

# Structure and Electrical Properties of Oxide Doped Rhombohedral $\text{Pb}(\text{Ni}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$ Ferroelectric Ceramics

Bijun Fang\*, Dun Wu, Qingbo Du, Limin Zhou, Yongyong Yan

School of Materials Science and Engineering, Changzhou University, Changzhou, China.  
Email: fangbj@cczu.edu.cn

Received February 28th, 2010; revised May 3rd, 2010; accepted May 5th, 2010.

## ABSTRACT

$0.7\text{Pb}(\text{Ni}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-}0.3\text{PbTiO}_3$  (0.7PNN-0.3PT) and 1 mol%  $\text{La}_2\text{O}_3$ -,  $\text{Y}_2\text{O}_3$ -, ZnO-,  $\text{MnO}_2$ - and  $\text{Nb}_2\text{O}_5$ -doped 0.7PNN-0.3PT ferroelectric ceramics were prepared by the conventional solid-state reaction method via the columbite precursor route. The ceramics sintered at  $1180^\circ\text{C}$  exhibit pure rhombohedral perovskite structure except the  $\text{Y}_2\text{O}_3$ -doped 0.7PNN-0.3PT ceramics. The oxide-doped 0.7PNN-0.3PT ceramics exhibit rather homogeneous microstructure and improved densification, especially for the  $\text{MnO}_2$ - and  $\text{La}_2\text{O}_3$ -doped 0.7PNN-0.3PT (defect) ceramics whose relative density is larger than 96%. All the above dopants decrease the dielectric loss of the 0.7PNN-0.3PT ceramics, whereas the values of the dielectric maximum ( $\epsilon_m$ ) and the temperature of  $\epsilon_m$  ( $T_m$ ), and the character of dielectric response vary differently. ZnO and  $\text{Nb}_2\text{O}_5$  doping increase remanent polarization  $P_r$ , and  $\text{La}_2\text{O}_3$ , ZnO,  $\text{MnO}_2$  and  $\text{Nb}_2\text{O}_5$  doping decrease coercive field  $E_c$  of the 0.7PNN-0.3PT ceramics. Piezoelectric property is greatly improved by  $\text{Y}_2\text{O}_3$ ,  $\text{MnO}_2$ ,  $\text{Nb}_2\text{O}_5$  and ZnO doping, where the  $\text{MnO}_2$ -doped 0.7PNN-0.3PT ceramics exhibit the largest value of piezoelectric constant  $d_{33}$ , which reaches 191 pC/N.

**Keywords:** Lead Nickel Niobate-Lead Titanate, Perovskite, Dielectric Property, Ferroelectric Property, Piezoelectricity Property

## 1. Introduction

Relaxor-based ferroelectric ceramics have arisen extensive research due to their high and nearly temperature insensitive dielectric constant, electromechanical constant and electro-optical performance, which make them potential revolution in electromechanical transducer and actuator applications and promising candidates for optical devices [1,2]. To meet the requirements of these applications, ideal materials should possess high relative dielectric constant and low dielectric loss. Recently, a novel methodology is devised to stabilize perovskite phase and develop piezoelectric materials by adding stable perovskite normal ferroelectrics to relaxor ferroelectrics. The formation of solid solutions increases the tolerance factor and electronegativity difference, leading to the stabilization of the perovskite structure [3,4].

Among relaxor ferroelectrics,  $\text{Pb}(\text{Ni}_{1/3}\text{Nb}_{2/3})\text{O}_3$  (PNN) is a typical relaxor ferroelectric with perovskite structure, which exhibits broad and diffused dielectric response peaks accompanied by apparent dielectric frequency dis-

persion.  $\text{PbTiO}_3$  (PT) is a typical normal ferroelectric sharing perovskite structure, which exhibits sharp and frequency independent dielectric response peaks at Curie temperature ( $T_C$ )  $490^\circ\text{C}$ . Since the arrangement of heterovalent cations in the perovskite structure, their electrostatic interactions and the morphotropic phase boundary (MPB) effects affect electrical properties of ferroelectrics greatly, the development of perovskite structure and the MPB composition of the solid solution  $(1-x)\text{-Pb}(\text{Ni}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-}x\text{PbTiO}_3$  (PNN-PT) have arisen great research attention [5,6].

