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Preparation and ferroelectric properties of barium-ion-doped strontium bismuth tantalate thin films

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Abstract

$(Sr_{0.5}Ba_{0.5})_xBi_yTa_2O_z$ (SBBT) films were prepared on $Pt/Ti/SiO_2/Si$ substrates by a metal-organic decomposition method. At low temperatures, the phase transformation of films from fluorite-type structure to SBBT structure was suppressed with increasing the amounts of bismuth ions. As temperature increased, the phase transformation was improved by excess bismuth ions. Adding excess bismuth ions also resulted in an increase in the grain size of the prepared films. The value of the remanent polarization of thin film was also increased by adding excess bismuth contents. It was found that the ferroelectric characteristics of these films were significantly affected by the composition in the films.

Keywords: A. Thin films; B. Chemical synthesis; D. Microstructure

1. Introduction

Recently, the layered-structure perovskites have attracted considerable attention for their applications of low-voltage and high-speed nonvolatile random access memory (NvRAM). The chemical formula of these layered-structure compounds is $(Bi_2O_2)^{2+}(A_{x-1}B_xO_{3x-1})^{2-}$, where A and B indicates cations, and x represents numbers of perovskite layers between two $(Bi_2O_2)^{2+}$ layers. These materials were synthesized by Aurivillus in 1949 and hence were named as Aurivillus compounds. Comparing with $Pb(Zr,Ti)O_3$-based materials, thin films of the Aurivillus compounds with $x = 2$, such as $SrBi_2Ta_2O_9$, $BaBi_2Ta_2O_9$, and $SrBi_2Nb_2O_9$, exhibit several advantages. The excellent properties of low leakage current, long retention time, fatigue-free, and stable imprint characteristics improve the applications in FeRAM [1–11]. The processes for preparing $SrBi_2Ta_2O_9$-based thin films on Si-based substrates have been widely examined.

Strontium bismuth tantalite ($SrBi_2Ta_2O_9$, SBT) is one of the promising materials of Aurivillus compounds with excellent ferroelectric properties of long fatigue endurance and large remanent polarization (P_r) [12–16]. The previous studies have revealed that the layered-structured perovskites exhibit the characteristics of low leakage current, low operating voltage, stable imprinted characteristics, and high polarization retention up to long switching cycles. Because of the slight difference of cation radii between Sr^{2+} and Ba^{2+}, the formation of solid solutions of these compounds is feasible. In present study, barium ions were doped into $SrBi_2Ta_2O_9$ films to form solid solutions. $(Sr_{0.5}Ba_{0.5})Bi_yTa_2O_z$ thin films were prepared via a metal-organic decomposition (MOD) method on $Pt/Ti/SiO_2/Si$ substrates. Varying the stoichiometry of bismuth ions, the formation of the layered-structure perovskites, crystallinity, and the ferroelectric properties were investigated in this study.

2. Experimental

Strontium 2-ethylhexanoate $[Sr(C_8H_{15}O_2)_2]$, barium 2-ethylhexanoate $[Ba(C_8H_{15}O_2)_2]$, bismuth 2-ethylhexanoate $[Bi(C_8H_{15}O_2)_2]$, and tantalate ethoxide $[Ta(OC_2H_5)_5]$ were used as the starting materials. MOD was employed to fabricate $(Sr_{0.5}Ba_{0.5})_xBi_yTa_2O_z$ (SBBT) thin films. The starting materials were mixed in toluene and then were

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spin-coated onto Pt/Ti/SiO_2/Si substrates. The as-deposited films were baked on the hot plate at 150 °C. After the solvent was removed, the films were pyrolyzed at 400 °C to burn out the remaining organics. The pyrolyzed films were annealed at 580–800 °C for 1 h with oxygen flow to enhance the crystallinity. The crystallite phases were identified by X-ray diffraction (XRD) at room temperature using a MAC Science MXP3 XRD system with Cu K_α radiation at

