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Synthesis and characterization of $0.65Pb(Mg_{1/3}Nb_{2/3})O_3$–$0.35PbTiO_3$ fibers with Pt core

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Abstract

This paper reports the synthesis and electromechanical characterization of $0.65Pb(Mg_{1/3}Nb_{2/3})O_3$–$0.35PbTiO_3$ (PMN–35PT) ceramics and fibers. To prevent the lead loss during the sintering of the fibers, lead-atmosphere was used during the sintering process. As a consequence, it was possible to ensure a good densification of the fiber and a pure perovskite phase. The electromechanical coupling factor and piezoelectric coefficient of the piezoelectric fiber were found to be $k_{31} = 0.20$ and $d_{31} = -130$ pC/N, respectively. These results are lower than ceramic sample properties ($k_{31} = 0.32$ and $d_{31} = -234$ pC/N). In order to determine reasons for these lower results in fiber shape sample, density and poling studies were performed. It is shown that fiber shape samples cannot be poled correctly because of the ratio between core and ceramic diameters.

Keywords: A. Ceramics; A. Inorganic compounds; C. X-ray diffraction

1. Introduction

There has been considerable interest in the perovskite-type solid solutions of $(1-x)Pb(Mg_{1/3}Nb_{2/3})O_3$–$xPbTiO_3$ due to their dielectric and piezoelectric properties. It exhibits excellent dielectric and piezoelectric properties by combining the advantages of both the relaxor PMN and its solid solution with the normal ferroelectric $PbTiO_3$ (PT). Moreover, it was proven that these properties were maximum at the morphotropic phase boundary (MPB) which marks the transition from rhombohedral to tetragonal PMN–PT compositions. From these results, we selected for our study the composition PMN–35PT ($x = 0.35$) belonging to the morphotropic zone.

In recent years, piezoelectric fibers with metal core were successfully fabricated. The advantage is first to obtain less brittle fiber than fibers without core. Besides, the metal core constitutes one of the two electrodes generating a radial electric field. Consequently, large displacements can be reached for limited voltages due to the lateral piezoelectricity [1,2]. The sintering process of such a material is the key to obtaining high density and perovskite fibers. Indeed, since fibers are not formed under hydraulic press as ceramics are, only the sintering process can increase

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the density of the material. This leads to high temperature and long sintering, which usually results in a high-lead loss and degradation of the perovskite into pyrochlore phase.

The effects of the fiber shaping process on the piezoelectric properties of the ceramic phase are still unclear. Starting with the piezoelectric properties, it is then possible to predict fiber behavior, which can be called a downward approach [3].

In order to understand the influence of the shape on the material properties, a chemical characterization and electromechanical characterization on lateral mode have been conducted on both PMN–35PT ceramics and fibers. Three possible explanations were studied:

- Microstructure of the synthesized materials.
- Density of samples.
- Effect of polarization.

2. Experimental procedure

High-purity chemical powders PbO, TiO_2, MgO and Nb_2O_5 were used as starting materials. PMN–35PT powder was synthesized using the two step columbite precursor technique [4]. Powders of magnesium oxide (MgO) and niobium oxide (Nb_2O_5) were ball-milled in water, using MgO excess and calcined at 1100 °C for 8 h in order to synthesize the $MgNb_2O_6$ phase. Magnesium niobate was then mixed with PbO and TiO_2 in the ratios of PMN:PT 65:35 in molar percentage. Excess of PbO (1 wt%) was added to compensate for PbO evaporation during heat treatments [5]. This mixture was calcined at 850 °C for 2 h. The resulting mixture was divided on two parts: the first was mixed with 10 wt% polyvinyl alcohol (PVA) solution and was pressed to prepare pellets under uniaxial stress. The pellets were first heated at 600 °C to burn out the PVA binder followed by sintering at 1250 °C for 4 h. Samples of 10 mm × 2 mm × 1 mm were used for the lateral mode electromechanical characterization.

The second part of powder was mixed with organic binder (poly vinyl butyral and additives such as dibutyl phtalate as a plasticizer and myryalim as a dispersant). The obtained paste was dried at 80 °C to get a clay-like mixture. The resulting paste was then extruded at room temperature under a pressure of 20 MPa by the extrusion apparatus shown in Fig. 1. The diameter of the nozzle was about 300 μm. For both ceramics and fibers, a lead-atmosphere ($PbZrO_3$) was used during sintering process.

The phase analysis of the grown crystals was performed by X-ray powder diffraction with a monochromatic selecting Cu Kα radiation (λ = 1.5418 Å). Bulk ceramic poling was realized by applying a dc electric field of 30 kV/cm at 50 °C. The fibers were poled using a 200 V voltage (2 kV/mm ''average'' electric field) in an oil bath heated up to 50 °C to facilitate domain reorientation. Fibers tested were 16 mm long on average with a diameter of 300 μm and a core diameter of 50 μm.

The characteristics of the lateral and planar mode were measured on samples using an HP4194A gain/phase analyzer at room temperature 24 h after poling according to IEEE standards on piezoelectricity [6].

3. Result and discussion

3.1. Crystallographic structure and microstructure

Fig. 2 shows the X-ray diffractogram of the PMN–35PT powder. It indicates a pure perovskite phase and no pyrochlore phase was detected within the sensitivity of the X-ray diffraction, meaning that $Pb(Mg_{1/3}Nb_{2/3})O_3$ and $PbTiO_3$ have formed a perfect solid solution with the perovskite structure. It also shows a mixture phase (rhombohedral and tetragonal phases) which is normal since that this formulation belongs to the morphotropic boundary MPB.

Fig. 3 shows X-ray diffraction patterns of ground samples, ceramic and fiber after sintering which indicate a pure perovskite phase. In most cases, XRD diagrams are carried out over narrow angular regions centered about the six pseudo-cubic reflections (1 0 0), (1 1 0), (1 1 1), (2 0 0), (2 2 0) and (2 2 2) from which it is possible to unambiguously determine the crystal symmetry. In our case, from the peak profiles of the pseudo-cubic (2 0 0) reflection shown in Fig. 3, the symmetry is clearly seen to be a mixture of rhombohedral and tetragonal symmetries for the two shapes. The