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# Effects of synthesis conditions on electrical properties of chemical solution deposition-derived $Pb(Mg_{1/3}Nb_{2/3})O_3$–$PbTiO_3$ thin films

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ABSTRACT

Relaxor ferroelectrics $Pb(Mg_{1/3}Nb_{2/3})O_3$–$PbTiO_3$ (PMN–PT) have attracted considerable attention because of their excellent electrical properties, which include high dielectricity and piezoelectricity. Their thin films are promising for use as super capacitors and piezoelectric actuators. However, the reported electrical properties of PMN–PT thin films, such as dielectric and piezoelectric properties, are markedly lower than those of bulk ceramics and single-crystals. This study investigated the effects of synthesis conditions such as annealing temperatures, excess lead amounts, and the molecular design of the precursor solution on the electrical properties of the Chemical Solution Deposition (CSD)-derived PMN–PT thin films to deposit single-phase perovskite PMN–PT thin films with superior electrical properties on a Si substrate at lower temperatures. Results of studies demonstrated effectively that suitable processing is necessary to elicit the enhanced electrical properties of PMN–PT thin films, such as introduction of suitable seeding layers and optimization of synthesis conditions. Results show that CSD-derived polycrystalline 0.65PMN–0.35PT thin films with preferred orientation exhibited a higher dielectric constant over 4000 (1 kHz, at room temperature) and higher remanent polarization of $P_r = 27.7\ \mu C/cm^2$ (1000 kV/cm, at room temperature) as well as a higher electrostrictive constant of $d_{33}$ about 200 pm/V. Further investigation and development are expected to improve these electrical properties of the PMN–PT thin films by stress engineering or residual stress.



## 1. Introduction

Relaxor ferroelectrics have attracted much attention because of their superior electrical properties such as high dielectricity and giant piezoelectricity [1]. In actuality, $(1-x)Pb(Mg_{1/3}Nb_{2/3})O_3 - xPbTiO_3$ (PMN–PT), so-called PMN–PTs, are typical relaxor ferroelectrics that have a perovskite-type structure with a morphotropic phase boundary (MPB) around a composition of $x = 0.35$ at room temperature [2]. Reportedly, a PMN–PT single crystal with a composition near the MPB exhibits a huge electrostrictive constant ($d_{33} = 2800$ pC/N) and electromechanical coupling coefficient ($k_{33} = 94\%$) [3], which means very high electromechanical energy conversion over 90% [4]. These electrical properties are superior to those of a typical commercially-available piezoelectric material: lead zirconate titanate (PZT). Therefore, PMN–PT is promising for application in superior piezoelectric actuators, sensors, and energy-harvesting devices. For these applications, size reduction and a high performance are necessary for cost-effective processing, especially for the case of micro-electromechanical systems. Therefore, thin film technology for piezoelectric materials on a Si substrate has been earnestly sought [5].

To date, deposition methods of various kinds, such as chemical solution deposition (CSD) [6–12], sputtering [13–15], and pulsed laser deposition [16–21], have been reported for the preparation of PMN-type thin films. Among these techniques, CSD is extremely useful for the PMN–PT thin films with complex compositions because of the easy composition control of precursor solutions and low-temperature deposition using higher potential energy of the gel, leading to cost-effective processing methods of thin film deposition on a Si substrate as an industrial use.

However, many earlier reports have described the formation of the pyrochlore phase with lower electrical properties, which should be avoided. This problem is ascribed to the similar formation energies of perovskite and pyrochlore phases. In addition, the reason remains unclear, but the reported electrical properties of PMN–PT thin films such as dielectric and piezoelectric properties are markedly lower than those of bulk ceramics and single crystals. For ceramics, it has been reported that *Columbite method* was effective to obtain a single-phase perovskite with excellent electrical properties [22]. For thin films, previous reports describe that single-phase perovskite was obtained using appropriate substrates or by introducing seeding layers between substrates and relaxor thin films such as the use of MgO [17] single-crystal substrate or the introduction of $BaTiO_3$ [21], PZT [10,14], or PbO [7] as seeding layers.

