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Effect of lead additive on the ferroelectric properties and microstructure of \( \text{Sr}_x\text{Pb}_y\text{Bi}_{2z}\text{Ta}_2\text{O}_9 \) thin films

San-Yuan Chen\(^{a}\) and Ving-Ching Lee

Department of Materials and Science Engineering, National Chiao-Tung University, 300 Hsinchu, Taiwan, People’s Republic of China

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Ferroelectric thin films of bismuth-containing layered perovskite \( \text{Sr}_x\text{Pb}_y\text{Bi}_{2z}\text{Ta}_2\text{O}_9 \) have been prepared using the metalorganic decomposition method. The effect of both \( \text{Sr} \) and \( \text{Pb} \) content on the crystal structure, microstructure, and ferroelectric properties of \( \text{Sr}_x\text{Pb}_y\text{Bi}_{2z}\text{Ta}_2\text{O}_9 \) films was investigated. A maximum remanent polarization of \( 2P_r = 19.2 \mu \text{C/cm}^2 \) was obtained for the \( \text{Sr}_x\text{Pb}_0\text{Bi}_{2z}\text{Ta}_2\text{O}_9 \) film with 20 mol \% \( \text{Sr}-\)deficient composition as prepared at 800 °C, which could be the compromising effects of \( \text{Sr} \) content on both grain growth and second phase formation of \( \text{BiTaO}_4 \). The substitution of \( \text{Pb} \) for \( \text{Bi} \) is accompanied by the occurrence of oxygen vacancies to compensate the charge balance, which is responsible for grain growth mechanism in \( \text{Sr}_x\text{Pb}_0\text{Bi}_{2z}\text{Ta}_2\text{O}_9 \) films. Fatigue endurance of \( \text{Sr}_x\text{Pb}_0\text{Bi}_{2z}\text{Ta}_2\text{O}_9 \) films becomes problematic after \( 10^9 \) cycles with a decrease in remanent polarization to 85\% of the original value. This phenomenon was related to electron injection and creation of electron traps due to the occupation of \( \text{Sr} \) vacancies by \( \text{Bi} \) cations. It is demonstrated that the fatigue endurance of \( \text{Sr}_x\text{Pb}_0\text{Bi}_{2z}\text{Ta}_2\text{O}_9 \) film can be improved by doping with 20 mol \% \( \text{PbO} \).

\(^{a}\)Author to whom correspondence should be addressed.

I. INTRODUCTION

Bismuth-containing layered perovskites were found to be ferroelectric by Smolenkii et al.\(^1,2\) They belong to the family of Aurivillius compounds with a general formula of \( (\text{Bi}_3\text{O}_5)^{2–} (\text{A}_n–1\text{B}_3\text{O}_{3m+1})^{2–} \), consisting of \( m \)-perovskite units sandwiched between bismuth oxide layers. (Here \( \text{A} \) and \( \text{B} \) are the two types of cations that enter the perovskite unit. \( \text{A} \) is \( \text{Bi}^{3+} \), \( \text{Ba}^{2+} \), \( \text{Sr}^{2+} \), \( \text{Pb}^{2+} \), or \( \text{K}^+ \); \( \text{B} \) is \( \text{Ti}^{4+} \), \( \text{Ta}^{5+} \), \( \text{Nb}^{5+} \), \( \text{Mo}^{6+} \) or \( \text{W}^{6+} \)).

Ferroelectric thin films of \( \text{SrBi}_2\text{Nb}_2\text{O}_9 \) (SBN), \( \text{SrBi}_2\text{Ta}_2\text{O}_9 \) (SBT) and their solid solutions are being widely investigated for applications in high density nonvolatile ferroelectric random access memories because of their excellent ferroelectric properties, characterized by limited polarization fatigue and low coercive field.\(^3,4\) Various deposition methods have been used to produce Bi layer-structured ferroelectric thin films, such as rf sputtering,\(^5\) laser ablation,\(^6\) metalorganic chemical vapor deposition,\(^7\) and wet-chemical processes [sol–gel or metalorganic decomposition (MOD)].\(^8–10\)

