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Optimized conditions for fabrication of La-dopant in PZT ceramics

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Abstract

The ferroelectric $Pb(Zr_xTi_{1-x})O_3$ ceramics are well known as piezoelectric materials for electro-mechanical transducers. The highest piezoelectric coupling coefficients as well as maximum permittivity are located near the morphotropic phase boundary (MPB). The region of phase transition between the tetragonal and rhombohedral structures in the $Pb(Zr_xTi_{1-x})O_3$ ceramic shows very adaptable piezoelectric characteristics due to the phase coexistence phenomena and exhibits a sensitivity of properties to the preparation method, the composition, the firing temperatures and the kinds of additives. The purpose of this research is to determine the optimum condition and the effect of doping La into $Pb(Zr_{0.52}Ti_{0.48})O_3$ ceramics prepared by solid state reaction. The properties, such as microstructure, physical properties, dielectric constant (ε_r) and piezoelectric properties (k_p and Q_m) of undoped and lanthanum-doped PZT ceramics were investigated. Several effects, such as firing temperature, grain size and dopant content on structure and properties of PZT have also studied. The undoped PZT ceramics with Zr/Ti at 52/48 indicated the highest $\varepsilon_r = 1101$ (sintering for 1 h) and $k_p = 0.39$ (sintering for 2 h). Doping with lanthanum ion led to an improvement in the ε_r but a reduced Q_m value. The optimum values of k_p is found to be 0.48 for PLZT (1/52/48) doped with 1.00 mol% La^{3+} and sintered at 1200 °C for 1 h.

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Keywords: PLZT; Piezoelectric; Morphotropic phase boundary

1. Introduction

The $Pb(Zr,Ti)O_3$-based solid solution systems have been investigated by the addition of various additives incorporation with other ABO_3-type perovskites for improving sinterability, dielectric and piezoelectric properties. After the reports of superior properties at the phase boundary in PZT [1], many researchers have tried to improve the properties of these materials using various techniques. In 1973–1974, Okazaki and Nagata [2] and Martirena and Burfest [3] showed that an increase in T_c and decreases in dielectric constant were resulted from decreasing grain size. Chandratreya et al. [4] and Hiremath et al. [5] proposed the reaction mechanisms involved in the formation of PZT and PLZT solid solution prepared via mixed oxides method in 1981–1983. Okada et al. [6] reported the production of the actuator from small particle PZT, which were synthesized by chemical preparation method. Moreover, the grain size increased with the calcining temperature. In 1999, Xue et al. [7] reported that high density PZT ceramics had been successfully prepared by skipping the phase formation calcinations at intermediate temperature, the sintered PZT ceramics exhibited a dielectric constant of 1340 and a dielectric loss of 0.6% at a frequency of 1 kHz. The higher density PZT prepared from chemical solution was reported by Tunkasiri [8], with addition of B_2O_3–Bi_2O_3–CdO into the dried PZT powder and sintered in a lead atmosphere. Kamiya et al. [9] and Hase et al. [10]

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observed that addition of the MnO_2 tended to increase Q_m and k_{31} but decrease the tetragonality. Moure et al. [11] reported the microstructure and piezoelectric properties of PZT doped with Fe^{3+} and Sb^{3+}. The grain boundary seemed to be weak when the weight loss increased. The $Pb(Sb_{1/2}Nb_{1/2})O_3$ suppressed the grain growth of PZT ceramics, and exhibit the planar coupling factor (k_p) as high as 0.65 [12]. There have been several reports PZT modified with some lanthanide ions. Haertling and Land [13] reported that Pb^{2+} ions could be substituted by the La^{3+} because of its comparable ionic size. A year later, the lowest calcining temperature to obtain the crystalline PLZT phase prepared by chemical method was 500 °C, 16 h and 400 °C in 1990, respectively [14,15]. In 1994–1995, it has been reported that substitution of Pb^{2+} by La^{3+} ion created vacancies in the A site of perovskite ABO_3 structured ferroelectric PZT ceramics and refined to improve the optical quality of PLZT [16–18]. Sharma et al. [19] found that the structure parameters of lanthanide modified PZT, were dependent on the ionic radius of lanthanide ions. The transparent PLZT (7/60/40) ceramics with large piezoelectric coefficient, $k_p = 0.71$ and small grain size of about 3.00 μm were prepared by Sun et al. [20]. Meanwhile, the PLZT (14/50/50) film showed the maximum charge density which are good for DRAM capacitors [21]. The purpose of the present work is to study the effect of doping rare earth ions into PZT (52/48) ceramics, especially on the structure and piezoelectric properties. The preparation was based on the conventional mixed oxide method. The La^{3+} ion was expected to substitute Pb^{2+} in the crystal on the basis of comparable size. The optimum heating conditions, both calcining and sintering, were investigated. The sintered products were characterized by determining their crystal structure, microstructure and density and composition analysis. Measurements and calculations of the dielectric constant (ε_r), electromechanical coupling factor (k_p) and mechanical quality factor (Q_m), were carried out.

