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# Low-temperature growth of lead magnesium niobate thick films by a hydrothermal process

Xiuli Chen, Huiqing Fan *, Laijun Liu, Shanming Ke

*State Key Laboratory of Solidification Processing, School of Materials Science and Engineering, Northwestern Polytechnical University, Xi'an 710072, China*

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**Abstract**

Pyrochlore free $PbMg_{1/3}Nb_{2/3}O_3$ (PMN) thick films were prepared by using a hydrothermal process from oxide-based suspension precursors. PMN thick films have been grown on titanium substrates at 150 °C for 8 h. The effect of processing parameters such as reaction durations and mineralization conditions on perovskite phase formation on the microstructures is very critical. By controlling the operating parameters, high quality PMN thick films on titanium substrates were fabricated. The films with a single perovskite structure were smooth and the surfaces were free of micrometer scale cracks. The thickness of the film was about 20 μm. Dielectric responses of the PMN films were characterized in detail. The samples showed excellent reproducibility in the measurement of dielectric responses.


*Keywords:* A. Films; B. Electron microscopy; C. Dielectric properties; D. Perovskites

## 1. Introduction

In recent years, the relaxor ferroelectric $PbMg_{1/3}Nb_{2/3}O_3$ (PMN) and its solid solutions with a normal ferroelectric $PbTiO_3$ (PT), have been the focus of intensive studies in view of their excellent dielectric and electromechanical properties [1]. PMN, which is the best-known and most widely studied relaxor, could be considered as a model object of relaxor materials. Characterized by interesting dielectric, electrostrictive, and piezoelectric properties in single crystal and bulk ceramic [2] forms, $(1-x)$ PMN $-$ $(x)$ PT films are potentially promising various microelectromechanical applications. It has, however, proven difficult to synthesize phase pure perovskite PMN films because of the relatively poor stability of the perovskite phase relative to, for example, the pyrochlore phase. One of the reasons for the difficulty of obtaining single perovskite phase in the PMN films is a severe loss of lead from the films at the post-annealing temperature around or above the evaporation temperature of PbO. The evaporation of PbO leads to the transformation of the perovskite phase PZN into the pyrochlore phases. Therefore, it is necessary to find an effective way at low-temperature to synthesize the PZN films with perovskite structure. A variety of thin film synthesis techniques have been used to fabricate $(1-x)$ PMN $-$ $(x)$ PT films, including chemical solution deposition [3–5], rf sputtering [6], pulsed laser ablation [7], and metal-organic chemical vapor deposition [8]. However, all of these methods require a high-temperature crystallization process in order to crystallize a PMN film. In contrast, hydrothermal epitaxy is a technique that utilizes aqueous chemical reactions that occur at low-temperatures to form heteroepitaxial thin films. As temperatures of only ~200 °C or lower are required, this technique potentially eliminates problems like cracking due to residual thermal stresses that are commonly associated with high processing temperatures. It can be accomplished at relatively mild temperatures and in a closed system. Moreover, it is a simple method to prepare films of single crystal with little post-treatments. The hydrothermal method utilizes the chemical reaction among different ions dissolved in the solution. Using this method, curved shaped materials can be made. And the film can be directly synthesized from an ionic reaction in solution, making it possible to get a chemical homogeneity ferroelectric thin film. Other superior property of films obtained using the hydrothermal method is its large thickness, its three-dimensional structure. So, hydrothermal method provides a very good choice for preparing PZN films. It has been considered as a

* Corresponding author. Tel.: +86 29 88494463; fax: +86 29 88492642.
*E-mail address:* hqfan3@163.com (H. Fan).

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superior method of low production cost due to energy and environmental considerations. It can be accomplished at relatively mild temperatures and in a closed system. This technique possessed the potential to produce well-crystallized PMN films with controlled morphology. But few works have been done to prepare PZN films by using the hydrothermal method yet.

Use of the hydrothermal technique to grow perovskite films like $PbTiO_3$ [9], and PZT [10] at temperature of 200 °C and lower were reported. This study presents an initial effort to synthesize PMN film on titanium substrate by the hydrothermal process. And the effect of processing parameters such as compositions, reaction durations and mineralization conditions on perovskite phase formation and dielectric properties are reported.

