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Stability and formation of pyrochlore phase in doped $\text{Sr}_{0.8}\text{Bi}_{2.3}\text{Ta}_2\text{O}_9$ thin films

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Abstract

Ferroelectric thin films of bismuth-containing layered perovskite $\text{Sr}_{0.8}\text{Bi}_{2.3}\text{Ta}_{2-x}\text{M}_x\text{O}_9$ (SBTM), where M is V, Ti, W, and Zr, have been prepared on Pt/Ti/SiO₂/Si substrates using the metal-organic decomposition method. The effect of the incorporated B-site cations on pyrochlore phase formation and microstructure evolution of SBTM films was investigated. The pyrochlore phase formation has been identified due to out-diffusion of titanium from underneath platinum layer to participate in the reaction with the films. Furthermore, the formation of pyrochlore phase in the SBTM films has been observed strongly dependent on the characteristics of incorporated M cation. The substitution of both W and V for Ta leads to the formation of pyrochlore phase at lower annealing temperature (750–800 °C). On the other hand, the addition of Zr can retard the formation of pyrochlore phase from 850 to 900 °C. A model based on the binding energy of octahedral structure is used to elucidate the formation and stability of the pyrochlore phase present in the SBT film.

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1. Introduction

Excellent fatigue resistance in $\text{SrBi}_2\text{Ta}_2\text{O}_9$ (SBT) films has made this material attractive for nonvolatile memory applications [1,2]. The SBT compound is part of the family of Aurivillius compounds with a general formula of $(\text{Bi}_2\text{O}_2)^{2+}(\text{A}_{m-1}\text{B}_m\text{O}_{3m+1})^{2-}$, consisting of *m*-perovskite units sandwiched between bismuth oxide layers. Here A

is the 12-fold coordinated cation in the perovskite structures, B is the octahedral site, and the bismuth forms the rock-salt type interlayer $(\text{Bi}_2\text{O}_2)^{2+}$ between the perovskite blocks $(\text{A}_{m-1}\text{B}_m\text{O}_{3m+1})^{2-}$ [3,4]. As the films were fired at high temperature, especially above 850 °C, a secondary phase having a pyrochlore structure was formed. Lu and Fang reported that the formation of the pyrochlore phase was primarily correlated with the interaction between the films and the titanium species that diffused outward from the titanium layer on substrates [5]. Rodriguez et al. studied the effect of Bi content on perovskite formation of SBT films and

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reported that the pyrochlore phase is easily developed above 775 °C. With the decrease of Bi content, the formation tendency of pyrochlore phase was stronger. The estimated stoichiometry of bismuth-deficient pyrochlore was $\text{Sr}_{0.2}(\text{Sr}_{0.5}\text{-Bi}_{0.7})\text{Ta}_2\text{O}_{6.75}$ [6]. Furthermore, once the pyrochlore phase forms, it will be deleterious to the formation of the SBT ferroelectric phase. Therefore, the pyrochlore phase is undesirable as the SBT films are used in ferroelectric memories. Thus, it is interesting to find ways to avoid formation of this pyrochlore phase. Excess Bi is usually required to compensate for Bi loss due to the high volatility of Bi during processing [7] and Bi diffusion into the bottom electrode during annealing [8]. However, the pyrochlore phase formation could be prevented or retarded by doping some elements because the pyrochlore structure was constructed via the 6-fold coordinated cation to the main framework of the unit cell in terms of binding energy, with additional cation incorporated into the framework of octahedral [9]. Therefore, the stability and formation of the pyrochlore phase will be influenced by the characteristics of 6-fold coordinated cation.

For realizing the contribution of dopants on the formation and stability of the pyrochlore phase, the substitutional replacements of various dopants with different binding energy for Ta^{5+} sites (B-site) were used in this work. The temperature dependence of the phase formation in the $\text{Sr}_{0.8}\text{-Bi}_{2.3}\text{Ta}_{2-x}\text{M}_x\text{O}_9$ (SBTM) films on Pt/Ti/SiO₂/Si substrates will be first investigated. The compositional distribution in the depth direction was examined to study the possible stoichiometry of pyrochlore structure in the SBT-based materials. Furthermore, the effect of various dopants on the formation of pyrochlore phase will be further studied and discussed.