Ferroelectric properties, crystal structure, and microstructure are remarkably influenced by the composition fluctuation in the bismuth layer structured compounds. Atsuki et al.\(^11\) reported that the remanent polarization \( P_r \) of \( \text{Sr}_x\text{Bi}_{2z}\text{Ta}_2\text{O}_9 \) \( (0.7 \leq x \leq 1.0, 2.0 \leq 2z \leq 2.6) \) increased with the decrease of the \( \text{Sr} / \text{Ta} \) mole ratio for films annealed at 800 °C. A maximum remanent polarization was obtained for the 20 mol \% \( \text{Sr}-\)deficient and 10 mol \% \( \text{Bi}-\)excess composition.\(^12\) Noguchi et al. attributed the enhancement of \( P_r \) with decreasing \( \text{Sr} \) content from \( x = 1.0 \) to 0.8 to the increase in grain growth. On the other hand, the decrease of \( P_r \) with further decreasing \( \text{Sr} \) content is due to the disappearance of the SBT phase and the formation of a \( \text{BiTaO}_4 \) second phase.\(^13\) On the other hand, Watanabe et al.\(^14\) reported that the dependence of \( P_r \) on \( \text{Sr} \) content in SBN films was entirely due to the sensitivity of grain orientation to \( \text{Sr} \) content. The randomly oriented \( \text{Sr}-\)deficient SBN films have larger remanent polarization than \( c \)-axis oriented stoichiometric SBN films. An asymmetric hysteresis loop was also observed in \( \text{Sr}-\)deficient SBTN films. Excess \( \text{Bi} \) is usually required to achieve stoichiometry due to the high volatility of \( \text{Bi} \) during processing\(^15\) and \( \text{Bi} \) diffusion into the bottom electrode during annealing.\(^16\) Watanabe et al.\(^17\) reported that the SBTN films grown with an excess bismuth of around 20\% \( (2z = 2.4) \) yields a maximum \( P_r \) value and a lower coercive field.

\( \text{PbBi}_2\text{Nb}_2\text{O}_9 \) is another ferroelectric compound that has a layered perovskite structure.\(^1\) It has a pseudotetragonal unit cell with lattice parameters \( a = 5.492 \AA \), \( b = 5.503 \AA \), \( c = 25.53 \AA \), and \( Z = 4.\) Subbarao et al.\(^19\) found well-defined hysteresis loops for \( \text{PbBi}_2\text{Nb}_2\text{O}_9 \)-based capacitors at 200 °C, but its relatively high coercive field made it difficult to obtain ferroelectric switching at room temperature.\(^20\) From the viewpoint of the general formula of Aurivillius compounds, \( \text{Pb} \), similar to \( \text{Sr} \) in the \( \text{SrBi}_2\text{Nb}_2\text{O}_9 \), occupies the \( \text{Bi} \) sites of \( \text{PbBi}_2\text{Ta}_2\text{O}_9 \). However, \( \text{Pb} \) and \( \text{Bi} \) are known to have 6 lone pair electrons and tend to form ionic bonds,\(^21\) and the occupancy of \( \text{Pb} \) for \( \text{Bi} \) was thought to be related to the improvement of the ferroelectric properties. A recent study by Millan et al.\(^22\) reported that when the \( \text{SrBi}_2\text{Nb}_2\text{O}_9 \) ceramic was doped with \( \text{PbO} \), the \( \text{Pb}^{2+} \) cation was incorporated into the orthorhombic structure, leading to a monoclinic distortion, which increases with the increased substitution of \( \text{Bi}^{3+} \) by \( \text{Pb}^{2+} \). From literature reports, it was found that vacancies usually play an important role in grain growth and have a remarkable effect on electrical properties of materials, especially for electronic ceramics such as...
BaTiO$_3$. Therefore, it is also relevant to study the effect of Pb$^{2+}$ incorporation in the composition Sr$_2$Bi$_2$Ta$_2$O$_9$ compound in order to identify its role in the structure of this compound. In this work, we explore the correlation between the Sr deficiency in SBT films and the observed enhanced polarization from the viewpoint of defect chemistry. Based on the similar structures of PbBi$_2$Ta$_2$O$_9$ and SrBi$_2$Ta$_2$O$_9$, the effect of Pb$^{2+}$ substitution on remanent polarization and fatigue properties of Sr$_2$Bi$_2$Ta$_2$O$_9$ composition was also investigated.

