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Investigation of dielectric and piezoelectric properties in $Pb(Ni_{1/3}Nb_{2/3})O_3$–$PbHfO_3$–$PbTiO_3$ ternary system

H. Tang [a,b], M.F. Zhang [a,c], S.J. Zhang [a,b,*], Y.J. Feng [b], F. Li [b], T.R. Shrout [a]

[a] Materials Research Institute, Pennsylvania State University, University Park, PA 16802, USA
[b] Electronic Materials Research Laboratory, Key Laboratory of the Ministry of Education & International Center for Dielectric Research, Xi'an Jiaotong University, Xi'an 710049, PR China
[c] Centre for Composite Materials, Harbin Institute of Technology, Harbin 150080, PR China

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Abstract

The dielectric and piezoelectric properties were investigated in the $(1-x)Pb(Hf_{1-y}Ti_y)O_3$–$xPb(Ni_{1/3}Nb_{2/3})O_3$ (PNN–PHT, $x=0.05$–0.50, $y=0.55$–0.70) ternary system. The morphotropic phase boundary (MPB) was determined by X-ray powder diffraction analysis. Isothermal map of Curie temperature (T_C) related to the compositions in the phase diagram was obtained. The optimum dielectric and piezoelectric properties were achieved in ceramics with the MPB compositions, with the maxima values being on the order of 6000 and 970pC/N, respectively. Rayleigh analysis was used to study the extrinsic contribution (domain wall motion) in PNN–PHT system, where the extrinsic contribution was found to be ~30% for composition 0.49PNN–0.51PHT(30/70), showing a high nonlinearity.

Keywords: $Pb(Ni_{1/3}Nb_{2/3})O_3$–$PbHfO_3$–$PbTiO_3$; Piezoelectric properties; Morphotropic phase boundary; Curie temperature; Rayleigh analysis

1. Introduction

$PbZrO_3$–$PbTiO_3$ (PZT) piezoelectric ceramics have been mainstay for numerous electronic devices, such as actuators, sensors and transducers due to their high dielectric and piezoelectric properties,[1–3] which are obtained with compositions in the vicinity of the morphotropic phase boundary (MPB). The MPB is a nearly temperature independent phase boundary separating ferroelectric phases with rhombohedral and tetragonal structures. The coupling between the two equivalent energy states, i.e., tetragonal and rhombohedral phases gives rise to enhanced polarizability, allowing optimum domain reorientation during poling.[4,5] Thus, extensive studies have been focused on the exploration of MPB compositions in binary or ternary PZT based systems. In addition, the relaxor ferroelectric lead nickel niobate [$Pb(Ni_{1/3}Nb_{2/3})O_3$, PNN] has been studied,[6–8] showing a broad dielectric maximum near −120 °C, with values being around 4000,[9] revealing a potential relaxor end member to form binary and/or ternary systems with MPB compositions, which were expected to possess enhanced dielectric/piezoelectric properties. For example, $Pb(Ni_{1/3}Nb_{2/3})O_3$–$Pb(Zr,Ti)O_3$[10–12] and $Pb(Ni_{1/3}Nb_{2/3})O_3$– $Pb(Zn_{1/3}Nb_{2/3})O_3$–$PbZrO_3$[13] exhibit high dielectric permittivities and piezoelectric coefficients near MPB compositions. Analogous to PZT, the $PbHfO_3$–$PbTiO_3$ (PH–PT or PHT) solid solution also exhibits MPB composition at ~50%PT.[14–16] Studies on $Pb(Mg_{1/3}Nb_{2/3})O_3$–PHT based ternary compositions shown improved dielectric and piezoelectric properties, comparable to PZT based counterparts,[17,18] however, no investigations on PNN–PHT ternary system was reported, which is the topic of this research.

2. Experiments

$(1-x)Pb(Hf_{1-y}Ti_y)O_3$–$xPb(Ni_{1/3}Nb_{2/3})O_3$ ($x=0.05$–0.50, $y=0.55$–0.70) polycrystalline ceramics were prepared using two-step precursor method.[19] Raw materials of NiO (99.9%, Alfa Aesar, Ward Hill, MA), Nb_2O_5 (99.9%, Alfa Aesar), HfO_2 (99.9%, Alfa Aesar) and TiO_2 (99.9%, Ishihara, San Francisco, CA) were used to synthesize precursors of $NiNb_2O_6$

* Corresponding author at: Materials Research Institute, Pennsylvania State University, University Park, PA 16802, USA. Tel.: +1 8148632639; fax: +1 8148657173.
E-mail address: soz1@psu.edu (S.J. Zhang).

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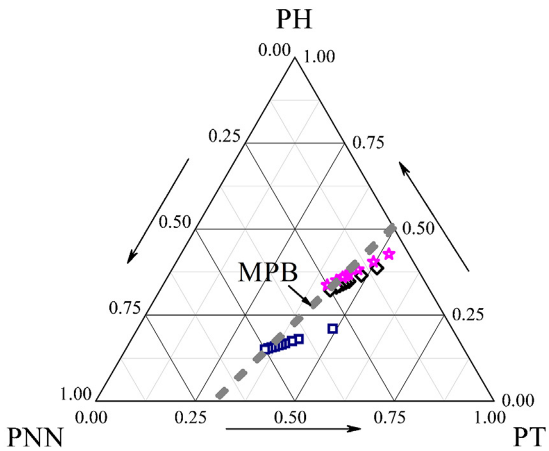

Fig. 1. Compositions studied in $(1-x)Pb(Hf_{1-y}Ti_y)O_3$–$xPb(Ni_{1/3}Nb_{2/3})O_3$ ternary system.

