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Pyroelectric and piezoelectric properties of yttrium-doped $0.15[Pb(Ni_{1/3}Nb_{2/3})O_3]–0.85[Pb(Zr_{1/2}Ti_{1/2})O_3]$ ceramics

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Abstract

We have studied the dielectric, pyroelectric and piezoelectric properties of $0.15[Pb(Ni_{1/3}Nb_{2/3})O_3]–0.85[Pb(Zr_{1/2}Ti_{1/2})O_3] + Y_2O_3$ (0, 0.5, 1.0, 3.0, 5.0 mol%) ceramic systems. For the sample doped with 1.0 mol% of Y^{3+} and higher, the diffraction peaks corresponding to (1 0 0) and (2 0 0) planes have been widened and are getting rather split. The dielectric constant increases with increasing Y^{3+}, which is related to the formation of extra phase. A well saturated *P*–*E* hysteresis loop is obtained for 0.15PNN–0.85PZT ceramic doped with 1.0 mol% Y^{3+}, and the values of $2P_r$ and $2E_c$ are reached 21 μC/cm^2 and 7.7 kV/cm, respectively. Good pyroelectric properties have been obtained for the 1.0 mol% Y^{3+}-doped sample with large figures of merit of $F_V = 0.018\,m^2/C$ and $F_D = 1.47 \times 10^{-5}\,Pa^{-1/2}$ at room temperature.

Keywords: C. Dielectric properties; C. Piezoelectric properties; Pyroelectric properties; Yttrium-doped lead nickel niobate titanate zirconia

1. Introduction

Ferroelectric ceramics based on $Pb(Zr,Ti)O_3$ (PZT) have been intensively studied for a large field of applications. A large number of researches have been carried out on ternary solid solution systems such as, $A(B_1B_2)O_3$-PZT type materials [1–3]. Solid solution system can be easily processed at relatively low sintering temperature, in polycrystalline form, with excellent physical properties. Lead nickel niobate [$Pb(Ni_{1/3}Nb_{2/3})O_3$, PNN] was one of the first known relaxor ferroelectrics reported by Smolenskii and Agranovskaya [4,5]. PNN–PZT systems were useful for multilayer ceramic (MLC) because PNN had a strong effect on lowering the Curie temperature of PZT. The addition of PNN helps in extending the compositional range for preparing ceramics with perovskite structure [6,7].

In order to choose suitable materials whose electric properties can reach the high values, it was necessary to investigate the dielectric, piezoelectric and pyroelectric properties of the PNN–PZT ternary system modified with other element substitution. Whatmore et al. [8,9] investigated the dielectric and piezoelectric properties of the modified PNN–PZT and found that piezoelectric activity and temperature stability could be improved. However, no detailed investigation had been made on the relationship between the pyroelectric and piezoelectric properties of the PNN–PZT system modified with Y^{3+} substitution.

In this work, the ternary compound system 0.15 $[Pb(Ni_{1/3}Nb_{2/3})O_3]–0.85[Pb(Zr_{1/2}Ti_{1/2})O_3]$ (PNN–PZT) ceramics were chosen, and modified with yttrium to investigate systematically dielectric, piezoelectric and pyroelectric properties.

2. Experimental procedure

The powder made by columbite precursor process was prepared by mixing of high purity NiO, Nb_2O_5, ZrO_2 and TiO_2 powders followed by calcinations at 1100 °C for 4 h. The more detail ceramic fabrication process using Coulmbite method was described in our previous paper [10].

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The calcined PNN–PZT powder was doped with Y_2O_3 (0, 0.5, 1.0, 3.0, 5.0 mol%). They were pressed into disk shape of 18 mm in diameter at the pressure of 100 MPa. The specimens were sintered at 1000 °C for 2 h in a covered alumina crucible. To prevent PbO evaporation from the pellets, $PbZrO_3$ was used as the bedding powder. The sintered pellets were polished into 0.8 mm in thickness and deposited platinum on the both surface sides in order to use electrode. Dielectric constant and loss were measured by impedance analyzer (HP4192). The ferroelectric properties were obtained using a modified Sawyer–Tower circuit at 60 Hz. For the piezoelectric measurement, samples were poled in a silicon oil bath at 120 °C with the dc electric field of 3 kV/mm. The piezoelectric properties of samples were measured by the resonance–antiresonance method using an impedance analyzer (HP4194A). The electric field induced strain were observed by the Michelson interferometer using He–Ne laser. The pyroelectric properties were tested using a digital electrometer interfaced with computer at a constant heating rate of 2 °C/min.

