Relaxor behavior of piezoelectric Pb(Yb$_{1/2}$Nb$_{1/2}$)O$_3$-PbTiO$_3$ ceramics sintered at low temperature

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Abstract A (100-x)Pb(Yb$_{1/2}$Nb$_{1/2}$)O$_3$-xPbTiO$_3$ [PYN-PTx] solid solution system with 49.0≤×≤51.0 was prepared using a conventional ceramics process and sintered at low temperature. When excess PbO was added into the PYN-PTx system, all samples were sintered at temperatures as low as 800°C with good dielectric and piezoelectric properties. It is suggested that a liquid phase with excess PbO was formed during the sintering and improved the densification of PYN-PTx ceramics at low temperatures. For the PYN-PTx binary system, it was found that the temperature dependence of the relative permittivity follows a Curie–Weiss Law above the deviation temperature (T$_D$) at high temperatures. Good piezoelectric properties of d_{33}= 510 pC/N, ε_r=2800 at RT, k_p=0.57, and k_t=0.42 with T$_c$= 373°C were obtained for PYN-PT49.5 ceramics sintered at 800°C for 8 h.

Keywords Piezoelectric Properties · Pb(Yb$_{1/2}$Nb$_{1/2}$)O$_3$-PbTiO$_3$ · Relaxor

1 Introduction

Recently, low temperature co-fired ceramic (LTCC) multi-layer devices, composed of alternating piezoelectric ceramics and internal metallic electrode layers, have been extensively investigated for the miniaturization of electronic components[1, 2]. LTCC multilayer devices consist of alternating piezoelectric ceramics and internal metallic electrode layers[1]. Ag has been widely used as a metallic electrode, because of its high conductivity and low cost. However, the melting temperature of Ag is low, about 961°C, whereas the sintering temperature of piezoelectric ceramics is generally above 1000°C. Therefore, for the fabrication of multilayer devices, it is necessary to develop piezoelectric ceramics having low sintering temperatures, which can be co-fired with Ag.

Pb-based perovskite compounds, expressed as Pb(B$_1$,B$_2$) O$_3$, have received considerable attention in the recent years because of their potential for application to many electronic ceramic devices such as actuators, sensors, capacitors, and transducers[3, 4]. Furthermore, there has been much interest in various phase transitions and crystal structures of mixed compositions of the ferroelectrics because of their high dielectric constants, high coupling coefficients, and high piezoelectric coefficients[5]. The Pb(Yb$_{1/2}$Nb$_{1/2}$)O$_3$-PbTiO$_3$ [PYN-PT] binary system is a good candidate for use in multilayer actuator (MLA) applications such as fuel injection systems where both large strain and high operating temperatures are required[6].

The piezoelectric properties and phase transitions of pseudo-binary solid solutions of PYN and PT have been investigated by X-ray powder diffraction analyses and dielectric measurements[7, 8]. It has been revealed that a PYN-PT(50:50) binary system as MPB sintered at 950°C exhibits good piezoelectric properties with the following values: T_c=350°C, ε_r=1650 at RT, k_p=52%, and k_t=43% [8]. Duran et al. reported the piezoelectric properties with d_{33}=508 pC/N and ε_r=1900 for 0.5PYN-0.5PT ceramics sintered at 950°C after conducting cold isostatic press (CIP)

