Synthesis and properties of BiScO₃–PbTiO₃ powders and thin films using metal-organic precursor solutions

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The BiScO₃–PbTiO₃ binary system is known to have a morphotropic phase boundary (MPB) and a higher Curie temperature than Pb(Zr,Ti)O₃ and to exhibit excellent dielectric and ferroelectric properties. Perovskite BiScO₃–PbTiO₃ powders and thin films were synthesized via a chemical process using metal-organic precursor solutions. Homogeneous and stable precursor solutions, perovskite BiScO₃–PbTiO₃ single-phase powders and thin films on Pt/TiO_x/SiO₂/Si substrates were successfully prepared by optimizing the processing conditions. The 0.35BiScO₃–0.65PbTiO₃ composition was close to the MPB and had a Curie temperature of around 470°C. The electrical properties of BiScO₃–PbTiO₃ thin films showed a maximum at this composition. The dielectric permittivity of the 0.35BiScO₃–0.65PbTiO₃ thin film at the MPB was approximately 1700, with a dielectric loss tangent of less than 5% at room temperature. Furthermore, BiScO₃–PbTiO₃ thin films showed a typical ferroelectric polarization (*P*)–electric field (*E*) hysteresis loop. The remnant polarization (*P_r*) and coercive field (*E_c*) of the 0.35BiScO₃–0.65PbTiO₃ film were approximately 23 μC/cm² and 70 kV/cm, respectively.

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1. Introduction

The lead zirconate titanate (Pb(Zr_{1–x}Ti_x)O₃, PZT) solid solution system has been extensively studied and widely used as ferroelectric and piezoelectric material. The highest values of the dielectric and piezoelectric properties in the PZT system are observed near the morphotropic phase boundary (MPB) composition that separates the rhombohedral and tetragonal phases.^{1),2)} Although the PZT has excellent ferroelectric properties, PZT ferroelectrics exhibit relatively low Curie temperatures (*T_C* = 386°C at MPB), which tend to limit the temperature range of their application.³⁾

Recently, high *T_C* ferroelectric perovskites in (1 – *x*)BiMO₃–*x*PbTiO₃ (*M* = Sc, In, Y, Fe, etc.)-type MPB systems have been discovered and investigated.^{4)–10)} Among them, the (1 – *x*)BiScO₃–*x*PbTiO₃ (BS-PT) system was reported to exhibit a *T_C* = 450°C and a peak piezoelectric coefficient *d*₃₃ = 460 pC/N (comparable to that of PZT) near the MPB composition (*x* = 0.64).^{4),5)} Furthermore, a ferroelectric material with a high Curie temperature tends to have a large crystallographic anisotropy, which often causes problems in practical applications, such as the requirement for orientation control. For example, Bi-layered perovskite Bi₄Ti₃O₁₂ (*T_C* = 675°C)¹¹⁾ and tungsten bronze PbNb₂O₆ (*T_C* = 560°C).¹²⁾ In these materials, crystal orientation control in the direction of polarization is indispensable for utilizing their excellent ferroelectric properties. A solid solution of BiMO₃ and PbTiO₃ does not have such a large crystallographic anisotropy. In addition to this, it is considered of value to study those materials that have excellent properties with lower lead content, because it is difficult to achieve the desired properties with current lead-free materials. These facts suggest that the BS-PT system is a potential candidate for applications

requiring excellent temperature-stable properties, such as ferroelectric and piezoelectric thin film devices. Epitaxial BS-PT thin films on LaAlO₃ substrates with preferred orientation fabricated by pulsed laser deposition (PLD) have been reported.^{13),14)} However, except for a *x* = 0.66 (MPB) composition, chemically prepared BS-PT thin films have not been reported.^{15),16)}

This paper describes the preparation of perovskite BS-PT powders and thin films near their MPB composition, with various PbTiO₃ concentrations, using a chemical process based on metal-organic precursor solutions. This chemical solution process is useful for acquiring high homogeneity, flexible control of the chemical composition, and for lower processing temperatures to reduce environmental load.^{17)–20)} The crystallization and phase transition of chemically synthesized BS-PT powders and thin films were investigated and dielectric and ferroelectric properties of the BS-PT films on Pt/TiO_x/SiO₂/Si substrates are also evaluated in this paper.