3. Results and discussion

Fig. 1 shows the X-ray diffraction patterns of the 0.15PNN–0.85PZT ceramics doped with different Y^{3+} contents. The XRD patterns revealed a single perovskite phase without second phase. For the undoped and 0.5 mol% doped samples, all of the diffraction peaks were observed corresponding to those of rhombohedral structure. For the sample doped with 1.0 mol% of Y^{3+} and higher, it can be seen that the diffraction peaks corresponding to (2 0 0) plane were split (0 0 2) and (2 0 0) planes clearly and had been widened with getting rather split. Furthermore, as the results of our lattice constant measurement (not shown in figure, see Table 1), the substitution of Y^{3+} for Pb^{2+} site has given rise to the enhancement of *c*/*a* ratio. So, the samples doped with 1.0 mol% Y^{3+} and higher, the main PNN–PZT phase was changed from rhombohedral to tetragonal structure. For the rhombohedral region, the substitution of Y^{3+} caused the reduction of lattice constant, but in the tetragonal region, the addition of Y^{3+} has given rise into the increase of the tetragonality ratio lineally by *c*/*a*. This can be understood based on the knowledge that Y^{3+} ionic radius (0.99 Å) is smaller than that of the Pb^{2+} (1.49 Å) in the PNN–PZT perovskite structure and possibly rather too difficult to be substituted for the Ni and Nb site. Beitollahi and Khezri [11] were also observed the limited solid solubility of Y^{3+} in PZT solutions.

Fig. 2 shows the variation of room temperature dielectric constant as a function of Y^{3+} contents. It was expected that the Curie temperature of the PNN–PZT modified with yttrium, can be measured at 322 °C. The observed variation for the dielectric constant and loss with doping level of Y^{3+} was rather complex. For the sample doped with 0.5 mol% Y^{3+}, there was initially a down in the magnitude of dielectric constant at the room temperature. This could be possibly related to the observed lower density of this sample (Table 1). However, it should be added other defect parameters, such as oxygen vacancies, antisite defects, domain wall mobility, and internal stresses have also seen to have a marked effect on the magnitude of the dielectric loss. By increasing doping level to the 1.0 mol% Y^{3+}, the dielectric constant was increased. This could be related to the formation of extra phases and possibly the higher density of this sample was compared to that of 0.5 mol% Y^{3+}-doped sample. However, for the sample doped with higher than 1.0 mol% Y^{3+}, the dielectric constant was maintained constant.

Fig. 3(a) shows the variation of polarization and strain of samples as a function of electric field with different Y^{3+} contents. The shape of hysteresis loops were changed with increasing Y^{3+}. It was well known that the polarization vector of the rhombohedral phase was (1 1 1) and has eight directions for dipole moment reorientation. Similarly the

