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Nonlinear piezoelectric coefficient of $Pb(Ni,Nb)O_3$–$Pb(Zn,Nb)O_3$–$PbZrO_3$–$PbTiO_3$ system ceramics

K. Ishii*, S. Tashiro, K. Nagata

Department of Materials Science and Engineering, The National Defense Academy, 1-10-20, Hashirimizu, Yokosuka 239-8686, Japan

Abstract

In order to obtain the piezoelectric ceramics with smaller nonlinear piezoelectricity, $Pb(Ni,Nb)O_3$–$Pb(Zn,Nb)O_3$–$PbTiO_3$–$PbZrO_3$ system ceramics having large piezoelectric *d*-constants were prepared using the conventional method with the solid reaction by calcination. The nonlinear piezoelectric coefficients at the MPB compositions decreased below a one-third of value compared with $Pb(Sn,Nb)O_3$–$PbTiO_3$–$PbZrO_3$ system ceramics which we have ever been studying about the nonlinearity. These small nonlinearity coefficients are discussed in the relationship with the large piezoelectric *d*-constants.

Keywords: Actuator; Grain size; Nonlinear piezoelectricity; Piezoelectric property; PZT

1. Introduction

Nonlinear phenomena which often appear in piezoelectric ceramics for high-power use have had serious problems with practical applications. The material development for the smaller nonlinearity is the most effective way to control the appearance of the nonlinear phenomena. In order to find out which materials have smaller nonlinearity, the influences of the composition, the grain size and the poling condition on the nonlinearity have been investigated by using $Pb(Sn,Nb)O_3$–$PbTiO_3$–$PbZrO_3$ system ceramics (PZT–PSN).[1–3] Table 1 shows the results of PZT–PSN system including 5 mol% $Pb(Sn_{1/2}Nb_{1/2})O_3$ as the third component. For the quantitative estimation of the nonlinear piezoelectricity, a nonlinear piezoelectric coefficient of the third higher term as a material constant, ξ_{D31}, was utilized. The ξ_{D31} expressed by Eq. (1) indicates the relationship between electric flex density on the upper and lower electrodes, D_3, and a third higher harmonic field generated in a rectangular thin plate sample poled in the thickness direction.[4]

$$E_3 = -\frac{g_{31}}{s_{11}^D} S_1 + \beta_{33}^S D_3 + \gamma_{D31} D_3^2 + \xi_{D31} D_3^3 \quad (1)$$

Here, the γ_{D31} is the nonlinear piezoelectric coefficient of the second higher term. The E_3 and S_1 are the electric field in the thickness direction and the stress in the transverse direction, respectively. The g_{31}, β_{33}^S and s_{11}^D are the piezoelectric *g*-constant, inverse permittivity and compliance, respectively. As shown in Table 1, the various dependences of ξ_{D31} have been made clear. The minimum ξ_{D31} value which we obtained in PZT–PSN system ceramics was about 3×10^{12} m^5V/C^3.

On the other hand, the ξ_{D31} has a negative dependence on d_{31} as shown in Table 1, except the acceptor-additive dependence. The d_{31} values of $Pb(Ni,Nb)O_3$–$Pb(Zn,Nb)O_3$–$PbTiO_3$–$PbZrO_3$ system ceramics (PZT–PZN–PNN) have been reported to be larger than those of PZT–PSN system ceramics.[5,6] Hence, it is expected that the nonlinear piezoelectricity in PZT–PZN–PNN system ceramics are smaller than that in PZT–PSN system ceramics. In this study, PZT–PZN–PNN system ceramics were prepared, and their ξ_{D31} values were compared with those of PZT–PSN system ceramics.

2. Experimental

The compositions of PZT–PZN–PNN system ceramics are expressed by $0.6Pb(Zr_\alpha Ti_{1-\alpha})O_3 + 0.4\{(1-\beta)Pb(Zn_{1/3}Nb_{2/3}) + \beta Pb(Ni_{1/3}Nb_{2/3})\} + 0.015\ MnCO_3$. The samples

* Corresponding author.

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with Zr/(Zr + Ti) ratio, α, of 32–49 mol% and with PNN/(PZN + PNN) ratio, β, of 26–100 mol% were prepared as listed in Table 2. These samples are represented as PNN–100β/100α.