## 2. Experimental procedure

Thick-film capacitors of composition PMN were grown by the hydrothermal process on Ti substrates. The PMN precursor suspensions were prepared according to the formula $PbMg_{1/3}Nb_{2/3}O_3$. The pressure vessel consisted of an inner Teflon-lined autoclave of 58 ml capacity. PbO, MgO, and $Nb_2O_5$ were used as source materials for the preparation of PMN suspension. To avoid pollution, the precursors were directly put into a Teflon-lined autoclave of 58 ml capacity, 60% of which was filled with deionized water. Hydroxide potassium (KOH), which was used as the mineralizer, was added slowly while stirring. After mixing the reactants, a piece of titanium metal (22 mm × 12 mm × 0.5 mm) was held at a certain height above the bottom of the vessel. The reaction vessels were slowly heated at a rate of 1 °C/min to a temperature 150 °C and for 8–12 h. Then, the reaction vessels were cooled to room temperature naturally and then the films were carefully washed with deionized water. Finally, Au dot electrodes of 0.5 mm in diameter were deposited on the surfaces of the films as top electrodes through a metal shadow mask in order to measure electrical properties. The titanium substrate was used as the bottom electrodes. Fig. 1 shows the cross-section structure of the PMN thick films on titanium substrate for the electric properties measurement.

Crystal X-ray diffraction (XRD) was used to characterize the films. Data were collected on an automated diffractometer (X'Pert PRO MPD, Philips, Eindhoven, Netherlands) with Cu $K\alpha_1$ radiation ($\lambda = 1.5406$ Å) and a $2\theta$ range from 20 to 60°.

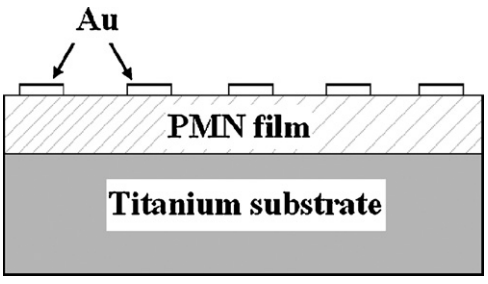


Fig. 1. Measurement structure of PMN thick films.

Microstructure evolution was observed through scanning electron microscopy (SEM; Mode JSM-5610LV, JEOL Technics, Tokyo, Japan). The dielectric properties were measured on the films using an impedance analyzer (HP4294A, Agilent, Palo Alto, CA, USA).

## 3. Results and discussion

It is well known that Pt electrodes often result in the formation of hillocks, which can electrically short the capacitors. Furthermore, ferroelectric thin films on Pt electrodes exhibit a significant fatigue after long bipolar switching pulses. So, in order to obtain high quality films, we used titanium metal as the substrate. The titanium metal could be used directly as the bottom electrode of the PZN films for dielectric measurement without a buffer layer or a seeding layer. And the reaction between the substrate and the solution would be used, so that the adhesive force between the substrates and films is sufficiently strong [10]. Fig. 2 shows the X-ray diffraction patterns (XRD) of PMN films that were hydrothermally synthesized at 150 °C for 8 h at different concentrations of KOH. It is evident from the curve in Fig. 2(a) that the phase consisted of substrate, pyrochlore, and perovskite PMN. The sample exhibits strong peaks corresponding to the (1 0 0) and (1 1 0) peaks, respectively. With increasing the concentration of KOH, intensities of the PLZT peaks decreased. And there was no peaks corresponding to substrate, or pyrochlore observed in Fig. 2(b). Fig. 2(b) indicates that the PMN thick film was crystallized completely. As increasing the concentration of KOH, such as 1.2 and 1.5 M, the substrate was eroded by the alkaline solution. This means that the KOH gives rise to form the perovskite phase. The micrographs observed in detail also confirm this point. Although the KOH favors synthesize of PMN films, the concentration of KOH should not too large, as KOH could erode the substrate. So, in this study, we consider the concentration is 1.0 M is the best.

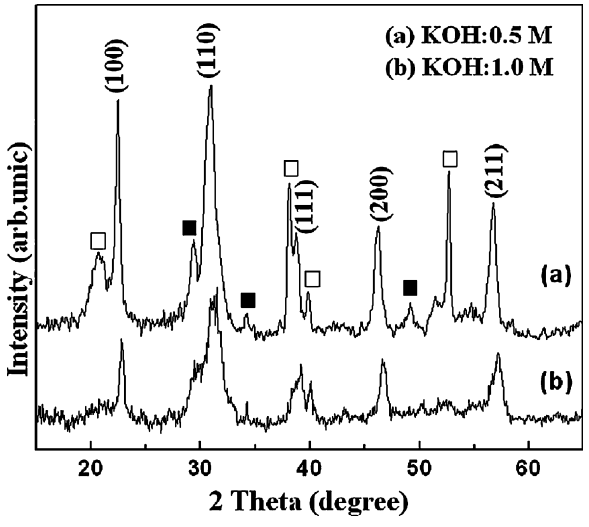


Fig. 2. XRD patterns of PMN films that were hydrothermally synthesized at 150 °C for 8 h at different concentrations of KOH: (a) 0.5 M, (b) 1.0 M. The solid square represents the pyrochlore phase, the open circle represents the substrate, and (*h k l*) represents the perovskite phase.