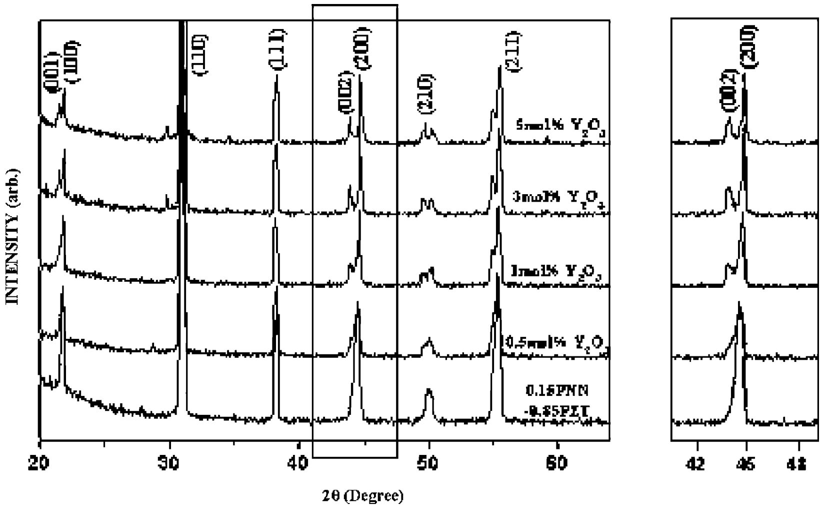
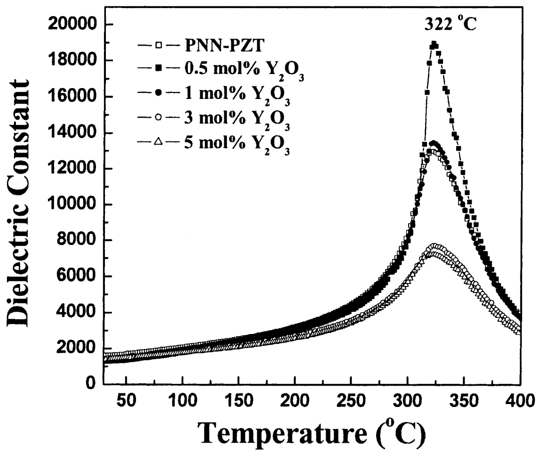


Fig. 1. XRD patterns of the 0.15PNN–0.85PZT ceramics at various Y^{3+} doping contents.

Table 1
Dielectric, piezoelectric and pyroelectric of Y^{3+}-doped 0.15PNN–0.85PZT ceramics

Y_2O_3 (mol.%)	Dielectric properties				Piezoelectric properties				Pyroelectric properties		Figures of merit	
									Pyro coefficient			
	Density (g/cm^3)	Strain (10^{-3})	ε_r at room temperature	$\tan\delta$ at room temperature	P_r (μC/cm^2)	E_c (kV/cm)	k_p (%)	Q_m	Room temperature (μA/m^2 K)	Maximum value (μA/m^2 K)	F_v (m^2/C^{-1})	F_D (10^{-5} Pa$^{-1/2}$)
PNN–PZT	7.53	0.51	1616	0.030	20	8	47.50	128	761	29646	0.019	1.75
0.5	7.38	1.53	1273	0.034	13	9.6	53.16	88	343	12435	0.011	0.86
1.0	7.6	0.89	1422	0.035	21	7.7	50.86	136	452	5008	0.018	1.47
3.0	7.46	0.52	1421	0.033	13	9.3	44.97	163	530	21581	0.004	0.37
5.0	7.44	0.49	1390	0.032	9.8	9.7	31.25	151	228	16774	0.008	0.70



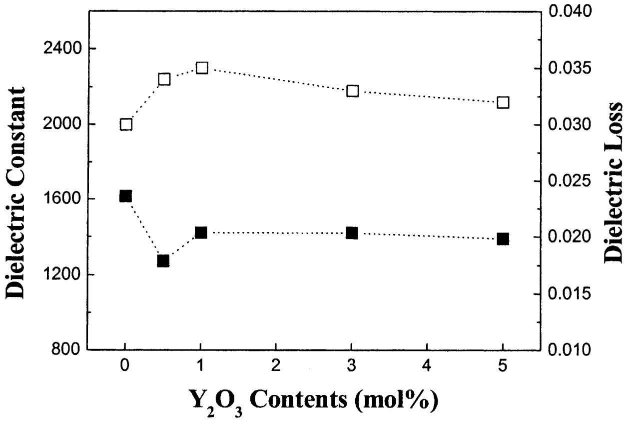


Fig. 2. Dielectric constant and loss of 0.15PNN–0.85PZT ceramics at various Y^{3+} doping contents.

