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Preparation and characterization of $Pb(Lu_{1/2}Nb_{1/2})O_3$-$Pb(Ni_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ ternary ferroelectric ceramics with high piezoelectric constant

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ABSTRACT

$Pb(Lu_{1/2}Nb_{1/2})O_3$-$Pb(Ni_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ ferroelectric ceramics were successfully prepared by a modified two-step columbite precursor method. The structural, dielectric, ferroelectric and piezoelectric properties were characterized by X-ray diffraction, ferroelectric and dielectric measurements. All the obtained samples have pure perovskite structure. The composition of 0.17PLN-0.47PNN-0.36PT within morphotropic phase boundary exhibits optimal properties with piezoelectric coefficient d_{33} = 378 pC/N, Curie temperature Tc = 142 °C, dielectric constant ε' = 4700, dielectric loss tangent $\tan\delta$ = 0.05, remnant polarization Pr = 27.1 μC/cm^2 and coercive field Ec = 8.89 KV/cm. According to Curie-Weiss Law and Lorentz-type quadratic relationship, the dielectric behavior was studied and the relaxor factor γ is between 1.55–1.87, indicating the character of diffuse phase transition of the $Pb(Lu_{1/2}Nb_{1/2})O_3$-$Pb(Ni_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ ceramics. The excellent piezoelectric properties and high Curie temperature make this system a promising material for high-power transducer applications in a broad temperature range.

1. Introduction

$Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN) and $Pb(Zn_{1/3}Nb_{2/3})O_3$ (PZN) exhibit large dielectric permittivity and typical relaxor behavior [1,2], which can form a solid solution with $PbTiO_3$ or other lead based compound with perovskite structure, such as $Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$(PMN-PT) [3], $Pb(Zn_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ (PZN-PT) [4], $Pb(Mg_{1/3}Nb_{2/3})O_3$-$Pb(Sc_{1/2}Nb_{1/2})O_3$-$PbTiO_3$ (PMN-PSN-PT) [5], $Pb(Zn_{1/3}Nb_{2/3})O_3$-$Pb(In_{1/2}Nb_{1/2})O_3$-$PbTiO_3$ (PZN-PIN-PT) [6]. These compounds have attracted great attention in the past decades because of their high piezoelectric constant and high dielectric permittivity of compositions near morphotropic phase boundary (MPB) region. The MPB region allows the coexistence of rhombohedral, tetragonal phases and other phases, showing the optimum domain reorientation during the process of poling [7]. Therefore, extensive studies focus on the compositions near the MPB region, in which potential excellent physical properties are expected [8,9].

$Pb(Ni_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ (PNN-PT) is a typical relaxor ferroelectric material, which shows excellent dielectric and piezoelectric properties near the MPB region [10]. However, the low Curie temperature of PNN-PT in MPB regions limits its applications at elevated temperature. In order to increase the Curie temperature of PNN-PT system, many studies focus on ternary system, such as $Pb(Ni_{1/3}Nb_{2/3})O_3$-$PbHfO_3$-$PbTiO_3$ (PNN-PH-PT) [11], $Pb(Ni_{1/3}Nb_{2/3})O_3$-$Pb(Sc_{1/2}Nb_{1/2})O_3$-$PbTiO_3$ (PNN-PSN-PT) [12], $Pb(Ni_{1/3}Nb_{2/3})O_3$-$Pb(Mg_{1/2}W_{1/2})O_3$-$PbTiO_3$ (PNN-PMW-PT) [13] and so on.

$Pb(Lu_{1/2}Nb_{1/2})O_3$(PLN) has been reported to exhibit a ferroelectric to anti-ferroelectric phase transition temperature at 30 °C [14] and an anti-ferroelectric to para-electric phase transition temperature near 270 °C [15]. It can easily form binary solid solution with $PbTiO_3$ (PT), which has high Curie temperatures and good piezoelectric properties within MPB region [16–18]. Therefore, we believe that the ternary system $Pb(Lu_{1/2}Nb_{1/2})O_3$-$Pb(Ni_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ (PLN-PNN-PT) will possess relative higher Curie temperature and excellent electrical properties. This paper reports the preparation and the phase structure, piezoelectric and ferroelectric properties of the PLN-PNN-PT ternary ceramics.