2. Experiment

The starting materials for the metal-organic decomposition (MOD) process were bismuth 2-ethylhexanoate [$\text{Bi}(\text{CH}_3(\text{CH}_2)_3\text{CH}(\text{C}_2\text{H}_5)\text{COO})_3$], strontium 2-ethylhexanoate [$\text{Sr}(\text{CH}_3(\text{CH}_2)_3\text{CH}(\text{C}_2\text{H}_5)\text{COO})_2$], lead 2-ethylhexanoate [$\text{Pb}(\text{CH}_3$

$(\text{CH}_2)_3\text{CH}(\text{C}_2\text{H}_5)\text{COO})_2$], titanium isopropoxide $\text{Ti}(\text{OC}_3\text{H}_7)_4$, zirconium *n*-propoxide, $\text{Zr}(\text{OC}_3\text{H}_7)_4$, vanadium isopropoxide $\text{V}(\text{OC}_3\text{H}_7)_5$, tungsten ethoxide $\text{W}(\text{OC}_2\text{H}_5)_6$ and tantalum ethoxide [$\text{Ta}(\text{OC}_2\text{H}_5)_5$] with 2-ethylhexanoic acid as the solvent. The metal-organic precursors were mixed to form solutions with compositions of $\text{Sr}_{0.8}\text{Bi}_{2.3}\text{-}(\text{Ta}_{2-x}\text{M}_x)\text{O}_9$, where M is Zr, Ti, V and W. Prior to film deposition, the substrate (Pt/Ti/SiO₂/Si) was cleaned in acetone and alcohol ultrasonic baths, and then blown dry with N₂ gas. The solutions were spin-coated onto the substrate at a speed of 3000 rpm. After each coating, the as-deposited film was dried on a hot plate at a temperature of about 350 °C to remove the solvent before application of the next coating. After the process was repeated 3 times, the as-deposited films were annealed at 700–900 °C in air for 30 min by directly placing the coated substrate into a preheated tube furnace.

The crystal structures of the films were analyzed by using X-ray diffraction (XRD) with Cu K α radiation and a Ni filter. The chemical composition of the films was determined using inductively coupled plasma (ICP) mass spectroscopy. Three samples were measured by ICP analysis. The Sr/Bi/Ta/Ti ratio normalized in $\text{Ta}=2$ for $\text{Sr}_{0.8}\text{-Bi}_{2.3}\text{Ta}_{2-x}\text{M}_x\text{O}_9$ films annealed at 850 °C/1 h was calculated with error deviation of ~5%. The secondary-ion mass spectroscopy (SIMS) of the films was performed with a surface analysis system. The film thickness was measured by surface profilometry. Field-emission scanning electron microscopy was performed to investigate the surface morphology of the films.

3. Results

3.1. Phase formation of $\text{Sr}_{0.8}\text{Bi}_{2.3}\text{Ta}_2\text{O}_9$ films

XRD studies of $\text{Sr}_{0.8}\text{Bi}_{2.3}\text{Ta}_2\text{O}_9$ films as a function of annealing temperature indicate that the films annealed at 600 °C are amorphous. At 650–700 °C, a broad diffraction peak appears at around $2\theta = 28.5$, which implies that the film is not fully crystallized. As the annealing temperature increases, at 750 °C, the (115) peak in the

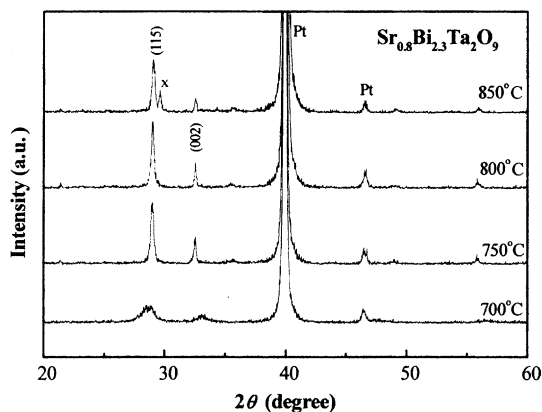


Fig. 1. XRD patterns of $\text{Sr}_{0.8}\text{Bi}_{2.3}\text{Ta}_2\text{O}_9$ films annealed at different temperatures for 0.5 h.

