Vol 18 No 10, October 2009
1674-1056/2009/18(10)/4511–04

Chinese Physics B

© 2009 Chin. Phys. Soc.
and IOP Publishing Ltd

Great enhancement in remnant polarisation of $SrBi_4Ti_4O_{15}$ thin films by A-site doping of Fe^{3+} ions

Sun Jia-Bao(孙家宝), Sun Hui(孙 慧),
Wang Wei(王 伟), Cai Hua(蔡 华), and Chen Xiao-Bing(陈小兵)†

College of Physics Science and Technology, Yangzhou University, Yangzhou 225002, *China*

(Received 30 September 2008; revised manuscript received 12 March 2009)

$SrBi_{4-x}Fe_xTi_4O_{15}$ (SBFT-x) thin films ($x = 0.00$, 0.05, 0.08, 0.15) have been synthesized on $Pt/Ti/SiO_2/Si$ (100) substrates by sol-gel method. This paper finds that Fe-doping does not change the crystal structure of $SrBi_4Ti_4O_{15}$ (SBTi). The coercive filed (E_c) and remnant polarisation (P_r) increase at first, then decrease with the increase of Fe doping content. At a maximum applied field of 229 kV/cm, the $2P_r$ reaches a maximum value of 91.1 $\mu C/cm^2$ at $x = 0.05$ and the corresponding E_c is 72 kV/cm. The $2P_r$ increases by about 260% and the E_c decreases by about 6%, respectively. Obviously, the ferroelectric property of $SrBi_4Ti_4O_{15}$ is greatly enhanced by Fe doping. The fatigue-endurance characteristic of the SBFT-0.05 is not improved. After 1.1×10^9 read/write cycles at a frequency of 50 kHz, the nonvolatile polarisations ($P_{nv} = P^* - P^\wedge$) decreased about 48% of its initial value.

Keywords: thin films, remnant polarisation, ferroelectrics, fatigue
PACC: 7780, 8140, 8270, 6820

1. Introduction

Ferroelectric thin films have attracted much attention for use in nonvolatile memory applications.[1] It is of great importance in such applications that the films should have large remnant polarisation ($2P_r$), low coercive field, low processing temperature, and be fatigue-free. Bismuth layer-structured ferroelectrics (BLSFs) are thought to be promising materials due to their fatigue-free nature.[2] Among them, $Bi_4Ti_3O_{12}$ (BIT) is known to be a typical kind of layer-structured ferroelectric material and has been widely investigated because of its good properties, such as large spontaneous polarisation, low switching field, and high Curie temperature.[3] Recent research studies have revealed that doping BIT by lanthanide series not only improves their fatigue-free property, but also increases its $2P_r$. For example, the $2P_r$ of $Bi_{3.25}La_{0.75}Ti_3O_{12}$ and $Bi_{3.15}Sm_{0.85}Ti_3O_{12}$ thin films are 20 $\mu C/cm^2$ and 49 $\mu C/cm^2$, respectively.[4,5] $SrBi_4Ti_4O_{15}$ (SBTi), whose crystalline structure is similar to BIT, is another typical layer-structured ferroelectrics, having a better fatigue-free property than that of BIT, but the relatively small P_r hindered its commercial use.[6] To enhance its ferroelectric properties, the same strategy of lanthanide substitution into SBTi has been performed and some positive results have been obtained.[6,7] All the doping studies are mainly focused on lanthanide ions, which possess the same chemical valence and similar ionic radius as the bismuth ion, since the doping effects are commonly attributed to the stability of lanthanide ions which suppress oxygen vacancies and lead to the enhancement of polarisation and improvement of fatigue endurance in BLSFs.[6,7] It is known that the origination of the ferroelectricity in such BLSFs is from the lattice distortion, especially from the distortion of pseudo-perovskite slab, the octahedron with a B-site cation in the center and six oxygens on the apexes. However, it has been shown that A-site lanthanide substitution for bismuth ion in BLSFs causes less structural distortion which results in smaller polarisation.[8] In other words, it still needs to be clarified if lattice distortion would play a more important role in ferroelectricity in BLSFs. Thus, an investigation on the lattice distortion induced by doping ions with the same valence but different radius into A-site in BLSFs is informative for the above question. Fe^{3+}, with the same valance as Bi^{3+}, has quite a large difference in ion radius from that of the bismuth ion (Bi^{3+}: $r = 0.96$ nm; Fe^{3+}: $r = 0.64$ nm). Therefore, doping some irons into A-site in BLSFs is quite a suitable method for under-