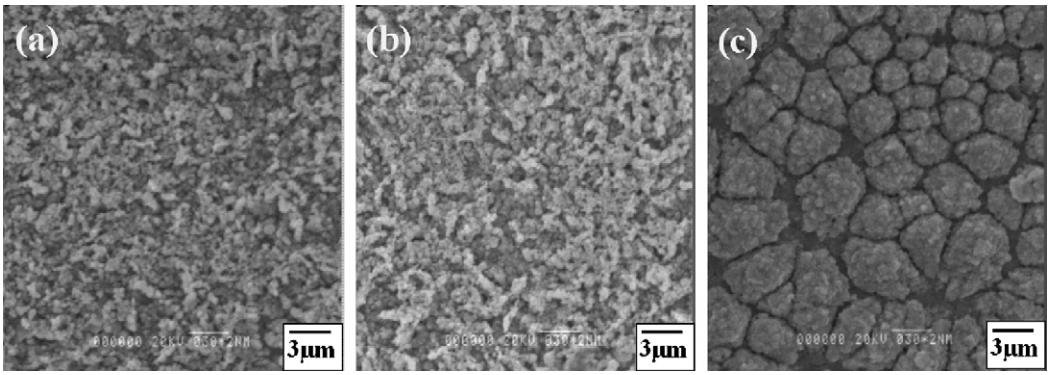


Fig. 3. SEM surface micrographs of the PMN films prepared by the hydrothermal process at 150 °C for: (a) 6 h, (b) 8 h, and (c) 10 h.

Besides the KOH concentration, the reaction durations have an influence on the final films. In the present work, we found the reaction duration affected the surface microstructure of the PMN thick films. Fig. 3 shows SEM surface micrographs of the PMN films prepared by the hydrothermal process at 150 °C for: (a) 6 h, (b) 8 h, and (c) 10 h, respectively. No pyrochlore phase is found in these photos. Fig. 3(a and b) was almost same. The average grain sizes of the films were about 0.3 μm. However, the XRD indicates that when the reaction duration was 6 h, the PMN film has some degree amorphous, and as 8 h, the films were fully crystallized. Another photos show the thick of the sample synthesized at 150 °C for 8 h is 20 μm. As prolong the reaction duration by 2 h, many cracks were formed on the surface of the film, as shown in Fig. 3(c). And the size of crystals became bigger.

The Ti metal substrate was used as the bottom electrodes. Fig. 1 shows the cross-section structure of the PMN thick film on Ti metal substrate for the electric properties measurement. The dielectric constant and dissipation factor measurements were made at room temperature as a function of frequency in the range of 100 Hz to 10 MHz for the thick film. The dielectric responses of the PMN thick film are shown in Fig. 4. The dielectric constant decreases from 1250 to 200 as the frequency increases. The experimental results show that the dielectric loss of the PMN thick films is low, but there is some degree of the dielectric relaxation.

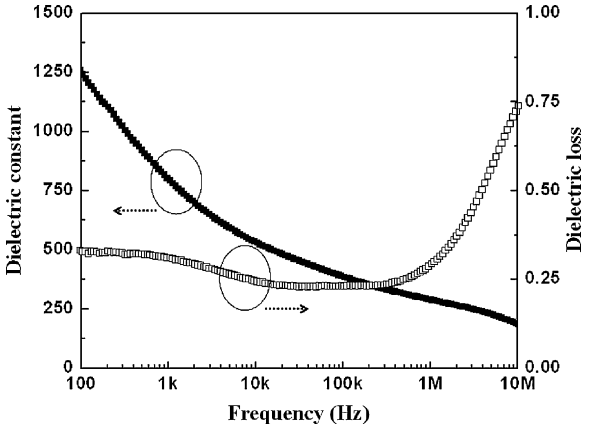


Fig. 4. Dielectric constant and loss of the PMN films synthesized at 150 °C for 8 h.

## 4. Conclusions

In summary, PMN thick films were prepared on Ti substrate with no seeding layer by the hydrothermal process. The route is more simplified and cheaper, and no delicate feedstock preparation is required. Both the KOH concentration and the reaction time had influences on the morphology and microstructure of the final crystals. The dielectric constant and dielectric loss were measured. The experimental results show that there is some degree of the dielectric relaxation. Although the quality of thick films derived from a hydrothermal process may usually not be as high as films deposited in vacuum, the greater thickness, three-dimensional structure as shown here is an attractive advantage for the hydrothermal deposition process.

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