The phase structure, electrical properties, and correlated characterizations of (Mn, Sb) co-tuned PZMnNS–PZT ceramics with relaxation behavior near the morphotropic phase boundary

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Abstract

A normal to relaxor ferroelectric transition was induced by (Mn, Sb) co-tuned $Pb[(Mn_xZn_{0.1-x})_{1/3}(Sb_xNb_{0.1-x})_{2/3}(Zr_{0.505}Ti_{0.4895})_{0.9}]O_3$ ($x=0-0.1$) ceramics near the morphotropic phase boundary using the precursor columbite method. To probe the crystal structure evolution, Raman scattering spectra and fine-scanning fitting curves for XRD patterns were obtained, showing that the B–O bonding energy and the fraction of tetragonal phase decreased with increasing x content. The relaxation degree (ΔT_{relax}), diffuseness degree ($\Delta T_{diff\ (1\ kHz)}$), and diffuseness exponent (γ) of ceramics increased with x content due to increase in the fraction of rhombohedral phase, inducing a short-range order. Correspondingly, the "hard" effect was enhanced and the mechanical loss Q_m^{-1} decreased from 0.01163 to 0.00063. The square ratio (R_{squ}) decreased with increasing x content relating to the increase in reduced amount of space charge and the decrease in Q_m^{-1}. Moreover, the temperature change rate of resonant frequency (TCF_r) and mechanical quality factor (TCQ_m) could be made approximately zero by adjusting x for temperatures of up to 100 °C. To retain the original resonant characterizations of power transducers at high temperature, the trade-off composition of ceramics was obtained at $x=0.08$ with properties: $k_p=0.50$, $Q_m^{-1}=0.00071$, $\varepsilon_{33}^T/\varepsilon_0=900$, $\tan\delta=0.0065$, $\gamma=1.65$, $TCF_r=-0.02\%$, and $TCQ_m=10.6\%$.

1. Introduction

Lead zirconate titanate, $Pb(Zr_{1-x}Ti_x)$, (PZT) is a widely used piezoelectric material because of its excellent electro-mechanical properties. Its highest electro-mechanical parameters can be obtained at the morphotropic phase boundary (MPB) between the rhombohedral (R3m) and tetragonal (P4mm) phases. Piezoelectric materials use the MPB-phase characterization in designing device applications, such as physiotherapy transducers, piezoelectric motors and transformers

[1,2]. These materials typically use the inverse piezoelectric effect to transform electrical energy into mechanical vibrations or displacements. To achieve electrical properties suited for transducers, sensors and actuators, doping ions and adding multiple relaxor compounds into PZT-based materials are effective approaches.

The $(1-x)Pb(Zn_{1/3}Nb_{2/3})O_3-xPb(Zr_yTi_{1-y})O_3$ (PZN–PZT) solid solution near the MPB has a high electro-mechanical coupling factor (k) and elastic strain coefficient (s) [3–5]. However, its small mechanical quality factor (Q_m) constrains its use in power piezoelectric devices. Therefore, relaxor-type compounds have been added to PZN–PZT material systems to improve their Q_m and temperature stability to meet the

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requirements of high-power ultrasonic transducers. According to a previous report [6], manganese (Mn) dopant induces the defect dipole ($Mn'' - Vo^{\bullet\bullet}$), inhibiting the domain wall motion that accompanies increases in the quality factor (Q_m). In contrast, antimony (Sb) dopant suppresses the space charge generation, resulting in a marked increase of k and a decrease of Q_m. Therefore, (Mn, Sb) co-dopants added to a PZT based material system are expected to effectively improve the Q_m while maintaining a high k. Yang et al. reported that the quaternary PMS–PZN–PZT system has a d_{33} value of 369 pC/N, a k_p value of 0.64 and a Q_m value of 1381 [7]. Later, Li et al. showed that individually doping WO_3 and ZnO into a material system can effectively lower the sintering temperature, resulting in $Q_m = 1852$ and 1899, $k_p = 0.58$ and 0.55, and $d_{33} = 243$ pC/N and 300 pC/N, respectively [8,9]. Previous studies investigated crystal structure and piezoelectric properties by using the molten salt synthesis (MSS). High piezoelectric coefficients were obtained using this method. However, the chemical flux processing is required to produce the synthesized powders. Thus, this method is not suitable for low-cost mass production.

