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Grain size effect on electromechanical properties and non-linear response of dense nano and microstructured PIN–PT ceramics

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Abstract

Nanopowders of $0.63Pb(In_{1/2}Nb_{1/2})O_3$–$0.37PbTiO_3$ were synthesized by solid state reaction using the continuous attrition milling followed by high-energy ball milling techniques in air at room temperature. After milling for 8 h nanopowders of 20–30 nm grain size are obtained. Sintering by hot pressing of PIN–37PT green pellets leads to dense ceramics with average grain size varying from 100 nm to 1 μm. The dielectric and piezoelectric properties of PIN–37PT nanostructured ceramics with grain size bigger than about 160 nm remain roughly unchanged and comparable to those of microstructured ceramics. In addition, the stability of the permittivity and dielectric losses under high ac electric field grows when the grain size decreases. The material becomes less non-linear with decreasing grain size. This result is attractive for acoustic transducer applications.

Keywords: A. Hot pressing; B. Grain size; C. Piezoelectric properties; D. Perovskites

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1. Introduction

Lead indium niobium ceramics $(1-x)Pb(In_{1/2}Nb_{1/2})$–$xPbTiO_3$ (PIN–PT) present a high Curie temperature and exhibit excellent dielectric and electromechanical properties at low and high signal, especially at compositions near the morphotropic phase boundary (MPB).[1] It is important to note that the higher the Curie temperature, the higher the coercive field, and the required electric field. This system, not extensively studied, represents a great interest for piezoelectric actuators, underwater and medical acoustic transducers.

Previous work on PIN–PT microstructured ceramics near the MPB ($x = 0.37$) had revealed a high Curie temperature $T_C \sim 300\,°C$,[1,2] high dielectric and piezoelectric properties (ε_{33}^{T} at 1 kHz = 2600, $k_p \sim 0.57$), a high coercive field ($E_c = 1600$ V/mm) and had observed a relatively good stability of dielectric constant under high ac field.[3] The X-ray diffraction and dielectric studies have shown that the MPB zone of PIN–PT system separates a rhombohedral phase for low PT compositions from a tetragonal phase for high PT compositions. The composition near the MPB, PIN–37PT ($x = 0.37$) presents a phase transition from a monoclinic phase to a tetragonal phase at $T_{F\text{–}F} \sim 150\,°C$.[4] Since PIN–PT ceramics are attractive for high-power sonar application, it is important to know if the ceramics with nano-size grains can improve the properties at high signal. However, the difficulty in preparing nanostructured ceramic materials includes not only the synthesis of nanopowders but also their consolidation, shaping, and subsequent sintering. The sintering by hot forging of nanostructured ceramics represents a compromise between pressure and temperature. The goal of this work is to show the influence of the grain size on structure, electromechanical properties and non-linear dielectric properties of nanostructured ceramics under high ac field. We compare these properties with those of conventional PIN–PT and of hard PZT[5] microstructured ceramics.

2. Experimental procedure

PIN–xPT ceramics were synthesized by a two-step solid state reaction via Wolframite. The Wolframite ($InNbO_4$) was formed

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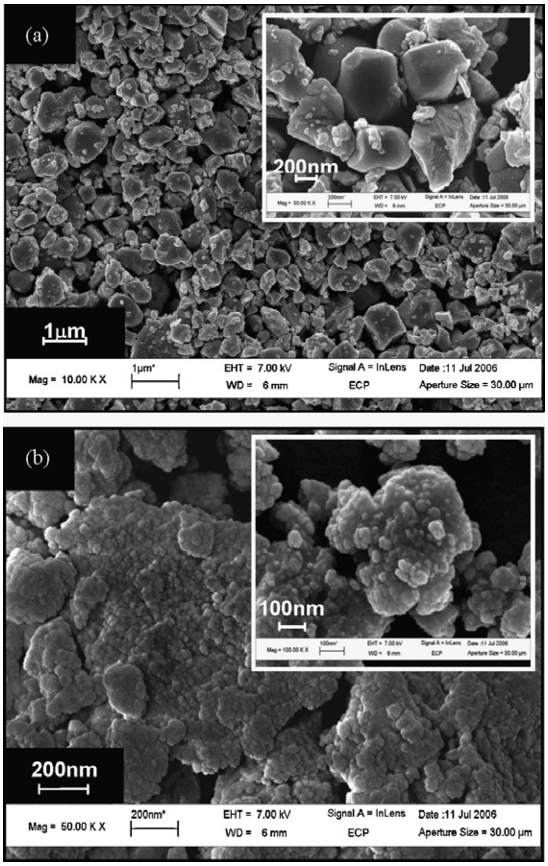

