JOURNAL OF MATERIALS SCIENCE 31 (1996) 4255–4259

Preparation of stabilized $Pb(Zn_{1/3}Nb_{2/3})O_3$(PZN) films by the sol–gel method

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$Pb(Zn_{1/3}Nb_{2/3})O_3$ thick films with the perovskite structure were prepared by the sol–gel method. Niobium ethoxide $Nb(OC_2H_5)_4$, lead acetate $Pb(CH_3COO)_2$, and Zinc 2-ethylhexanoate $Zn(O_2C_8H_{15})_2$ were reacted in 2-methoxyethanol to form the precursor. Titanium isopropoxide, $Ti(O\cdot i\text{-}C_3H_7)_4$ and barium isopropoxide $Ba(O\cdot i\text{-}C_3H_7)_4$ were added into the precursor solution to stabilize the formation of the perovskite phase. Films of upto 10 μm thickness were obtained by controlling the viscosity of the solution and the dipping speed of silicon wafers. The phase evolution was investigated using differential thermal analysis (DTA) and X-ray diffraction techniques. The thickness-dependent dielectric constant of the resultant films is also reported.

1. Introduction

Much attention has been directed in recent years towards the lead based ferroelectric perovskite structured compounds for use in electrostrictive actuator and capacitor applications [1–4]. Amongst these materials, lead zinc niobate (PZN) is one of the few compositions with both a high dielectric transition temperature ($T_c \sim 140\,^\circ C$) and a high resistivity. A high T_c allows the use of many types of shifters to move T_c to approximately room temperature. However, a disadvantage of PZN is the difficulty in obtaining a pure perovskite phase in ceramic form due to pyrochlore-phase formation [5–7].

In the past, several additives such as $SrTiO_3$ (ST), $BaTiO_3$ (BT), $Ba(Zn_{1/3}Nb_{2/3})O_3$(BZN), and $PbTiO_3$ (PT) have been successfully used to stabilize the perovskite phase, and the dielectric and piezoelectric properties of these systems have been studied extensively [1, 8–10]. Amongst these different additives, only 6–7 mol % of BT is required to stabilize PZN in the perovskite structure, whereas 10 mol % BZN, 10 mol % ST, and up to 30 mol % PT are required to stabilize PZN in the perovskite structure. On the other hand, small amounts of excess PbO are reported to eliminate the pyrochlore phase and enhance densification through liquid-phase sintering [11]. However, traditional ceramic processes usually induce local inhomogeneities in the composition and thereby reduce the effect of the stabilization.

Recently, the sol–gel method has become a novel technique for the synthesis of advanced glasses and ceramics [12]. This technique can lead to homogeneity, stoichiometry, and high purity on the molecular scale and also provides great flexibility due to the large variety of precursor chemicals that are available. In this paper, PZN films were prepared by using organometallic precursors that allowed us to fabricate films of a desired thickness and with a high volume fraction of stabilized perovskite structured PZN phase.

2. Experimental procedure

The precursors were prepared by reacting niobium ethoxide and zinc 2-ethylhexanoate (in the ratio Nb:Zn = 2:1) with anhydrous lead acetate in 2-methoxyethanol. A mixed solution of barium isopropoxide and titanium isopropoxide was added into the precursor solution. The compositions selected for the present study were $Pb_{1.05}(Zn_{1/3}Nb_{2/3})$ O_3-0.07(BaO,TiO_2). Fig. 1 illustrates the procedure for the preparation of PZN coatings by the sol–gel method. To the fully mixed solution 2-ethylhexanoic acid was added in the molar ratio of Pb:acid = 1:5 in order to modify the structure of the solution. The resultant solutions became very stable and highly resistant to hydrolysis. Once the solutions possessed a viscosity of 1–5 poise, the PZN gel films were obtained by dipping silicon wafers into the solutions and slowly withdrawing them at $5\ \mathrm{cm\,min^{-1}}$. The coated film was then preheated at 300 °C for two hours. The dipping and preheated processes were repeated until the desired thickness of the coatings was achieved. Ceramic PZN films were obtained by heat treating these gel films at temperatures between 700–900 °C in air.