In this paper  $0.7\text{Pb}(\text{Ni}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-}0.3\text{PbTiO}_3$  (0.7PNN-0.3PT) ferroelectric ceramics were prepared by the columbite precursor method. This composition was chosen since 0.7PNN-0.3PT locates around the MPB composition and exhibits typical rhombohedral structure, which reveals enhanced microstructure and electrical properties, and was easy to research the effects of chemical doping on structure and performance of the ferroelectric solid solution.  $\text{La}_2\text{O}_3$ ,  $\text{Y}_2\text{O}_3$ , ZnO,  $\text{MnO}_2$  and  $\text{Nb}_2\text{O}_5$  were used as dopants to investigate the influence on stabilization of

the perovskite structure, electrical properties and MPB effects of the PNN-PT system. By the way, special efforts should be undertaken on ceramic processing and sintering profile for the preparation of the lead-containing ferroelectric ceramics in order to suppress the evaporation of lead during sintering [7].

## 2. Experimental Procedure

0.7PNN-0.3PT and 1 mol%  $\text{La}_2\text{O}_3$ -,  $\text{Y}_2\text{O}_3$ -,  $\text{ZnO}$ -,  $\text{MnO}_2$ - and  $\text{Nb}_2\text{O}_5$ -doped 0.7PNN-0.3PT ferroelectric ceramics were prepared by the conventional solid-state reaction method via the columbite precursor route. The chemical compositions were designed as below:

To maintain stoichiometry, the analytical-purity raw oxides were dried separately before weighing and the synthesized columbite precursors were weighed and introduced into the batch calculation. The columbite precursors,  $\text{NiNb}_2\text{O}_6$ ,  $\text{ZnNb}_2\text{O}_6$  and  $\text{MnNb}_2\text{O}_6$ , were synthesized by calcining of a mixture of stoichiometric  $\text{NiO}$ ,  $\text{ZnO}$  and  $\text{MnO}_2$  with  $\text{Nb}_2\text{O}_5$ , respectively, at  $1000^\circ\text{C}$  for 4 h. Stoichiometric  $\text{PbO}$ ,  $\text{TiO}_2$  and chemical dopants (zinc and manganese were introduced in the form of  $\text{ZnNb}_2\text{O}_6$  and  $\text{MnNb}_2\text{O}_6$  columbite precursors) were added to  $\text{NiNb}_2\text{O}_6$ , and the well-mixed powders were calcined at  $900^\circ\text{C}$  for 2 h. The calcined powders were then dry-pressed into pellets with the addition of 1 wt% polyvinyl alcohol (PVA) binder and sintered at different temperatures. Detailed preparation of the ceramics was described elsewhere [8].

The sintered ceramics were ground and polished to obtain flat and parallel surfaces. For electrical property measurement, silver paste was coated on both surfaces of the well-polished pellets and fired at  $550^\circ\text{C}$  for 30 min to provide robust electrodes. Detailed phase structure characterization, micromorphology observation and electrical properties measurement procedures were described elsewhere [7-8].

## 3. Results and Discussion

For the preparation of lead-containing PNN-PT ferroelectric ceramics, special attention should be paid for the control of the evaporation of lead during sintering, which helps to determine the appropriate sintering conditions

combined with the collective assessments of fabrication cost and electrical properties. The 0.7PNN-0.3PT and 1mol% oxide-doped 0.7PNN-0.3PT ceramics were sintered at  $1100\text{-}1220^\circ\text{C}$ . The columbite precursor method exhibits superiority and feasibility in synthesizing complex relaxor-based ferroelectric ceramics since the weight loss during sintering is relatively low and phase-pure perovskite structure can be obtained. Based on the results of preliminary experiments, the appropriate sintering condition for 0.7PNN-0.3PT is  $1180^\circ\text{C}$  for 2 h.