†Corresponding author. E-mail: xbchen@yzu.edu.cn

standing the effect of structural distortion caused by dopant size. In this work, Fe-doped SBTi thin films were prepared and their structure and electrical properties were studied.

2. Experimental details

Considering that the film-growing technique and the subsequent processing steps play key roles in the quality of the films, a standard sol-gel process was therefore employed for preparing the SBFT-x thin films. The precursor solutions were prepared with strontium acetate, bismuth (III) acetate (99.99%), titanium (IV) n-butoxide (99%), iron (III) acetylacetonate (99%) as starting materials, acetic acid (99.5%) and propanol (99%) as solvents, and acetylacetone (99%) as stable agent. The final concentration of the precursor solution was 0.1 mol/L. With the proper processing, the films were deposited on a Pt substrate ($Pt/Ti/SiO_2/Si$) by spin coating with 3000 rpm for 30 s, and the coated films were baked at 250∼400 °C in air for 3 min and 5 min, respectively. The baked films were then annealed per-layer at 750 °C for 10 min in flowing oxygen atmosphere. The spinning-baking-annealing process was repeated for 5 times till the films reached a proper thickness.

The crystal structure of the films was characterized by the x-ray diffraction (XRD) (M03XHF22) with Cu Kα radiation at a tube voltage of 40 kV and a tube current of 40 mA. Raman spectra were recorded in backscattering geometry by using a JY T64000 triple monochromator. The surface and cross-sectional images of the films were obtained by an environment scanning electron microscopy (ESEM) (XL-30ESEM). The ferroelectric hysteresis loops and the fatigue properties were measured by an RT66 standard ferroelectric test system (Radiant Technologies).

3. Results and discussion

3.1. Structural analysis

Figure 1 shows the XRD patterns of the SBFT-x (x = 0.00, 0.05, 0.08 and 0.15) thin films. The diffraction peaks are indexed according to the standard diffraction data of SBTi. The pure bismuth layered perovskite structure appears with the random orientation. The coincidence of diffraction peaks of SBFT-x and SBTi indicates that Fe doping does not affect the layered perovskite structure of SBTi. The reason is the fact that the chemical valence of Fe^{3+} is the same as that of Bi^{3+}, and the amount of Fe^{3+} is very small though the radius of Fe^{3+} is much smaller.

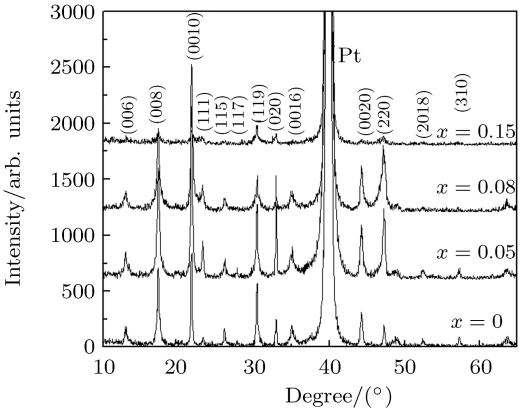


Fig.1. X-raydiffraction patterns of SBFT-x thin films.

