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Dielectric, ferroelectric and piezoelectric studies of neodymium-modified PLZNT ceramics for sensor and actuator applications

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Abstract

This paper highlights donor Nd-modified PLZNT $Pb_{0.985}La_{0.015}Nd_y][Zr_{0.524}Ti_{0.476}]_{0.99-(y/4)}Nb_{0.005}O_3$ ceramic compositions where $y = 0, 0.25, 0.50, 0.75$ and 1.0 mol% synthesized through solid-state reaction method were characterized for microstructure, dielectric, ferroelectric and piezoelectric properties. Scanning electron microscopy studies exhibited grain growth inhibition and the room temperature dielectric constant enhanced with decreasing Curie temperature. It was observed that increasing Nd content with donor cations in A-site and B-site had influenced the ferroelectric properties, viz. remanent and spontaneous polarization. The optimum dielectric and piezoelectric properties (d_{33} and k_p) were observed in 1 mol% Nd-modified PLZNT composition which could be suitable for possible sensor and actuator applications.

Keywords: PLZT; Ferroelectrics; Scanning and transmission electron microscopy; Dielectric response

1. Introduction

Lead zirconate titante Pb(Zr,Ti)O_3—PZT have been modified with several donor dopants like La_2O_3, Nd_2O_3, Nb_2O_5, ThO_2, CrO_3, etc. due to their wide application in various piezoelectric, ultrasonic, underwater devices, and various sensors and actuators [1–3]. The morphotrophic phase boundary (MPB) which separates the two different regions, viz. Ti-rich region is tetragonal symmetry and Zr-rich region is rhombohedral symmetry and the best electrical and mechanical properties can be derived where Zr/Ti ≈ 52:48 [4]. There are two types of dopants, viz. hard (acceptor doping) and soft (donor doping).

In PZT perovskite structure, the acceptor (hard) dopants such as K^+, Rb^+, Na^+ (occupy A-site, i.e., Pb-site) and Sc^{3+}, Mg^{2+}, Fe^{3+}, Fe^{2+}, Co^{2+}, Co^{3+}, Mn^{2+}, Mn^{3+}, Ni^{2+}, Ga^{3+}, In^{3+}, Al^{3+}, Cr^{3+} (occupy B-site, i.e., Zr/Ti-site) in the perovskite structure. For example, when Pb^{2+} ions are replaced by two acceptor ions or two acceptor ions replaces Zr^{4+}/Ti^{4+}, one oxygen vacancy is formed which cannot be removed by sintering the ceramic in oxygen atmosphere. The properties of hard doping are lower dielectric constant, lower dielectric loss, higher coercive field, low k_p and high Q_m where different acceptor doping ions affect different properties. While donor (soft) dopants such as La^{3+}, Nd^{3+} and rare earths Bi^{3+}, Sb^{3+}, Th^{4+} (occupy A-site, i.e., Pb-site) and Nb^{5+}, Ta^{5+}, Sb^{5+}, W^{6+} (occupy B-site, i.e., Zr/Ti-site) in the perovskite structure. For example, when two A-sites are occupied by two cations with a valence of 3+, one Pb vacancy is created in the lattice to maintain electroneutrality. The properties of soft doping are high dielectric constant, high k_p, k_t, d_{33} and low coercive field, Q_m, etc. The isovalent substitutions Sr^{2+}, Ca^{2+}, Ba^{2+} replace Pb^{2+} and Sn^{4+} replaces Zr^{4+}/Ti^{4+}. The monovalent substitution Ag^+ (occupy A-site, i.e., Pb-site) and the vacancies occur at B-site similar to La^{3+} or Nd^{3+}.