XRD patterns of the 0.7PNN-0.3PT and 1 mol% oxide-doped 0.7PNN-0.3PT ceramics sintered at the optimized conditions are shown in **Figure 1**. All the sintered ceramics exhibit pure rhombohedral perovskite structure except for  $\text{Y}_2\text{O}_3$ -doped 0.7PNN-0.3PT, where slight content of  $\text{Pb}_3\text{Nb}_4\text{O}_{13}$ -type pyrochlore phase appears. The appearance of pyrochlore phase can be attributed to the ionic radius difference between  $\text{Pb}^{2+}$  and  $\text{Y}^{3+}$ , and the evaporation of lead during sintering and the deterioration of the stabilization of perovskite structure induced by  $\text{Y}_2\text{O}_3$  doping. The content of pyrochlore phase of the  $\text{Y}_2\text{O}_3$ -doped 0.7PNN-0.3PT ceramics can be determined by an approximate method  $\% \text{pyrochlore} = I_{\text{pyro}} \times 100 / (I_{\text{perov}} + I_{\text{pyro}})$ , where  $I_{\text{perov}}$  and  $I_{\text{pyro}}$  are the relative intensity of the (110) perovskite diffraction peak and the (222) pyrochlore diffraction peak, respectively, being 4.59%.

Cell parameters and density of the pure and oxide-doped 0.7PNN-0.3PT ceramics are shown in **Table 1** based on XRD results and density measurement by Archimedes water-immersed method. Since pure rhombohedral perovskite structure forms in the oxide-doped 0.7PNN-0.3PT ceramics except  $\text{Y}_2\text{O}_3$ -doped one, the doped cations tend to occupy A- or B-site of the perovskite structure. However, due to the difference of the ionic radius between the doping and the replaced cations, the perovskite structure distorts, leading to the variation of cell parameters and cell volume of the perovskite structure. The relative density of 0.7PNN-0.3PT is not high enough at this experimental conditions, which confirms again the difficulty of the preparation of complex perovskite ferroelectric ceramics [9]. Therefore, the ceramic processing

---

$0.7\text{Pb}(\text{Ni}_{1/3}\text{Nb}_{2/3})\text{O}_3 - 0.3\text{PbTiO}_3$	abbr. as: 0.7PNN - 0.3PT
$(\text{Pb}_{0.99}\text{La}_{0.01})(\text{Ni}_{1/3}\text{Nb}_{2/3})_{0.7}\text{Ti}_{(0.3-0.01/4)}\text{O}_3$	abbr. as: $\text{La}_2\text{O}_3$ -doped 0.7PNN - 0.3PT
$(\text{Pb}_{0.99}\text{La}_{0.01})(\text{Ni}_{1/3}\text{Nb}_{2/3})_{0.7}\text{Ti}_{0.3}\text{O}_3$	abbr. as: $\text{La}_2\text{O}_3$ -doped 0.7PNN - 0.3PT (defect)
$(\text{Pb}_{0.99}\text{Y}_{0.01})(\text{Ni}_{1/3}\text{Nb}_{2/3})_{0.7}\text{Ti}_{(0.3-0.01/4)}\text{O}_3$	abbr. as: $\text{Y}_2\text{O}_3$ -doped 0.7PNN - 0.3PT
$0.7\text{Pb}[(\text{Ni}_{0.99}\text{Zn}_{0.01})_{1/3}\text{Nb}_{2/3}]\text{O}_3 - 0.3\text{PbTiO}_3$	abbr. as: $\text{ZnO}$ -doped 0.7PNN - 0.3PT
$0.7\text{Pb}[(\text{Ni}_{0.99}\text{Mn}_{0.01})_{1/3}\text{Nb}_{2/3}]\text{O}_3 - 0.3\text{PbTiO}_3$	abbr. as: $\text{MnO}_2$ -doped 0.7PNN - 0.3PT
$0.7\text{Pb}(\text{Ni}_{1/3}\text{Nb}_{2/3})\text{O}_3 - 0.3\text{Pb}(\text{Ti}_{0.99}\text{Nb}_{0.01})\text{O}_3$	abbr. as: $\text{Nb}_2\text{O}_5$ -doped 0.7PNN - 0.3PT