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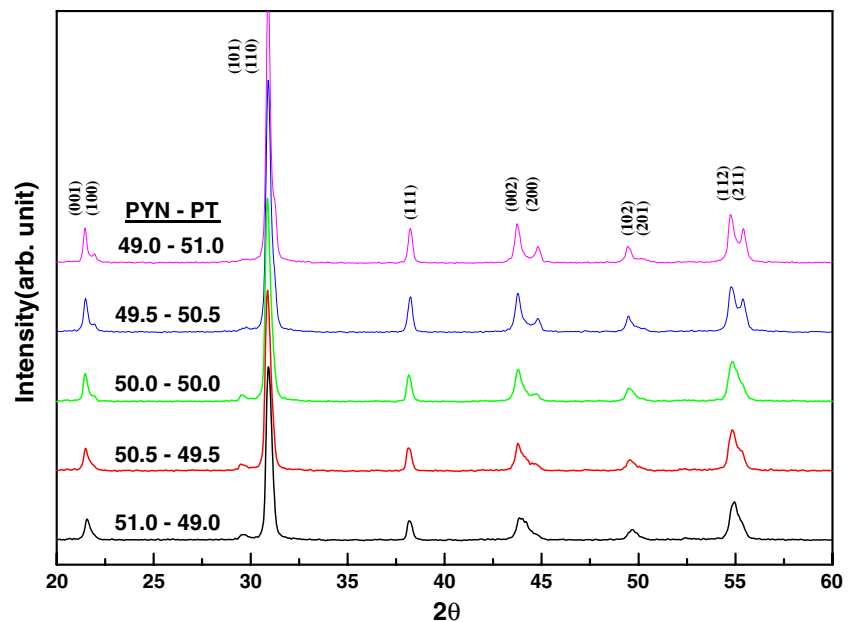University Park,
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[9]. Kim also reported good dielectric and piezoelectric properties for PYN-PT(50:50); i.e., d_{33}=300 pC/N and ε_r= 2400 at RT with T_c=385°C. However, the sintering was conducted at 1050°C with 2 wt% excess PbO[10].

Despite its interesting characteristics, few studies have been conducted on the piezoelectric properties of the PYN-PT binary system at low temperatures for application to multilayer devices. Since previous studies have introduced the possibility of developing new piezoelectric ceramics sinterable at fairly low temperatures (below 900°C), it could be used for LTCC application. In this work, Pb_3O_4 as a sintering aid was added to PYN-PT to further reduce the sintering temperature of PYN-PT having small particle size and the effect of Pb_3O_4 addition on the piezoelectric properties was studied. Furthermore, more detailed morphotropic phase boundary (MPB) for PYN-PT binary system and its frequency dependence of dielectric permittivity as relaxor behavior were characterized.

2 Experimental procedure

Conventional mixed oxide processing was used to prepare the $(100-x)Pb(Yb_{1/2}Nb_{1/2})O_3$-$xPbTiO_3$ [PYN-PTx] solid solution system. Samples in the binary system were fabricated with high-purity oxide powders: Pb_3O_4 (99.9%, MCP Inc.), Yb_2O_3 (99.9%, PIDC), Nb_2O_5 (99.9%, Ferro), and TiO_2 (99.99%, Aldrich Chemical). $YbNbO_4$ was first prepared at 1200°C for 4 h prior to reaction with PbO using the columbite precursor method [11] in a PYN-PTx formation.

The powders for PYN and PT were stoichiometrically weighed and mixed for 24 h using ball milling in an anhydrous ethanol solution with stabilized zirconia media. These mixtures were then dried and calcined at 850°C for 3 h to form the desired perovskite phase. The calcined powders were vibratory-milled to decrease the particle size of PYN-PTx, resulting in the average particle size of <1.0 μm. Subsequently, excess 2 wt% Pb_3O_4 as a dopant was added to the PYN-PTx to improve the densification of PYN-PTx. the samples were sintered at 775°C~800°C for 4 h and 8 h, respectively.

The phase purity and microstructure were examined by X-ray powder diffraction (XRD; PAD V diffractometer, Scintag Inc., Cupertino, CA) and scanning electron microscopy (SEM; S-3500 N, Hitachi). The densities of the sintered samples were measured by the Archimedes method. The dielectric permittivity and dielectric loss were determined using a multifrequency LCR meter (HP4284A, Hewlett-Packard, Palo Alto, CA) over a temperature range of RT~400°C in a temperature-controlled furnace. The polarization-electric field hysteresis (P-E) loops were measured using a modified Sawyer-Tower circuit driven at a field of 20 kV/cm supplied by a high-voltage power supply (TREK Model 610, TREK, Median, NY).