Among donor dopants, lanthanides (e.g., La and Nd) are unique in producing significant effects on properties of bulk PZT materials. La^{3+} ions are known to promote uniform grain growth and homogeneous densification of a single-phase ceramics. The addition of Nd^{3+} ions in bulk PZT ceramics was found to increase the dielectric constant while enhancing the sintering process [5]. PLZT(9/65/35) ceramics doped with Eu^{3+}, Nd^{3+} and Cr ions synthesized through sol–gel method are investigated [6]. The effect of Nd^{3+} concentration in PLZT transparent ferroelectric ceramics was investigated [7]. The ferroelectric behaviour and charge carriers in Nd-doped $Bi_4Ti_3O_{12}$ thin films

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Table 1
Nd-modified PLZNT solid solutions

	Formulae
General formula	$[Pb_{1-x-y}La_xNd_y][Zr_zTi_{1-z}]_{1-(x/4)-(y/4)-(5/4w)}Nb_wO_3$
Chemical formula	$[Pb_{0.985}La_{0.015}Nd_y][Zr_{0.524}Ti_{0.476}]_{0.99-(y/4)}Nb_{0.005}O_3$
$y = 0$ mol%	$[Pb_{0.985}La_{0.015}][Zr_{0.524}Ti_{0.476}]_{0.99}Nb_{0.005}O_3$
$y = 0.25$ mol%	$[Pb_{0.9825}La_{0.015}Nd_{0.0025}][Zr_{0.524}Ti_{0.476}]_{0.989375}Nb_{0.005}O_3$
$y = 0.50$ mol%	$[Pb_{0.98}La_{0.015}Nd_{0.005}][Zr_{0.524}Ti_{0.476}]_{0.98875}Nb_{0.005}O_3$
$y = 0.75$ mol%	$[Pb_{0.9775}La_{0.015}Nd_{0.0075}][Zr_{0.524}Ti_{0.476}]_{0.988125}Nb_{0.005}O_3$
$y = 1$ mol%	$[Pb_{0.975}La_{0.015}Nd_{0.010}][Zr_{0.524}Ti_{0.476}]_{0.9875}Nb_{0.005}O_3$

were investigated [8]. Undoped and lanthanide (La and Nd)-doped $Pb(Zr_xTi_{1-x})O_3$, i.e., PZT, ferroelectric thin films were prepared and found that electrical properties enhanced with lanthanide concentrations [9]. It has been reported that the effect of doping of Sm^{3+} and Nd^{3+} are similar to La^{3+}-doped lead zirconate titanate ceramics. The effect of Nd_2O_3 in PZT near MPB was investigated and found to have high dielectric and electromechanical properties [10,11]. The system with mixed compounds especially with neodymium has been investigated such as $BaNd_2Ti_5O_{14}$ (BNT), $BaNd_2Ti_4O_{12}$ and $BaNd_2Ti_3O_{10}$ [12]. The effect of neodymium substitution on the ferroelectric properties of $Bi_4Ti_3O_{12}$ was investigated and synthesized by sol–gel method [13].

The PZT ceramics modified with La^{3+} ions have been extensively studied for both piezoelectric and electro-optical applications. However, such studies with other rare-earth oxides are very limited. Therefore, in this study, La, Nd and Nb were chosen as dopants in PZT to form PLNZNT compositions which were investigated for their effects on the microstructure, dielectric, ferroelectric and piezoelectric properties. The general chemical formulae and compositions synthesized have been presented in Table 1.

2. Experimental procedure

2.1. Ceramic processing

Analytical reagent grade powders (purity 99.99%) of PbO, La_2O_3, Nd_2O_3, ZrO_2, Nb_2O_5 and TiO_2 were used as starting materials and the solid solutions were prepared through solid-state reaction method. Initially, all the batch compositions were added with excess 2–6 wt% PbO and were synthesized. The ceramic compositions with excess 4 wt% and 6 wt% PbO were not consistent in phase formation, whereas, 5 wt% PbO-added compositions had shown consistency in phase formation since starting stoichiometric materials participate in the chemical reaction to form end product, while excess PbO compensates the lead volatilization during high-temperature sintering. Thus, weighed starting reagents were mixed in suitable stoichiometric ratios (as batch powders) with the addition of excess 5 wt% PbO to compensate lead volatilization during high-temperature sintering. The batch powders were ball-milled using zirconia balls and ethanol as media for 24 h. As-dried powders were calcined at 925 °C for 3 h in alumina crucible by maintaining air atmosphere. Calcined powders were ball-milled using zirconia balls and ethanol as media for 24 h to crush agglomerates and to minimize the particle size. The calcined fine powders were mixed with 5 wt% polyvinyl alcohol (PVA, as binder) and were pressed into pellets of 12 mm diameter and 2–3 mm thickness using steel die and hydraulic press with uniaxial pressure of 700–900 kg/cm^2. Binder was burned off at 500 °C for 3 h and sintered at 1225 °C for 3 h. The sintering process was conducted in a lead-rich environment and fired in closed alumina crucible to minimize lead oxide volatilization. After sintering process, the specimens were cooled to the room temperature along with furnace.