Differential thermal analysis (DTA) studies of the dried precursor were conducted using a DuPont 2000 thermal analyser at a heating rate of $5\,^\circ\mathrm{C\,min^{-1}}$. The PZN dried gel and PZN powders prepared at different temperatures were evaluated by X-ray diffraction (XRD) (using CuK_α radiation). The viscosity of the precursors was measured using a cone rheometer of a Mettler–Toledo AG instrument. The thickness of the films was measured from a scanning electron microscopy (SEM) micrograph. The temperature dependence of the dielectric constant was measure at 1 kHz

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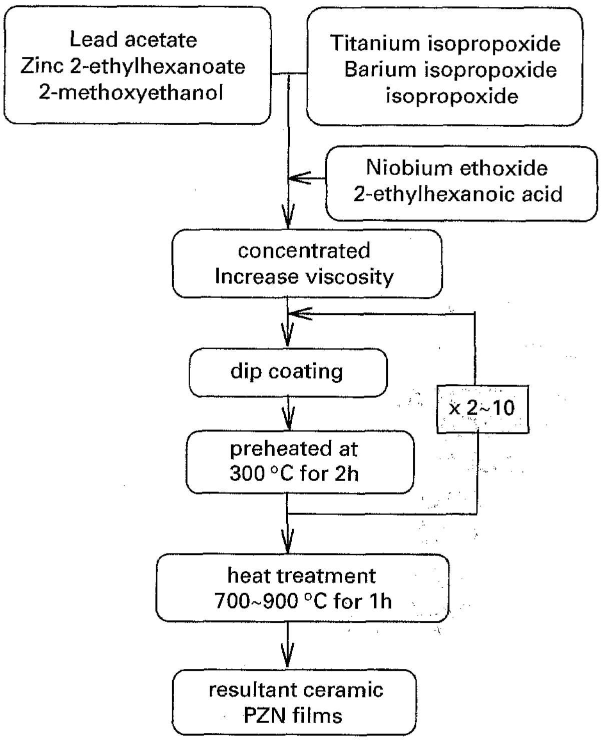

Figure 1 Flow chart of the sol–gel method to prepare the PZN films.

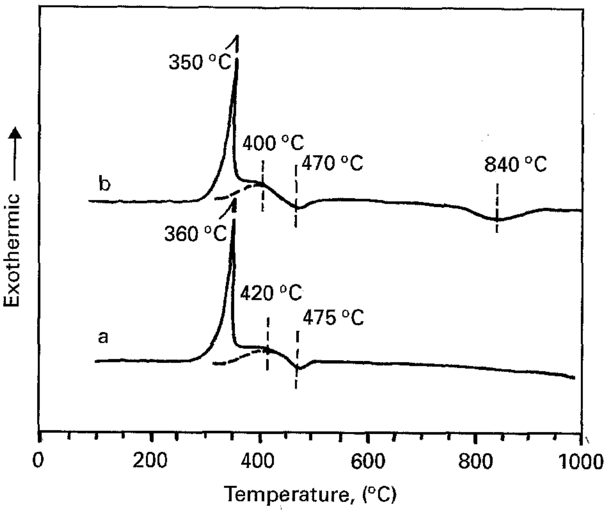

Figure 2 Differential thermal analysis (DTA) curves of the dried precursor A (without stabilizers) and dried precursor B (with stabilizers).

using an automated LCR meter (YHP 4275A) in the temperature range of −50–250 °C. In order to measure the dielectric properties, a sandwich structure of the type substrate/Pt/PZN film/gold was used.