3 Results and discussion

Figure 1 shows XRD patterns for the PYN-PTx solid solution system with 49.0≤×≤51.0 sintered at 800°C for 8 h. The XRD patterns for PYN-PTx indicate that perovskite structures formed as the majority phase, and

Fig. 1 XRD pattern of PYN-PTx ceramics with 49.0≤×≤51.0 sintered at 800°C for 8 h

only a trace amount of pyrochlore was developed over the entire range of the solid solution system. In fact, pyrochlore formation has not yet been clearly described in PYN-based systems. As shown in Fig. 1, the change in the peak split related to the structural phase transition was confirmed in PYN-PTx. For $x=49.0$, all peaks were indexed to a rhombohedral phase that shows only one peak for (200) ranging from $2\theta=42^{\circ}-45^{\circ}$. For $x=49.5$, a peak at $2\theta=42^{\circ}-45^{\circ}$ started to split into two peaks for (002) and (200), and then its intensity increased with PT content; this indicates that the structure was changed to a tetragonal phase. Therefore, it can be considered that the PYN-PTx solid solution system is mainly rhombohedral below a PT of 49.5 and tetragonal above 50.0, and the MPB between the rhombohedral and tetragonal phases can exist for PT range of 49.5~50.0 of PT.

Figure 2 shows the variations in the relative density of PYN-PTx as a function of sintering temperature. The relative density of a sample sintered at 775°C for 4 h was very low, approximately 92% of the theoretical density. Increasing the sintering temperature significantly increased the density; it reached the saturated value of 96.5% for a sample sintered at 800°C for 8 h. Pb_3O_4 is usually decomposed into $3PbO+1/2O_2$ at about 550°C[12]. In addition, the melting temperature of PbO is 875°C, but it starts to melt at 760°C[13]. Therefore, it can be inferred that the excess PbO exists as a liquid phase during the sintering and improves the densification and grain growth of the PYN-PTx. To clarify the effect of the liquid phase of PbO on the densification of PYN-PTx, SEM analysis was conducted to observe the microstructure of these samples. The fractured surface of PYN-PT49.5 as an MPB composition was observed in inset of Fig. 2 with different

sintering temperatures. For a sample sintered at 775°C for 4 h in the inset(a), the porous microstructure was formed with small grains, approximately ~2 μm. However, when the sintering temperature was increased to 800°C, the microstructure became dense even at a holding time of 4 h and 8 h, showing the grain size of 5 μm and 8 μm, respectively[see the inset (b) and (c) in Fig. 2]. In addition, a liquid phase was found near the grain boundaries of the samples indicated by arrows, as shown in the inset(c) of Fig. 2. Therefore, as observed in other excess PbO-containing ceramics[14, 15], both the excess PbO resulting in the formation of liquid phase and small particle size of PYN-PTx cause the improvement of densification and grain growth at a low sintering temperature.

The temperature dependence of the dielectric permit tivity for PYN-PTx was measured at 1 kHz, as shown in Fig. 3. PYN-PTx exhibited phase transitions at T_c and at the Rhom./Tetra. transition temperature (T_{r-t}) as a function of the amount of PT. The variation in T_c was found to be a linear function of PT content. As shown, increasing the amount of PT (T_c~490°C) increased T_c by about 7°C/mol% addition. On the other hand, T_{r-t} was observed to decrease with increasing PT content and then disappeared. The phase transition temperature normally exhibits compositional dependence. Therefore, it is considered that the addition of PT (T_c~490°C) increases the tetragonality, which causes T_c to increase and T_{r-t} to decrease in PYN-PTx system. The inset in Fig. 3 shows temperature dependences of the inverse relative permittivity for PYN-PTx. In this case, due to space— charge polarization contributions at high temper-atures and lower measurement frequency, the 1 MHz data is presented as no space— charge polarization contribution was detected. As shown, the inverse relative permittivity of