2.2. Structural characterization

An X-ray diffractometer (XRD: Model PW-1710 Philips powder X-ray diffractometer) with Cu Kα radiation with Ni filter at room temperature was used to characterize phase modification in sintered specimens. The XRD patterns were recorded at a scan rate of 1°/min and $2\theta = 20$–$60°$. As-sintered ceramic surfaces were polished, thermally etched at 1150 °C for 1 h and gold coated using a sputtering technique to analyze microstructure. Fractured surfaces of the ceramics were also coated with gold for scanning electron microscopy studies. Microstructural studies were observed through scanning electron microscopy (SEM) of JEOL Model JSM 840A. The average grain sizes were measured by the linear interception method with scanning electron micrographs. The particle size of the calcined powder was studied by using a transmission electron microscope JEOL JEM 1200. The apparent densities of sintered ceramics were measured using the Archimedes method.

2.3. Dielectric, ferroelectric and piezoelectric characterization

The lapped pellets were electroded with silver paste painted on both faces and fired at 600 °C for 1 h. The electroded specimens were characterized for room temperature dielectric constant (ε_{RT}), dielectric maximum (ε_{Tc}), Curie temperature (T_c), dissipation factor ($\tan\delta$) and temperature-dependent dielectric response (ε) at 1 kHz using 4192A HP Impedance Analyzer. In this study, the temperature change was provided by an automatic temperature chamber (Delta 2300) controlled by a HP computer.

The electroded specimens were poled in silicon oil bath at 100 °C by applying a dc field of 20 kV/cm. After 24 h ageing, the poled specimens were characterized for ferroelectric properties, viz. remanent (P_r), spontaneous (P_s) polarization and coercive field (E_c) with modified sawyer-tower circuit.

The piezoelectric planar coupling coefficient (k_p) of the poled specimens was characterized using a HP-4192A impedance analyzer through the resonance and anti-resonance technique. The piezoelectric charge coefficient (d_{33}) was characterized using a Berlincourt piezo-d-meter.

3. Results and discussion

3.1. XRD characterization

Fig. 1 depicts X-ray diffraction patterns of undoped and Nd-modified lead lanthanum zirconium niobium titanate (designated as PLNZNT) ceramics. XRD studies revealed that Nd^{3+} doping at A-site of PLZNT resulted in enhancing the tetragonality near MPB. In this study, the MPB has been taken as Zr:Ti = 52.4:47.6 where XRD patterns indicate a FE_{TET} exhibiting peak splitting at (0 0 2) with arising subpeak (2 0 0) and

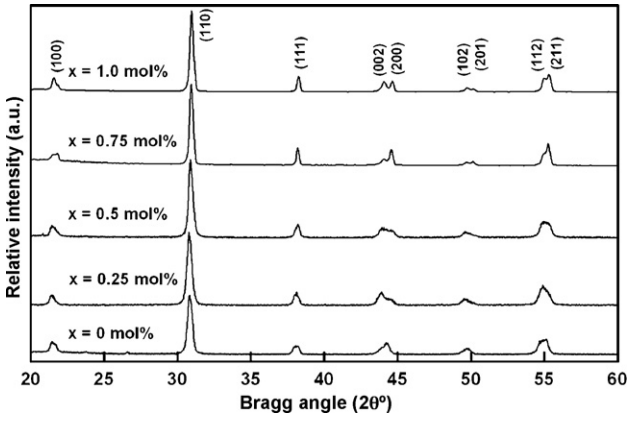

Fig. 1. X-ray diffraction patterns of undoped and Nd-modified lead lanthanum zirconium niobium titanate (designated as PLNZNT) ceramics.