2. Experimental procedure

Figure 1 shows the experimental procedure for preparing BiScO₃–PbTiO₃ precursor solutions, crystalline powders, and thin films. Bi(O⁺C₅H₁₁)₃, Sc(O⁺C₃H₇)₃, Pb(CH₃COO)₂, and Ti(O⁺C₃H₇)₄ (Kojund Chemical, Japan) were selected as starting materials for preparing (1 – *x*)BiScO₃–*x*PbTiO₃ (*x* = 0.50, 0.60, 0.65, 0.70) precursor solutions. 2-Methoxyethanol (Kishida Chemical, Japan) was dried over a molecular sieve and distilled prior to use. The desired amounts of starting materials with 5 mol % excess Bi and Pb were dissolved in absolute 2-methoxyethanol. In this case, the addition of excess Bi and Pb was performed to compensate for the loss due to the Bi and Pb volatilization during the heat treatment of precursor powders and films. Then, the mixed solution was heated at 100°C for 20 h yielding a 0.1 M homogeneous precursor solution. The entire procedure was conducted in a dry nitrogen atmosphere.

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Fig. 1. Experimental procedure for preparing BiScO₃-PbTiO₃ precursor solutions, crystalline powders and thin films.

Thin films were fabricated using the precursor solution by spin-coating on Pt/TiO_x/SiO₂/Si substrates. As-deposited BS-PT precursor films were dried at 150°C for 5 min and calcined at 400°C at a rate of 10°C/min for 1 h in an oxygen flow. Then, the calcined films were crystallized at 750°C at a rate of 10°C/min for 1 h in an oxygen flow. The thickness of the BS-PT films was adjusted to be approximately 250 nm by repeating the coating/calcining cycle.

To study the crystallization and thermal behavior of the chemically derived BS-PT powders, the precursor powders of BS-PT were prepared by removing the solvent from the precursor solutions. The precursor powders were heat-treated at 800°C in an oxygen flow to yield the crystalline BS-PT powders.

The crystallographic phases of the prepared BS-PT powders and thin films were characterized by X-ray diffraction analysis (XRD; Rigaku, RAD RC) using CuKα radiation with a monochromator. The thermal behavior of the crystallized BS-PT powder was analyzed by differential scanning calorimetry (DSC) [Rigaku, Tas-300] in air from room temperature to 600°C with a temperature ramp rate of 20°C/min. The surface morphology of the crystallized thin films was observed using atomic force microscopy (AFM; Olympus, NV-2000). The electrical properties of the films were measured using a 0.2-mm diameter Pt top electrode deposited by DC sputtering onto the surface of the BS-PT films followed by annealing at 400°C for 1 h. The Pt layer of the Pt/TiO_x/SiO₂/Si substrate was used as the bottom electrode. The electrical properties of the films were evaluated using an impedance/gain phase analyzer (SI-1260, Toyo Corp.) and a ferroelectric test system (FCE-1, Toyo Corp.) at room temperature.

3. Results and discussion

3.1 Crystallization and phase transition of BS-PT powders

Homogeneous and stable BiScO₃-PbTiO₃ precursor solutions were successfully prepared by reacting starting metal-organic compounds in 2-methoxyethanol. In the BS-PT system, the crystallographic structure change and the MPB were observed by varying the BS-PT composition.^{5),8)} The MPB region has been confirmed to be around $x = 0.64$ in the $(1-x)$ BiScO₃- x PbTiO₃ system by analyses of the detailed X-ray and electron diffraction patterns, dielectric properties and DSC data of BS-PT single crystals and polycrystals.^{5),8)} In this study, the crystallization of