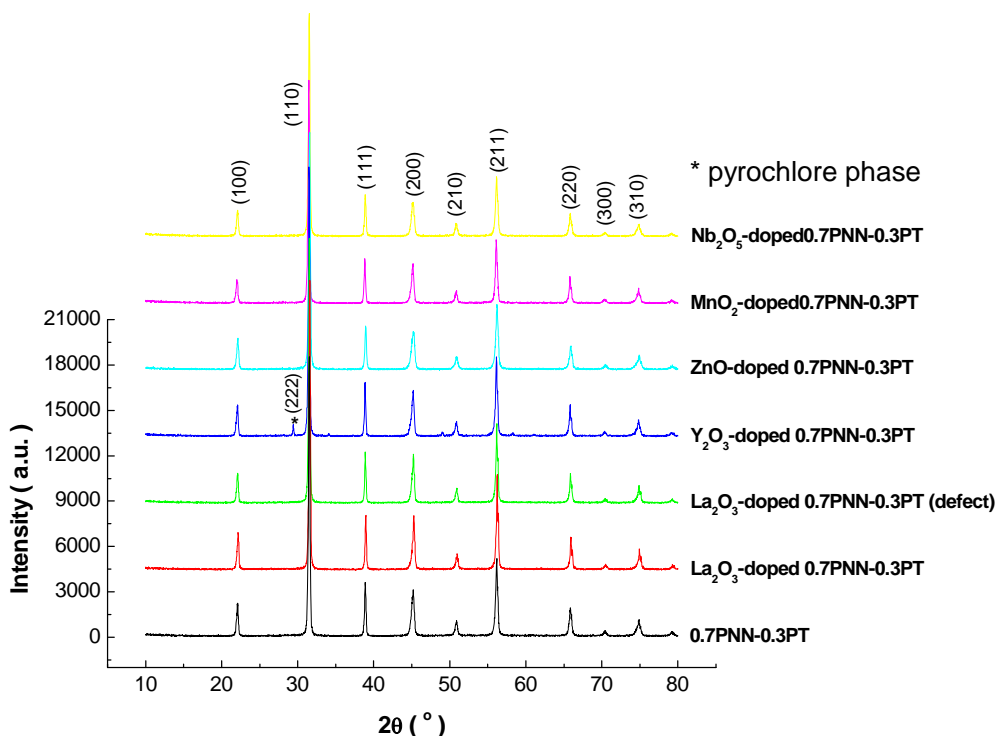


Figure 1. XRD patterns of the pure and oxide-doped 0.7PNN-0.3PT ceramics sintered at 1180°C for 2 h

Table 1. Cell parameters and density of the pure and oxide-doped 0.7PNN-0.3PT ceramics

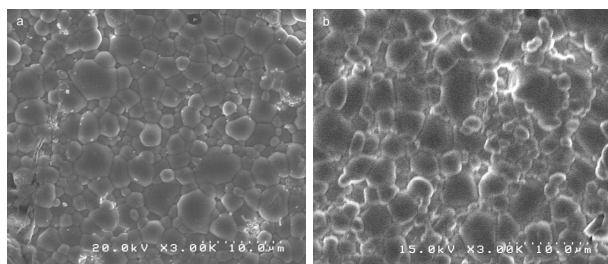
Composition	$a = b = c$ (Å)	$\alpha = \beta = \gamma$ (°)	Cell volume (Å <sup>3</sup> )	Theoretical density (g/cm <sup>3</sup> )	Bulk density (g/cm <sup>3</sup> )	Relative density (%)
0.7PNN-0.3PT	4.0039(8)	90.012(81)	64.187	8.4497	7.520	88.99
La <sub>2</sub> O <sub>3</sub> -doped 0.7PNN-0.3PT	4.0057(9)	90.037(137)	64.271	8.4179	7.398	87.88
La <sub>2</sub> O <sub>3</sub> -doped 0.7PNN-0.3PT (defect)	4.0028(13)	89.991(137)	64.135	8.4389	8.424	99.82
Y <sub>2</sub> O <sub>3</sub> -doped 0.7PNN-0.3PT	~4.0082(16)	~90.022(165)	~64.395	~8.3888	7.073	~84.31
ZnO-doped 0.7PNN-0.3PT	4.0054(41)	90.091(428)	64.256	8.4410	7.692	91.13
MnO <sub>2</sub> -doped 0.7PNN-0.3PT	4.0035(27)	90.064(280)	64.166	8.4522	8.140	96.31
Nb <sub>2</sub> O <sub>5</sub> -doped 0.7PNN-0.3PT	4.0039(26)	90.070(265)	64.187	8.4532	7.347	86.91

