Preparation of $0.055\text{BaZrO}_3\text{--}0.935(\text{K}_{0.45}\text{Na}_{0.5}\text{Li}_{0.05})\text{NbO}_3\text{--}0.01(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$ piezoelectric thin films from precursor solution by Pechini method

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Lead-free piezoelectric thin films of $0.055\text{BaZrO}_3\text{--}0.935(\text{K}_{0.45}\text{Na}_{0.5}\text{Li}_{0.05})\text{NbO}_3\text{--}0.01(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$ (BZ–KNLN–BNT) were fabricated on (100)- $\text{LaNiO}_3/\text{SiO}_2/\text{Si}$ substrates. The Pechini (polymeric precursor) method was carried out to prepare the complicated multi-component precursor solution. This method was suited for controlling the complex components accurately. The films crystallized at 700°C showed a $(100)_{\text{pc}}$ -oriented perovskite structure, whose grain size was about 200 nm and thickness was about 700 nm. The Curie temperature T_c of the films was 292°C that was near to that of the bulk ceramics. The preparation method used in this work provided a possibility for the application of multi-component lead-free piezoelectric films.

Keywords: Lead-free piezoelectric materials; thin films; Pechini method; sol–gel method.

1. Introduction

Lead-based piezoelectric materials are widely used in piezoelectric devices because of their large piezoelectric coefficients.^{1–5} However, because of environmental pollution caused by PbO contained in lead-based piezoelectric devices, research and development of high-performance lead-free piezoelectric materials have attracted much attention in recent years.⁶ Potassium sodium niobate (KNN)-based lead-free piezoelectric materials with high piezoelectric properties have been widely reported.^{7–11} In our previous study, one of the lead-free piezoceramics with vertical morphotropic phase boundary (MPB) was investigated by adjusting MPB slope of $(\text{K}, \text{Na}, \text{Li})\text{NbO}_3\text{--}\text{BaZrO}_3$ (KNLN–BZ) binary system using rhombohedral $(\text{Bi}, \text{Na})\text{TiO}_3$ (BNT) as the third component. The piezoceramics were supposed to exhibit the temperature-stability of the piezoelectric properties in a wide temperature range.⁶

The object of this study is an attempt to prepare $0.055\text{BaZrO}_3\text{--}0.935(\text{K}_{0.45}\text{Na}_{0.5}\text{Li}_{0.05})\text{NbO}_3\text{--}0.01(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$ (BZ–KNLN–BNT) thin films. Many thin film fabrication techniques have been applied in piezoelectric thin films, such as sputtering, laser ablation, metalorganic chemical vapor deposition (MOCVD) and sol–gel method.^{12–15} The BZ–KNLN–BNT thin films contained eight metallic elements. So the sol–gel method was considered a suitable method used for such multi-component system thin films because of its controllability of accurate composition.¹⁶ Pechini method, as a modified sol–gel method, has been reported to be available for synthesis of lead-free

piezoelectric ceramics and thin films.^{17–28} The Pechini method is associated with the formation of a metallic complex using a hydroxycarboxylic acid, such as citric acid (CA). Polymerization is promoted by heating the complex in the presence of a polyhydroxy alcohol, such as ethylene glycol (EG). A homogeneous polymeric precursor could be produced, in which the metal ions are uniformly distributed within the organic matrix.²⁹ In this work, the Pechini method was adopted to prepare the precursor solution of BZ–KNLN–BNT thin films.

2. Experimental Methods

The process of synthesis of BZ–KNLN–BNT precursor solution is shown in Fig. 1. All raw materials were weighed according to the formula of BZ–KNLN–BNT. Firstly, Nb_2O_5 was dissolved in HF at 80°C and then $\text{NH}_3\cdot\text{H}_2\text{O}$ was tardily added into the above solution until the pH became 10. $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ formed after filtering, washing and drying the sediment at 80°C for 10 h. The Nb-source was then obtained by dissolving the $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ in CA solution. Other metal–CA solutions were prepared under the conditions listed in Table 1. Na_2CO_3 , K_2CO_3 and Li_2CO_3 were directly dissolved in CA solution. BaCO_3 was dissolved in CA solution and then the pH was quickly adjusted to 8 by adding $\text{NH}_3\cdot\text{H}_2\text{O}$. $\text{Bi}(\text{NO}_3)_3\cdot 5\text{H}_2\text{O}$ was dissolved in the alkali CA solution. By heating mixtures of $\text{Ti}[\text{O}(\text{CH}_2)_3\text{CH}_3]_4/\text{Zr}[\text{O}(\text{CH}_2)_3\text{CH}_3]_4$ and CA solutions at 80°C until the solution became transparent, the Ti and Zr sources were obtained, respectively.