The compositions of PZT–PSN system ceramics are expressed by $(1-\gamma)Pb(Zr_{\delta}Ti_{1-\delta})O_3-\gamma Pb(Sn_{1/2}Nb_{1/2})O_3+0.015MnO$. The Zr/(Zr + Ti) ratio, δ, ranged from 49 to 53%. The prepared samples with PSN/(PSN + PZT) ratio, γ, of 4, 5 and 6 mol% were represented by PSN-4/100δ, PSN-5/100 δ and PSN-6/100 δ, respectively. All the samples were prepared using a conventional method. Raw materials with small particle sizes under 1 μm were used, and the calcined powders were mixed and ground by a ball-mill in ethanol. The calcining and sintering temperatures of PZT–PZN–PNN system ceramics and PZT–PSN system ceramics are 870 and 1240, 850 and 1270 °C, respectively. The densities of all the prepared samples exceeded to 97% of the theoretical densities. All the prepared samples were confirmed not to include any pyrochlore phases by an X-ray diffraction method.

The configurations of the samples are a rectangular thin plate of the size 31×4×1 mm and a flat disk of the size ϕ12×1 mm. A pair of silver electrodes were fired on the upper and the lower surface of the samples, and were poled under an electric field of 3 kV/mm for 10 min in the silicone oil bath kept at 120 °C. Fig. 1 shows the temperature dependence of the relative permittivity in the samples with the compositions near to MPB.

Table 1
The various factors exerting on ξ_{D31} and d_{31} in PSN–5/100δ[1–3]

Change of states	Change of ξ_{D31} and d_{31}	
	ξ_{D31}	d_{31}
Increase of poling field	down	up
Increase of temperature	down	up
Zr/Ti ratio→closer to MPB composition	down	up
Increase of acceptor	down	down
Increase of grain size	down	up

Table 2
PZT–PZN–PNN sample list

PNN/(PZN + PNN) ratio (%)	26	60	100
			32
			34
		35	35
			36
			37
		38	38
Zr/(Zr + Ti) ratio (%)		40	40
		41	
		42	42
	44	44	
	45		
	47		
	49		

While the Curie points, T_c, of PZT–PSN system ceramics are larger than 300 °C, these of PZT–PZN–PNN system ceramics are 190–240 °C which are low compared with PZT–PSN system ceramics. For these low Curie points in PZT–PZN–PNN, we kept to applying the poling field until cooled down to 60 °C after the poling at 120 °C in PZT–PZN–PNN system ceramics.

For the measurement of ξ_{D31} values, the samples were driven at around the fundamental resonance frequency of the length extensional 1/2 λ mode by a signal generator (HP, 3325B) and a power amplifier (NF, 4020) in the constant-current circuit as shown in Fig. 2. The waveforms of the sample current and the sample voltage were accumulated and stored into a digital storage scope (Lecroy, LT344) simultaneously. Using the

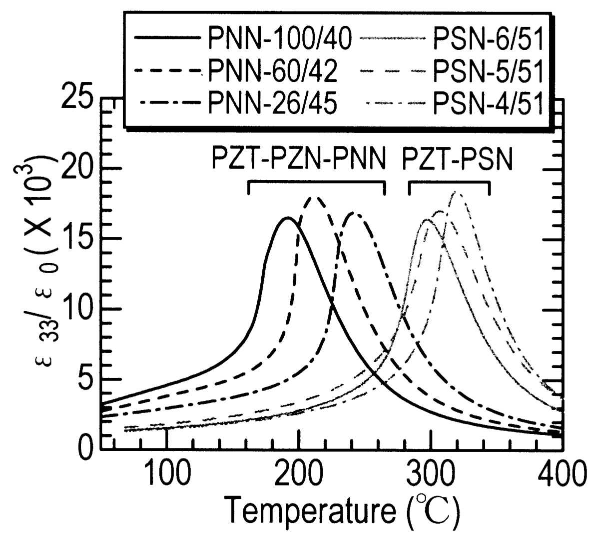

Fig. 1. Temperature dependence of the relative permittivity in PZT–PZN–PNN and PZT–PSN system ceramics with the compositions near MPB.

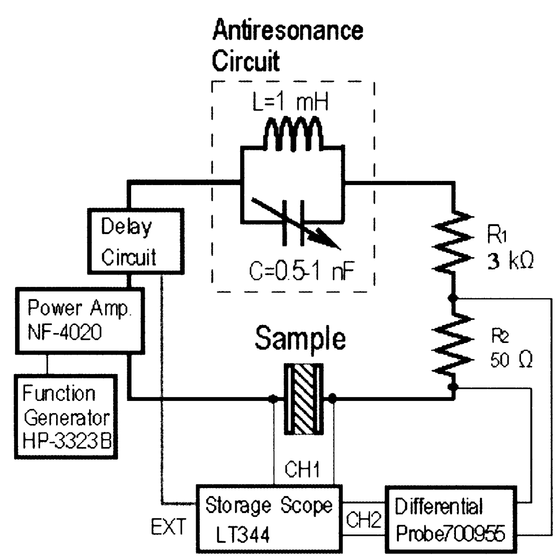

Fig. 2. Measuring circuit for the nonlinear coefficient.