2. Experimental procedure

All chemicals used in this study were of high purity grade (at least 99.0% pure). The starting material, which were lead oxide (PbO), zirconium dioxide (ZrO_2), titanium dioxide (TiO_2) and lanthanum oxide (La_2O_3) were mixed in stoichiometric proportion to obtain $Pb_{1-x}La_x(Zr_{0.52}Ti_{0.48})_{1-x/4}O_3$ when x (mole fraction) = 0.00, 0.01, 0.02 and 0.06. In order to compensate the loss of PbO during high temperature firing, 2% (by weight) excess of PbO was added. The formulation was based on the assumption that La^{3+} would substitute Pb^{2+} on A site [22–24]. Each mixture was wet milled in ethanol using ZrO_2 balls in a polyethylene jar for 24 h, and then evaporated to dryness before calcination at 800 °C for 2 h. The calcined powders were sieved through a 75 μm (200 mesh) sieve, and pressed into pellets using polyvinyl alcohol as a binder. The pellets were also isostatically pressed at 28446 psi before sintering at 1200 °C in a closed alumina crucible. Lead zirconate was used as a covering material, together with a small amount of PbO_2, in order to reduce the PbO vaporization from the pellets. Phases of both calcined and sintered products were identified by powder X-ray diffraction technique using Cu Kα ($\lambda = 1.54056$ Å) radiation (Bruker D8Advance). Energy dispersive X-ray spectrometry was chosen for investigating the chemical composition of PLZT samples. In this study, the same samples used for microstructure observation were carried out in a JEOL-LMS-6400 SEM together with a link series 300 EDS. The acceleration voltage for electron is 20 kV. The microstructures of calcined and sintered products were obtained by using a scanning electron microscopy (SEM). Meanwhile the samples were cracked into small pieces and fixed on the brass stub, and were than coated with Pt and Pd sputtered coating in order to increases conductivity. The samples were viewed and photographed under a scanning electron microscope and grain sizes were investigated on the surface of sintered product without polishing and etching.

The pellets were cut into thin discs by a fine saw. The thin discs were polished by SiC paper and alumina powder to obtain smooth surface and cleaned discs were electroded by screening silver paste (Ag_2O) on both sides, and then fired at 700 °C for 30 min. Ag_2O was decomposed to metallic silver and therefore the surfaces became electrodes. The dielectric properties at 300 kHz the electroded discs were measured. A 3.0 kV/mm electric field was applied to each pellet in silicone oil at 100 °C for 30 min for poling treatment and was kept for 24 h at room temperature after poling before dielectric and piezoelectric measurement. The capacitances of unpoled discs were measured from an HP 4192A LF Impedance Analyzer at 300 kHz. Similar measurements were also performed for poled samples at 1 kHz. Fig. 1 shows the sample alignment in the impedance analyzer. The sample was placed such that poles of the silver electrode and the test fixture had the same sign. The value of k_p, planar coupling factor, could be determined via the resonance and antiresonance method by measuring the frequencies corresponding to the minimum and maximum impedance of the sample $k_p = \sqrt{\frac{1.265(f_a^2 - f_r^2)}{f_a^2}}$, where f_r and f_a are resonance frequency and antiresonance frequency, respectively. The mechanical quality factor Q_m could be obtained obtained as $Q_m = \frac{f_a^2}{2\pi f_r Z_r C^F (f_a^2 - f_r^2)}$, where Z_r and

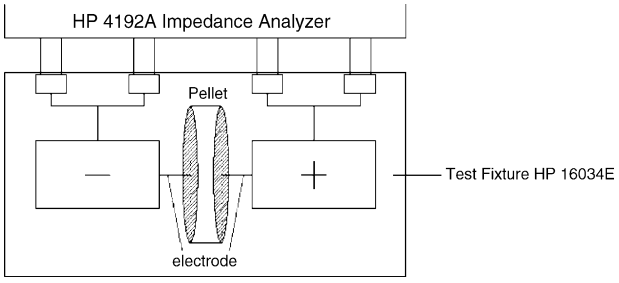

Fig. 1. Sample alignment for measurement of the capacitance, resonance and antiresonance frequency.