3. Results and discussion

Differential thermal analysis (DTA) curves of the dried gel from the precursor without (precursor A) and with (precursor B) addition of barium and titanium oxides are shown in Fig. 2. It was found that large exothermic peaks existed at about 360 and 350 °C for precursors A and B, respectively. Following this strong exothermic reaction a small and broad exothermic peak was also found in each precursor (420 °C for precursor A and 400 °C for precursor B). In addition, small endothermic reactions were observed at about 475 °C for precursor A and 470 °C for precursor B. Examination of the X-ray powder diffraction patterns, shown in Figs 3 and 4 for both precursors heated at different temperatures, show that the powders are amorphous at 300 °C and only have a low crystallinity when heat treated at 350 °C for one hour. This indicates that the strong exothermic reaction can be attributed to the decomposition of the organic groups. The removal of both acetyl and 2-ethylhexanoate groups and their combustion is reported to take place at about 300 °C [13, 14]. However, the formation of the metal–organic complex would shift the exothermic peak to lower or higher temperatures. Such a shift of the exothermic peak has been observed in the thermal decomposition of the 2-ethylhexanoate group of $Pb(O_2C_8H_{15})_2$ [14]. The mixture of $Pb(O_2C_8H_{15})_2$ with metal alkoxides changed the pyrolysis behaviour to a lower or higher peak temperature. Therefore, the shift of the pyrolysis of the organic groups from 300 °C to 350 °C or even

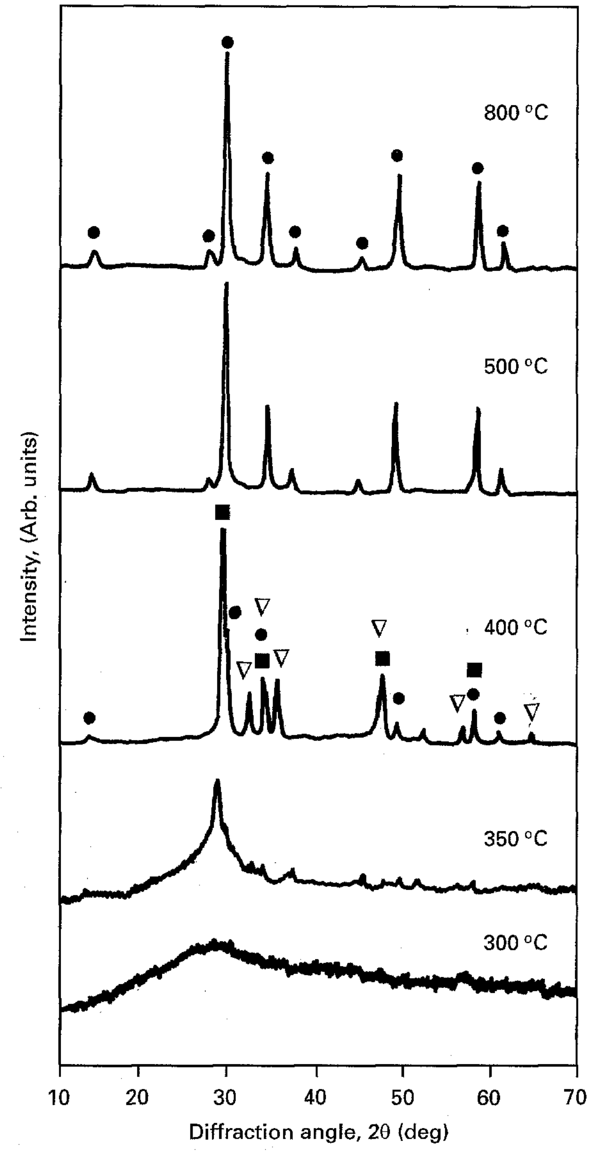

Figure 3 X-ray diffraction patterns of the PZN powder after calcining precursor A at different temperatures. ■: $Pb_3Nb_2O_8$, ∇: ZnO, ●: pyrochlore phase.