Fourier-transform function in LT344, the magnitudes of the third harmonic voltage were computed from the accumulated waveforms of the voltage. The details of the measurement method are described in previous reports.[4] The electromechanical coupling constants, k_p and k_{31}, were measured by the resonance–antiresonance method using an LF impedance analyzer (HP, 4192A), and piezoelectric d_{31} constant was calculated from k_{31}.

3. Results and discussion

As shown in Table 1, it has already made clear that the MPB composition of Zr/(Zr + Ti) ratio gives us the minimum ξ_{D31} in PSN-5/100δ. This reason is considered to be that the MPB compositions are easily poled because of their small crystal anisotropy since the easy poling decreases the remaining domain wall density due to the non-oriented domains. The nonlinear piezoelectricity are believed to be caused by nonlinear motions of the residual domain walls.[2] The Zr/(Zr + Ti) ratios giving the MPB compositions were investigated in PZT–PZN–PNN system ceramics. Figs. 3 and 4 show the relationships between Zr/(Zr + Ti) ratio and k_p in PZT–PZN–PNN and PZT–PSN system ceramics. The k_p has a maximum value when the Zr/(Zr + Ti) ratios are 45, 42 and 40 mol% in PNN-26/100 α, PNN-60/100 α and PNN-100/100 α, respectively. In PSN-4/100 δ, PSN-5/100 δ and PSN-6/100 δ, the maximum k_p values are always observed at the Zr/(Zr + Ti) ratios of 51 mol%. Hence, these Zr/(Zr + Ti) ratios are regarded as the MPB compositions of each material. The measurements for deriving ξ_{D31} value were done using these samples of the MPB compositions (PNN-26/45, PNN-60/42, PNN-100/40, PSN-4/51, PSN-5/51, PSN-6/51), since the minimum ξ_{D31} is expected.

Fig. 5 represents the relationship between ξ_{D31} and d_{31} in the six kinds of the samples. The data dispersion among the samples with the same composition will be mainly due to the cutting and grinding accuracy of each sample. While ξ_{D31} values of PZT–PSN system ceramics are 3.2–4.4×10^{12} (m^5V/C^3), those of PZT–PZN–PNN system ceramics are 1.0–1.2×10^{12} (m^5V/C^3). Fig. 5 indicates that theξ_{D31} values of PZT–PZN–PNN system ceramics are about one-third compared with PZT–PSN system ceramics.

The driving conditions for the occurrence of current jump phenomena, which is one of the typical nonlinear phenomena in piezoelectric ceramics, are strongly influenced by ξ_{D31} value.[7,8] Since the minimum driving voltage and the minimum input power which can induce the current jump are proportional to $|\xi_{D31}|^{-0.5}$ and $|\xi_{D31}|^{-1}$, the PZT–PZN–PNN system ceramics are stable in high-power driving without the current jumping, even when the input power is three times higher than the upper limit for the stable driving in the PZT–PSN system ceramics.

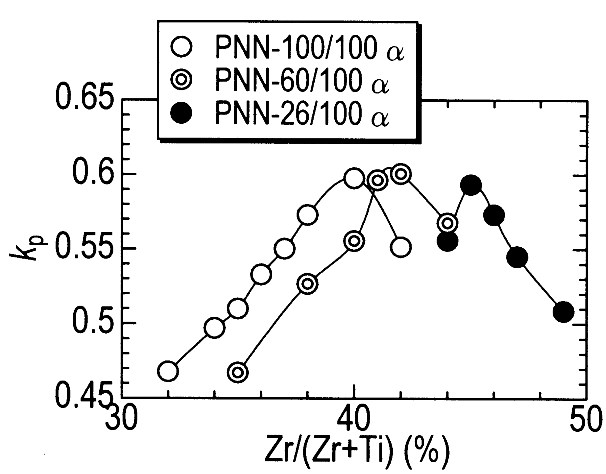

Fig. 3. Influence of Zr/(Zr + Ti) ratio on k_p in PZT–PZN–PNN system ceramics.

