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Synthesis of pyrochlore free PMN–PZT ceramics via a seeding method

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Abstract

Pyrochlore free (x)PMN–$(1-x)$PZT ceramics were synthesized successfully by a seeding method. In this method, the mixture of PbO, MgO and Nb_2O_5 was added to the prepared PZT sol to from PMN–PZT gel. The gel was fired to vaporize the organic contents of gel and obtain powder. Two-step sintering process was used to produce pyrochlore free ceramics. The samples produced by this method showed higher relative densities, lower sintering temperature and higher dielectric properties relative to the mixed oxide method, mostly due to the higher homogeneity of the prepared powder. The measured dielectric properties of PZT-rich and PMN-rich materials were high while the other samples exhibited low dielectric properties.

Keywords: Lead magnesium niobate; Lead zirconate titanate; Sol–gel; Seeding method

1. Introduction

Both PMN and PZT ceramics are from lead-based piezoelectric family materials. They are promising candidates for electronic and microelectronic devices. The PMN ceramic exhibits high dielectric properties, low loss, non-hysteric behavior and low sintering temperatures [1–4]. Also, the Curie temperature for PMN ceramics is below room temperature. The PZT ceramic is one of the piezoelectric ceramics, which is used widely due to its high dielectric and electrostrictive properties [1,2]. But, some of the disadvantages, such as high Curie temperature and low piezoelectric properties at room temperature, which would limit its use at room temperature. Therefore, it was thought that by introducing the PMN to PZT ceramic, the advantages of both ceramics can be utilized.

The major problem in lead-based piezoelectric ceramics is the formation of pyrochlore phases, which show low electric properties and cause negative effect on the piezoelectric ceramic. This fact is more important in PMN preparation due to the easier production of pyrochlore phases. The easiest preparation route for PMN–PZT ceramics is a mixed powder method [3–5], in which PMN and PZT powders were produced separately, mixed together and sintered to produce a PMN–PZT ceramic. There are very different methods of the PMN and PZT production of single-phase powders. The PZT single-phase ceramics can be synthesized by solid state [6], mechanical activation [7,8] or sol–gel [9–11] methods. With respect to the PMN powder, the processing routes for single-phase PMN production will limit the more specific routes, which are columbite route [12–15], mechanical activation process [16–18], reaction sintering process [19–21] and sol–gel method [22,23].

Also, there are other routes proposed by other authors for PMN–PZT production such as mixed oxide method [24], columbite or corundum routes [25] and wet chemical routes [26,27].

Considerable works have been conducted in sol–gel-derived PZT ceramics [9–11]. The sol–gel-derived ceramics show low sintering temperature and very high homogeneity. The addition of crystallographic suitable seed particles in the sol–gel-derived ceramics has been reported earlier [28–31]. It was suggested that the addition of seeds to the gel would modify the phase selection, lower the crystallization temperature or modify the microstructure development [28]. Also, as the seeds disperse uniformly in the solution, the obtained gel would be of high homogeneity which would raise the final product properties. But, still there are few works conducted to use seeding method in the preparation of lead-based piezoelectric ceramics [28–30]

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and the use of this method in preparation of PMN–PZT ceramics has not been reported yet.

In the present work, PMN–PZT ceramics with different compositions were synthesized by the seeding method and the results compared with the prepared samples by the mixed powder method. The single-phase PZT powder was obtained by a sol–gel method. The milled mixture of PbO, MgO and Nb_2O_5 were mixed with PZT sol and PZT calcined powder in the seeding and mixed powder methods, respectively. After preparing the samples, a two-step sintering process was used to prevent pyrochlore formation. Finally, single-phase PMN–PZT ceramics with different compositions were synthesized successfully by both methods and their properties were studied.

2. Experimental procedure

In this work, a seeding method was used to prepare PMN–PZT ceramics and the results were compared with the samples prepared by the mixed powder method. Hence, the production procedure for both methods can help better understand the results.

A milled mixture of PMN ($Pb(Mg_{1/3}Nb_{2/3})O_3$) starting materials (named as mPMN powder) was prepared for use in both methods. In this regard, laboratory grade PbO (Merck, 99.0%), MgO (Merck, 98.0%) and Nb_2O_5 (Merck, 99.9%) were milled in a high energy disc mill (Siebtechnik T100) with Tungsten Carbide (WC) vial and discs at a speed of 1000 rpm for 90 min.

To maintain the highest homogeneity and prevent PZT pyrochlore phase formation, PZT ($Pb(Zr_{0.52}Ti_{0.48})O_3$) sol was synthesized via a sol–gel method. To do so, lead acetate trihydrate ($Pb(CH_3COO)_2{\cdot}3H_2O$, Nacalai tesque, 99.5%), zirconium *n*-propoxide ($Zr(OCH_2CH_2CH_3)_4$, Fluka 70% in *n*-propanol) and tetra-isopropyl titanate ($Ti(OCH(CH_3)_2)_4$, Nacalai tesque, 99.5%) were used as starting materials and the acetic acid was used as a chelating agent. The lead acetate trihydrate was dissolved in acetic acid and stirred at 120 °C to form a Pb-sol. The zirconium *n*-propoxide with extra acetic acid was added to the sol and stirred at 100 °C for a while to form a PZ-sol. At the final step, tetra-isopropyl titanate with additional acetic acid were added to the sol and stirred at 80 °C for 30 min to form PZT sol.