XRD pattern becomes sharper and the full width at half-maximum decreases indicating better crystallinity and an increase in grain size. However, when the films were annealed at 850 °C, besides the presence of the SBT perovskite, a small amount of pyrochlore phase was found to generate as shown in the XRD patterns of Fig. 1 (labeled with x). Furthermore, upon increasing annealing temperatures, the amount of SBT phase decreases with the corresponding increase in pyrochlore phase.

3.2. Formation of pyrochlore phase in doped-SBT films

The peak at 29.7° shown in XRD patterns was not only found in the pure SBT but also in oxide-doped SBT systems. Vanadium (V) has the same valence as tantalum (Ta) but a smaller ionic radius than Ta. It was found that the (1 1 5) reflection in Fig. 2 for 800 °C – annealed $\text{Sr}_{0.8}\text{Bi}_{2.3}(\text{Ta}_{2-x}\text{V}_x)\text{O}_9$ (SBTV) films is slightly shifted to the lower diffraction angle with increasing vanadium content, indicating that the V ions could be dissolved into TaO_6 octahedral structure to substitute for Ta ions. Nevertheless, further excess vanadium (x) beyond 0.2, the peak intensity of (1 1 5) rapidly decreases along with the accelerating formation of the pyrochlore phase that implies the layered perovskite structure becomes unstable. When the vanadium content was added above 0.4, complete

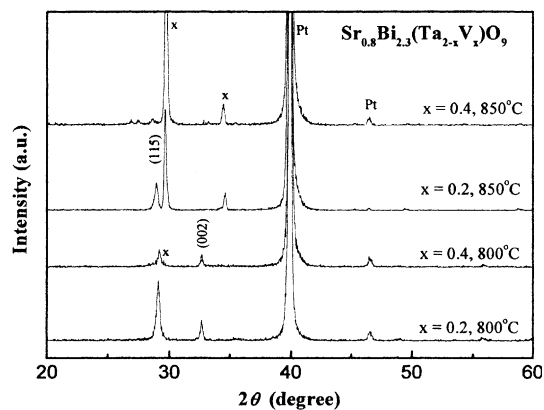


Fig. 2. XRD patterns of $\text{Sr}_{0.8}\text{Bi}_{2.3}\text{Ta}_{2-x}\text{V}_x\text{O}_9$ films annealed at 800 and 850 °C for 0.5 h.

secondary phase with no trace of perovskite has been developed in the SBTV films at 850 °C. In contrast, although the pyrochlore phase can be detected for the undoped SBT films ($x = 0$), the film is primarily composed of perovskite phase.

For confirmation, the Pt/SiO₂/Si (without Ti) substrate was used and no pyrochlore phase was detected for the SBT films annealed at 850 °C for 1 h. In contrast, as the SBT films were deposited on Pt/Ti/SiO₂/Si (with Ti) substrate, well-crystallized pyrochlore phase has been completely developed at the same annealing condition. Furthermore, the surface morphology (Fig. 3) of SBT film on the former (without Ti) substrate is much different from that on the latter (with Ti) substrate. However, it was doubted that the Ti out-diffused from the substrate directly either reacts with the atoms of SBT or first forms TiO₂ phase prior to reacting with SBT structure to form the pyrochlore phase. For realizing the effect of Ti on the formation of pyrochlore phase, $\text{Sr}_{0.8}\text{Bi}_{2.3}\text{Ta}_{2-x}\text{Ti}_x\text{O}_9$ (SBTT) films were heated at various temperatures. The obtained XRD patterns shown in Fig. 4 illustrate that, at 850 °C, even though the pyrochlore phase can be identified, the peak intensity is much weaker compared to that of undoped SBT films.