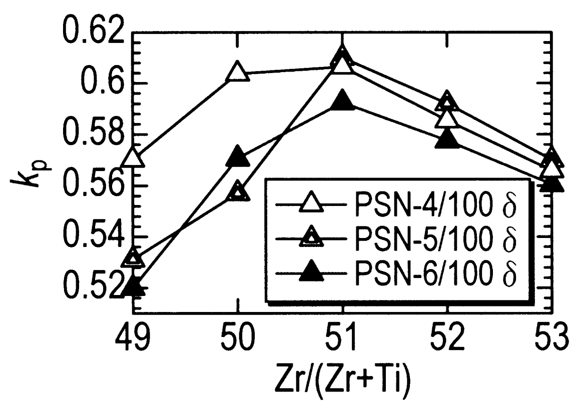

Fig. 4. Influence of Zr/(Zr + Ti) ratio on k_p in PZT–PSN system ceramics.

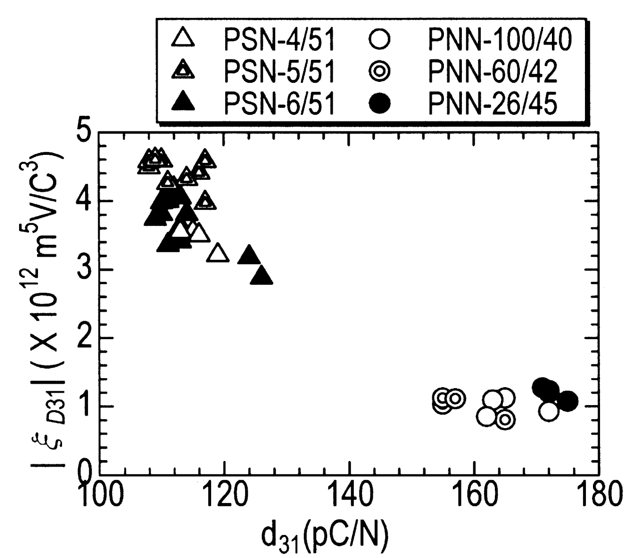

Fig. 5. Relationship between nonlinear piezoelectric coefficient ξ_{D31} and piezoelectric d_{31} constant.

Table 3
Averaged ξ_{D31}, d_{31} and grain sizes in each sample

	PZT–PSN	PNN–26/45	PNN–60/42	PNN–100/40
$\|\xi D31\|(\times 10^{12}\ m^5V/C)$	3.2–4.4	1.1	1.2	0.98
d_{31} (pC/N)	111–120	171	156	165
Grain size ($\times 10^{-6}$ m)	1.4–1.5	3.2	2.7	2.3

The ξ_{D31}, d_{31} constants and average grain sizes of each sample are summarized in Table 3. The d_{31} values of PZT–PZN–PNN system ceramics are about 50% larger than the values of PZT–PZN–PNN system ceramics. In addition to this fact, the average grain sizes of PZT–PZN–PNN system ceramics are about twice larger compared with those of PZT–PZN–PNN system ceramics. These tendencies in PZT–PZN–PNN system ceramics to PZT–PSN system ceramics correspond to the tendencies of ξ_{D31} as shown in Table 1. That is, the present results are compatible with those of the studies for the nonlinear piezoelectricity in PSN-5/51.[1–3] However, the dependences of ξ_{D31} on averaged grain size, d_{31} and PNN/(PZN + PNN) ratio were not found clearly in the samples of PZT–PZN–PNN system ceramics.

Although there is a paper in which the d_{31} value increased with increasing of PNN content in the MPB compositions,[5] such tendency is not found in the present samples of PZT–PZN–PNN system ceramics. Furthermore, d_{31} shown in Fig. 5 is a little smaller than the values previously reported (~200 pN/C).[5] These facts suggest that the sample preparation of this study has not yet been optimized enough. Since ξ_{D31} often decreases with the optimization for the sample preparation, it is expected that the real minimum value in PZT–PZN–PNN system ceramics is smaller than the reported values in this paper.

4. Conclusions

1. PZT–PZN–PNN system ceramics having smaller nonlinearity were prepared using a conventional method. The minimum value of nonlinear piezoelectric coefficient, ξ_{D31}, was a one-third of value compared with PZT–PSN system ceramics.
2. A negative dependence of ξ_{D31} on d_{31} was confirmed between PZT–PZN–PNN and PZT–PSN system ceramics with MPB compositions.

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