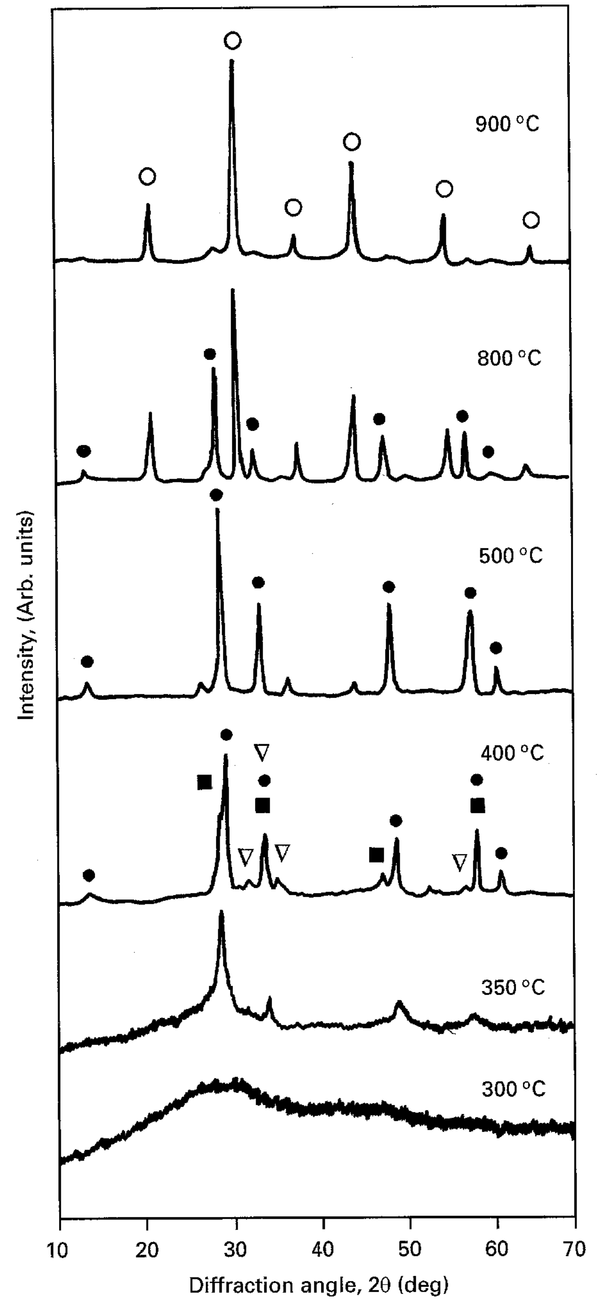

Figure 4 X-ray diffraction patterns of the PZN powder after calcining precursor B at different temperatures. ●: $Pb_3Nb_2O_8$, ∇: ZnO, ●: pyrochlore phase, O: perovskite PZN.

higher temperatures results from the formation of a metal–organic complex in the solution.

The small exothermic reactions at about 420 °C for precursor A and 400°C for precursor B seems to be related to the formation of $Pb_3Nb_2O_8$ and ZnO as observed in the X-ray diffraction pattern for the precursors heated at 400 °C (Fig. 3), although a pyrochlore phase (P_3N_4) is also found at this temperature. These crystalline phases must be formed in the organic burn-off reaction. The small endothermic reactions at 475 °C for precursor A and 470 °C for precursor B seem to be due to the reaction between $Pb_3Nb_2O_8$ and ZnO to form the pyrochlore phase, since the X-ray diffraction pattern shows only the pyrochlore phase to be present in each precursor after heating at 500 °C. Heat treatments at higher temperatures for precursor A (without stabilizers) do not show any further reaction as judged from the DTA and X-ray patterns. However, a small endothermic peak from 780–920 °C for precursor B (containing stabilizers) is observed and attributed to the perovskite phase formation identified in the X-ray diffraction patterns as shown in Fig. 4. This is consistent with the results of the heat treatment, since the perovskite phase was not observed at temperatures below 700 °C.