polarization vector (0 0 1) for the tetragonal phase and had six directions for the dipole moment reorientation. Because the rhombohedral and tetragonal phases were coexisted at the 1.0 mol% Y^{3+} content, there were fourteen directions for dipole moment reorientation. Thus the remanent polarization at the doped with 1.0 mol% Y^{3+} was higher than that of the rhombohedral or tetragonal phases. A well saturated *P–E* hysteresis loop was confirmed for 0.15PNN–0.85PZT ceramics with 1.0 mol% Y^{3+}, and the values of $2P_r$ and $2E_c$ were reached 21 μC/cm^2, and 7.7 kV/cm, respectively.

Fig. 3(b) shows the strain hysteresis parallel to the electric field for the Y^{3+}-doped PNN–PZT ceramics in the room temperature. In a cycle with small maximum electric field, the field induced strain curve appeared nearly linear, and can be called 'inverse piezoelectric effect'. However, with the increase of the maximum electric field, the hysteresis loop became larger, and finally transforms to the symmetric butterfly shape when the electric field exceeds a coercive field. This was caused by the change of polarity in ferroelectric domains under applied electric field, including a different state of polarization. A well saturated strain–electric field hysteresis loop was confirmed for 0.15PNN–0.85PZT ceramics

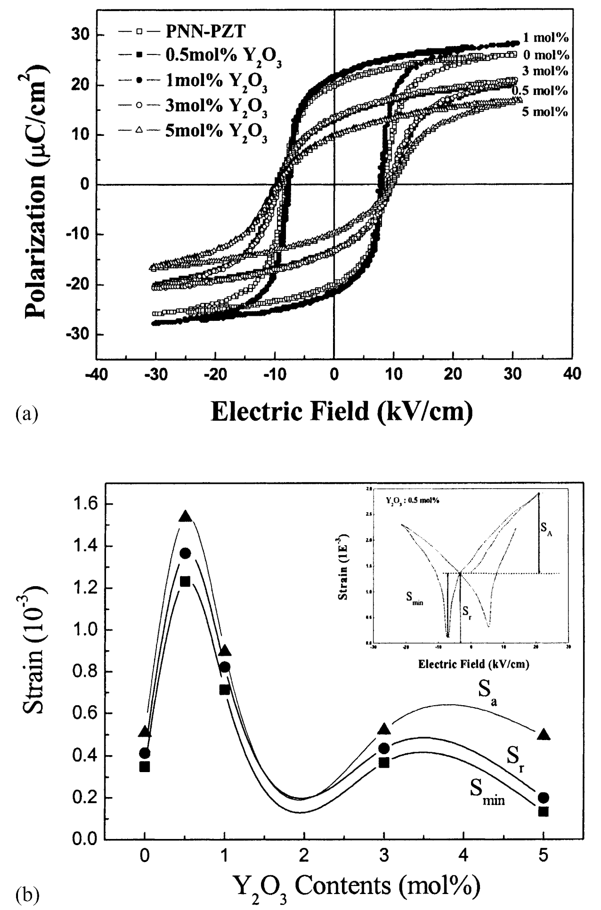


Fig. 3. The variation of polarization and strain of 0.15PNN–0.85PZT ceramics as a function of electric field at various Y^{3+} doping contents.