should be tailored further. Small content of oxide doping exhibits great effect on the densification of the 0.7PNN-0.3PT ceramics. Among which, the MnO<sub>2</sub>- and La<sub>2</sub>O<sub>3</sub>-doped 0.7PNN-0.3PT (defect) ceramics exhibit the largest relative density, being more than 96% of the theoretical density, which is especially suitable for the electronic industry applications. Above results indicate that chemical doping is an efficient way to improve densification of ferroelectric ceramics.

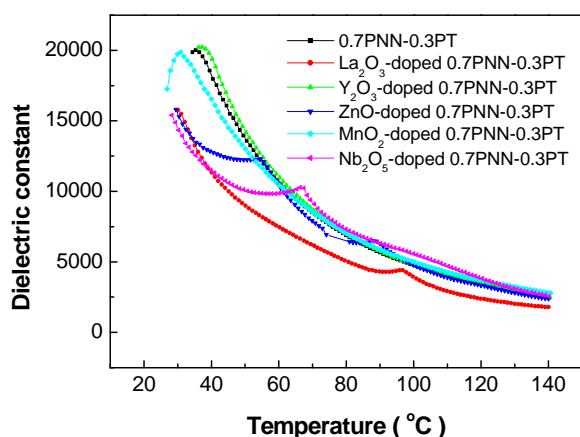
The improved densification of the sintered MnO<sub>2</sub>- and La<sub>2</sub>O<sub>3</sub>-doped 0.7PNN-0.3PT (defect) ceramics is further confirmed by SEM observation, which is shown in Figure 2. The both oxide-doped 0.7PNN-0.3PT ceramics exhibit rather homogeneous microstructure morphology, where almost no gas pores exist and exaggerated growth of abnormal grains are few. Such results conform well to the

density measurement, where the bulk density of the MnO<sub>2</sub>- and La<sub>2</sub>O<sub>3</sub>-doped 0.7PNN-0.3PT (defect) ceramics is 8.140 and 8.424 g/cm<sup>3</sup>, which reaches 96.31% and 99.82% of the theoretical density, respectively. Liquid-phase sintering mechanism inevitably takes partial effect in the densification of the oxide-doped lead-containing ferroelectric ceramics since most grains exhibit round morphology [10].

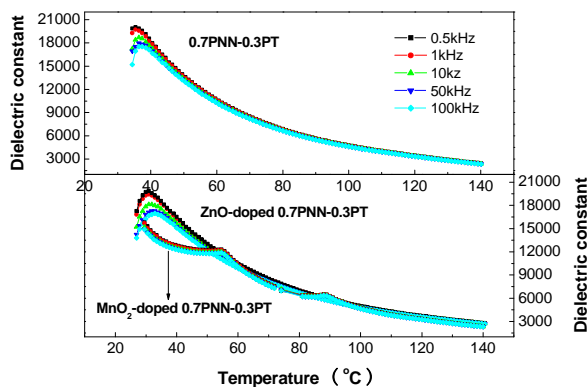
Temperature dependence of dielectric constant of the pure and oxide-doped 0.7PNN-0.3PT ceramics is shown in Figure 3. The dielectric anomalies appeared at different temperatures are generally ascribed to the ferroelectric phase transition (FPT) from rhombohedral ferroelectric phase to cubic paraelectric phase with the increase of temperature [11]. Due to the oxide doping, the temperature of dielectric maximum ( $T_m$ ) varies accompanied by



**Figure 2.** SEM images of free surface of the  $\text{MnO}_2$ - (a) and  $\text{La}_2\text{O}_3$ -doped 0.7PNN-0.3PT (defect) (b) ceramics sintered at  $1180^\circ\text{C}$  for 2 h after thermal etching at  $825^\circ\text{C}$  for 30 min