Fig. 2. XRD patterns of the $(1-x)$ BiScO₃- x PbTiO₃ (BS-100xPT) crystalline powders: (a) $x = 0.50$ (BS-50PT); (b) $x = 0.60$ (BS-60PT); (c) $x = 0.65$ (BS-65PT); (d) $x = 0.70$ (BS-70PT).

chemically prepared BS-PT precursor powders was investigated at various PbTiO₃ concentrations prior to the fabrication of the BS-PT films. **Figure 2** illustrates the XRD profiles of $(1-x)$ BiScO₃- x PbTiO₃ (BS-100xPT) precursor powders after heat treatment at 800°C. In this case, the excess Bi and Pb concentration of the precursor powders was determined when the perovskite BS-PT phase having the highest crystallinity without the formation of second phase was obtained. At compositions of $x = 0.5$ and $x = 0.6$, the BS-50PT and BS-60PT precursor powders crystallized in the rhombohedral (pseudo cubic) perovskite phase. This is consistent with previously reported results where BS-PT with $x \leq 0.60$ had a rhombohedral perovskite BS-PT phase.^{5),8)} At $x = 0.7$ (BS-70PT) composition, the main crystallographic phase was considered to be the tetragonal BS-PT phase because of the separation of 002 and 200 diffractions, as shown in Fig. 2(d). Furthermore, at $x = 0.65$, the BS-65PT precursor powder might crystallize in a mixture of rhombohedral and tetragonal BS-PT phases, as shown in Fig. 2(c), which is enlarged for the range of $2\theta = 43.5\text{--}46.5^\circ$ in the figure. From Fig. 2, the MPB of the chemically derived BS-PT powders was considered to be located at around the $x = 0.65$ composition of $(1-x)$ BiScO₃- x PbTiO₃.

To confirm the ferroelectric phase transition behavior of BS-65PT (at MPB composition), DSC measurements were conducted on perovskite BS-65PT powder, because DSC, or differential thermal analysis (DTA), is useful for detecting the exo- and endothermic behavior of ferroelectrics during phase transition.^{8),21),22)} **Figure 3** illustrates a DSC curve for the BS-65PT powder from room temperature to 600°C. The phase transition from ferroelectrics to paraelectrics was endothermic. Although the DSC curve was broadened, the Curie temperature of BS-65PT was observed to be 470°C, which is almost the same as the temperature of bulk BS-PT ceramics.^{4),5)} Thus, chemically synthesized BS-65PT maintained the high Curie temperature of bulk BS-PT ceramics and was ferroelectric over a wide temperature range.

3.2 Crystallization of BS-PT thin films on substrates

Figure 4 illustrates the XRD patterns of $(1-x)$ BiScO₃- x PbTiO₃ (BS-100xPT, $x = 0.50, 0.60, 0.65, 0.70$) thin films fabricated on Pt/TiO_x/SiO₂/Si substrates after heat treatment at 750°C. Although the crystallographic phase was similar to the cubic (pseudo cubic) phase, BS-PT thin films ($x = 0.60, 0.65, 0.70$) were found to crystallize in the perovskite BS-PT single phase, without any second phase, like pyrochlore. On the other

Fig. 3. DSC curve of the $0.35\text{BiScO}_3\text{-}0.65\text{PbTiO}_3$ (BS-65PT) crystal-line powder.

Fig. 4. XRD patterns of the $(1-x)\text{BiScO}_3\text{-}x\text{PbTiO}_3$ (BS-100xPT) thin films: (a) $x = 0.50$ (BS-50PT); (b) $x = 0.60$ (BS-60PT); (c) $x = 0.65$ (BS-65PT); (d) $x = 0.70$ (BS-70PT).

hand, the BS-50PT ($x = 0.50$) thin film crystallized in the perovskite BS-PT phase with a small amount of the pyrochlore phase, as shown in Fig. 4(a). The end member of perovskite BiScO_3 is known to have an unstable perovskite structure because of its low tolerance factor ($t = 0.907$).⁴ In the BS-PT system, the stability of the perovskite phase decreases with increasing BiScO_3 concentration. This evidence corroborates our finding that the BS-PT thin films with $x = 0.60$, 0.65 and 0.70 compositions crystallized solely in the perovskite phase while the film with $x = 0.50$ composition crystallized in a mixture of perovskite and pyrochlore phases.