Fig. 1. SEM micrograph of PIN–PT perovskite micropowder obtained by attrition milling (a) and nanopowder obtained by high-energy milling (b).

by mixing In_2O_3 with Nb_2O_5 at 1100 °C for 24 h and then mixed with PbO and TiO_2. The mixture was ball-milled, dried and calcined at 850 °C for 2 h to form stoichiometric perovskites. The ultra fine perovskite powder (Fig. 1a), exhibiting high specific areas, $S_{BET} = 12\ m^2/g$, consists of a major grains of about 0.4 μm and nanoparticles upon their surface; it was obtained by continuous attrition milling. Then, a specially equipped Retsch mill PM400 was used for high-energy ball milling during 8–10 h. The high-energy-milled powder consists of agglomerates constituted by crystalline nanograin sizes (primary particle sizes of ∼20 nm, Fig. 1b). The energy dispersive X-ray analysis of powders shows that contamination by Zr from ZrO_2 milling media was below 300 ppm.

Nanopowders were first uniaxially pressed at 300 MPa and green ceramics pellets with density of about 50–60% were obtained. The green PIN–PT pellets were embedded in Al_2O_3 powder and then sintered by hot pressing at temperatures ranging between 750 °C and 1200 °C for 1 h under pressures ranging between 0 MPa and 500 MPa. Different PIN–PT ceramics with high relative densities (>98% of the theoretical density) and different grain size were prepared.

High resolution X-ray diffraction (XRD) measurements were performed on a highly accurate two-axis diffractometer in a Bragg-Brentano geometry with Cu-K_β wavelength issued from an 18 kW Rigaku rotating anode generator, using a furnace operating between RT and 400 °C. Structural refinement was carried out on these XRD patterns at 350 °C and 200 °C with the XND program[6] in order to determine the lattice parameters of the cubic and tetragonal phases.

The average grain size of nanopowders and nanostructured ceramics was measured, using the line intersection method, on scanning electron microscope (SEM) images obtained at room temperature and compared to the average grain size obtained by refinement of XRD patterns recorded for the cubic phase at 350 °C. The attrition milled and high-energy-milled powders consist of pure perovskite phase, without the presence of amorphous phase or pyrochlore phases. XRD refinement results in a size of about 20–22 nm which is coherent with SEM observations.

For electric measurements, silver paint was deposited on the polished faces and fired at 500 °C during 30 min. Ceramics were poled by field cooling process. Dc electric fields, 2.5–3 kV/mm, were applied to samples in silicon oil at 170 °C and then cooled down to 40 °C. Temperature dependence of the dielectric constant was measured at 1 kHz using a HP 4192A impedance analyzer. Electromechanical properties were measured according to the IRE standard method with an Agilent 4294A impedance analyser. Drift measurements or electric field dependences of the dielectric constant and dielectric losses were measured up to 1 kV/mm. The sinusoidal signal at 1 kHz, generated from a HP 3314A function generator, was amplified by a Kepco Bipolar Amplifier. A EG&G 5210 Lock-in Amplifier and an integration capacitance allow to measure the capacitance and the dielectric losses (tan δ) at fundamental frequency.

3. Results and discussion

3.1. Phase transitions and ferroelectric distortion

Ceramics obtained from attrition milled powder, by using the conventional sintering at ambient pressure and at 1200 °C, exhibit homogeneous microstructure with a 1–2 μm grain size. Fig. 2 shows the SEM micrographs of PIN–37PT dense ceramics sintered from nanopowder by hot forging at different pressures. Ceramics present homogeneous microstructures with a grain size of about 250–300 nm, 125–180 nm and 50–125 nm (Fig. 2a–c), respectively. For easier presentation, we annotate these ceramics by using their average grain size: 1 μm, 300 nm, 160 nm and 100 nm, respectively.

Fig. 3 shows the pseudo-cubic (2 0 0) X-ray diffraction peak of PIN–37PT microstructured and nanostructured ceramics for different temperatures. As expected, the pattern at 350 °C (>T_C) shows single peaks characteristic of the cubic phase (Fig. 3a). When decreasing the temperature to 200 °C, the (2 0 0) reflection of the microstructured ceramic becomes asymmetric due to the diffuse shoulder on its left side, attributed to the transition into a tetragonal phase. The (2 0 0) reflection of the nanostructured ceramic remains symmetric (Fig. 3b), but the small broadening shows that its tetragonal distortion is lower than that of the microstructured one. At room temperature, the (2 0 0) reflection of PIN–37PT microstructured ceramic is broader and more diffuse than the (2 0 0) reflection of PIN–37PT nanostructured ceramic (Fig. 3c). It was shown that a mixture of a tetrago-