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The molecular design of the precursor solutions and optimization of the processing parameters including thermal treatment conditions are also extremely important to obtain good thin films using CSD. Studies of the optimization of these processing parameters have been conducted for the PMN-type thin films [6–12]. Previous studies revealed that slight inhomogeneity of the composition caused the formation of the pyrochlore phase. The *Columbite method* has overcome this difficulty to form single-phase perovskite ceramics. However, optimization of the processing parameters remains insufficient for thin films compared with the bulk ceramics and single-crystals because of the unique difficulty in thin film deposition. Therefore, a suitable processing method with optimized conditions must be developed to deposit single-phase perovskite relaxor thin films in this system with a dense microstructure at low temperature to elicit excellent electrical properties.

For lead-based ferroelectrics, excess lead is generally added to precursors to compensate for their lack of lead content, which engenders the formation of the pyrochlore phase during thermal treatment, especially in the case of CSD. However, too much excess lead induces formation of residual PbO phase, leading to reduced electrical properties even in the case of ceramics [23,24]. Furthermore, optimization of the excess lead is necessary for thin film processing because the excess lead diffuses into a Si substrate to degrade the electrical properties.

This study investigated the effects of synthesis conditions, including the molecular design of the precursor solution on the electrical properties of the CSD-derived polycrystalline PMN–PT thin films with preferred orientation, to prepare single-phase perovskite PMN–PT thin film with superior properties on a Si substrate at lower temperatures. Many factors such as film orientation, compositions, and residual stress affect the electrical properties of the perovskite relaxor thin films. Therefore in this study, a lanthanum nickelate ($LaNiO_3$:LNO) thin film electrode with preferred orientation [25] was introduced as a seeding layer for the orientation control and the single perovskite phase formation at low temperatures. This LNO seeding layer will engender the deposition of PMN–PT thin films with preferred orientation to improve their electrical properties.

In addition, this study investigated the effects of the preannealing temperature and annealing temperature on the dielectric and ferroelectric properties of the resulting PMN–PT thin films to optimize these processing parameters and to ascertain the optimum amount of Pb added to precursor solutions.

## 2. Experimental procedure

For this study, PMN–PT and LNO thin films were prepared using CSD. The starting reagents used for LNO precursor solution were lanthanum nitrate [$La(NO_3)_3 \cdot 6H_2O$] and nickel acetate [$Ni(CH_3COO)_2 \cdot 4H_2O$]. Details of the LNO thin film deposition are presented elsewhere [25]. The starting reagents for PMN–PT precursor solution were lead acetate [$Pb(OCOCH_3)_2 \cdot 3H_2O$], titanium isopropoxide [$Ti(i\text{-}OC_3H_7)_4$], magnesium ethoxide [$Mg(OC_2H_5)_2$], and niobium ethoxide [$Nb(OC_2H_5)_5$]. To remove the crystal water, $Pb(OCOCH_3)_2 \cdot 3H_2O$ was dried. It was then refluxed with $NH_3$ flow in ethanol for 2 h at 50 °C. Excess lead (0, 10, 15, 20, 25, and 30 mol.%) was added to the precursor solutions to compensate for the lack of lead by volatilization and diffusion into the electrode. The addition of too much excess lead will leave residual lead oxide. Therefore, determination of the suitable amount of excess lead is necessary to optimize the electrical properties of the resultant thin films. On the other hand, sources of the B-site cations of the perovskite structure, $Ti(i\text{-}OC_3H_7)_4$, $Mg(OC_2H_5)_2$, and $Nb(OC_2H_5)_5$, were refluxed in ethanol for 4 h at 78 °C because Columbite method is effective to suppress the formation of the pyrochlore phase in the case of bulk ceramics. These solutions were mixed and reacted for 2 h at 78 °C. Then, 2-aminoethanol was added to stabilize the obtained precursor solutions. A concentration and composition of precursor solutions were, respectively, 0.6 M and MPB composition with $x = 0.35$.

