

PVP-Assisted Sol-Gel Preparation of BaBi₄Ti₄O₁₅ Thin Films and Dielectric Properties

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BaBi₄Ti₄O₁₅ thin films were prepared on Pt/Ti/SiO₂/Si substrates from Ba(CH₃COO)₂ - Bi(C₇H₁₅COO)₃ - Ti(OC₃H₇)₄ - polyvinylpyrrolidone (PVP) - H₂O - CH₃COOH - CH₃OC₂H₄OH - C₇H₁₅COOH solutions by the sol-gel method. The sol was concentrated, and then aged for various periods of time. Fired films prepared from solutions without PVP contained Bi₂Ti₂O₇ as the second phase, while the films from solutions with PVP were single-phase in BaBi₄Ti₄O₁₅. By concentrating the solution, crack-free, as thick as 0.93 μm films could be obtained via non-cycled deposition, but the dielectric constant was as small as 14-16, and no hysteresis was seen in *P-E* characteristics. When the sol aging time was increased from 22 to 246 days, the film thickness increased by about 37%, several tens nm wide gaps appeared between the grains, and the number of sites where dielectric constant could not be measured increased. Crack-free, 3.2 μm thick BaBi₄Ti₄O₁₅ films could be prepared by 5 cycles of deposition, which had dielectric constant of 270 and dielectric loss of 0.08 at 1 kHz, and exhibited *P-E* hysteresis at 60 Hz with remnant polarization of 8.0 μC cm⁻² and coercive field of 78 kV cm⁻¹.

Key words: Sol-gel method, BaBi₄Ti₄O₁₅, Thin films, Ferroelectrics

1. INTRODUCTION

Great number of papers have been published so far on PbTiO₃, Pb(Zr,Ti)O₃ and (Pb,Lu)(Zr,Ti)O₃, which are used as high frequency filters, ultrasonic sensors, pyroelectric sensors and ultrasonic motors, based on their piezoelectric properties. Research on thin films to be used as nonvolatile memories have also been made intensively [1]. These materials, however, (1) contain non-environment benign lead, and (2) undergo fatigue under alternating field [2].

Bismuth layer-structured ferroelectric materials (Bi₂O₂)(A_{m-1}B_mO_{3m+1}) [3-5] are attracting much attention as lead free materials showing much less fatigue under alternating field. Among them, (Bi₂O₂)(A_{m-1}B_mO_{3m+1}) with *m* = 4 including CaBi₄Ti₄O₁₅, SrBi₄Ti₄O₁₅ and PbBi₄Ti₄O₁₅ have been prepared in the form of thin films by sol-gel method, and expected to be applied as FeRAM [6-8]. Kato et al. prepared CaBi₄Ti₄O₁₅ and SrBi₄Ti₄O₁₅ thin films by sol-gel method with cycled deposition [6,7]. The CaBi₄Ti₄O₁₅ films obtained were about 0.3 μm thick, and had remnant polarization *P_r*, coercive field *E_c* dielectric constant *ε'* and dielectric loss tan *δ* of 9.4 μC cm⁻², 106 kV cm⁻¹, 300 and 0.033, respectively [6]. The SrBi₄Ti₄O₁₅ films had *P_r*, *E_c* *ε'* and tan *δ* of 2.9 μC cm⁻², 55 kV cm⁻¹, 330 and 0.04, respectively [7]. Park et al. prepared PbBi₄Ti₄O₁₅ thin films via cycled sol-gel deposition, 0.34 μm in thickness, and of *P_r*, *E_c* *ε'* and tan *δ* of 8 μC cm⁻², 60 kV cm⁻¹, 270 and 0.03, respectively [8].

Thickness over submicron is often demanded in ferroelectric ceramic thin films. However, over submicron thick ceramic coatings are difficult to be obtained without cracking via non-cycled sol-gel deposition. Therefore, gel film deposition and firing are cycled in laboratories, which is time-consuming and unrealistic in industries. Our group reported that addition of polyvinylpyrrolidone (PVP) in coating

solutions is effective in increasing uncracking critical thickness (the maximum thickness achievable without cracking via single-step deposition) [9-13]. Utilizing the technique, the authors recently have prepared BaBi₄Ti₄O₁₅ thin films from Ba(CH₃COO)₂ - Bi(C₇H₁₅COO)₃ - Ti(OC₃H₇)₄ solutions containing PVP. Crack-free, 0.4 μm thick, single-phase BaBi₄Ti₄O₁₅ films could be obtained via single-step deposition [14]. In the present work, preparation of thicker BaBi₄Ti₄O₁₅ films was attempted by increasing the sol viscosity via concentrating the sol, and examined the stability of the sol by preparing thin films from sols aged for various periods of time.