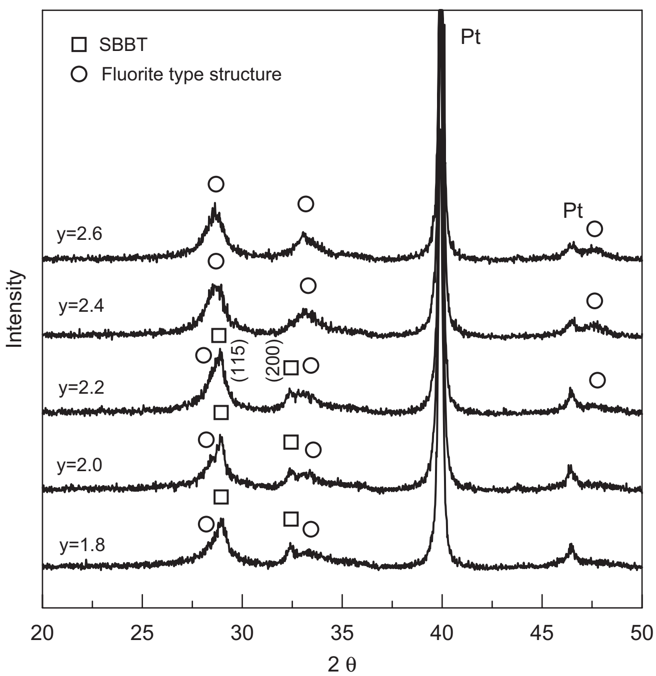

Fig. 1. XRD patterns of $(Sr_{0.5}Ba_{0.5})Bi_yTa_2O_z$ thin films with different y values annealed at 630 °C for 1 h.

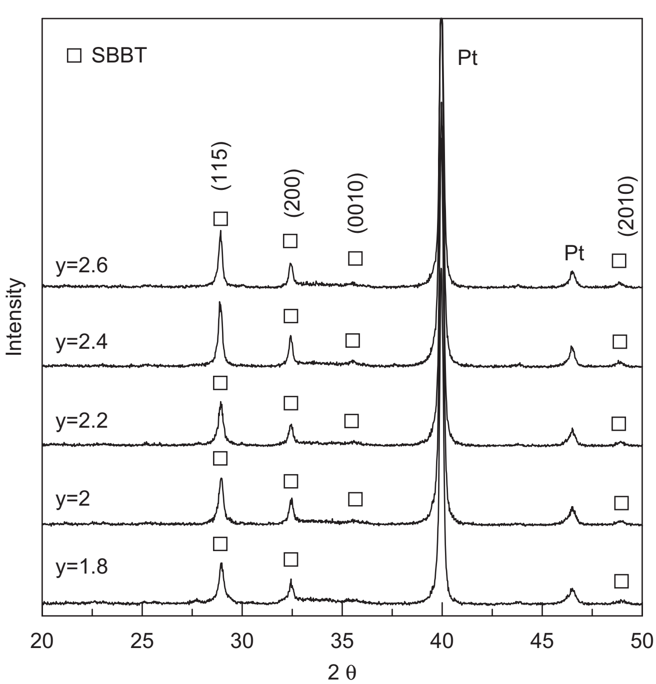

Fig. 2. XRD patterns of $(Sr_{0.5}Ba_{0.5})Bi_yTa_2O_z$ thin films with different y values annealed at 730 °C for 1 h.

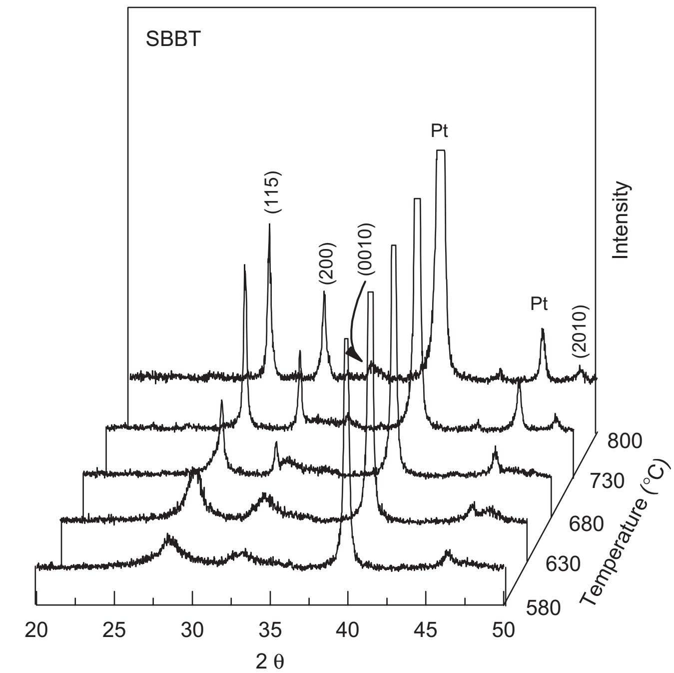

Fig. 3. XRD patterns of $(Sr_{0.5}Ba_{0.5})Bi_{2.4}Ta_2O_z$ thin films heated at (a) 580 °C, (b) 630 °C, (c) 680 °C, (d) 730 °C, and (e) 800 °C.