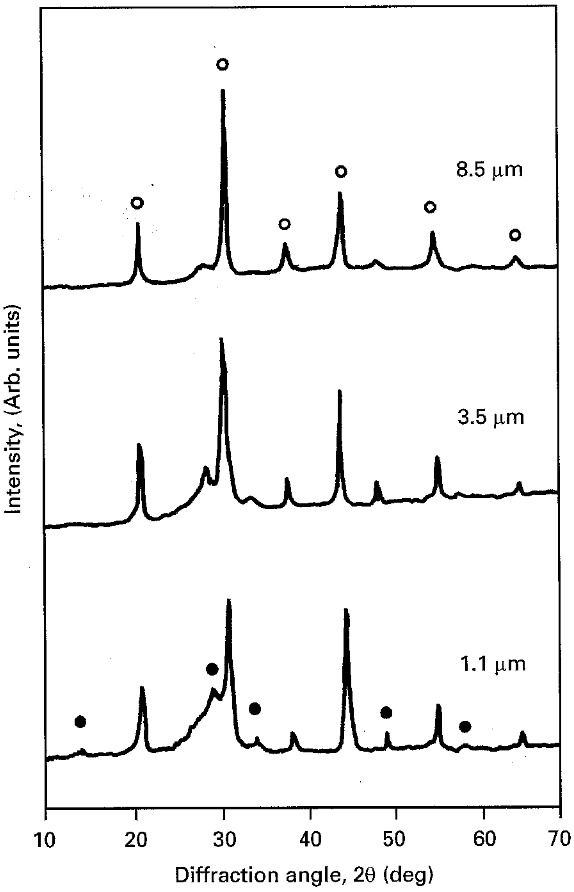

Figure 5 X-ray diffraction patterns of the PZN films with different thickness. All films are heat treated at 900 °C for one hour. ●: pyrochlore phase, O: perovskite PZN.

The present study shows that Ba and Ti oxides combined together are excellent additives for stabilizing the perovskite structure in PZN. The stabilization of the perovskite phase by $BaTiO_3$ has been explained in terms of the electronegativity difference and tolerance factor by Halliyal *et al.* [15]. The analysis reveals that perovskite compounds with tolerance factors near unity ($t = 1$) and large electronegativity differences are very stable perovskites. The PZN compound has a considerably lower electronegativity than $BaTiO_3$ or $PbTiO_3$ and a somewhat lower tolerance factor and is found to be difficult to synthesize in the perovskite structure. In this study it tends to form the more covalent bonded pyrochlore structure such as the $Pb_3Nb_2O_8$(P_3N_2 pyrochlore) phase.

Fig. 5 shows the X-ray diffraction patterns of the films on a (1 1 1) silicon wafer that were heated at 900 °C for 30 min. The perovskite phase is the major phase in these films, however there is still a small volume of pyrochlore phase that can be observed. Fig. 6 shows the SEM photographs of ceramic films of different thickness. The thickness of these films reached 10 μm and depended on the coating times. It is