3.3. SIMS analysis of $\text{Sr}_{0.8}\text{Bi}_{2.3}\text{Ta}_{2-x}\text{M}_x\text{O}_9$ films

The SIMS analysis in Fig. 5 illustrates that the titanium has diffused into the SBT film during

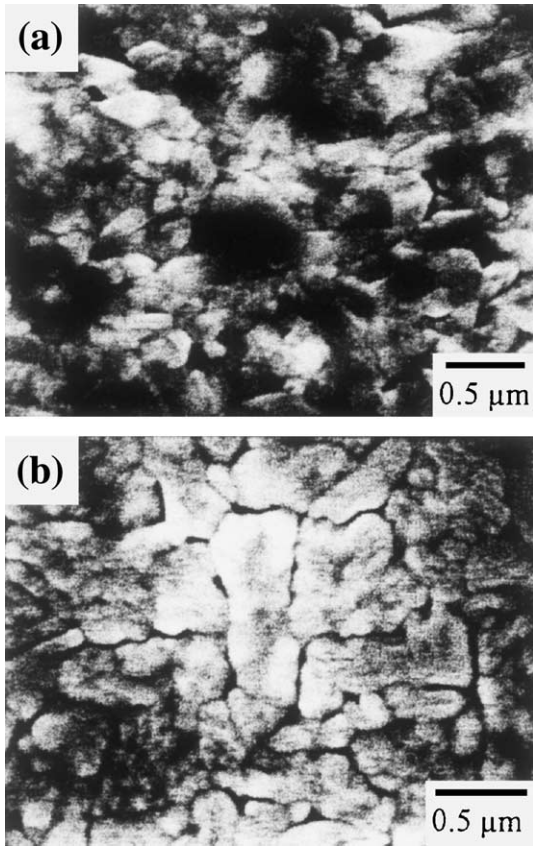


Fig. 3. SEM plan views of $\text{Sr}_{0.8}\text{Bi}_{2.3}\text{Ta}_2\text{O}_9$ films deposited on (a) Pt/Ti/SiO₂/Si and (b) Pt/SiO₂/Si substrates annealed at 850 °C for 1 h.

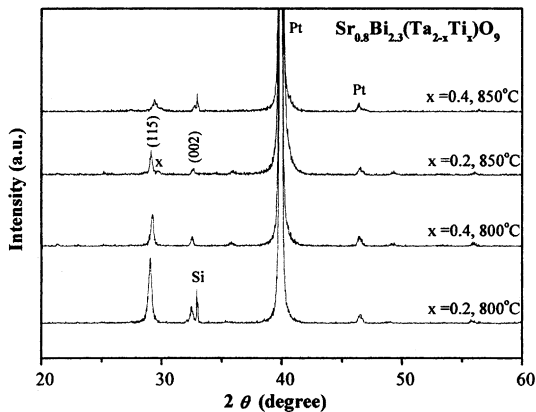


Fig. 4. XRD patterns of $\text{Sr}_{0.8}\text{Bi}_{2.3}\text{Ta}_{2-x}\text{Ti}_x\text{O}_9$ films annealed at 800 and 850 °C for 0.5 h.

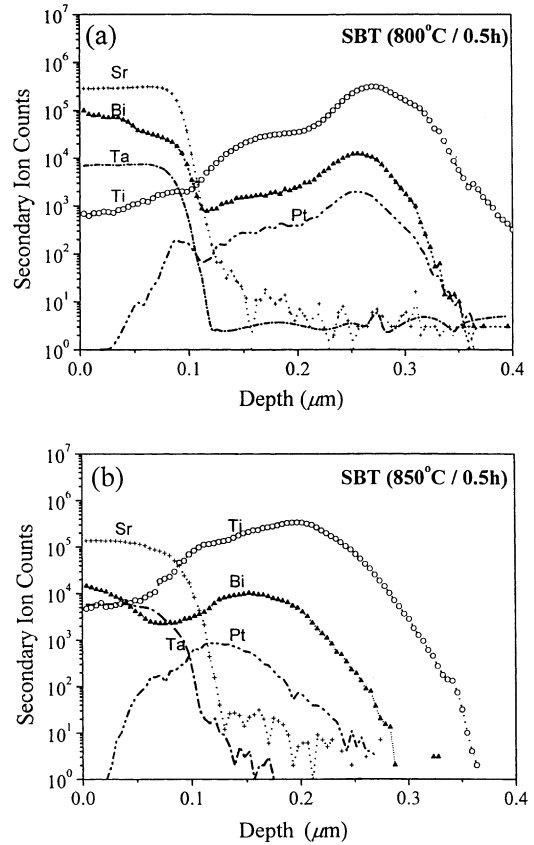


Fig. 5. Secondary ion mass spectroscopy of $\text{Sr}_{0.8}\text{Bi}_{2.3}\text{Ta}_2\text{O}_9$ films deposited on Pt/Ti/SiO₂/Si substrate and annealed at (a) 800 °C and (b) 850 °C for 0.5 h.