Four LNO layers were deposited on a Si substrate by spin coating to increase the film thickness to about 180 nm. The PMN–PT layers were deposited repeatedly on the LNO/Si substrate by spin coating to increase the film thickness up to 600 nm. The as-deposited PMN–PT layer was dried at 150 °C and then preannealed at 350 or 450 °C. It was then annealed at 650 or 750 °C for 5 min.

In the CSD method, the as-deposited wet precursor film is dried and preannealed to remove water and the residual solvent. It is then annealed for crystallization. For better heat treatment, residual organics should be removed completely before final annealing because evaporation of residual organics during annealing will form pores in the film, leading to the lower density or electrical properties. Therefore, optimization of the heat treatment and the excess amount of lead are crucially important.

Thermogravimetry and differential thermal analysis (TG-DTA) were conducted (TG 8120; Rigaku Corp.) with a heating ratio of 10 °C/min in an oxygen atmosphere. The crystal structure was identified using X-ray diffraction (XRD, D8 Advance; Bruker Analytik) θ-2θ scan using Cu Kα with a scan speed of 3.3 deg/min. The thin film microstructure was observed using field-emission type scanning electron microscopy (FE–SEM, JSM-7001F; JEOL), of which the operating voltage was 15 kV. Ferroelectricity was evaluated using a ferroelectric test system (FCE-PZ type; Toyo Technica Inc.). The local piezoelectric response was observed using an atomic force microscope (AFM, SPI3800N; SII Nano Technology Inc.) equipped with a piezoelectric force mode. A Rh coated Si tip with the resonant frequency of around 129 kHz (the stiffness of tip: 14 N/m) was used for this measurement (Hitach High-Tech Science Corp., Japan). The electric field was applied between the top Pt electrode with a 60 μm diameter and the bottom electrode of the thin film. The local piezoelectric response ($d_{33}$) was evaluated by the deflection of the cantilever by applying the triangle wave (±20 V, 5 Hz) and sin wave (5 Vrms, 5 kHz) simultaneously. The sin wave response was detected by rock-in amplifier.

## 3. Results and discussion

### 3.1. Effect of preannealing temperature

Fig. 1 presents results of TG-DTA for PMN–PT powders obtained from the precursor solution after drying. Two exothermic peaks were observed at about 315 °C and 400 °C. Weight losses were observed with these exothermic peaks. Therefore, results suggest that the evaporation of the organics occurred at each temperature. Fig. 2 presents dielectric constants of the PMN–PT thin films preannealed at 350 °C after the first exothermic peak or preannealed at 450 °C after the second one. The final annealing temperature and excess lead amount were, respectively, 750 °C and 20 mol.%. This result demonstrated that

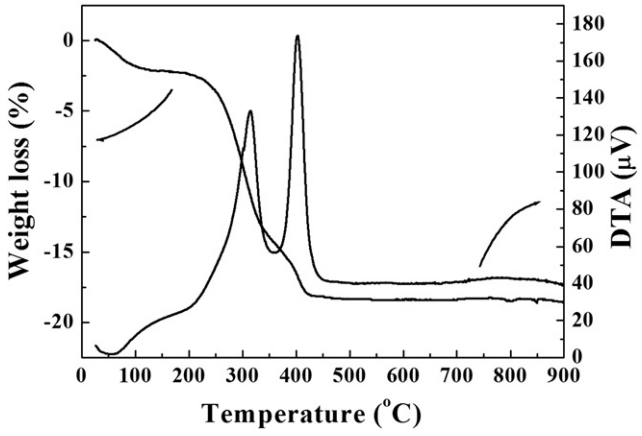


**Fig. 1.** TG-DTA of PMN–PT powders obtained from dried precursor solution with 20 mol.% lead excess.