2. EXPERIMENTAL

Ba(CH₃COO)₂, C₇H₁₅COOH solution of Bi(C₇H₁₅COO)₃ (Bi metal wt% of 25%), Ti(OC₃H₇)₄, PVP (K90, viscosity average molecular weight of 6.3 x 10⁵), CH₃COOH, CH₃OC₂H₄OH and ion-exchanged water were used as the raw materials. A starting solution of mole ratio, Ba(CH₃COO)₂ : Bi(C₇H₁₅COO)₃ : Ti(OC₃H₇)₄ : PVP : H₂O : CH₃COOH : CH₃OC₂H₄OH : C₇H₁₅COOH = 1 : 4 : 4 : 4 : 4 : 27 : 69.7 : 5.48, was prepared, where the mole ratio for PVP was defined for the monomer. 100 mL starting solution was concentrated at 134°C into a final volume of 75 mL, followed by addition of 7.94 mL CH₃COOH, and aged at room temperature in a sealed container for various periods of time before use. In some cases, the resultant solution was further refluxed at 80°C for 10 h. Gel films were deposited on Pt/Ti/SiO₂/Si substrates by spin-coating at 6000 rpm, heated at 300°C for 10 min, followed by heating at 800°C for 10 min. The number of the deposition cycles was 1 or 5.

Crystalline phases of the films were identified with an X-ray diffractometer with a thin film attachment at an incident angle of 1°. Infrared absorption spectra of

the solutions were measured by an FT-IR spectrophotometer with an ATR attachment.

Dielectric constants of the films were measured at 1 kHz using an LCR meter, and polarization-electric field (P - E) characteristics were examined at 60 Hz at voltages of 5 or 90 V, where Pt electrodes 0.2 mm in diameter were deposited on the film surface.

3. RESULTS

3.1 Effects of the addition of PVP in solution

When PVP was added to the solution, the thickness of the fired films increased from 0.09 to over 0.68 μm (A0R0, A22R0, A103R0 and A246R0 in Table 1). The fired film prepared without PVP had $\text{Bi}_2\text{Ti}_2\text{O}_7$ as the second phase, while those prepared with PVP were single-phase in $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$ (A0R0 and A22R0 in Fig. 1). The films prepared without PVP were cracked at thickness over 0.14 μm , whereas even 0.93 μm thick films were crack-free when prepared with PVP.

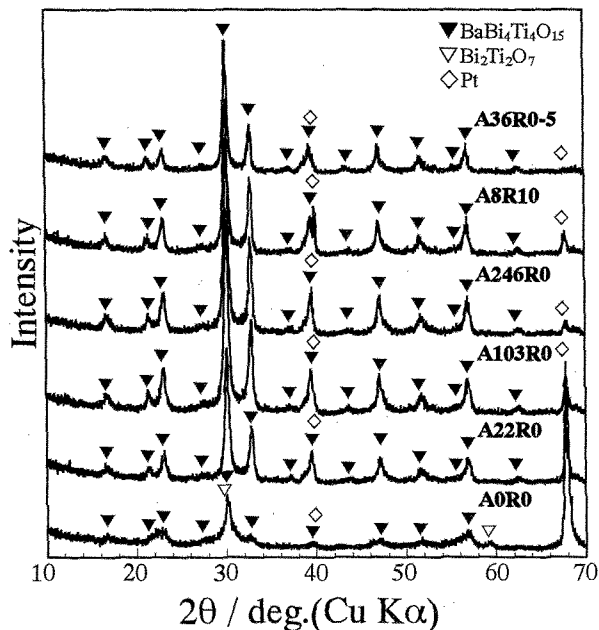


Fig. 1 XRD patterns of the films on Pt/Ti/SiO₂/Si substrates prepared under various conditions.