II. EXPERIMENT

The starting materials for the MOD process were bis-muth 2-ethylhexanoate [Bi(CH$_3$(CH)$_2$CH(C$_2$H$_5$)COO)$_3$], strontium 2-ethylhexanoate [Sr(CH$_3$(CH)$_2$CH(C$_2$H$_5$)COO)$_2$], lead 2-ethylhexanoate [Pb(CH$_3$(CH)$_2$CH(C$_2$H$_5$)COO)$_2$], and tantalum ethoxide [Ta(OCH$_2$CH$_3$)$_3$] with 2-ethylhexanoic acid as the solvent. The metalorganic precursors were mixed to form solutions with compositions of Sr$_x$Pb$_{1-x}$Bi$_2$Ta$_2$O$_9$. Prior to film deposition, the substrate (Pt/Ti/SiO$_2$/Si) was cleaned in acetone and alcohol ultrasonic baths, then blown dry with N$_2$ 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 four times, the as-deposited films were sintered at 750–800 °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 Siemens D5000 x-ray diffraction (XRD) with Cu Kα radiation and a Ni filter. The chemical composition of the films was determined using inductively coupled plasma (ICP) mass spectroscopy (Perkin Elmer, SCIEX ELAN 5000). The film thickness was measured by Dektak surface profilometer. Field-emission scanning electron microscopy Hitachi S4000 was performed to investigate the surface morphology of the films. Patterned top Au electrodes through a shadow mask on an area of 8.0×10$^{-4}$ cm$^2$ area were sputter deposited onto the SBT layers to define capacitors in order to perform electrical measurements. A ferroelectric testing system (RT-66A, Radiant Technologies Inc.) operating in the virtual-ground mode was used to obtain the remanent polarization ($P_r$)-coercive field ($E_c$) hysteresis characteristics and fatigue properties. Fatigue tests of the films were conducted using a bipolar square wave of 5 V at 1 MHz.

III. RESULTS

A. Sr$_x$Bi$_2$Ta$_2$O$_9$ thin films

1. Microstructure and phase evolution

XRD analysis was used to investigate the effect of Sr content on the phase development of Sr$_x$Bi$_2$Ta$_2$O$_9$ film (0.5 ≤$x$≤ 1.2) annealed at 800 °C for 0.5 h. As shown in Fig. 1, an unknown phase at 2θ= 29.5° was observed for Sr$_{0.8}$Bi$_2$Ta$_2$O$_9$ film and the peak intensity increased with increasing Sr deficiency. This peak might originate from the formation of BiTaO$_4$ (JCPDS 16-0906) according to the report of Hase et al. TABLE I lists the chemical compositions of Sr$_x$Bi$_2$Ta$_2$O$_9$ films annealed at 800 °C for 0.5 h. The molar numbers of Sr, Ta, and Bi in those films are very close to the compositions in the precursor solutions for Sr-deficient Sr$_x$Bi$_2$Ta$_2$O$_9$ films.

In other words, the films with Sr deficiency show no obvious Bi loss. However, for the films with Sr ($x$) = 1, a partial loss of Bi was found compared to those in precursor solutions. This might indicate that the occupation of Sr vacancies by Bi cations reduces the evaporation of Bi$_2$O$_3$ or Bi loss. Similarly, for Sr-deficient Sr$_{0.8}$Pb$_{0.2}$Bi$_2$Ta$_2$O$_9$ films, except for the loss of Pb, the reduction of Bi was also observed.

The microstructure evolution of SrBi$_2$Ta$_2$O$_9$ films changes substantially as a function of Sr content, as shown in Fig. 2. The grain size is larger for Sr-deficient Sr$_x$Bi$_2$Ta$_2$O$_9$ films than for Sr$_{0.8}$Bi$_2$Ta$_2$O$_9$ films annealed at 800 °C for 0.5 h. The molar numbers of Sr, Ta, and Bi in those films are very close to the compositions in the precursor solutions for Sr-deficient Sr$_x$Bi$_2$Ta$_2$O$_9$ films.