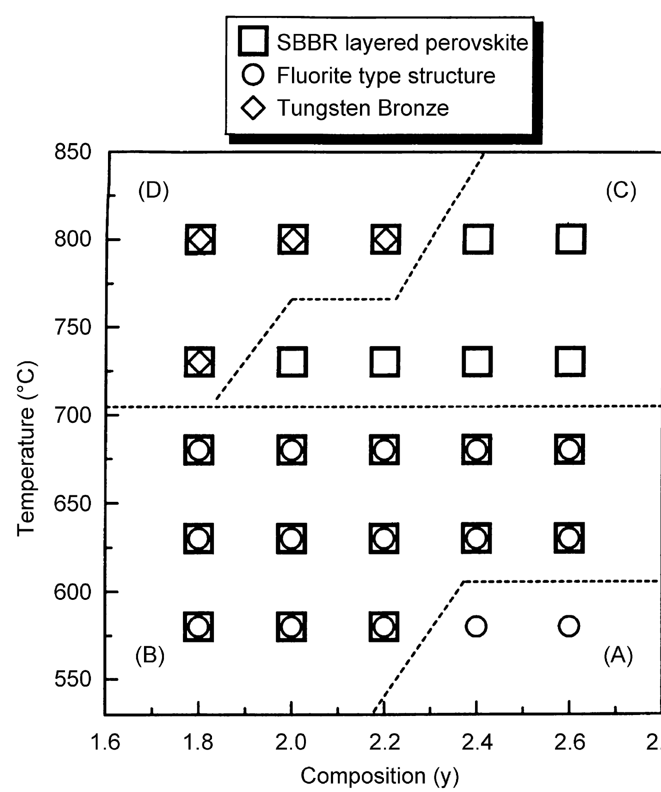

Fig. 4. Phase diagram of formation of $(Sr_{0.5}Ba_{0.5})Bi_yTa_2O_z$ thin films.

40 kV and 30 mA. The surface morphologies and structure were examined by scanning electron microscopy (Hitachi model S-800 microscope, 20 kV) and atomic force microscopy using tapping mode with amplitude modulation (Nanoscope IIIa, Digital Instruments Company, Santababara). The ferroelectric hysteresis measurements were conducted on films in metal–ferroelectric–metal configuration using a standardized ferroelectricity test system in the virtual ground.

3. Results and discussion

3.1. Formation of $(Sr_{0.5}Ba_{0.5})Bi_yTa_2O_z$ thin films

Fig. 1 shows the XRD patterns of $(Sr_{0.5}Ba_{0.5})Bi_yTa_2O_z$ thin films with different y values annealed at 630 °C. At $y = 1.8$–2.2, two structures, layered-structure perovskites (SBBT structure) and fluorite-type structure, are observed. With an increase in y, only fluorite-type structure is