Figure 2 shows the Raman spectra of the SBFT-x thin films. The 57 cm^{-1} mode is assigned as a "rigid-layer" mode, strongly related to the rigid movement of the Bi_2O_2 layer against the perovskite layer.[9] If Bi^{3+} in the Bi_2O_2 is replaced by Fe^{3+}, this mode should shift, for Fe^{3+} has a smaller mass than Bi^{3+}. Since this mode remains unchanged as $x \leq 0.08$, it implies that Fe^{3+} is unlikely incorporated into the Bi_2O_2 layer when Fe^{3+} content is less than 0.08. When the amount of Fe^{3+} is 0.15, the 57 cm^{-1} mode down-shifts slightly and becomes vague, which indicates that when the amount of Fe^{3+} is increased to 0.15, the Fe^{3+} will occupy partially in the Bi_2O_2 layer.

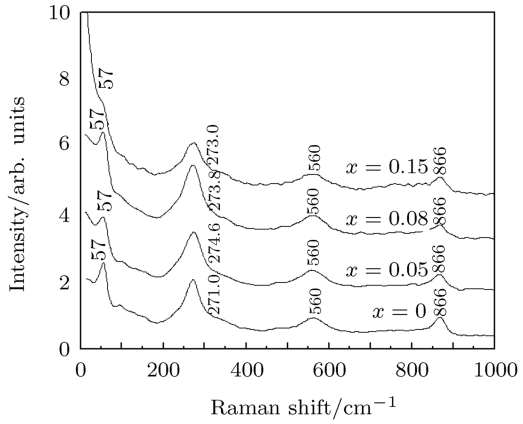


Fig.2. Raman scattering spectra of SBFT-x thin films.

It is also seen from the Raman spectra of the SBFT-x films that the 271 cm^{-1} mode, assigned to

Bi ions at A-site of BLSFs, changes with the variation of Fe^{3+} content, suggesting that Fe ions mainly substitute for Bi ions in the perovskite slabs when the amount of Fe^{3+} is small. The higher modes of 560 cm^{-1} and 866 cm^{-1} keeps unchanged since those modes correspond to Ti–O octahedral. Therefore, it may conclude that Fe substitution is not involved with Ti ions.

Figures 3(a), 3(b), 3(c) and 3(d) show the surface topographic images of SBFT-0.00, SBFT-0.05, SBFT-0.08 and SBFT-0.15 thin films, respectively, examined by ESEM. It is seen that all samples have dense surfaces without any cracks, and show rod-like grains.

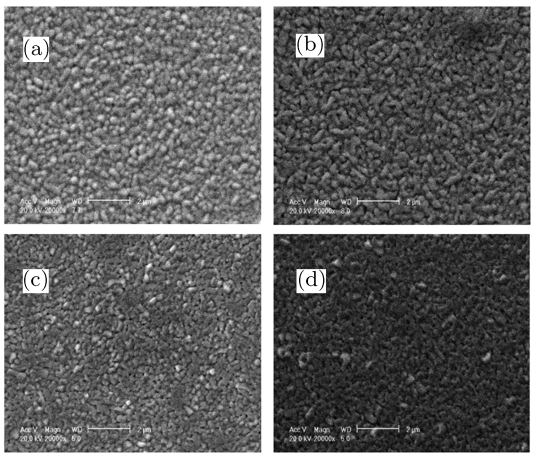


Fig.3. The surface topographic images of SBFT-x thin films.

Figure 4 shows the cross-sectional ESEM morphology of the SBFT-0.05 thin film. A clear and sharp boundary exists between the film layer and Pt electrodes, suggesting no obvious inter-diffusion across the capacitor structure. The thickness of the film is quite uniform, being estimated to be 700 nm.

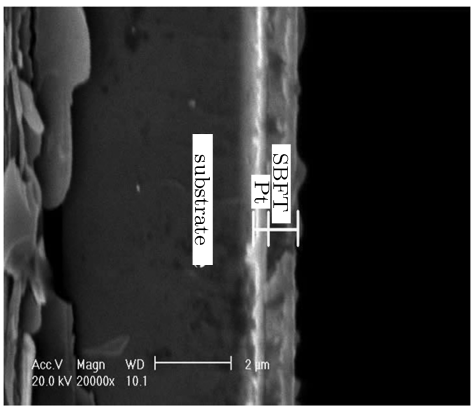


Fig.4. The cross-sectional ESEM morphology of the SBFT-0.05 thin film.