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![Fig. 1. XRD patterns of Sr$_x$Bi$_2$Ta$_2$O$_9$ films annealed at 800 °C for 0.5 h.](image)

**TABLE I.** Sr/Pb/Bi/Ta ratio normalized in Ta$^2+$ for Sr$_{0.8}$Bi$_2$Ta$_2$O$_9$ films.

<table>
<thead>
<tr>
<th>Precursor solution</th>
<th>Films prepared at 800 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sr/Pb/Bi/Ta</td>
<td></td>
</tr>
<tr>
<td>0.8/0/0.2/0.2</td>
<td>0.8787/0.0/2.05/2</td>
</tr>
<tr>
<td>0.8/0/2.3/2</td>
<td>0.7939/0.2/3.1/2</td>
</tr>
<tr>
<td>1.00/0/2.0/2</td>
<td>0.9797/0.0/2.04/2</td>
</tr>
<tr>
<td>1.00/2.3/2</td>
<td>0.9697/0.2/2.4/2</td>
</tr>
<tr>
<td>0.80/2.2/0.2</td>
<td>0.7920/0.183/1.98/2</td>
</tr>
<tr>
<td>0.80/2/2.3/2</td>
<td>0.7890/0.186/2.24/2</td>
</tr>
<tr>
<td>1.00/2/0.2/2</td>
<td>0.9710/0.175/1.97/2</td>
</tr>
<tr>
<td>1.00/2/2.3/2</td>
<td>0.9760/0.172/2.19/2</td>
</tr>
</tbody>
</table>
be about 190, 145, 100, and 70 nm for $x=0.6$, 0.8, 1.0, and 1.2, respectively.

2. Electrical properties

Figure 3 shows the P–E hysteresis curves of both $\text{SrBi}_2\text{Ta}_2\text{O}_9$ and $\text{Sr}_{0.8}\text{Bi}_2\text{.3Ta}_2\text{O}_9$ films annealed at 800 °C. The $2P_r$ value of $\text{Sr}_{0.8}\text{Bi}_2\text{.3Ta}_2\text{O}_9$ film was measured to be about 15.9 $\mu$C/cm$^2$, which is larger than that of $\text{SrBi}_2\text{.3Ta}_2\text{O}_9$ films ($2P_r=6.7 \mu$C/cm$^2$) for an applied voltage of 5 V. Here, the hysteresis curves of Sr-deficient SBT film often exhibit little horizontal shifts along the voltage axis as compared with that of stoichiometric SBT film. The $P_r$ value was also found to be strongly dependent on Sr content in $\text{Sr}_x\text{Bi}_2\text{.3Ta}_2\text{O}_9$ compositions for a variety of Bi content ($2y=2.0–2.3$) (Fig. 4). When the Sr content exceeded 20% ($x=1.2$), there is no hysteresis curve. However, the $2P_r$ value increased with the decrease in Sr content from Sr=1.1 to Sr=0.8 and then decreased with further decreasing Sr content from Sr=0.8 to Sr=0.6. The maximum value of $2P_r$ was obtained at the $\text{Sr}_x\text{Bi}_2\text{.3Ta}_2\text{O}_9$ films with Sr=0.8. A similar phenomenon was also observed for the $\text{Sr}_{2}\text{Bi}_{2.0}\text{Ta}_2\text{O}_9$ films.

Fatigue endurance was tested with 1 MHz bipolar pulses at 5 V. Figure 5 shows the fatigue behavior of $\text{Sr}_x\text{Bi}_2\text{Ta}_2\text{O}_9$ films prepared at 800 °C for 0.5 h. Most of the $\text{Sr}_x\text{Bi}_2\text{Ta}_2\text{O}_9$ films show no appreciable fatigue after $10^9$ cycles. However, a partial loss of $2P_r$ after fatigue was observed for $\text{Sr}_{0.8}\text{Bi}_2\text{.3Ta}_2\text{O}_9$-based capacitors. The percentage of the remanent polarization after $10^9$ cycles was approximately 87% of the initial value. Similar dependence of fatigue endurance on composition was also observed by Noguchi et al. 12