annealing at 800 °C. As the vanadium was added to substitute for tantalum ion, the SIMS analysis of $\text{Sr}_{0.8}\text{Bi}_{2.3}(\text{Ta}_{1.8}\text{V}_{0.2})\text{O}_9$ films in Fig. 6(b) shows that no significant amount of strontium and tantalum was detected in the platinum layer at 800 °C as compared to that of undoped $\text{Sr}_{0.8}\text{Bi}_{2.3}\text{Ta}_2\text{O}_9$ films in Fig. 5(a). However, at 850 °C (Fig. 6(b)), it was found that a small quantity of Sr with little Ta appears in the platinum layer for $\text{Sr}_{0.8}\text{Bi}_{2.3}(\text{Ta}_{1.8}\text{V}_{0.2})\text{O}_9$ films. Furthermore, the relative content of Ti in the $\text{Sr}_{0.8}\text{Bi}_{2.3}(\text{Ta}_{1.8}\text{V}_{0.2})\text{O}_9$ films is higher than that in SBT films. On the other hand, as shown in Fig. 7, with the addition of incorporated Zr cation, the diffusion of Ti into the films is retarded. Therefore, a lower ratio of Ti/Ta can be obtained for the Zr-added SBT films compared to

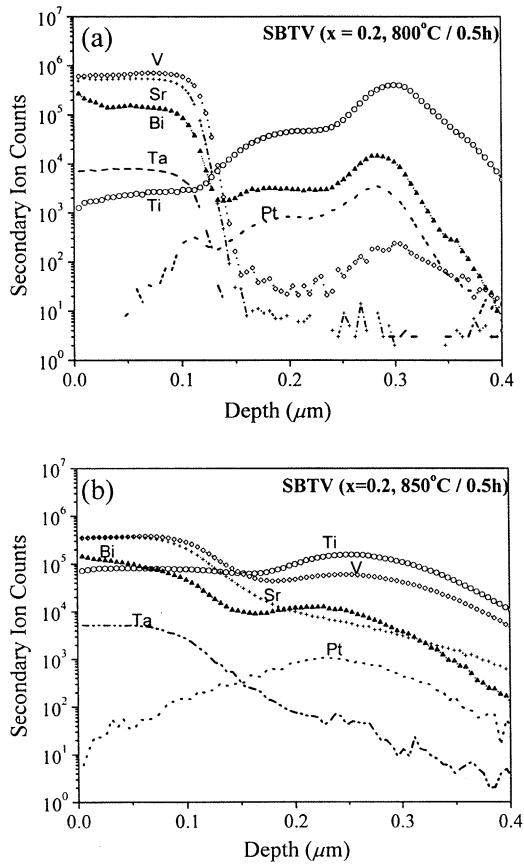


Fig. 6. Secondary ion mass spectroscopy of $\text{Sr}_{0.8}\text{Bi}_{2.3}\text{Ta}_{1.8}\text{V}_{0.2}\text{O}_9$ films deposited on Pt/Ti/SiO₂/Si substrate and annealed at (a) 800 °C and (b) 850 °C for 0.5 h.

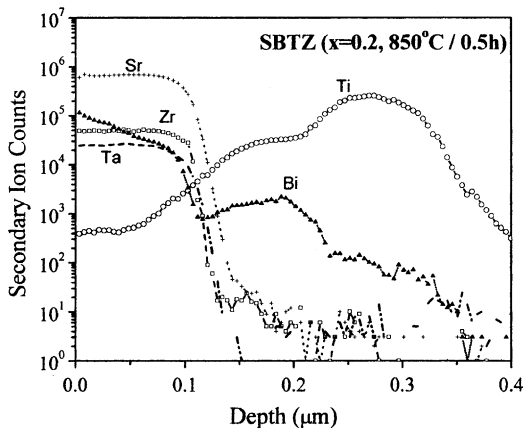


Fig. 7. Secondary ion mass spectroscopy of $\text{Sr}_{0.8}\text{Bi}_{2.3}\text{Ta}_{1.8}\text{Zr}_{0.2}\text{O}_9$ films deposited on Pt/Ti/SiO₂/Si substrate and annealed at 850 °C for 0.5 h.

the films added with the V and W (not shown here).