3.2. Ferroelectricity

The ferroelectric hysteretic loops of the SBFT-x thin films, obtained under an applied electric field of 229 kV/cm at room temperature, are plotted in Fig.5. The $2P_r$ of the SBFT-x thin films is significantly enlarged by the Fe-substitution, in which the $2P_r$ of the SBFT-0.05 sample, reaching about 91.1 $\mu C/cm^2$, is much larger than that of undoped SBTi films ($2P_r \sim$ 25.3 $\mu C/cm^2$ by sol-gel and $\sim$6.2 $\mu C/cm^2$ by PLD-grown, and $\sim$ 14.4 $\mu C/cm^2$ by MOD-grown[10−12]). This value is also much larger than that doped by lanthanides.[6,7] The variation of $2P_r$ is most likely caused by the structural distortion, because the radius of Fe^{3+} ions is quite different from Bi^{3+} ions. To explore the relationship between remnant polarization and structural distortion in SBFT-x, the lattice constants of the SBFT-x thin films are refined from the XRD data and summarized as listed in Table 1.

From Table 1, it can be seen that the lattice constants a and b are changed as Bi is substituted by Fe, resulting in a notable change in the orthorhombicity, defined as $2(a-b)/(a+b)$ of the samples.[8] When the Fe content is 0.05, the orthorhombicity reaches at a maximum value of 5.71×10^{-3} together with the maximum value of P_r = 45.5 $\mu C/cm^2$. The coincidence of maxima both in polarization and orthorhombicity confirms that the great enhancement of polarization is attributed to the increase of structural distortion.

Fatigue properties of the SBFT-x thin films tested at room temperature using 171 kV/cm and 50 kHz bipolar square wave are displayed in Fig.6. Except for the SBFT-0.15 (stars), the fatigue endurance behavior of the thin films is unpromising. The P_{nv} (the difference between switched and non-switched polarisation)

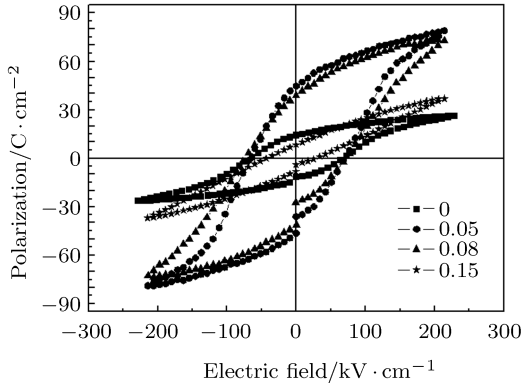


Fig.5. Ferroelectric hysteresis loops of SBFT-x under an applied field of 229 kV/cm.

Table 1. Lattice constants, orthorhombicities calculated from the refined structural parameters, and remnant polarisations of SBFT-x thin films (1 Å = 0.1 nm).

	SBFT-0.00	SBFT-0.05	SBFT-0.08	SBFT-0.15
a/Å	5.44904(8)	5.46903(7)	5.43156(6)	5.44447(2)
b/Å	5.43346(4)	5.43787(3)	5.42100(9)	5.43513(4)
c/Å	40.8389(5)	40.8636(8)	40.9162(3)	40.9346(8)
$2(a-b)/(a+b)$	2.86×10^{-3}	5.71×10^{-3}	1.95×10^{-3}	1.70×10^{-3}
$P_r/\mu C\cdot cm^{-2}$	12.7	45.5	40.0	8.30

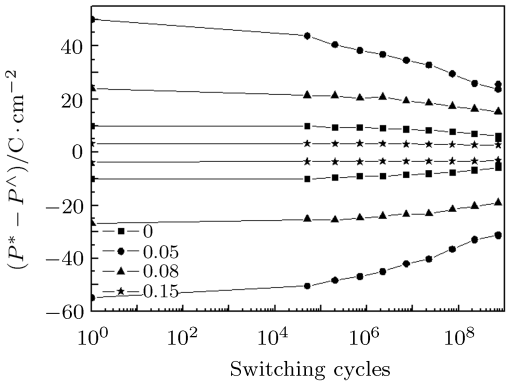


Fig.6. Fatigue properties of SBFT-x thin films after being subjected to 1×10^9 read/write cycles at a frequency of 50 kHz.