Fig. 2 Variation of the relative density for PYN-PTx ceramics as a function of sintering temperatures

fractured surface for PYN-PT49.5 as an MPB
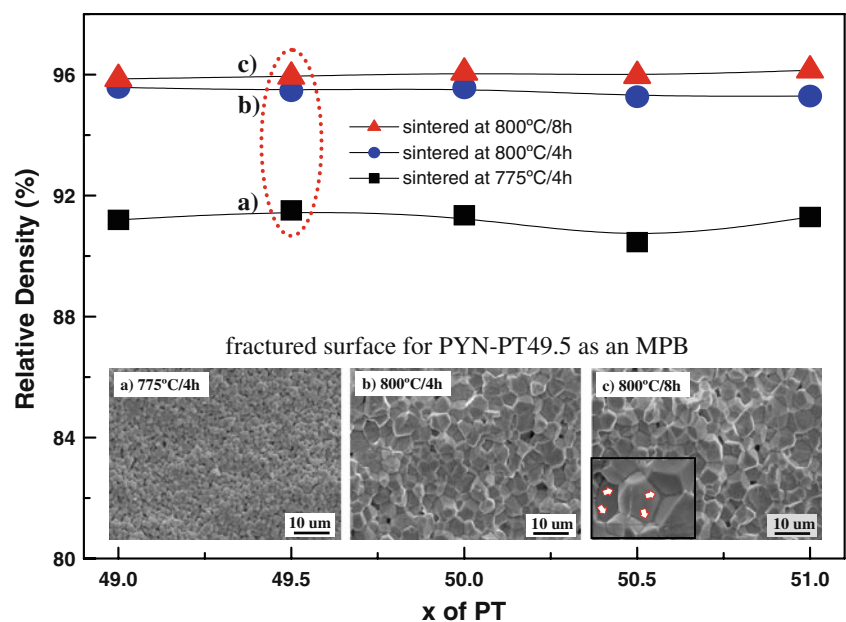
Fig. 3 Temperature dependence of dielectric permittivity for PYN-PTx ceramics. The inset shows the inverse dielectric permittivity as function of temperatures
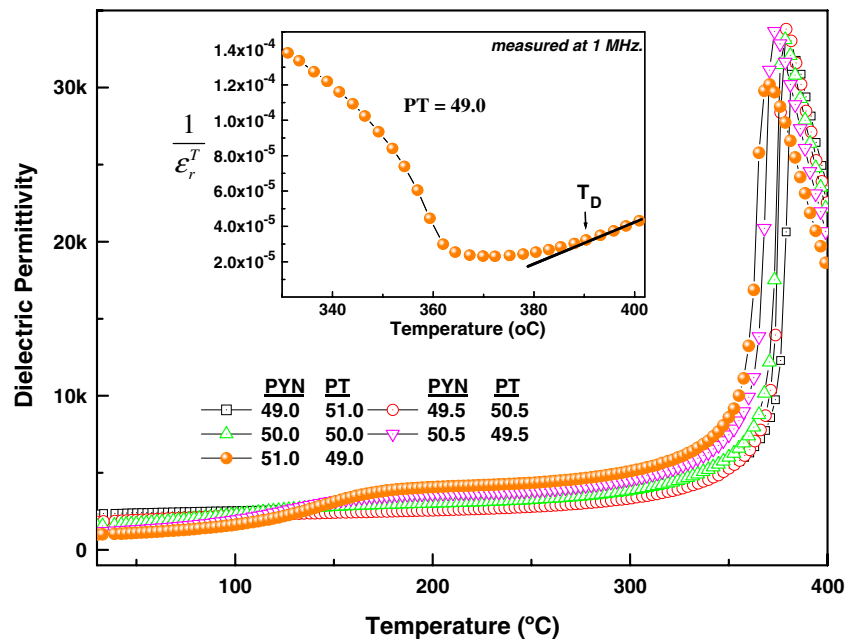
PYN-PTx against temperature followed a Curie- Weiss Law above the deviation temperature (T_D) while the permittivity shows large deviation below T_D. The diffuseness of the permittivity maxima can be described by an empirical expression previously developed by Smolenskii and Kirillov[16, 17] as