B. $\text{Pb}_y\text{Bi}_2\text{Ta}_2\text{O}_9$ thin films

Figure 6 shows the XRD patterns of $\text{Pb}_{y}\text{Bi}_2\text{Ta}_2\text{O}_9$ (PBT) films fired at 800 °C for 0.5 h. Some peaks at $2\theta=29.4$, 32.6, and 34.1, corresponding to BiTaO$_4$ phase in $\text{Sr}_{0.8}\text{Bi}_2\text{Ta}_2\text{O}_9$ film, began to develop. Furthermore, these peak intensities increased with decreasing Pb content in $\text{Pb}_y\text{Bi}_2\text{Ta}_2\text{O}_9$ films. The dependence of grain size on Pb content in PBT films was completely different from that of Sr in SBT films. As shown in Fig. 7, a fine-grained microstructure was developed in the $\text{Pb}_y\text{Bi}_2\text{Ta}_2\text{O}_9$ film with Pb=0.6 and...
accompanied with the formation of pores because of volume shrinkage during the amorphous/crystalline transformation. With increasing Pb content, clusters appeared [for stoichiometric PBT films, Fig. 7(c)], probably originated from a single nucleus, similar to spherulites commonly seen in amorphous-to-crystalline transitions. Some clusters with pores appear located near the center of each cluster and on the grain boundaries. Even for Pb-rich PBT films, the clusters are still seen [Fig. 7(d)].

The hysteresis curve of Pb$_{0.6}$Bi$_{2.0}$Ta$_2$O$_9$ films with $y = 0.7$ and 1.0 were further measured under an applied voltage of 5 V. The film with $y = 1.0$ displayed a remanent polarization $P_r$ of 3.3 $\mu$C/cm$^2$ but the remanent polarization could not be measured for Pb-deficient Pb$_{0.8}$Bi$_{2.3}$Ta$_2$O$_9$ films such as $y = 0.7$. The fatigue behavior of Pb$_{1.0}$Bi$_{2.0}$Ta$_2$O$_9$ films were also tested and no appreciable loss after $10^9$ cycles was observed.

C. Sr$_x$Pb$_{1-x}$Bi$_2$Ta$_2$O$_9$ thin films

Both SrBi$_2$Ta$_2$O$_9$ and PbBi$_2$Ta$_2$O$_9$ are Aurivillius-structure layered bismuth compounds of (Bi$_2$O$_2$)$^2^+$. When Sr$_{0.6}$Pb$_{1.4}$Bi$_{2.3}$Ta$_2$O$_9$ films were annealed at 750–800 °C for 0.5 h, a maximum value of $2P_r$ was obtained near the composition of Sr$_{0.6}$Bi$_{2.3}$Ta$_2$O$_9$. Moreover, as the Sr content increases, the $2P_r$ changes little up to $x = 0.7$ and then a sharp drop of $2P_r$ is observed at $x = 1$. When the annealing temperature was raised to 800 °C, a second phase was detected in the Pb-rich Sr$_{0.7}$Pb$_{0.3}$Bi$_2$Ta$_2$O$_9$ composition as observed in Pb-deficient Pb$_{1.0}$Bi$_2$Ta$_2$O$_9$ film (Fig. 6), therefore, causing the remanent polarization to be apparently reduced, especially for a Pb$_{1.0}$Bi$_2$Ta$_2$O$_9$ film. Consequently, a maximum remanent polarization ($2P_r = 16.7$ $\mu$C/cm$^2$) was obtained near the composition of Sr$_{0.6}$Pb$_{0.4}$Bi$_{2.3}$Ta$_2$O$_9$ film ($x = 0.7$). In this case, the results also reflect the fact that the minor addition of Pb into Sr$_{0.6}$Bi$_{2.3}$Ta$_2$O$_9$ films does not strongly influence the dependence of Sr content on $P_r$ value.

In order to further clarify the role of Pb additive in Sr$_x$Bi$_{2.3}$Ta$_2$O$_9$ films, the electrical properties and microstructural morphology of Sr$_x$Bi$_{2.3}$Ta$_2$O$_9$ films doped with 20 mol % PbO were studied. The XRD results show that no changes in the diffraction pattern were observed except for a slight variation in the intensity of some diffraction peaks. The dependence of film morphology on Sr content in the Sr$_x$Pb$_{0.2}$Bi$_{2.1}$Ta$_2$O$_9$ compositions is shown in Fig. 9. As the Sr$_{0.6}$Bi$_{2.3}$Ta$_2$O$_9$ film is doped with 20 mol % PbO, i.e., Sr$_{0.6}$Pb$_{0.4}$Bi$_{2.3}$Ta$_2$O$_9$, the grains begin to grow and coalesce with each other. Therefore, some large grains were formed along with finer pores located near the center of a large grain or at the grain boundaries. Obviously, the addition of PbO promotes the grain growth of Sr$_{0.6}$Bi$_{2.3}$Ta$_2$O$_9$ film. Furthermore, as compared with the grain size of SEM micrographs.
in Fig. 2 for Sr$_{1-x}$Bi$_2$Ta$_2$O$_9$ films, a larger-grain microstructure was obtained for Sr$_0.2$Bi$_2$Ta$_2$O$_9$ films. The average grain size of Sr$_0.2$Bi$_2$Ta$_2$O$_9$ films, similar to Sr$_{1-x}$Bi$_2$Ta$_2$O$_9$ compositions, decreases with the increase of Sr content. The average grain size was measured to be around 210 nm at the compositions of $x=0.8$ and 150 nm at $x=1.0$.