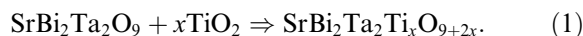
4. Discussion

4.1. Pyrochlore phase development of $\text{Sr}_{0.8}\text{Bi}_{2.3}\text{Ta}_{2-x}\text{M}_x\text{O}_9$ films

As well known, SBT films are usually required to sinter at 750–800 °C for obtaining good ferroelectric properties. However, depending on the cation ratio of the SBT compounds, a mixture of at least three phases: a pyrochlore structure, perovskite SBT and Sr–Bi-oxide compound was observed and reported for the film stoichiometry of 1.0:2.0:2.0 fired at 775 °C [6]. On the other hand, when the films were annealed above 850 °C, besides the presence of the SBT perovskite, pyrochlore phase was generated as shown in the XRD patterns of Fig. 1 (labeled with x). This phenomenon implies that SBT becomes unstable and tends to be converted into the pyrochlore phase. Similar diffraction peaks were also observed by Desu [10] and Lu and Fang [5]. In general, the pyrochlore structure displays an affinity for the 6-fold coordinated cation to establish the main framework of the unit cell in terms of binding energy. In other words, with additional cation incorporated into the framework of octahedra (TaO₆), the formation and stability of cation-defect structure was remarkably influenced [9].

Some reports mention that the pyrochlore phase is usually observed at higher temperature annealing and the phase formation results from the interaction between SBT film and substrate [5–7]. As evidenced from SIMS analysis in Fig. 5, the titanium has diffused into the SBT film during annealing at 800 °C. Therefore, it can be assumed that the phase formation was strongly dependent on the diffusion of Ti. Abe et al. reported that the titanium on Pt/Ti/SiO₂/Si substrates did out-diffuse from the intervening layer into the platinum layer at elevated temperatures, and some titanium atoms reached the outside surface of the platinum layer and were oxidized to become TiO₂ [11]. Furthermore, a rough and granular morphology was usually observed on the platinum layer due to

the formation of TiO_2 [12]. Based on the above discussion, the Ti in the pyrochlore phase apparently results from the outward diffusion under the Pt electrode. Therefore, the pyrochlore phase could be considered due to the direct reaction between TiO_2 and SBT to form the compound as follows:



In addition, the XRD patterns in Fig. 2 illustrate that when excess vanadium ($x > 0.4$) was added to substitute for the Ta in the SBT films, complete secondary phase with no trace of perovskite has been developed in the SBTV films at 850 °C compared to the undoped SBT films ($x = 0$). This finding reveals that the addition of vanadium causes the TaO_6 perovskite structure to be more unstable and promotes the formation of pyrochlore phase that is probably due to the smaller ionic radius of V ion compared to that of Ta ion. However, in this work, with the Bi content fixed, i.e., $\text{Bi} \sim 2.3$ (enough for evaporation loss), and changing the V content, it was found that the pyrochlore phase is easily developed in the SBTV than pure SBT system. This phenomenon demonstrates that the formation of pyrochlore phase is not only dependent on Bi content but also strongly dependent on the stability of sub-perovskite structure.

In addition, it was found (not shown here) that as the Ta ion in the SBT films was replaced by the zirconium (Zr) ion to form $\text{Sr}_{0.8}\text{Bi}_{2.3}(\text{Ta}_{1.8}\text{Zr}_{0.2})\text{O}_9$ (SBTZ), the perovskite phase becomes more stable and the formation of pyrochlore phase was hampered in the SBTZ film at 850 °C. However, as the tungsten (W) ion was used to substitute for Ta ion in the SBT films, an enhanced transformation of perovskite into pyrochlore phase was observed. Namely, at 800 °C, a strong peak of the pyrochlore phase has been identified in the XRD patterns of $\text{Sr}_{0.8}\text{Bi}_{2.3}(\text{Ta}_{1.8}\text{W}_{0.2})\text{O}_9$ films.