$$\frac{1}{\varepsilon_r^T} - \frac{1}{\varepsilon_{max}} = \frac{(T_D - T_{max})^\gamma}{2\varepsilon_{max}\delta^\gamma}$$

where ε^T_r is permittivity, ε_{max} is the permittivity at T_{max}, T_D is deviation temperature from the Curie-Weiss behavior, δ is the diffuse parameter describing the width of the diffuse phase transition, and γ is the critical exponent that varies from $\gamma=1$ for a purely normal ferroelectric to $\gamma=2$ for a purely relaxor ferroelectric[18]. In addition, Curie constant (C) corresponding to high temperature paraelectric phase driven by a displacive transition with $C\sim10^5$°C and by the order-disorder transition with $C\sim10^3$°C[19] was calculated from a log— log plot of $[1/\varepsilon_r -1/\varepsilon_{max}]$ vs. $[T-T_{max}]$. At the high temperature region, it was observed that the inverse

permittivity for a PYN-PT0.49 followed C–W behavior from~400°C to T_D (393°C) with the diffuseness parameters of $\gamma=1.59$, $\delta=39.57°$ and Curie constant of 202×10^5°C. With increasing the content of PT, the value of γ was found to be gradually decreased down to 1.16, indicating a transition from relaxor to normal ferroelectrics. Furthermore, even though Curie constants were revealed to decrease, all Curie constants in PYN-PTx system were~10^5°C, resulting in typical of displacive based transition at high temperature paraelectric phase. In the case of the diffuse parameter (δ), it was observed to be increased with increasing the contents of PT. From the above results, therefore, it can be suggested that the increase in the amount of PT leads to the degree of tetragonality in PYN-

Table 1 Summary of the ε_{max}, T_{max}, δ and γ values for PYN-PTx with $0.00\leq\times\leq0.05$ measured at 1 MHz

Composition	ε_{max}	T_{max}(°C)	Diffuseness Parameter		
			δ(°)	γ	C($\times10^5$°C)
PYN-PT49.0	26015	373	39.57	1.59	202
PYN-PT49.5	27248	375	36.62	1.51	149
PYN-PT50.0	29003	379	62.81	1.30	123
PYN-PT50.5	29047	381	54.08	1.33	112
PYN-PT51.0	29762	383	90.82	1.16	98
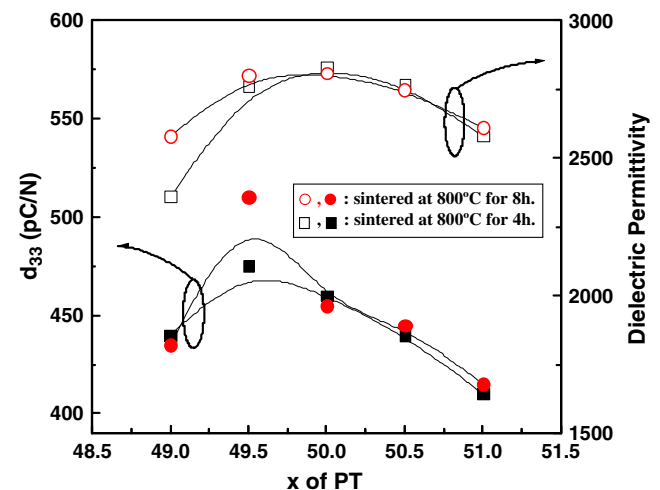
Fig. 4 Variations in d_{33} and dielectric permittivity of PYN-PTx ceramics
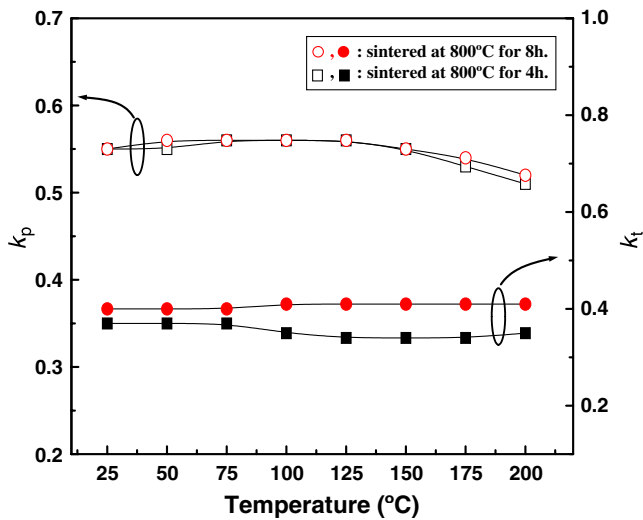
Fig. 5 Variations of the planar and thickness electromechanical coupling factors as a function of temperatures