In order to compare the effect of 20 mol % PbO on the remanent polarization of Sr$_{1-x}$Bi$_2$Ta$_2$O$_9$ films, the $2P_r$ values of Sr$_{0.8}$Bi$_2$Ta$_2$O$_9$ films were measured at 5 V. As shown in Fig. 4, the film with 20% Sr deficiency ($x=0.8$) still gives a maximum $2P_r$ of 19.2 $\mu C/cm^2$ for Sr$_0.2$Bi$_2$Ta$_2$O$_9$ compositions. Figure 10 shows the fatigue behavior of Sr$_0.2$Bi$_2$Ta$_2$O$_9$ films excited with 5 V pulses. The fatigue of Sr$_0.2$Bi$_2$Ta$_2$O$_9$ film is also placed in Fig. 10 for comparison. Most of the Sr$_0.2$Bi$_2$Ta$_2$O$_9$ films exhibit good fatigue endurance except for Sr$_0.2$Bi$_2$Ta$_2$O$_9$ films having a slight degradation of 9%. The fatigue endurance of Sr$_0.2$Bi$_2$Ta$_2$O$_9$ film was obviously enhanced by 20 mol % PbO additions.

**IV. DISCUSSION**

**A. Microstructure and polarization properties**

The $2P_r$ values increased with the decrease in Sr content from Sr=1.1 to Sr=0.8 for Sr$_{1-x}$Bi$_2$Ta$_2$O$_9$ films annealed at 800 °C. The enhanced $P_r$ could be attributed to the grain growth and grain orientation as reported in the literature. However, in our case, no preferred orientation was observed in the XRD pattern for Sr$_{1-x}$Bi$_2$Ta$_2$O$_9$ films, but the microstructure of Fig. 2 indeed revealed a grain morphology transitioned from rod- to round-like as the Sr content increased. For Sr-deficient Sr$_{1-x}$Bi$_2$Ta$_2$O$_9$ compositions, the BiTaO$_4$ phase was identified according to the XRD analysis of Fig. 1. Furthermore, the number of Sr defects would increase with the decrease in Sr content and therefore, the probability of domain pinning would increase, resulting in a reduced $2P_r$. Although the Sr$_{0.8}$Bi$_2$Ta$_2$O$_9$ film has larger grain size, both Sr vacancy concentration and second phase formation of BiTaO$_4$ microcrystals overcome the grain-size effect. Therefore, a maximum polarization was obtained at Sr=0.8 for both Sr$_{0.2}$Bi$_2$Ta$_2$O$_9$ and Sr$_{1-x}$Bi$_2$Ta$_2$O$_9$ films. The enhanced remanent polarization of the former composition could be attributed to the larger grain size compared to the latter composition without Pb.

As compared to SrBi$_2$Ta$_2$O$_9$, the PbBi$_2$Nb$_2$O$_9$ ceramic has a lower crystallization temperature and sintering temperature. Therefore, at the lower annealing temperature of 750 °C, Pb-rich composition (i.e., $x=0$) in Sr$_{1-x}$Bi$_2$Ta$_2$O$_9$ ($0<x<1$) films gives a larger remanent polarization as compared to the film with $x=1$. At 800 °C, however, a second phase was observed in the Pb-rich films as shown in the XRD pattern of Fig. 6 for PbBi$_2$Ta$_2$O$_9$ composition, and thus, the remanent polarization was strongly reduced for increasing Pb content (or decreasing Sr content). An optimal $2P_r$ of 16.7 $\mu C/cm^2$ was attained around the composition of Sr$_{0.7}$Pb$_{0.3}$Bi$_2$Ta$_2$O$_9$. Here, further increasing Sr content leads to the decrease of remanent polarization since grain size was remarkably reduced.