3.2 Effects of the sol aging time

The fired films were single-phase in $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$ even when the sol aging time was increased from 22 to 246 days (A22R0, A103R0 and A246R0 in Fig. 1), where the thickness increased by about 37%. Although ϵ' remained low at 14-16 and $\tan \delta$ was not changed greatly at 0.030-0.047 by the increased sol aging time, the

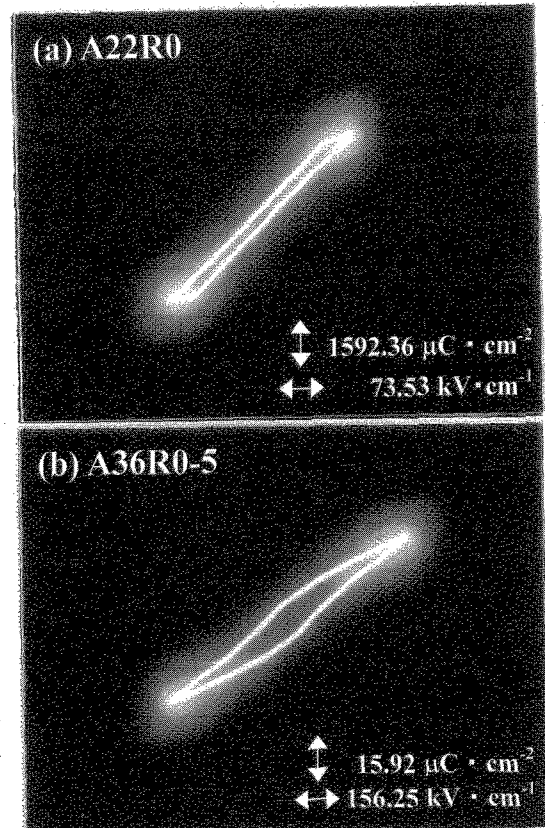


Fig. 2 P - E hysteresis loops of the films deposited on Pt/Ti/SiO₂/Si substrates. (a) A22R0, 1 time deposition, 5V, (b) A36R0-5, 5 times deposition, 90V.

number of sites where they could not be measured probably due to the leak current increased with sol aging time (A22R0, A103R0 and A246R0 in Table 2). P - E hysteresis was not seen in these films (Fig. 2 (a)).

Grains ca. 150 - 350 nm in size were observed in the surface of the fired films (Fig. 3 (a)). When the sol aging time was increased from 22 to 246 days, the grain size showed no great change, while ca. 70 nm wide gaps appeared between the grains (Fig. 3 (b) and (c) compared with (a)). The crystallite size was almost constant at about 22-34 nm (A22R0, A103R0 and A246R0 in Table 2), indicating that the grains observed in the SEM images are secondary particles.

Infrared absorption spectra of the sols were measured. When the sol aging time was increased from 22 to 246 days, C-O (1240 cm^{-1}) and C=O (1740 cm^{-1}) stretching vibration peaks of esters increased, and C-O (1290 cm^{-1}) and C=O (1710 cm^{-1}) peaks of carboxylic acid dimers decreased.

Table 1 Preparation conditions and thickness of the films deposited on Pt/Ti/SiO₂/Si substrates.

Sample	PVP / $\text{Ba}(\text{CH}_3\text{COO})_2$ mole ratio	Sol aging time / day	Refluxing time / h	Coating times	Film thickness / μm
A0R0	0	0	—	1	0.09
A22R0	4	22	—	1	0.68
A103R0	4	103	—	1	0.82
A246R0	4	246	—	1	0.93
A8R10	4	8	10	1	1.1
A36R0-5	4	36	—	5	3.2

Table 2 Crystallite size, dielectric constant and loss tangent of the films deposited on Pt/Ti/SiO₂/Si substrates.

Sample	Crystallite size d / nm	Dielectric constant	Loss tangent	Remarks
A22R0	$23 \leq d \leq 34$	6.9 ± 0.6	0.029 ± 0.015	
A103R0	$19 \leq d \leq 30$	14 ± 1	0.047 ± 0.018	Could not be measured on most of the electrodes.
A246R0	$22 \leq d \leq 34$	16 ± 1	0.030 ± 0.005	Could not be measured on most of the electrodes.
A8R10	$22 \leq d \leq 31$	Could not be measured	Could not be measured	
A36R0-5	$34 \leq d \leq 47$	270 ± 10	0.080 ± 0.007	