3.3 Surface morphology of crystalline BS-PT thin films

The surface morphologies of the BS-PT films with $x = 0.60$, 0.65 , 0.70 compositions were examined because they were determined to crystallize solely in the perovskite phase as described in 3.2. **Figure 5** shows the AFM images of synthesized BS-60PT, BS-65PT, and BS-70PT thin films on $\text{Pt}/\text{TiO}_x/\text{SiO}_2/\text{Si}$ substrates. These AFM images reveal that the average grain size of the BS-PT thin films varied from 50 to 100 nm depending on the amount of PbTiO_3 : at $x = 0.60$ (BS-60PT), the grain size of the film was approximately 50 nm; whereas, at $x = 0.7$ (BS-70PT), the grain size increased to around 100 nm. Similarly for the $(1-x)\text{BiMO}_3\text{-}x\text{PbTiO}_3$ ($M = \text{Sc, Ga, Fe}$) solid solution

Fig. 5. AFM images of the $(1-x)\text{BiScO}_3\text{-}x\text{PbTiO}_3$ (BS-100xPT) thin films: (a) $x = 0.60$ (BS-60PT); (b) $x = 0.65$ (BS-65PT); (c) $x = 0.70$ (BS-70PT).

Table 1. Dielectric constant (ϵ_r) and loss ($\tan \delta$) of the $(1-x)\text{BiScO}_3\text{-}x\text{PbTiO}_3$ thin films (BS-100xPT, $x = 0.60, 0.65, 0.70$) fabricated at 750°C on $\text{Pt}/\text{TiO}_x/\text{SiO}_2/\text{Si}$ substrates

Composition	ϵ_r	$\tan \delta$
BS-60PT	1200	0.047
BS-65PT	1700	0.039
BS-70PT	1000	0.048

[Measured at 100 Hz and at room temp.]

ceramic systems, the crystal grains of polycrystalline samples are also known to grow larger as the PbTiO_3 concentration increases.^{23,24} Furthermore, the BS-60PT and BS-65PT thin films had relatively homogeneous surfaces and less roughness compared to the BS-70PT thin film, as illustrated in Fig. 5. The root mean square (RMS) values of the films were approximately 3.3, 2.9, and 4.6, corresponding to the $x = 0.60$, 0.65 , and 0.70 compositions, respectively. To clarify grain growth behavior of BS-PT thin films, detailed cross-sectional observation of the films is required and will be carried out in the future.

3.4 Electrical properties of perovskite BS-PT thin films

For the thin film samples that crystallized in the perovskite BS-PT single phase, the dielectric properties were evaluated at room temperature. **Table 1** summarizes the dielectric constant (ϵ_r) and dielectric loss ($\tan \delta$) of the $(1-x)\text{BiScO}_3\text{-}x\text{PbTiO}_3$ (BS-100xPT) thin films crystallized at 750°C . The measurement was performed at a frequency of 100 Hz and at room temperature. Additionally, the thickness of the films was confirmed to be around 250 nm by scanning electron microscopy (SEM) observations. The values of ϵ_r were approximately 1200, 1700, and 1000, corresponding to the $x = 0.60$ (BS-60PT), 0.65 (BS-65PT), and 0.70 (BS-70PT) compositions, respectively. The maximum value of ϵ_r appeared at $x = 0.65$ (BS-65PT), and the values of the dielectric constant were consistent with those of polycrystalline BS-PT ceramics.⁵ For the BS-PT thin films in this study,

Fig. 6. Dielectric properties of the 0.35BiScO₃-0.65PbTiO₃ (BS-65PT) thin film as a function of measured frequency. [Measured at room temperature.]