4.2. Estimated stoichiometry of pyrochlore phase

Since the pyrochlore phase has been fully developed in the $\text{Sr}_{0.8}\text{Bi}_{2.3}(\text{Ta}_{1.8}\text{V}_{0.2})\text{O}_9$ at 850 °C, we can infer that the pyrochlore phase should contain smaller concentrations in Sr, Bi, larger content in

Ti and almost equal to Ta content than the perovskite phase. Therefore, the stoichiometric composition of pyrochlore phase can be postulated to be approximately to $\text{Sr}_{0.8-x}\text{Bi}_{2.3-y}\text{Ta}_2\text{Ti}_z\text{O}_m$.

The chemical compositions of $\text{Sr}_{0.8}\text{Bi}_{2.3}\text{Ta}_2\text{O}_9$ films after annealed at 800 °C for 0.5 h were analyzed by ICP, showing that the molar ratio of Sr, Ta, and Bi in the film is very close to the compositions in the precursor solutions except for a partial loss of Bi and an extra detectable Ti compared to those in precursor solutions. This might indicate that the bismuth indeed diffused into the platinum layer, and the Ti out-diffused from the substrate into the SBT films. As the SBT film was further annealed at 850 °C for 1 h, Table 1 shows that the bismuth content was much reduced and a great quantity of titanium has been diffused into the SBT film. The Sr/Bi/Ta/Ti ratio normalized in $\text{Ta} = 2$ for the 850 °C-annealed film is approximately to 0.71/2.03/2.0/1.67. For comparison, the ICP analysis was made for the SBTV and SBTZ with $x = 0.2$ films annealed at 850 °C for 1 h. For the SBTV films where the pyrochlore phase has been completely formed, the Sr/Bi/Ta/Ti/V ratio normalized in $\text{Ta} = 2$ was calculated to be approximately 0.73/2.21/2.0/1.89/0.14. According to Eq. (1), the possible stoichiometry for the pyrochlore phase was estimated and expressed as $\text{SrBi}_2\text{Ta}_2\text{Ti}_{2-x}\text{M}_y\text{O}_{13}$ compound. Since the exchange of Sr/Bi is possible [13,14] as well as both Ti and M cations are assumed to occupy at B-sites and the possible stoichiometry of the pyrochlore phase is very close to $\text{SrBi}_2\text{Ta}_2\text{Ti}_2\text{O}_{13}$ compound and the crystal structure is depicted in Fig. 8 that

Table 1
Sr/Bi/Ta/Ti/M ratio normalized in $\text{Ta} = 2$ for $\text{Sr}_{0.8}\text{Bi}_{2.3}\text{Ta}_{2-x}\text{M}_x\text{O}_9$ films annealed at 850 °C/1 h (where M is V or Zr)

Precursor solution	Annealed SBTM films
Sr/Bi/Ta 0.8/2.3/2.0	Sr/Bi/Ta/Ti 0.71/2.03/2.0/1.67
Sr/Bi/Ta/V 0.8/2.3/1.8/0.2	Sr/Bi/Ta/Ti/V 0.73/2.21/2.0/1.89/0.14
Sr/Bi/Ta/Zr 0.8/2.3/1.8/0.2	Sr/Bi/Ta/Ti/Zr 0.81/2.32/2.0/0.79/0.21

The calculated data are averaged from three samples with the error deviation of ~5%.