Few papers have investigated the coexisting phase structure ratio of (Mn, Sb) co-tuned PZN–PZT ceramics on physical and electrical properties near the morphotropic phase boundary (MPB) using the precursor columbite method (wolframite method). This method has been used in PZT based material systems with good dielectric and piezoelectric properties [10,11]. Therefore, an extension to the research on dielectric, ferroelectric and piezoelectric properties related with the degree of diffuseness behavior for piezoelectric transducers is the main purpose. The evolution of phase structure induced by (Mn, Sb) co-doping was closely investigated by the X-ray diffraction (XRD) and Raman spectroscopy analysis. Furthermore, the dielectric relaxation relating to temperature stability and space charge was determined.

2. Experimental procedures

The compositions of $Pb[(Mn_xZn_{0.1-x})_{1/3}(Sb_xNb_{0.1-x})_{2/3}$ $(Zr_{0.505}Ti_{0.495})_{0.9}]O_3$ (PMSZNZT–100x, where $x = 0$, 0.02, 0.04, 0.06, 0.08, 0.1) were prepared using the precursor columbite method (wolframite method). Ceramics specimens with various compositions were prepared to investigate the dielectric relaxation, ferroelectric, piezoelectric properties, and temperature stability.

Commercially available PbO, Sb_2O_3, ZnO, Nb_2O_5, $MnCO_3$, ZrO_2, and TiO_2 oxide powders (with purity > 99%) were used as the starting materials. First, the $(Zr_{0.505},Ti_{0.495})O_2$ precursor powder was ball-milled, dried, sieved and calcined at 1400 °C for 4 h. According to the formulation ratio, the precursor powder with other oxide powders and excess 1 mol% PbO were weighted and ball-milled for 24 h. After being dried, the powders were calcined at 850 °C for 3 h, and then ball-milled for 24 h and dried. Afterward, 8 wt% polyvinyl alcohol binder solution was added to the dried powders, and then the mixture was filtered using a 200 mesh sieve. The granulated powders were pressed into disc shapes, 12 mm in diameter and 1.5 mm

in thickness, with an average green density of 5.2 g/cm³. The specimens were sintered at 1150 °C for 4 h in a covered alumina crucible. Then, the sintered disc specimens were polished to the desired thickness and the silver paste was screen-printed on both faces, followed by firing at 750 °C for 10 min.

The bulk densities of the specimens were measured using the Archimedes method. The structure of the sintered pellets was determined by X-ray diffraction (XRD) using a Seimens D-5000 diffractometer. Microstructures were analyzed by field emission scanning electron microscopy (FESEM) using a Hitachi SU8000 microscope. The phase transition temperature (Curie temperature, T_c) of un-poled specimens was measured in the frequency range from 1 kHz to 1 MHz with a 0.5 V_{rms} oscillation signal in a controlled furnace from 20 °C to 500 °C. The capacitance and loss factor of un-poled specimens were measured using an Agilent-4294A precision impedance analyzer. The direct-current (dc) insulation resistance of un-poled specimens was measured using an ohm meter (HIOKI SM-8215 super megohmmeter; HIOKI, Nagano, Japan) at room temperature. Then the dc conductivity (σ) was calculated using the relation $\sigma = A/(R_b t)$, where R_b is the measured bulk resistance, A is the electrode area of the specimen and t is the ceramics thickness. To measure the piezoelectric properties and temperature stability of the specimens, the electrode specimens were poled using a dc electric field of 3 kV/mm for 30 min in a 150 °C silicon oil bath, and then the poled specimens were aged for one week to obtain stable values. The resonance frequency (f_r), anti-resonance frequency (f_a), resonance resistance (R) and static capacitance (C) at 1 kHz were measured using an Agilent-4294A precision impedance analyzer. The inverse mechanical quality factor (mechanical loss, Q_m^{-1}) and electromechanical coupling factor (k_p) were calculated using the resonance and anti-resonance method as follows [12]:

$$\frac{1}{k_p^2} = 0.395 \times \frac{f_r}{f_a - f_r} + 0.574$$

$$Q_m^{-1} = 2\pi R C f_r [1 - (f_r/f_a)^2]$$

3. Results and discussion

3.1. Phase structure and microstructure analysis

3.1.1. XRD analysis

The XRD patterns for PMSZNZT − 100x ($x = 0$, 0.02, 0.04, 0.06, 0.08, 0.1 mol) specimens are shown in Fig. 1(a). All specimens exhibit a pure perovskite structure without observing a second phase. The splitting of (200) reflection peak near the 2θ angle of 45° is commonly used to evaluate the phase transformation. To clearly demonstrate the phase transformation, the expanded XRD patterns of the (002) and (200) peaks in the 2θ angles range of 42–48° for all specimens are shown in Fig. 1(b). As can be seen, there is a phase transformation occurs from the rich tetragonal phase ($x = 0$) to the rich rhombohedral phase ($x = 0.1$) with increasing x content.