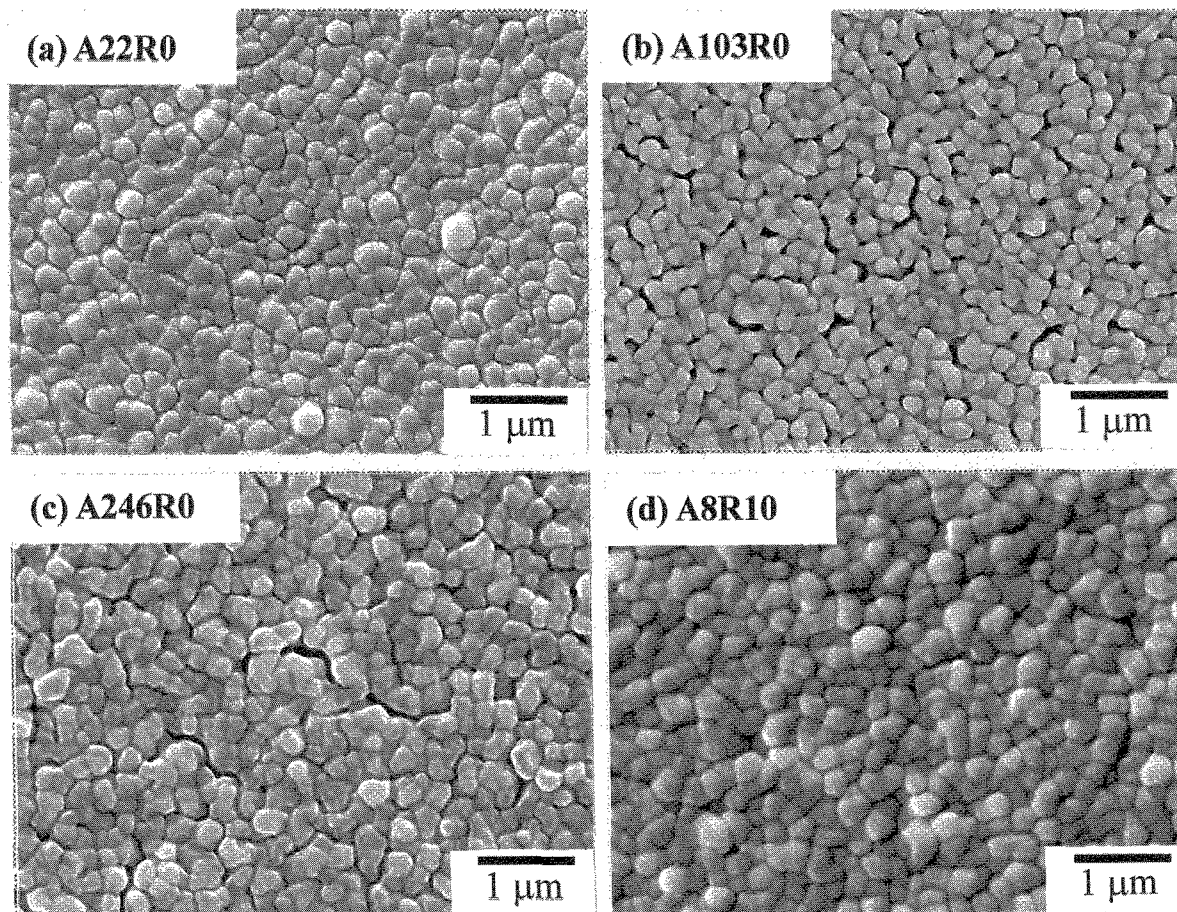


Fig. 3 SEM pictures of the surface of the films deposited on Pt/Ti/SiO₂/Si substrates via non-repetitive deposition using solutions prepared under various conditions. Sol aging time was (a) 22, (b) 103 and (c) 246 days, and for (d) the sol was refluxed for 10 h after aging for 8 days.

3.2 Effects of refluxing

When the sol was refluxed for 10 h, the fired film remained single-phase in BaBi₄Ti₄O₁₅ (A8R10 in Fig. 1), while the thickness increased by about 62% (A22R0 and A810 in Table 1). ϵ' and $\tan \delta$ could not be measured probably due to the leak current (A8R10 in Table 2). Grain size and crystallite size were almost the same as those prepared without refluxing, ca. 180-350 nm (Fig. 3 (d)) and 22-31 nm (A8R10 in Table 2), respectively. However, gaps appeared between the grains (Fig. 3 (d)). As in the case of prolonged sol aging, C-O (1240 cm⁻¹) and C=O (1740 cm⁻¹) peaks of esters increased, and C-O (1290 cm⁻¹) and C=O (1710 cm⁻¹) peaks of carboxylic

acid dimers decreased in the infrared absorption spectra of the sols when the sol was refluxed.