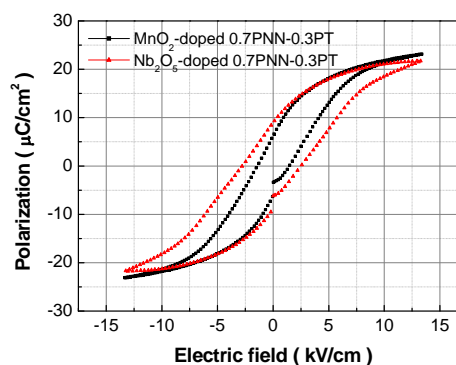
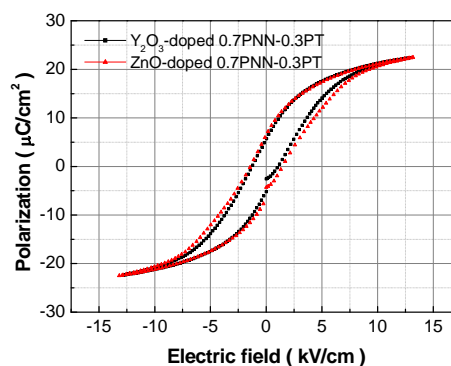
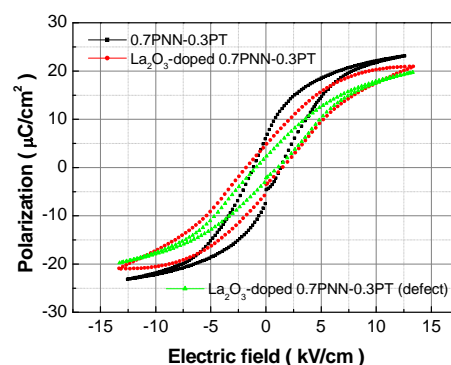
**Figure 3.** Temperature dependence of dielectric constant of the pure and oxide-doped 0.7PNN-0.3PT ceramics measured at 0.5 kHz upon heating



**Figure 4.** Temperature dependence of dielectric constant of the pure, ZnO- and  $\text{MnO}_2$ -doped 0.7PNN-0.3PT ceramics measured at several frequencies upon heating

the variation of the value of dielectric constant maximum ( $\epsilon_m$ ). The variation of the values of  $T_m$  and  $\epsilon_m$  can be attributed to the distortion of the perovskite structure, which is induced by oxide doping.

Detailed dielectric properties are shown in **Figure 4** using the pure, ZnO- and  $\text{MnO}_2$ -doped 0.7PNN-0.3PT ceramics as examples. The dielectric response peaks of



**Figure 5.** P-E dielectric hysteresis loops of the pure and doped 0.7PNN-0.3PT ceramics measured at room temperature

the both oxide-doped 0.7PNN-0.3PT ceramics are broadened. However, the dielectric peaks of the ZnO-doped 0.7PNN-0.3PT ceramics exhibit more diffused and much apparent dielectric frequency dispersion character as compared to that of the pure 0.7PNN-0.3PT ceramics. The enhanced diffused phase transition occurs mainly due to compositional fluctuation and/or substitutional disorder in the arrangement of the B sites of the perovskite structure induced by oxide doping. As a comparison, the dielectric peaks of the  $\text{MnO}_2$ -doped 0.7PNN-0.3PT ceramics are

just broadened, whereas the frequency dispersion of the dielectric behavior becomes almost vanish. The additional dielectric anomalies appearing at elevated temperature cannot be interpreted now, which maybe correlate with relaxation polarization or thermal activated conduction mechanism.

P-E dielectric hysteresis loops of the pure and oxide-doped 0.7PNN-0.3PT ceramics are shown in **Figure 5**. All the ceramics exhibit symmetric and fully saturated P-E loops, where no apparent evidence of pinning effect is observed [12]. The narrow character of the hysteresis loops accompanied by small value of coercive field ( $E_c$ ) is characteristic of rhombohedral ferroelectrics. From the fully saturated hysteresis loops, the values of the saturation polarization ( $P_s$ ), remanent polarization ( $P_r$ ) and  $E_c$  can be determined, which is shown in **Table 2**. The values of  $P_s$ ,  $P_r$  and  $E_c$  varies slightly due to the oxide doping.  $E_c$  of the  $\text{La}_2\text{O}_3$ -doped 0.7PNN-0.3PT (defect) ceramics is the smallest, being 1.23 kV/cm and  $P_r$  of the  $\text{Nb}_2\text{O}_5$ -doped 0.7PNN-0.3PT ceramics is the largest, being  $8.96 \mu\text{C}/\text{cm}^2$ . Therefore, ferroelectric properties of 0.7PNN-0.3PT can be tailored by oxide doping.