**B. Role of Pb in Sr$_x$Pb$_{y}$Bi$_2$Ta$_2$O$_9$ films**

From electronic structure, both Pb and Bi have a lone pair of out-shell electrons of 6s$^2$. This chemical aspect could be significant since the lone-pair electrons of Pb and Bi are known to have a large polarizability and to promote strong ferroelectricity. However, from the viewpoint of ferroelectricity, Pb in PbBi$_2$Ta$_2$O$_9$, as similar to Sr in SrBi$_2$Ta$_2$O$_9$, i.e., it occupies the A site in Aurivillius compounds and the radii of Pb (1.18 Å), Sr (1.16 Å) and Bi (1.02 Å) are very close. It will be interesting to study the role of Pb in SrBi$_2$Ta$_2$O$_9$ film in order to identify the key chemical and structural elements that lead to optimal polarization and polarization fatigue.

Assuming Pb can completely substitute for Sr in the SrBi$_2$Ta$_2$O$_9$ composition, the PbBi$_2$Ta$_2$O$_9$ film should display a specific ferroelectricity. However, since PbO, after being annealed at high temperature, is easily evaporated, the PbBi$_2$Ta$_2$O$_9$ composition probably became Pb$_2$Bi$_2$Ta$_2$O$_9$ ($z<1$). Furthermore, if the role of Pb is similar to Sr, the measured polarization of Pb$_2$Bi$_2$Ta$_2$O$_9$ film should have been...
considered that Sr deficiency was compensated by excess Bi in SrBi$_2$Ta$_2$O$_9$ or SrBi$_2$Ta$_2$O$_9$ films show no appreciable polarization of Sr$_0.8$Bi$_{2.3}$Ta$_2$O$_9$ film. In the other model, the electron/hole injection and traps due to the occupation of Bi for Sr vacancies will be trapped at domain boundaries to pin domain boundaries, which increases the coercive field to polarize the film. This was proposed to originate from the interaction of charge carriers with defects, which may be trapped at domain boundaries.

There are several proposals that attempt to explain the fatigue behavior of ferroelectric thin films, especially for PZTs.24 According to the fatigue model proposed by Warren et al.25 For Sr$_{0.8}$Bi$_{2.3}$Ta$_2$O$_9$ films, it is plausible for Pb to occupy the Sr vacancies and produce free Bi which will be readily evaporated from the surface because of the high vapor pressure of Bi at high temperatures.

C. Fatigue behavior of Sr$_{1-x}$Pb$_x$Bi$_{2.3}$Ta$_2$O$_9$ films

Ferroelectric thin films of bismuth-containing layered perovskite such as SrBi$_2$Ta$_3$O$_9$ and SrBi$_2$Nb$_3$O$_9$ have been reported to have excellent good fatigue resistance. Our results, although Sr-deficient SrBi$_2$Ta$_3$O$_9$ film shows an optimal remanent polarization of $2P_r = 15.9 \mu C/cm^2$, a loss of Pr of 15% was measured after $10^9$ cycles. A similar phenomenon was also reported by Noguchi et al.22 In contrast, the SrBi$_2$Ta$_2$O$_9$ or SrBi$_2$Ta$_3$O$_9$ films show no appreciable polarization under the same applied voltage of 5 V.

There are several proposals that attempt to explain the fatigue behavior of ferroelectric thin films especially for piezoelectric transducers (PZTs). These proposals are all related to defects, which may be trapped at domain boundaries to lower their mobility. However, there have been different views of the species of the defects and the location of the trapping sites. Oxygen vacancy and electron/hole injection have been suggested as possible mechanisms for the fatigue of PZT films.24,25 Support for the oxygen vacancy model was drawn from the observation that oxygen vacancy was produced in PZT film because PbO was easily evaporated during high temperature annealing. In our case, however, the Sr$_0.8$Bi$_2$Ta$_3$O$_9$ film prepared with both 20 mol % deficiency Sr and 15 mol % excess Bi should have very few oxygen vacancies. Therefore, the oxygen vacancy mechanism is not applicable in explaining the fatigue behavior of Sr$_0.8$Bi$_2$Ta$_3$O$_9$ film. In the other model, the electron/hole mechanism states that the injection of charge carrier (mainly electrons) will be trapped at domain boundaries to pin domains. The tendency for this to occur increases when the material is donor doped.25 For Sr$_0.8$Bi$_2$Ta$_3$O$_9$ film, it was considered that Sr deficiency was compensated by excess Bi since both radius of Sr (1.16 Å) and Bi (1.02 Å) are very close.11,26 The electron can be produced by substituting Bi for Sr vacancy according to the defect reaction as follows:

$$2\text{Bi}_2\text{O}_3 \rightarrow 2\text{Bi}^+ + 2\text{O}^\bullet + 2e^-.$$ (2)

With 15 mol % excess Bi, the Sr-deficient Sr$_0.8$Bi$_2$Ta$_3$O$_9$ film is probably considered as donor doped and the chance for electron injection is high. Therefore, after cycling, the injected electron was trapped by the ions Bi$^\bullet$, which in turn could pin the domain boundary movement, causing the switchable polarization to decrease. This is in agreement with our fatigue data shown in Fig. 5. Furthermore, the number of Sr defects would increase with the decrease in Sr content and therefore, cause a larger coercive field to polarize the film.

Although Pb is a volatile species, the anion (oxygen) vacancies accompanied by the substitution of Pb for Bi do not seem to adversely affect the fatigue resistance as evidenced in Fig. 10. This gives clearer evidence to rule out the oxygen vacancy mechanism for fatigue that has been proposed for PZT films.84 According to the fatigue model proposed by Warren et al.25 and Eq. (2), the released electronic charge trapping at domain walls can inhibit the domain motion and lead to the partial suppression of the switchable polarization in Sr$_0.8$Bi$_2$Ta$_3$O$_9$ film. However, as indicated in Table I, Sr$_0.8$Bi$_2$Ta$_3$O$_9$ film shows almost no loss of Bi, but the addition of Pb induces the reduction of Bi in the Sr$_0.8$Pb$_{0.2}$Bi$_{2.3}$Ta$_2$O$_9$ film. It is plausible for Pb to occupy the Sr vacancies and produce free Bi which will be readily evaporated from the surface because of the high vapor pressure of Bi at high temperatures. Therefore, the reaction in Eq. (2) is probably partially inhibited by doping Pb into the Sr$_0.8$Bi$_2$Ta$_3$O$_9$ film so that the electronic charge cannot be easily released. Alternatively, the released electrons due to the Bi substitution for Sr can be possibly compensated from the hole or oxygen vacancies produced from the substitution of Pb for Bi as shown in Eq. (1). Consequently, the fatigue behavior of Sr$_0.8$Pb$_{0.2}$Bi$_{2.3}$Ta$_2$O$_9$ film can be improved by incorporating 20 mol % PbO into Sr$_0.8$Bi$_2$Ta$_3$O$_9$ film.

V. CONCLUSIONS

Sr$_2$Bi$_3$Ta$_2$O$_9$ and Pb$_2$Bi$_3$Ta$_2$O$_9$ films have shown completely different dependence of microstructure evolution and ferroelectric properties on A site (Sr or Pb) content in Aurivillius compounds of (Bi$_2$O$_2$)$_{2m}$ (A$_{m-1}$Bi$_m$O$_{3m+1}$)$_{2m}$.26 Ferroelectric properties of Sr$_2$Bi$_3$Ta$_2$O$_9$ films could be further enhanced by the addition of 20 mol % Pb.

The addition of Pb is responsible for the enhanced grain growth in Sr$_0.8$Pb$_{0.2}$Bi$_2$Ta$_3$O$_9$ films.

Fatigue endurance of Sr$_0.8$Bi$_2$Ta$_3$O$_9$ films in this study become problematic after $10^9$ cycles with decreasing Sr content. This was proposed to originate from with electron injection and traps due to the occupation of Bi for Sr vacancies.

Fatigue behavior of Sr$_0.8$Bi$_2$Ta$_3$O$_9$ film can be improved by incorporating 20 mol % PbO because the release of electronic charge could be partially inhibited by doping Pb to occupy the Sr vacancies.
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