3.4 3.2 μm thick film via cycled deposition

A crack-free, 3.2 μm thick film could be prepared by cycling the gel film deposition and firing 5 times. The film was single-phase in BaBi₄Ti₄O₁₅ (A36R0-5 in Fig. 1), and had ϵ' of ca. 270 and $\tan \delta$ of 0.08 at 1 kHz, the former of which is about 40 times larger than that of the film prepared by non-cycled deposition (A36R0-5 in Table 2). P - E hysteresis was also observed (Fig. 2 (b)), where P_r and E_c were 8.0 μC cm⁻² and 78 kV cm⁻¹, respectively, at 60 Hz. The crystallite size was about

34-47 nm, about 40-50 % larger than that without deposition cycles.

4. Discussion

The addition of PVP in solution was effective in increasing the uncracking critical thickness and allowed the formation of single-phase BaBi₄Ti₄O₁₅. The C=O groups of PVP could coordinate the metal atoms and also could make hydrogen bonds with H₂O and/or OH ligands of the metal complexes. This might achieve high homogeneity in metal atom distribution in solutions and in gel films, facilitating the formation of the single-phase complex oxide.

The fired film thickness increased by about 37% when the sol aging time increased from 22 to 246 days, which might have resulted from the increased sol viscosity. Therefore, the sol cannot be said to be extremely stable. Microscopic gaps came to appear between the grains, and the number of sites where dielectric constant could not be measured increased, both of which again suggest that the sol is not extremely stable.

Longer sol aging resulted in the increased number of sites where dielectric constant could not be measured, and the sol refluxing made the dielectric properties non-measurable. General possible causes are decrease in crystallite size, and leak current along the gaps between the grains. The crystallite size was not changed by the increase in sol aging time or by the sol refluxing. Therefore, it would be the gaps provided by the sol aging or refluxing that made the dielectric properties of fired films non-measurable.

Infrared absorption spectra revealed that esters form when the sol is aged or refluxed. Because esters may be formed via condensation between alcohols and carboxylic acids, they would have larger molecular weight. In other words, higher molecular weight species increased in the sols in fraction, which may generate the gaps on thermal decomposition.

3.2 μm thick films could be prepared by 5 cycles of deposition, which had about 40 times larger dielectric constants than that prepared by single-step deposition. Also the film exhibited *P-E* hysteresis characteristic of ferroelectrics. These may be provided by the increase in the crystallite size by ca. 40-50% (Table 2) and by the possible decrease in leak current due to the increased thickness. When the deposition is cycled, the underlayers undergo longer heat-treatment in total. This would be the reason why the crystallite size was larger for the sample prepared via 5 cycles of deposition. ϵ' of 270 is slightly larger than that reported by Kim et al. on sintered, polycrystalline BaBi₄Ti₄O₁₅ [15], and P_r of 8.0 μC cm⁻² and E_c of 78 kV cm⁻¹ are smaller and larger than those reported by Irie et al. [16] on BaBi₄Ti₄O₁₅ single crystals, 14.8 μC cm⁻² and E_c of 32.0 kV cm⁻¹, respectively. Lower bulk density than the single crystals would be the reason for the difference in the values.

5. CONCLUSIONS

BaBi₄Ti₄O₁₅ thin films were prepared on Pt/Ti/SiO₂/Si substrates from Ba(CH₃COO)₂ - Bi(C₇H₁₅COO)₃ - Ti(OC₃H₇)₄ - PVP - H₂O - CH₃COOH - CH₃OC₂H₄OH - C₇H₁₅COOH solutions by the sol-gel method.

- (1) The fired films prepared without PVP had Bi₂Ti₂O₇ as the second phase, while those prepared with PVP were single-phase in BaBi₄Ti₄O₁₅.
- (2) By concentrating the solution, crack-free, as thick as 0.93 μm films could be obtained via non-cycled deposition, but ϵ' was as small as 14-16, and no *P-E* hysteresis was seen.
- (3) When the sol aging time was increased from 22 to 246 days, the fired films remained single-phase in BaBi₄Ti₄O₁₅, but the thickness increased by about 37%, several tens nm wide gaps appeared between the grains, and the number of sites where dielectric constant could not be measured increased. Similar changes were observed when the sol was refluxed.
- (4) Crack-free, 3.2 μm thick BaBi₄Ti₄O₁₅ films could be prepared by 5 cycles of deposition, which had ϵ' of 270 and $\tan \delta$ of 0.08 at 1 kHz, and exhibited *P-E* hysteresis at 60 Hz with P_r of 8.0 μC cm⁻² and E_c of 78 kV cm⁻¹.

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