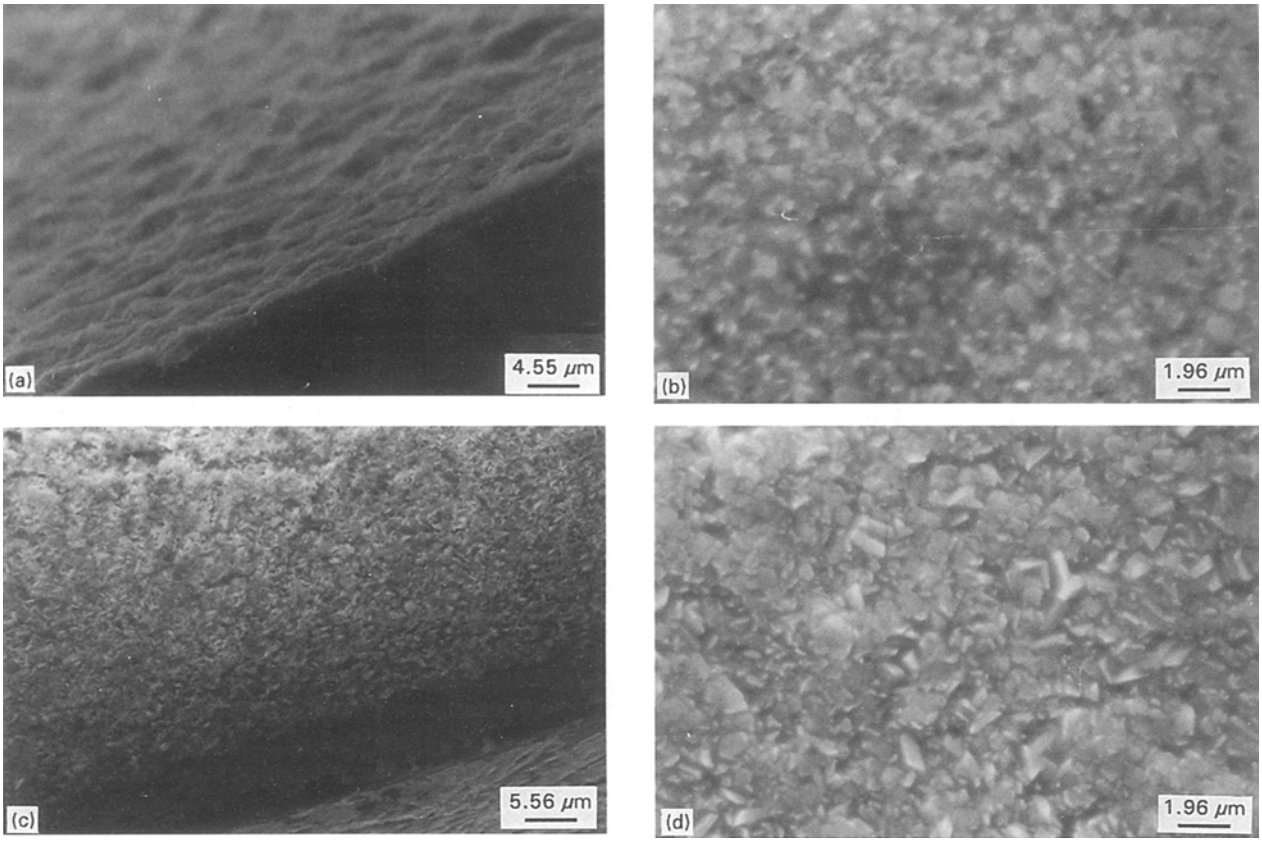

Figure 6 Scanning electron micrograph of the PZN films prepared at 900 °C. The thickness of films (a) and (b) is about 1.8 μm and that of films (c) and (d) is about 9 μm.

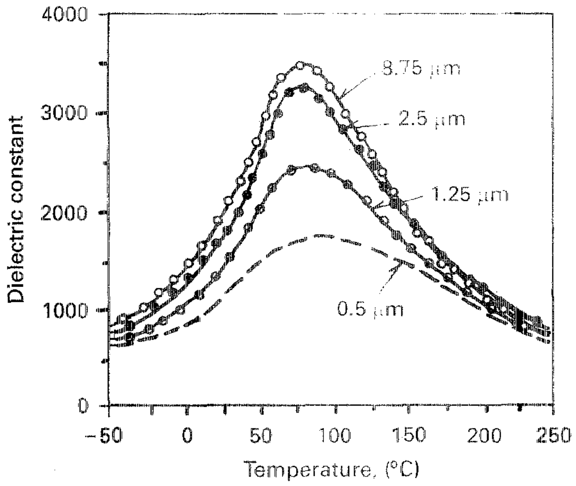

Figure 7 Variation of dielectric constant (1 kHz) with temperature for PZN films of different layer thickness.

noted that larger grains are observed in the thicker film as is shown in Fig. 6d.

Fig. 7 shows the relationship between the dielectric constant and the temperature of the ceramic films of different thickness that were heated at 900 °C for one hour. It is found that the apparent dielectric constant increases with layer thickness. A variety of effects, including Shottky barrier formation, changes in grain size, density and grain growth variations, have been adopted to explain the thickness-dependent properties for thin-layer dielectric [16–18]. The increase in the grain size as observed in Fig. 6 could be the major factor that causes the increase of apparent dielectric constant. However, the low dielectric constant of the sol–gel derived thin films may be due to the thin interfacial layers of low dielectric constant material as reported by Francis and Payne [19]. The effect of the microstructure of the PZN films on the dielectric properties and improvements in the preparation methods will be further investigated.

4. Conclusions

$Pb(Zn_{1/3}Nb_{2/3})O_3$ films with the perovskite structure have been successfully prepared by the sol–gel method. The stabilized perovskite structured PZN phase was obtained by the addition of barium and titanium alkoxides to the precursor solution. The perovskite phase is transformed from the pyrochlore phase which forms from the reaction between $Pb_3Nb_2O_8$ and ZnO. The apparent dielectric constant increases with the thickness of the PZN films.

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Received 10 August 1995
and accepted 21 December 1995