2. Experimental procedures

The ceramics of (1-x-y)PLN-xPNN-yPT were prepared by a modified two-step columbite precursor method. The appropriate amount of high purity (99.9%) oxide powers, PbO, Lu_2O_3, NiO, Nb_2O_5 and TiO_2 were used as raw materials with 4 mol% excess of PbO to suppress the formation of pyrochlore phase during sintering. First, the precursors of B-site ions were calcined using the columbite and wolframite method.

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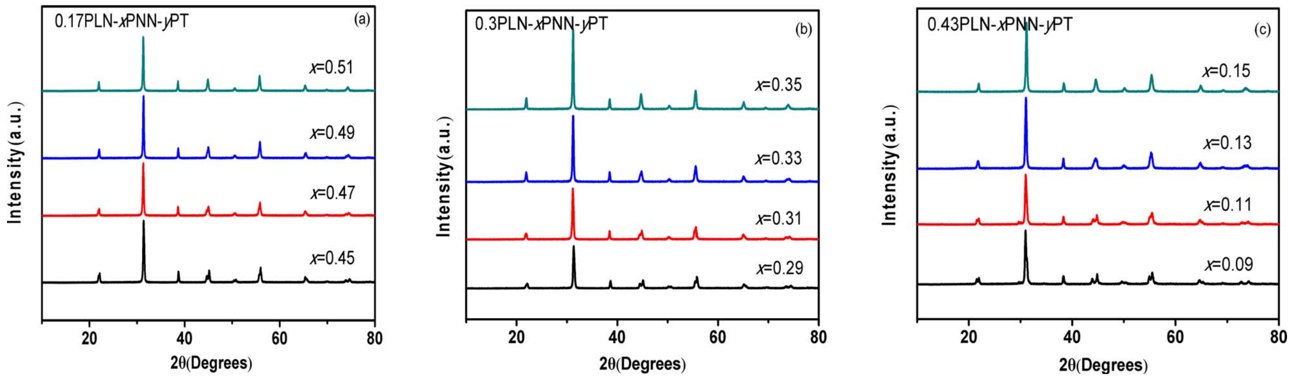

Fig. 1. XRD patterns of the PLN-PNN-PT ceramics at room temperature (a) 0.17PLN-*x*PNN-*y*PT (b) 0.30PLN-*x*PNN-*y*PT (c) 0.43PLN-*x*PNN-*y*PT.

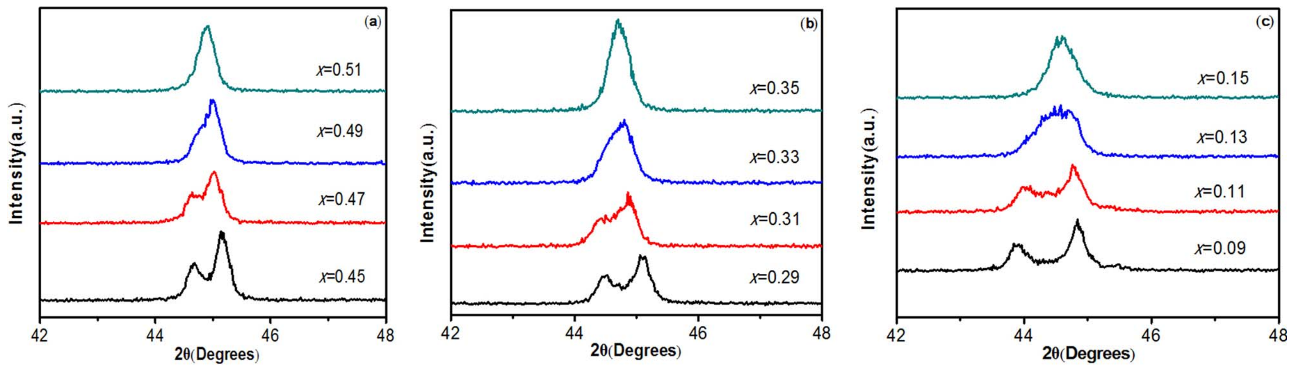

Fig. 2. (200) reflection peaks for (a) 0.17PLN-*x*PNN-*y*PT (b) 0.30PLN-*x*PNN-*y*PT (c) 0.43PLN-*x*PNN-*y*PT.