Polarization conditions and piezoelectric property of the pure and oxide-doped 0.7PNN-0.3PT ceramics are shown in **Table 3**.  $\text{Y}_2\text{O}_3$ , ZnO,  $\text{MnO}_2$  and  $\text{Nb}_2\text{O}_5$  doping increases piezoelectric constant  $d_{33}$  of the 0.7PNN-0.3PT ceramics, among which the  $\text{MnO}_2$ -doped 0.7PNN-0.3PT ceramics exhibit the largest value of  $d_{33}$ , being 191 pC/N, as compared to 65 pC/N of the pure 0.7PNN-0.3PT ceramics. Therefore, dopant doping can improve piezoelectric property of the 0.7PNN-0.3PT ceramics, which can be attributed to the variation of composition, microstructure, domain and crystal defect configuration.

#### 4. Conclusions

0.7PNN-0.3PT and 1 mol% oxide-doped 0.7PNN-0.3PT ferroelectric ceramics were prepared by the conventional

**Table 2. Ferroelectric properties of the pure and oxide-doped 0.7PNN-0.3PT ceramics measured at room temperature**

Composition	$P_s$ ( $\mu\text{C}/\text{cm}^2$ )	$P_r$ ( $\mu\text{C}/\text{cm}^2$ )	$E_c$ (kV/cm)
0.7PNN-0.3PT	23.2	6.33	1.58
$\text{La}_2\text{O}_3$ -doped 0.7PNN-0.3PT	20.9	4.70	1.68
$\text{La}_2\text{O}_3$ -doped 0.7PNN-0.3PT (defect)	19.7	2.17	1.23
$\text{Y}_2\text{O}_3$ -doped 0.7PNN-0.3PT	22.4	5.57	1.24
ZnO-doped 0.7PNN-0.3PT	22.5	6.40	1.66
$\text{MnO}_2$ -doped 0.7PNN-0.3PT	23.1	6.19	1.64
$\text{Nb}_2\text{O}_5$ -doped 0.7PNN-0.3PT	21.7	8.96	2.84

**Table 3. Polarization conditions and piezoelectric property of the pure and oxide-doped 0.7PNN-0.3PT ceramics**

Composition	Polarization electric field (kV/mm)	Leakage current (mA)	$d_{33}$ (mean value, pC/N)
0.7PNN-0.3PT	2.83	0.003	65
$\text{La}_2\text{O}_3$ -doped 0.7PNN-0.3PT	3.03	0.001-0.002	21
$\text{La}_2\text{O}_3$ -doped 0.7PNN-0.3PT (defect)	4.33	0.003	44
$\text{Y}_2\text{O}_3$ -doped 0.7PNN-0.3PT	3.14	0.002	79
ZnO-doped 0.7PNN-0.3PT	4.20	0.001	87
$\text{MnO}_2$ -doped 0.7PNN-0.3PT	3.29	0.001-0.002	191
$\text{Nb}_2\text{O}_5$ -doped 0.7PNN-0.3PT	2.08	0.003	89

ceramic processing via the columbite precursor method. Phase pure rhombohedral perovskite structure can be obtained for the ceramics sintered at  $1180^\circ\text{C}$  except the  $\text{Y}_2\text{O}_3$ -doped 0.7PNN-0.3PT ceramics. The oxide-doped 0.7PNN-0.3PT ceramics exhibit rather homogeneous microstructure and improved densification, where the relative density of the  $\text{MnO}_2$ - and  $\text{La}_2\text{O}_3$ -doped 0.7PNN-0.3PT (defect) ceramics reaches 96.31% and 99.82% of the theoretical density, respectively. Oxide doping decreases dielectric loss of the 0.7PNN-0.3PT ceramics accompanied by the variation of the value of dielectric constant and  $T_m$ , and the character of dielectric frequency dispersion. Ferroelectric and piezoelectric properties of the 0.7PNN-0.3PT ceramics can also be tailored by oxide doping.