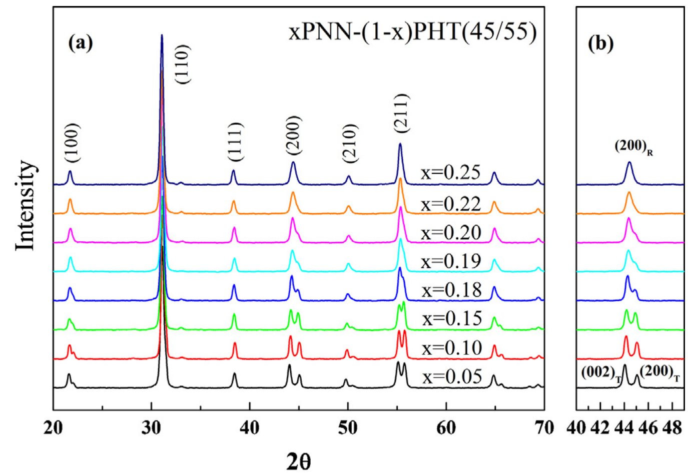

Fig. 3. (a) XRD patterns for xPNN–$(1-x)$PHT(45/55) (the small peaks around 33° are due to the pyrochlore second phase); (b) corresponding expanded XRD patterns of the compositions in the range of 2θ from 42° to 48°.

and $Hf_{1-y}Ti_yO_2$ at 1000 °C and 1200 °C, respectively. Pb_3O_4 (99.5%, Alfa Aesar), $NiNb_2O_6$ and $Hf_{1-y}Ti_yO_2$ powders were then batched stoichiometrically according to the nominal compositions as shown in Fig. 1. The mixed powders were calcined at 1000 °C for 4 h and then vibratory milled in alcohol for 12 h, subsequently granulated and pressed into pellets with 12 mm in diameter. Following binder burnout at 550 °C, the pellets were sintered in sealed crucibles at the temperature of 1250–1280 °C for 2 hs. The phase purity and structure were determined using X-ray powder diffraction (XRD) on the grounded samples. The density was measured by Archimedes method. The microstructure was determined by SEM on fractured surface. For electrical measurements, the samples were polished and then electrode on the parallel surfaces using fire-on silver paste. Poling was carried out in silicon oil at 120 °C for 10 min with an electric field of 30 kV/cm. Dielectric measurements were performed using a multi-frequency precision LCRF meter (HP 4184A). Curie temperatures were determined from the temperature dependent dielectric behavior, measured by the same LCR meter, connecting to a computer controlled high temperature furnace. The piezoelectric coefficients were measured using a Berlincourt d_{33} meter. Polarization hysteresis was determined using a modified Sawyer–Tower circuit driven by a high voltage power supply (TREK Model 610, TREK, Medina, NY). The planar electromechanical coupling factor k_p was determined from resonance and antiresonance frequencies, which were measured using an Impedance Gain-phase analyzer (HP 4194A) according to IEEE standards on piezoelectricity.[20,21] The electric-field-induced strain was measured using a linear variable differential transducer driven by a lock-in amplifier (Stanford Research system, Model SR830). For Rayleigh analysis, the maximum amplitude of the applied electric field was selected to be smaller than half of the coercive field.[22]

3. Results and discussions

Scanning electron microscope (SEM) images of xPNN–$(1-x)$PHT(45/55) ceramics are shown in Fig. 2. All samples exhibited intergranular fracture, with very few pores observed, revealing high densities, being consistent with the densities measured by Archimedes method, around >97% of the theoretical values. The grain size was found to be 4–8 μm for samples with $x = 0.05$, maintained the similar values with increasing PNN content, being 5–8 μm for $x = 0.15$, while decreasing to 2–4 μm for rhombohedral composition ($x = 0.22$).

XRD patterns of xPNN–$(1-x)$PHT(45/55) ceramics with x ranging from 0.05 to 0.25 are shown in Fig. 3(a). All the samples were found to be pure perovskite phase. It was observed that with increasing PNN content, the (2 0 0)/(0 0 2) peaks gradually merged to one peak, as shown in Fig. 3(b), indicating a phase transformation from tetragonal to rhombohedral phase,

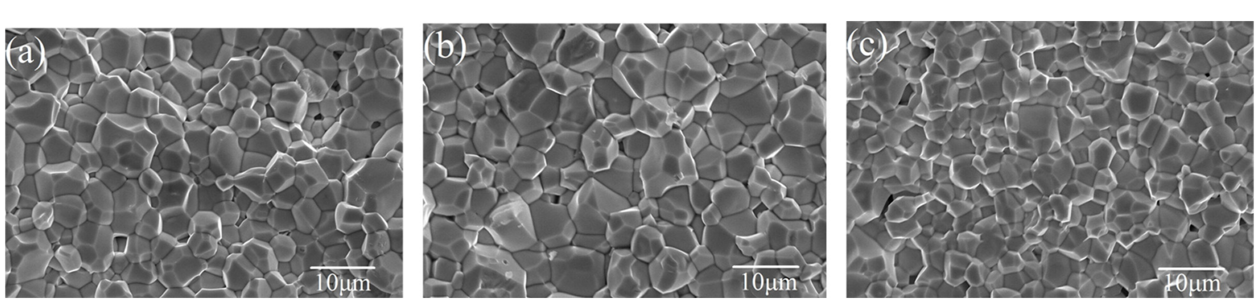

Fig. 2. SEM images of xPNN–$(1-x)$PHT(45/55) (a) $x = 0.05$; (b) $x = 0.15$; (c) $x = 0.22$.