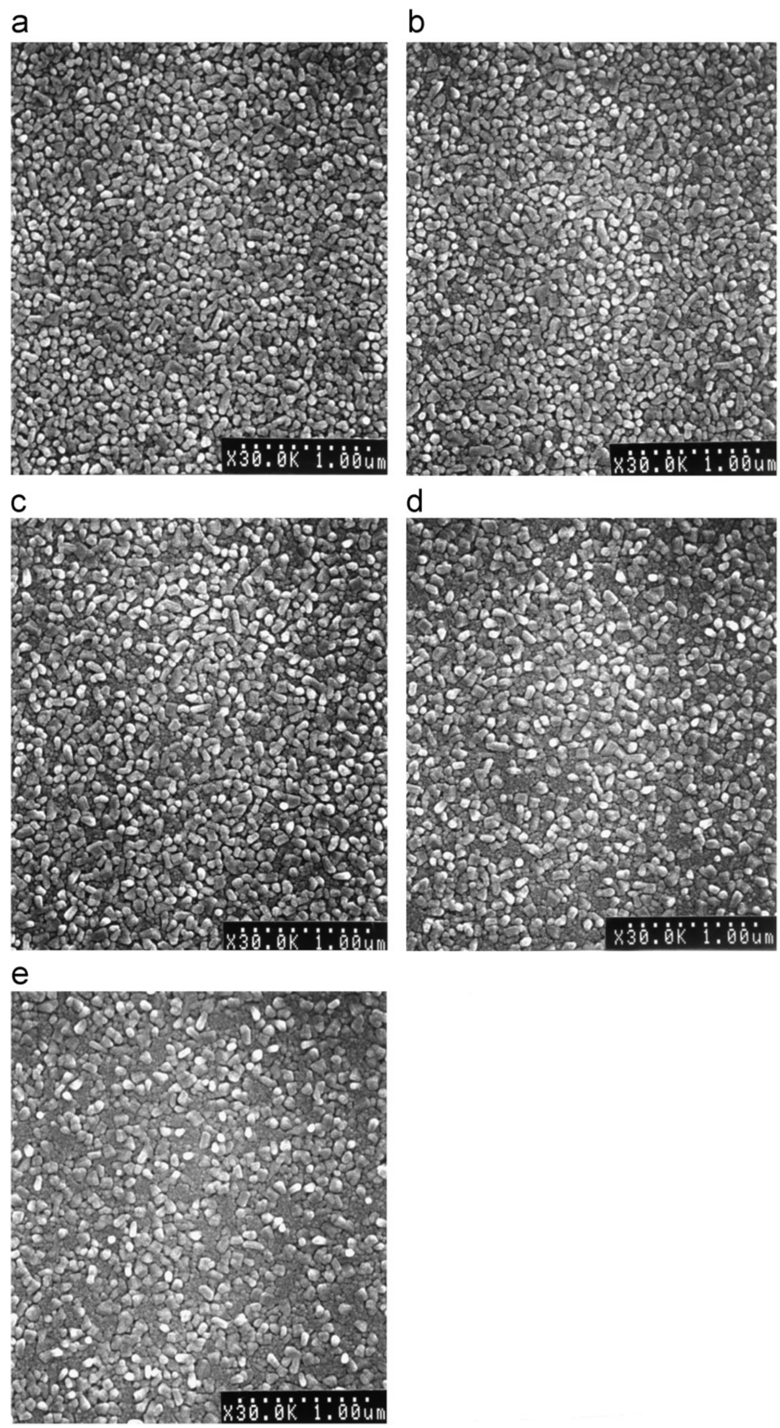

Fig. 5. Microstructures of $(Sr_{0.5}Ba_{0.5})Bi_yTa_2O_z$ thin films annealed at 730 °C: (a) $y = 1.8$, (b) $y = 2.0$, (c) $y = 2.2$, (d) $y = 2.4$, and (e) $y = 2.6$.

obtained, and the SBBT structure disappears. When the films are annealed at 630 °C, SBBT structure and fluorite-type structure coexist regardless of variations in y. Fig. 2 illustrates the XRD patterns of $(Sr_{0.5}Ba_{0.5})Bi_yTa_2O_z$ thin films with different y values annealed at 730 °C. As the annealing temperature increases to 730 °C, the SBBT structure becomes the dominant phase for $y = 2$–2.6. For $y = 1.8$, a minor tungsten bronze type coexists with the perovskite structure. It is observed that there is a phase transformation from fluorite-type structure to SBBT structure with increasing temperature. In addition, it is also found that increasing the bismuth contents can enhance the crystallinity of the films.

Fig. 3 illustrates the XRD patterns of the films at $y = 0.4$ heated at various temperatures. At 580 °C, only the fluorite structure exists. After heating at 630 °C, the crystallinity of the fluorite structure increases. The layered structure starts to form from 680 °C; however, a small amount of fluorite phase still remains. After heating at 730 °C, pure layered structure is completely formed.

Fig. 4 illustrates the phase diagram of SBBT. At 580 °C, the coexistence of SBBT structure and fluorite-type structure at $y = 1.8$–2.2 indicates that the phase transformation takes place with less bismuth-ion doped at low temperatures. The phase transformation of fluorite type to SBBT structure is suppressed when excess bismuth-ion is doped. When temperature arises, this transformation is facilitated by excess bismuth-ion. Therefore, the fluorite-type structure has transferred to SBBT structure completely above 730 °C. However, the thin films decompose at high temperature, and tungsten bronze-type oxide is formed.

In order to examine the effects of bismuth contents on the preferred orientation of the prepared films, the degree of orientation is defined as follows:

$$D_{(200)} = \frac{[I_{(200)}/I_{(115)}]_{\text{Film}}}{[I_{(200)}/I_{(115)}]_{\text{Powder}}} - 1, \tag{1}$$

where I_{200} and I_{115} are the diffraction intensity of the (2 0 0) and (1 1 5) planes, respectively. It is found that when the value of y increases from 1.8 to 2.6, the degree of orientation in a-axis significantly decreases. It reveals that adding excess bismuth-ion suppresses the preferred orientation in a-axis.