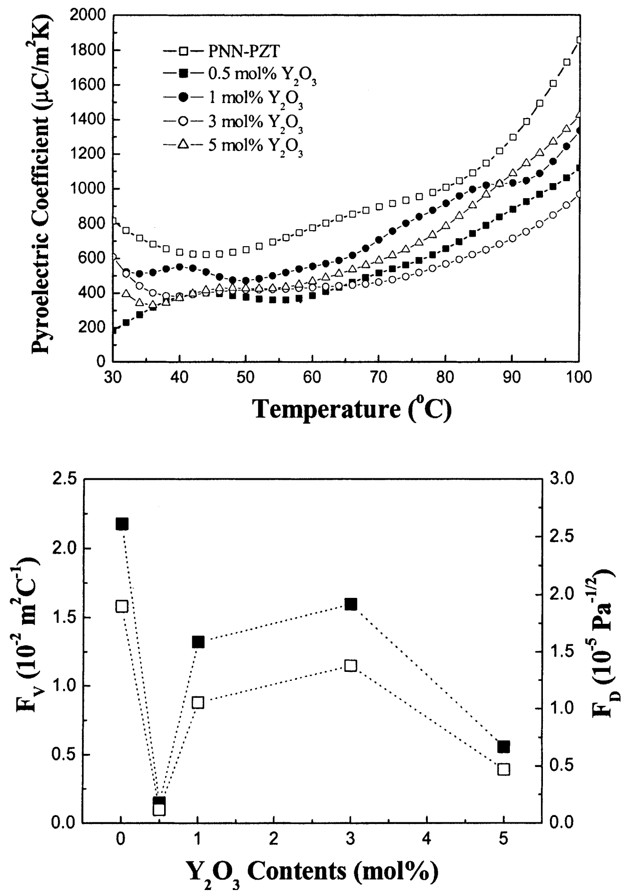


Fig. 4. The variation of pyroelectric coefficient and figure of merit of 0.15PNN–0.85PZT ceramics at room temperature at various Y^{3+} doping contents.

with 1.0 mol% Y^{3+}, and the value of maximum strain was reached 1.5×10^{-3} at the applied electric field of 20 kV/cm.

Fig. 4 shows room temperature pyroelectric coefficients and figures of merit for the PNN–PZT samples doped with different Y^{3+}. The samples were poled by dc electric field of 3 kV/mm in the silicon oil bath temperature of 120 °C before measurement. The pyroelectric behavior was evaluated in the ferroelectric state to determine the pyroelectric coefficient (p) and the figures of merit (F_D, F_V) at room temperature. Table 1 summarized measured physical values for Y^{3+}-doped PNN–PZT ceramics. A suitable material for pyroelectric applications should have a large pyroelectric coefficient, a relative small dielectric constant, low dielectric losses, and large figures of merit. From the examined compositions, 1.0 mol% Y^{3+}-doped sample was chosen to study practical applications as pyroelectric sensors. A large value of figures of merit was confirmed for 0.15PNN–0.85PZT ceramics with undoped and 1.0 mol% Y^{3+}, and the values of maximum pyroelectric coefficient and figures of merit (F_V and F_D) were obtained to 761, 452 μC/m² K and 0.019, 0.018 m²/C and 1.75×10^{-5}, 1.47×10^{-5} $Pa^{-1/2}$ at room temperature, respectively. Note that we could select the 1.0 mol% doped PNN–PZT ceramic as suitable materials for pyroelectric sensors because of their good figures of merit result.

4. Conclusions

We have demonstrated the dielectric, piezoelectric and pyroelectric properties of $0.15[Pb(Ni_{1/3}Nb_{2/3})O_3]$–$0.85[Pb(Zr_{1/2}Ti_{1/2})O_3]$ ceramics doped with Y^{3+}. The substitution of Y^{3+} for Pb^{2+} site has given rise to the enhancement of c/a ratio and the main PNN–PZT phase was changed from rhombohedral to tetragonal structure. A well saturated P–E hysteresis loop was confirmed for 0.15PNN–0.85PZT ceramics with 1.0 mol% Y^{3+}, and the values of $2P_r$ and $2E_c$ were reached 21 μC/cm², and 7.7 kV/cm, respectively. For the 0.15PNN–0.85PZT ceramics with 1.0 mol% Y^{3+}, the value of maximum strain was reached 1.5×10^{-3} at the applied electric field of 20 kV/cm. For the 0.15PNN–0.85PZT ceramics with undoped and 1.0 mol% Y^{3+}, the values of maximum pyroelectric coefficient and figures of merit (F_V and F_D) were obtained to 761, 452 μC/m² K, $F_V = 0.019$, 0.018 m²/C and $F_D = 1.75 \times 10^{-5}$, 1.47×10^{-5} $Pa^{-1/2}$ at room temperature, respectively.

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