Fig. 7. P - E hysteresis loops of the $(1-x)\text{BiScO}_3$ - $x\text{PbTiO}_3$ (BS-100xPT) thin films: (a) $x = 0.60$ (BS-60PT); (b) $x = 0.65$ (BS-65PT); (c) $x = 0.70$ (BS-70PT). [Measured at 1 kHz and at room temperature.]

enhancement of the dielectric constant at around $x = 0.65$ was considered to be caused by the presence of the MPB as in the case of bulk BS-PT.^{4),5),8)} **Figure 6** shows the dielectric properties of the BS-65PT thin film crystallized at 750°C as a function of measured frequency. Although the ϵ_r values indicated a small dependence on frequency, ϵ_r values higher than 1380 and $\tan \delta$ less than 10% were observed for the film over a wide frequency range.

P - E hysteresis measurements were also performed to characterize the ferroelectric properties for the perovskite BS-PT thin films crystallized at 750°C. **Figure 7** shows the P - E hysteresis loops of 250-nm thick BS-60PT, BS-65PT, and BS-70PT thin films, measured at a frequency of 1 kHz and at room temperature. These thin films showed typical ferroelectric hysteresis loops at an applied voltage of 10 V. The remnant polarization (P_r) and coercive field (E_c) of the films were 19, 23, 14 $\mu\text{C}/\text{cm}^2$ and 97, 70, 80 kV/cm^2 , corresponding to the $x = 0.60$, 0.65, and 0.70 compositions, respectively, as summarized in **Table 2**. The enhancement of P_r at the $x = 0.65$ (BS-65PT) composition was attributed to the presence of the MPB, as was the behavior of the dielectric constant at $x = 0.65$, described above. However, the P_r values of synthesized BS-100xPT ($x = 0.60$, 0.65, 0.70) thin films were lower than (and thus inferior to) those reported for bulk ceramics^{4),5)} and epitaxial films.^{13),16)} Moreover, the E_c values and square character of the P - E hysteresis loops were also inferior to those of BS-PT ceramics and epitaxial films.

Table 2. Remanent polarization (P_r) and coercive field (E_c) values of the $(1-x)\text{BiScO}_3$ - $x\text{PbTiO}_3$ thin films (BS-100xPT, $x = 0.60$, 0.65, 0.70) fabricated at 750°C on Pt/TiO_x/SiO₂/Si substrates

Composition	P_r	E_c
BS-60PT	18 $\mu\text{C}/\text{cm}^2$	100 kV/cm
BS-65PT	23 $\mu\text{C}/\text{cm}^2$	70 kV/cm
BS-70PT	13 $\mu\text{C}/\text{cm}^2$	80 kV/cm

[Measured at 1 kHz and at room temp.]

Improvement of the ferroelectric properties through controlling the crystal growth orientation, as well as low-temperature fabrication of perovskite BS-PT thin films are important for practical applications and are currently under investigation.

4. Conclusions

Ferroelectric $(1-x)\text{BiScO}_3$ - $x\text{PbTiO}_3$ (BS-100xPT) thin films were successfully synthesized using a chemical solution deposition process. Homogeneous and stable BS-PT precursor solutions were prepared by controlling the reaction of starting metal-organic compounds in 2-methoxyethanol. Our findings indicated that the MPB was located around the $x = 0.65$ (BS-65PT) composition. Additionally, a relatively high ferroelectric phase transition temperature (around 470°C) is also maintained. Perovskite BS-60PT, BS-65PT, and BS-70PT thin films were crystallized on Pt/TiO_x/SiO₂/Si substrates at 750°C. Among them, the BS-65PT thin film had the highest dielectric permittivity of approximately 1700 at room temperature. The BS-65PT thin film also showed the highest values of ferroelectric properties with a P_r of 23 $\mu\text{C}/\text{cm}^2$ and an E_c of 70 kV/cm at an applied field of 400 kV/cm . The existence of the MPB composition at around $x = 0.65$ contributed to these results.

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