Fig. 1. Synthesis route of BZ-KNLN-BNT precursor by using Pechini method.

Table 1. Preparing conditions of metal-CA solutions.

Metal-CA	Metal:CA (mol.)	pH	Temperature (°C)
Ba-CA	1:3	8	-
K, Na and Li-CA	1:3	-	-
Bi-CA	1:30	8	-
Ti-CA	1:30	-	80
Zr-CA	1:30	-	80

Note: “-”: no controlling.

Then, the metal sources were mixed. The ratio of CA/EG was 1/4 and pH was regulated to 10. Finally, the precursor was obtained by heating at 120°C for 24 h.

The films were expected to grow along with (100)_{pc} orientation (the pseudocubic perovskite indication was used in our work.). So (100)-LaNiO₃(LNO)/SiO₂/Si substrates were used. The substrates were prepared as follows: a SiO₂ layer was formed by wet-thermal oxidation of a Si wafer at 900°C for 1 h, and then the bottom electrode of (100)-LNO films was grown by RF magnetron sputtering at 200°C for 60 min.^{30,31} BZ-KNLN-BNT thin films were fabricated on (100)-LNO/SiO₂/Si substrates by spin coating at 500 rpm for 5 s and then 1700 rpm for 30 s. Each layer was dried at 120°C for 10 min in air, and pyrolyzed at 400°C for 30 min. After 3–5 circulations of spin coating and pyrolyzing, the samples were crystallized at 700°C for 2 h in O₂. The Pt top electrode with a diameter of 1 mm was formed by DC sputtering.

3. Results and Discussion

To determine the heat treatment condition, differential thermal analysis (DTA) and thermogravimetric analysis (TG) were carried out. Figure 2 shows the TG/DTA spectrum of the precursor solution. The endothermic valleys below 200°C showed the volatilization of NH₃·H₂O, H₂O and organic components. An exothermic peak at 550°C referred to the crystallization. Above 650°C, the weight loss became steady at -96.5%, and crystallization of the thin films finished. Therefore, the crystallization temperature was determined to be 700°C.

Fig. 2. TG/DTA spectrum of the precursor solution.

Figure 3(a) shows X-ray diffraction (XRD) pattern of BZ-KNLN-BNT powders from the heated precursor solution at 700°C which showed a perfect perovskite structure. Figure 3(b) shows the XRD pattern of BZ-KNLN-BNT thin

Fig. 3. XRD patterns of (a) BZ-KNLN-BNT powders, (b) thin films on (100)-LNO/SiO₂/Si substrate, and (c) (100)-LNO/SiO₂/Si substrate.

Fig. 4. SEM photos of (a) surface and (b) cross-section of the thin films on (100)-LNO/SiO₂/Si substrates crystallized at 700°C.

films crystallized on (100)-LNO/SiO₂/Si substrates at 700°C. For comparison, the XRD pattern of the (100)-LNO/SiO₂/Si substrate is shown in Fig. 3(c). The (100)_{pc} and (200)_{pc} peaks of the thin films were observed at $2\theta = 22.88^\circ$ and 45.46° , and the (100) and (200) peaks of LNO were observed at $2\theta = 23.22^\circ$ and 47.36° , respectively. According to the XRD patterns, the perovskite structure of (100)-orientated thin films was confirmed.

Scanning Electron Microscope (SEM) photos of surface and cross-sectional views of the thin films are shown in Fig. 4. From Fig. 4(a), the grain size was about 200 nm. From Fig. 4(b), the thickness of BZ–KNLN–BNT thin films and the LNO layer were about 700 nm and 280 nm, respectively.

The temperature dependence of dielectric constant of BZ–KNLN–BNT thin films at 100 kHz is shown in Fig. 5. It shows that the Curie temperature of the films was 292°C and

this value was near to that of bulk ceramics in our previous research.

4. Conclusions

A complex multi-component lead-free thin films with the molecular formula of BZ–KNLN–BNT were prepared from precursor solution by Pechini method. The films crystallized at 700°C exhibit a perovskite of (100) orientation on (001)-LNO/SiO₂/Si substrates and a Curie temperature of 292°C. The results in this work indicated an importance in application of preparation of multi-component lead-free piezoelectric films. The BZ–KNLN–BNT films are expected in applications of piezoelectric devices.

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Fig. 5. Temperature dependence of dielectric constant of BZ–KNLN–BNT films at 100 kHz.

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