of the SBFT-0.00, SBFT-0.05 and SBFT-0.08 samples decreased about 42%, 48%, and 30%, respectively, of their initial values. We think that the fatigue properties of SBFT-x thin films may be affected by the two following facts, the one is the reduction of oxygen vacancies, because Fe ion is more stable than Bi ion at high temperatures, so the oxygen ions near the Fe ions are likely to be more stable than those near Bi ions, the fact that one Bi^{3+} is substituted by one Fe^{3+} can reduce one and a half oxygen vacancies, and the other fact is the defect induced by the chemical valance change of Fe ion, because Fe^{3+} ion is unstable and easy to change into Fe^{2+} ion, but the fact that one Fe^{3+} ion changes into one Fe^{2+} ion can only induce half oxygen vacancy, so the generation of oxygen vacancies in pseudo-perovskite blocks is restrained by the Fe^{3+} substitution for Bi^{3+}, which enhanced the fatigue behavior of the thin films. The difference in ion radius and binding energy between the Fe ion and Bi ion should give rise to more internal stress in SBFT-x (for $x > 0$).[13]

4. Conclusions

In summary, XRD, polarisation and Raman studies of SBFT-x (x = 0.00, 0.05, 0.08, 0.15) thin films revealed that Fe-doping increases the structure distortion then enhances the polarisation. It is seen that appropriate content of Fe not only increases the $2P_r$ to a very large value of 91.1 $\mu C/cm^2$ but decreases the coercive field. For the SBFT-0.05 thin film, a poor fatigue-endurance behaviour appears at the frequency of 50 kHz, the reason of the poor fatigue-endurance behavior of the SBFT-0.05 thin films will be seriously studied in future.

References

[1] Shimakawa Y, Kubo Y, Tauchi Y, Kamiyama T, Asano H and Izumi F 2000 *Appl. Phys. Lett.* **77** 2749
[2] Paz de Araujo C A, Cuchlaro J D, McMillan L D, Scott M C and Scott J F 1995 *Nature* (London) **374** 627
[3] Cummins S E and Cross L E 1968 *J. Appl. Phys.* **39** 2268
[4] Park B H, Kang B S, Bu S D, Noh T W, Lee J and Jo W 1999 *Nature* **401** 682
[5] Chon U, Kim K B, Jang H M and Yi G C 2001 *Appl. Phys. Lett.* **79** 3137
[6] Chen Y P, Yao Y Y, Bao Z H, Bao P, Zhu J S and Wang Y N 2003 *Mater. Lett.* **57** 3623
[7] Zhu J, Lu W P, Mao X Y, Hui R and Chen X B 2003 *Jpn. J. Appl. Phys.* Part 1 **42** 5165
[8] Shimakawa Y, Kubo Y, Tauchi Y, Asano H, Kamiyama T, Izumiand F and Hiroi Z 2001 *Appl. Phys. Lett.* **79** 279
[9] Kojima S, Imaizumi R, Hamazaki S and Takashige M 1994 *Jpn. J. Appl. Phys.* Part 1 **33** 5559
[10] Zhang S T, Sun B, Yang B, Chen Y F, Liu Z G and Ming N B 2001 *Mater. Lett.* **47** 334
[11] Zhang S T, Yang B, Chen Y F, Liu Z G, Yin X B, Wang Y, Wang M and Ming N B 2002 *J. Appl. Phys.* **91** 3160
[12] Watanabe H, Mihara T, Yoshimori H and Paz de Araujo C A 1995 *Jpn. J. Appl. Phys.* **34** 524
[13] Lee J K, Kim C H, Suh H S and Hong K S 2002 *Appl. Phys. Lett.* **80** 3593