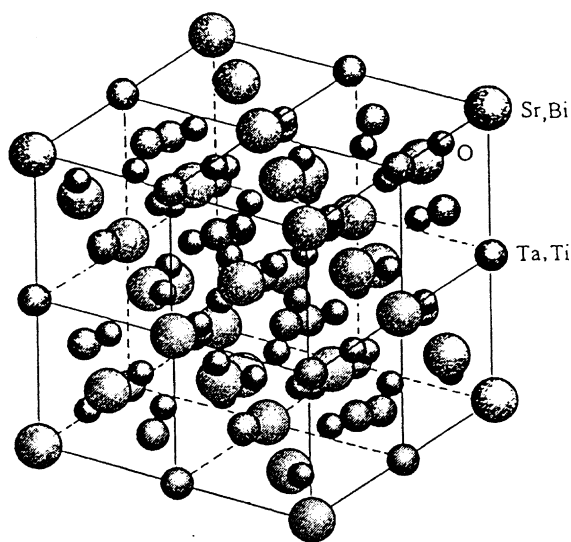


Fig. 8. Crystal structure of $\text{SrBi}_2\text{Ta}_2\text{Ti}_2\text{O}_{13}$ pyrochlore phase (Ref. [15]).

has a $Fd3m$ symmetry [15]. In this structure, (Ta,Ti), O(1) and (Bi,Sr) were assigned to sites 16c, 48f and 16d, respectively. The other O(2) is located in 8b. On the other hand, for the SBTZ with $x = 0.2$ film (no trace of pyrochlore phase observed), the Sr/Bi/Ta/Ti/Zr ratio is approximately to 0.81/2.32/2.0/0.79/0.21 that is significantly deviated from the stoichiometric composition of the pyrochlore phase. Therefore, the pyrochlore phase formation was inhibited because the less Ti content existed in the SBTZ films.

4.3. Stabilization of pyrochlore phase

In general, the pyrochlore structure displays an affinity for the 6-fold coordinated cation to establish the main framework of the unit cell in terms of binding energy, with additional cation incorporated into the framework of octahedra. From above discussion, it was implied that the formation extent of pyrochlore phase is strongly correlated with the addition of incorporated cation (M element). In other words, in addition to sintering conditions (temperature and time), the stabilization of perovskite structure will be influenced by the addition of M element. Titanium, vanadium, tungsten, and zirconium were selected in this

work to study the effect of M substitution for Ta on the stability of pyrochlore phase. If we neglect the Bi_2O_3 layer in the bismuth-based ferroelectric layered structure, the stabilization of TaO_6 octahedral structure was considered from the viewpoint of having the substitution of M atom for Ta. According to Pauling's rule, when a cation with higher valency (Z) and smaller ion radius (r) was placed in the center of polyhedron such as octahedral structure, the octahedral tends to become unstable since the cation substitution probably induces lattice strain and distortion of TaO_6 octahedral structure. Therefore, the higher the Z/r value, the unstable the octahedral structure is. A reconstruction of octahedral structure was easier preceded and converted into a pyrochlore phase at a lower annealing temperature. The Z/r ratio for the Ta substitution by W, V, Ta, and Zr is 1.223:1.051:1:0.77 in the above-mentioned doped-SBT systems that are consistent with our experimental results if based on the same stoichiometric composition of $\text{Sr}_{0.8}\text{Bi}_{2.3}(\text{Ta}_{1.8}\text{M}_{0.2})\text{O}_9$. That is, the tendency to form the pyrochlore phase for SBT with V added film is higher than that with Zr added. The fact that the addition of Zr can retard the formation of pyrochlore phase can be further evidenced from the SIMS analysis as shown in Fig. 7. A lower ratio of Ti/Ta can be obtained for the Zr-added SBT films compared to the films added with the V and W (no shown here). Therefore, a model based on the binding energy of octahedral structure can be used to explain the formation and stability of the pyrochlore phase present in the SBT film.

5. Conclusions

- (1) The out-diffusion of Ti from the underlayer Pt during annealing process plays a very important role in the formation of pyrochlore phase.
- (2) The estimated stoichiometry of the pyrochlore phase was approximately to $\text{SrBi}_2\text{Ta}_2\text{Ti}_{2-y}\text{M}_x\text{O}_{13}$ compound based on ICP analysis.
- (3) A pyrochlore phase was always observed at high temperature annealing irrespective of M-doped SBT compositions.

- (4) The formation temperature of the pyrochlore phase in M-doped SBT films was dependent on the characteristics and added amount of M cation.
- (5) The relative stability of the perovskite to pyrochlore structures in the SBTM films can be accounted for by the binding energy of TaO₆ octahedral structure.

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