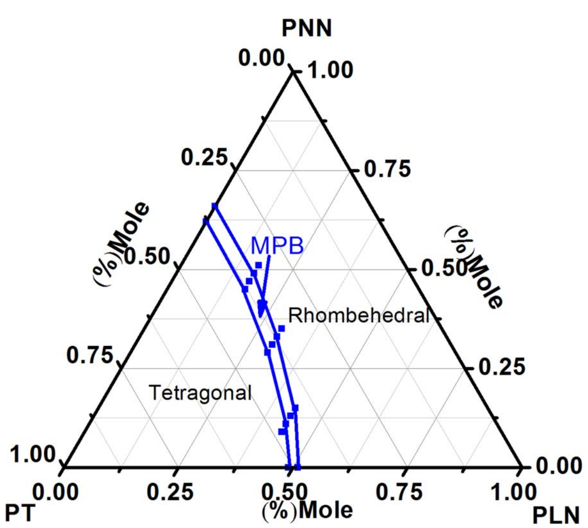

Fig. 3. MPB region of the PLN-PNN-PT ternary system at room temperature.

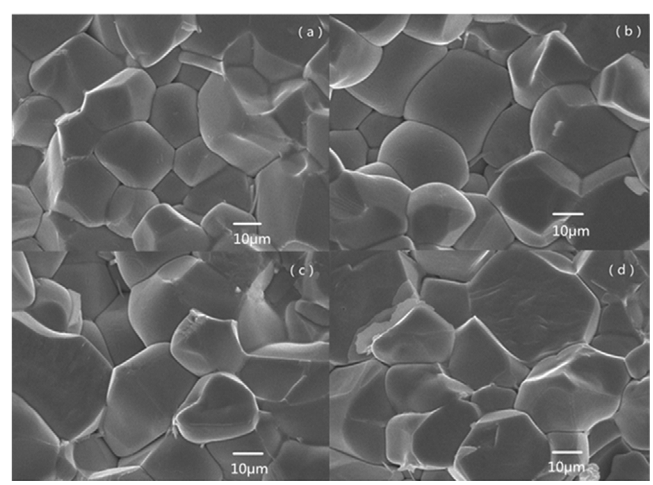

Fig. 4. SEM micrographs of a fracture surface of 0.17PLN-*x*PNN-*y*PT (a) 0.17PLN-0.45PNN-0.38PT (b) 0.17PLN-0.47PNN-0.36PT (c) 0.17PLN-0.49PNN-0.34PT (d) 0.17PLN-0.51PNN-0.32PT.

$LuNbO_4$ was calcined at 1250 °C for 1 h and $NiNb_2O_6$ was calcined at 1000 °C for 6 h according to the stoichiometric proportions respectively. Second, the $LuNbO_4$ and $NiNb_2O_6$ were subsequently ball-milled with the PbO and TiO_2 for 24 h, pressed into pellets and then calcined at 800 °C (4 h). Finally, the calcined powders were milled and mixed with 5 wt% polyvinyl alcohol and pressed into pellets at the pressure of 8 MPa. The pellets were sintered at various temperatures ranging from 1050 °C to 1150 °C for 2 h in a sealed Al_2O_3 crucible after burning out at 550 °C for 2 h. As a lead source, the $PbZrO_3$ powders were used to suppress the lead loss.

For structural studies, the powders of sintered samples were measured by X-ray diffraction technique with CuKα radiation (Rigaku, MinFlex II, Japan). In order to measure electrical properties, the ceramics were polished and pasted with silver as electrodes. The density of the pellets was measured by Archimedes principle. A scanning electron microscope (SEM, JSM-6700F, JEOL, Tokyo, Japan) was used to study the microstructure of the fracture surface of sintered ceramic samples. The dielectric properties were analyzed using a computer-controlled Alpha-A broad band dielectric/impedance spectrometer (Novo-control GmbH), with an AC signal of 1.0 V (peak-to-peak) applied. An aix-ACCT2000 analyzer (f = 4 Hz) was used to measure the ferroelectric hysteresis loops at room temperature. The piezoelectric coefficient d_{33} was measured using a quasi-static d_{33} meter (Institute of Acoustics, Chinese Academy of Sciences, model ZJ-4AN).