In the mixed powder method, the PZT sol was stirred further at 80 °C for 50 min to form the PZT gel and dried at 150 °C for 4 h and calcined at 800 °C for 2 h with heating rate of 10 °C/min to obtain PZT single-phase powder. PZT powder was mixed with the mPMN powder in different PMN to PZT ratios (i.e. PMN:PZT is 0.1:0.9, 0.3:0.7, 0.5:0.5, 0.7:0.3, and 0.9:0.1).

As for the seeding method, the seeds (mPMN powder) were added to the PZT sol and stirred at 80 °C to obtain (x)PMN–$(1-x)$PZT gel (where x is 0.1, 0.3, 0.5, 0.7 and 0.9). The obtained gel was dried at 150 °C for 4 h. It was heated at 450 °C, which is below calcination temperature of both PMN and PZT, for 2 h at a heating rate of 5 °C/min to obtain powder.

The schematic route for preparation of PMN–PZT powder by mixed powder and seeding methods has been shown in Fig. 1.

The prepared PMN–PZT powder was pressed under 280 MPa of pressure to produce disc shape samples with a diameter

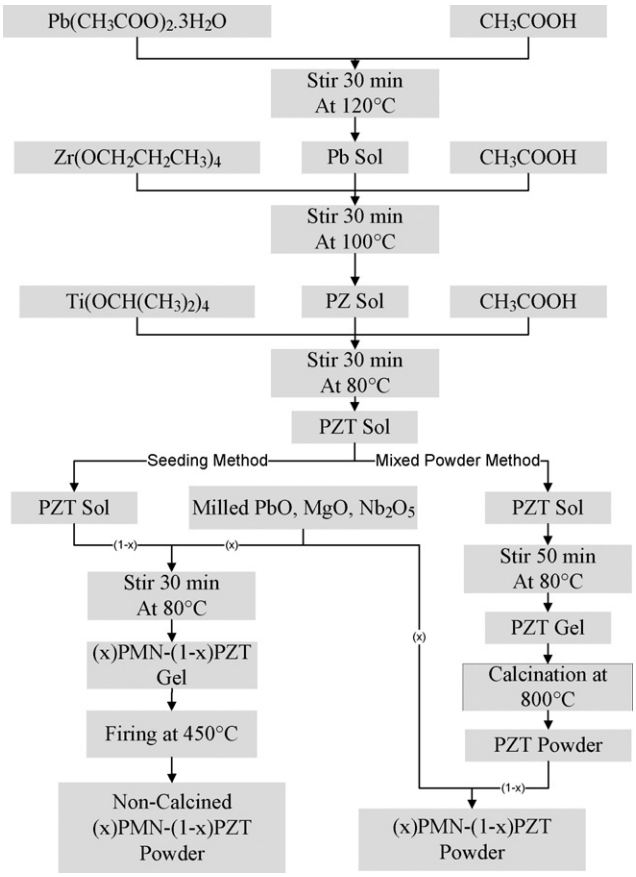

Fig. 1. Preparation route of PZT–PMN powder by mixed powder and seeding methods.

of about 10 mm and a thickness of about 1–2 mm. The samples were placed in a sealed alumina crucible. The atmosphere was controlled by the addition of small amounts of pure PbO in the crucible without any contact with the specimen. The two-step sintering process at different sintering temperatures (1250–1300 °C) was used to obtain single-phase PMN–PZT ceramics with the composition of $(x)Pb(Zr_{0.52}Ti_{0.48})O_3-(1-x)Pb(Mg_{1/3}Nb_{2/3})O_3$, where x is equal to 0.1, 0.3, 0.5, 0.7 and 0.9. In this process, the samples were heated to 900 °C for 1 h and heated to sintering temperatures (e.g. 1250 or 1300 °C) for 2 h with a heating rate of 10 °C/min for both steps. The sintering temperatures of 1250 and 1300 °C were chosen based on the variety of sintering temperatures reported in literature [4,5,25,32] earlier.

The phase formation of powders and sintered specimens was studied by an X-ray diffractometer. The XRD patterns were recorded at room temperature with Cu Kα radiation in a Bruker D-4 diffractometer. Diffraction intensity was measured between 4° and 70° with a 2θ step of 0.02° for y s per point.

Density of the sintered ceramics was measured by Archimedes method. Microstructure characterization was conducted by the fractured surface of specimens using scanning electron microscopy (SEM, PHILIPS XL30) and average grain sizes of sintered specimens were estimated by a linear intercept method from SEM micrographs.