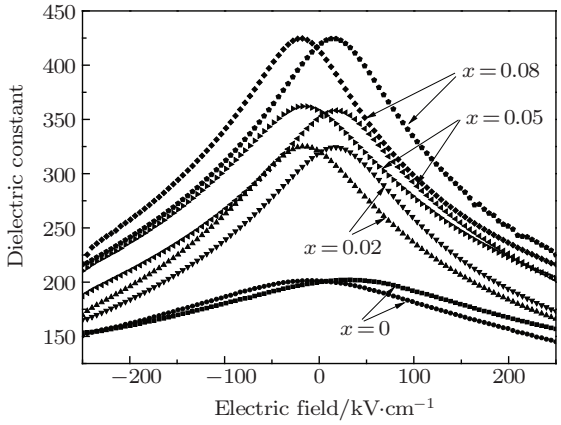


Fig. 6. The ε–V curves of the $Ba_{0.6}Sr_{0.4-x}K_xTiO_3$ thin films.

A tunable microwave circuit should take advantage of a high tunability together with a low dielectric loss factor ($\tan\delta$). Figure of merit (FOM) is a frequently used parameter to characterize the correlations between tunability and dielectric loss $\tan\delta$, which is defined as the ratio of tenability against $\tan\delta$, which is desirable to be as high as possible. The FOM value implies the fact that a tunable microwave device cannot take full advantage of high tunability if the dielectric loss is too high. As shown in Table 1, the FOM value of undoped BST thin films is 4.6, and those of 0.02-mol, 0.05-mol, and 0.08-mol K-doped BST thin films are 23.8, 18.5, and 11.4, respectively. In the case of 0.02-mol K-doped BST film, the tunability and dielectric loss are 48% and 0.020, respectively. Although the tunability is lower than that of the 0.08-mol K-doped BST film, the loss is even lower. As a result, the FOM has been improved. Considering the trade-offs between dielectric loss and tunability, the optimal doping content of K is 0.02 mol.

Table 1. Dielectric constant, dielectric loss tangent, tunability, and FOM of $Ba_{0.6}Sr_{0.4-x}K_xTiO_3$ thin films.

K content/mol	ε	$\tan\delta$	η	FOM
0	200	0.057	26%	4.6
0.02	321	0.020	48%	23.8
0.05	368	0.025	46%	18.5
0.08	464	0.044	50%	11.4

4. Conclusion

Our investigation demonstrates that K doping has a strong influence on the material properties of BST thin films. We have improved dielectric and tunable properties for K-doped BST thin films relative to that of pure BST films. Considering the trade-offs between

dielectric loss and tunability, the optimal doping content of K is 0.02 mol. The measured values of dielectric constant, dielectric loss tangent, tunability, and FOM of 0.02-mol K-doped BST thin films were 321, 0.02, 48%, and 23.8, respectively. The highest FOM value of 23.8 suggests that 0.02-mol K-doped BST thin film is the best choice for tunable device applications.

References

[1] Fu C L, Yang C R, Chen H W, Hu L and Wang Y X 2005 *Mater. Lett.* **59** 330

[2] Aygun S M, Daniels P, Borland W and Maria J P 2008 *J. Appl. Phys.* **103** 084123

[3] Cao Y H and Di G Q 2011 *Acta Phys. Sin.* **60** 037702 (in Chinese)

[4] Romanyuk V L, Gremenok V F, Merkulov V S, Emelyanov V A, Syakersky V S, Chyhir R R and Abetkovskaia S O 2009 *Phys. Stat. Sol.* C **6** 985

[5] Zhong S, Alpau S P, Cole M W, Ngo E, Hirsch S and Demaree J D 2007 *Appl. Phys. Lett.* **90** 092901

[6] Lü Y G, Liang X L, Tan Y H, Zheng X J, Gong Y Q and He L 2011 *Acta Phys. Sin.* **60** 2 (in Chinese)

[7] Zhigalina O M, Vorotilov K A and Kumskov A S 2006 *Ferroelectrics* **335** 13

[8] Yang X J, Yao X and Zhang L Y 2004 *Ceram. Int.* **30** 1525

[9] Su B and Button T W 2004 *J. Appl. Phys.* **95** 1382

[10] Wang S Y, Cheng B L, Wang C, Lu H B, Zhou Y L, Chen Z H and Yang G Z 2003 *J. Cry. Growth* **259** 137

[11] Ye Y and Guo T L 2009 *Ceram. Int.* **35** 2761

[12] Gao L N, Zhai J W and Yao X 2009 *Appl. Surf. Sci.* **255** 4251

[13] Fan Y H, Yu S H, Sun R, Li L, Yin Y S, Wong K W and Du R X 2010 *Appl. Surf. Sci.* **256** 6531

[14] Cole M W, Nothwang W D, Hubbard C and Ervin M 2003 *J. Appl. Phys.* **93** 11

[15] Lee S Y, Chiou B S and Lu H H 2008 *Mater. Chem. Phys.* **108** 55

[16] Sun X H, Zhu B L, Liu T, Li M Y, Zhao X Z, Wang D Y, Sun C L and Chan L W 2006 *J. Appl. Phys.* **99** 084103

[17] Wang S X, Guo M S, Liu T, Guo S S, Li M Y and Zhao X Z 2007 *J. Cry. Growth* **306** 22

[18] Yu J, Liao J X, Jin L, Wei X B, Wang P, Wei X B and Xu Z Q 2011 *Acta Phys. Sin.* **60** 077701 (in chinese)

[19] Zhang T J, Wang J, Jiang J, Pan R K and Zhang B S 2007 *Thin Solid Films* **515** 7721

[20] Hong S H, Hwang I R, Choi J S, Lee J H, Kim S H, Jeon S H, Kang S O, Alishev V S and Park B H 2008 *J. Korean Phys. Soc.* **52** 2

[21] Patil D R, Lokare S A, Devan R S, Chougule S S, Kanamadi C M, Kolekar Y D and Chougule B K 2007 *Mater. Chem. Phys.* **104** 254

[22] Zhang J J, Zhai J W, Jiang H T and Yao X 2009 *Sci. China Ser.* E: *Tech. Sci.* **52** 1