3.2. Microstructures and ferroelectric properties of $(Sr_{0.5}Ba_{0.5})Bi_yTa_2O_z$ thin films

The scanning electron micrographs of $(Sr_{0.5}Ba_{0.5})Bi_yTa_2O_z$ thin films heated at 730 °C are shown in Fig. 5. When $y = 1.8$, the grain size of the films is around 90 nm. When y increases to 2.6, the grain size of the films also increases to around 200 nm. This indicates that increasing the bismuth contents results in an increase in the grain size of the films. The ferroelectric characteristics of the prepared films heated at 730 °C are analyzed by the hysteresis measurement. The obtained data are illustrated in Fig. 6. When the value of y is small, the values of $2P_r$ and $2E_c$ of thin films are also small. Increasing the contents of bismuth ions, the values of $2P_r$ and $2E_c$ gradually increases. When y is equal to 2.4, the values of $2P_r$ and $2E_c$ of thin films becomes 12.459 μC/cm^2 and 28.44 kV/cm, respectively. After 10^{10} switching cycles, these films exhibit good anti-fatigue properties. The value of $2P_r$ only slightly decreases 3.55%. The above results reveals that $(Sr_{0.5}Ba_{0.5})Bi_yTa_2O_z$ with good ferroelectric films are successfully prepared in this study.

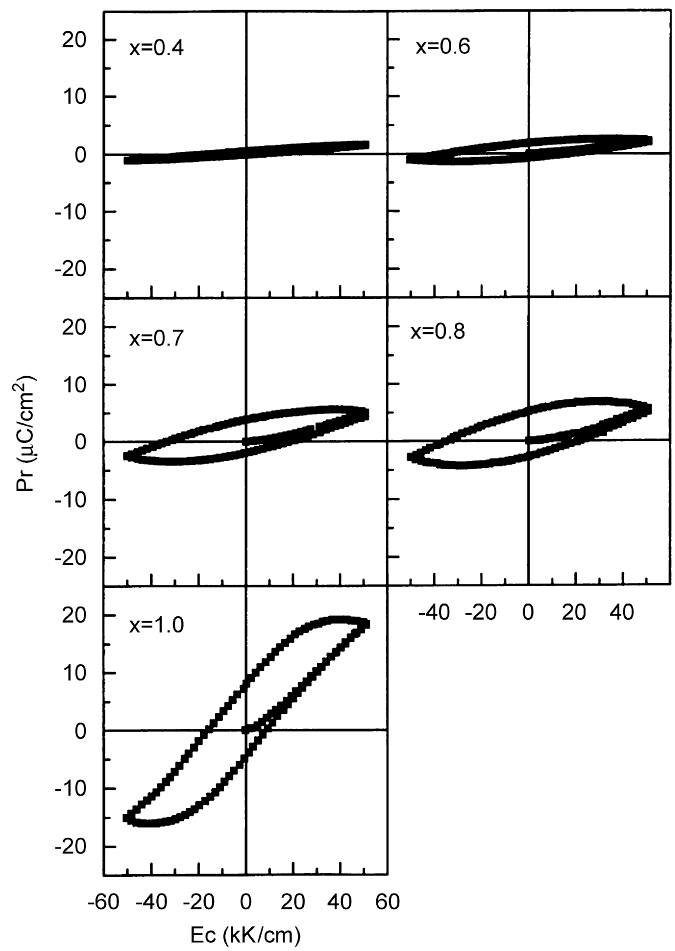

Fig. 6. Ferroelectric characteristics of $(Sr_{0.5}Ba_{0.5})_xBi_{2.4}Ta_2O_z$ films annealed at 730 °C for 1 h.

4. Conclusions

$(Sr_{0.5}Ba_{0.5})_xBi_yTa_2O_z$ films were synthesized on Pt/Ti/SiO_2/Si substrates by a metal-organic decomposition method with different contents of strontium, barium, and bismuth ions. At low temperature, the phase transformation of films from fluorite-type structure to SBBT structure was suppressed with increasing quantity of bismuth ions. As temperature increased, the phase transformation was improved by excess bismuth ions and decomposition was also avoided. Adding excess bismuth ions caused an increase in the grain size of the prepared films. The value of the remanent polarization of thin film was also increased by adding excess bismuth contents. It was found that the ferroelectric characteristics of these films were substantially influenced by the bismuth contents in the films.

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