#### 5. Acknowledgements

The authors thank the International Scientific Cooperation Project of Changzhou Scientific Bureau (Grant No. CZ 2008014) and the Natural Science Fundamental Research Project of Jiangsu Colleges and Universities (Grant No. 08KJB430001) for financial support.

#### REFERENCES

- [1] T. R. ShROUT and A. Halliyal, "Preparation of Lead-Based Ferroelectric Relaxors for Capacitors," *American Ceramic Society Bulletin*, Vol. 66, No. 4, 1987, pp. 704-711.
- [2] X. Wan, H. Xu, T. He, D. Lin and H. Luo, "Optical Properties of Tetragonal  $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})_{0.62}\text{Ti}_{0.38}\text{O}_3$  Single Crystal," *Journal of Applied Physics*, Vol. 93, No. 8,

4766-4768.

- [3] Z.-G. Ye, "Crystal Chemistry and Domain Structure of Relaxor Piezocrystals," *Current Opinion in Solid State and Materials Science*, Vol. 6, No. 1, February 2002, pp. 35-44.
- [4] T. R. Shrout, S. L. Swartz and M. J. Haun, "Dielectric Properties in the  $\text{Pb}(\text{Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3\text{-Pb}(\text{Ni}_{1/3}\text{Nb}_{2/3})\text{O}_3$  Solid-Solution System," *American Ceramic Society Bulletin*, Vol. 63, No. 6, 1984, pp. 808-810, 820.
- [5] P. Xiang, N. Zhong and X. Dong, "Single-Calcination Synthesis of Pyrochlore-Free  $\text{Pb}(\text{Ni}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$  Using a Coating Method," *Solid State Communications*, Vol. 127, No. 11, September 2003, pp. 699-701.
- [6] C. Lei, K. Chen and X. Zhang, "Dielectric and Ferroelectric Properties of  $\text{Pb}(\text{Ni}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$  Ferroelectric Ceramic near the Morphotropic Phase Boundary," *Materials Letters*, Vol. 54, No. 1, May 2002, pp. 8-12.
- [7] B. Fang, R. Sun, Y. Shan, K. Tezuka and H. Imoto, "On the Feasibility of Synthesizing Complex Perovskite Ferroelectric Ceramics via a B-Site Oxide Mixing Route," *Journal of Materials Science*, Vol. 42, No. 22, November 2007, pp. 9227-9233.
- [8] B. Fang, C. Ding, Q. Du and L. Zhou, "Effect of Oxide Doping on Electrical Properties of Tetragonal Perovskite  $\text{Pb}(\text{Ni}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$  Ferroelectric Ceramics," *Ferroelectrics*, Vol. 393, No. 1, 2009, pp. 94-105.
- [9] B. Fang, Y. Shan, K. Tezuka and H. Imoto, "High Curie temperature  $\text{Pb}(\text{Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3$ -based ferroelectrics:  $0.40\text{Pb}(\text{Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3\text{-}0.34\text{PbZrO}_3\text{-}0.26\text{PbTiO}_3$ ," *Physica Status Solidi A*, Vol. 202, No. 3, 2005, pp. 481-489.
- [10] S.-J. Park, H.-Y. Park, K.-H. Cho, S. Nahm, H.-G. Lee, D.-H. Kim and B.-H. Choi, "Effect of CuO on the Sintering Temperature and Piezoelectric Properties of Lead-Free  $0.95(\text{Na}_{0.5}\text{K}_{0.5})\text{NbO}_3\text{-}0.05\text{CaTiO}_3$  Ceramics," *Materials Research Bulletin*, Vol. 43, 2008, pp. 3580-3586.
- [11] B.-G. Kim, S.-M. Cho, T.-Y. Kim and H.-M. Jang, "Giant Dielectric Permittivity Observed in Pb-Based Perovskite Ferroelectrics," *Physical Review Letters*, Vol. 86, No. 15, April 2001, pp. 3404-3406.
- [12] X. Wen, C. Feng, L. Chen and S. Huang, "Dielectric Tunability and Imprint Effect in  $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$  Ceramics," *Ceramics International*, Vol. 33, No. 5, July 2007, pp. 815-819.