PTx system, which induce a soft optic mode condensation or a displacive transition[20]. Detailed ε_{max}, T_{max}, and diffuseness parameters for PYN-PTx with $49.0 \leq \times \leq 51.0$ were summarized in Table 1, which are similar to PZN[18] and PMN[21], respectively.

Figure 4 shows d_{33} and the dielectric permittivity of PYN-PTx with $49.0 \leq \times \leq 51.0$ sintered at 800°C for 4 h and 8 h. It was difficult to measure the dielectric and piezoelectric properties of the samples sintered at 775°C for 4 h because of their low density. For the samples sintered at 800°C, d_{33} exhibited a maximum value at $x = 49.5$ and decreased for $x > 49.5$, while the dielectric permittivity had an optimal value at $x = 50.0$. In general, the MPB composition shows the highest dielectric and piezoelectric properties as a result of the large number of polarization directions available. In this study, the highest value of d_{33} was 510 pC/N and occurred at $x = 49.5$. In the case of dielectric permittivity, however, the maximum was found to be 2810 for PYN-PT50 sintered at 800°C for 8 h. Therefore, it is suggested that PYN-PTx solid solutions possess an MPB region between $x = 49.5$ and 50.0.

The electromechanical coupling factors (k_p, k_t) for PYN-PT49.5 sintered at 800°C for 4 h and 8 h were measured as a function of temperature. IEEE resonance measurements were carried out using a HP 4194A Impedance/Gain-phase

analyzer to measure the material constants by resonance method[22]. As shown in Fig. 5, it was found that k_p increased to 0.56 at 125°C, and then gradually decreased until at 200°C it was 0.51 for 4 h and 0.52 for 8 h; this was owing to the phase transformation (T_{r-t}) whereas k_t was unchanged. A variety of sample geometries were prepared to investigate the set of low-field properties for PYN-PT49.5 sintered at 800°C for 8 h. The elastic compliance constants (s_{33}^E, s_{33}^D, s_{11}^E, and s_{11}^D), the electromechanical coupling factors (k_{33} and k_{31}), and the piezoelectric coefficient d_{31} were derived from the measured resonant frequency and the anti-resonant frequency of the sample impedance. All the measured dielectric and piezoelectric properties for PYN-PT49.5 as an MPB sintered at 800°C for 8 h were summarized in Table 2 and compared to commercial PZT5A(TRS210). It can be seen that PYN-PT49.5 sintered at low temperature is comparable to commercial PZT5A(TRS210).

4 Summary

A solid solution PYN-PTx system with $49.0 \leq \times \leq 51.0$ was sintered with excess 2 wt% PbO to induce liquid-phase sintering at a low temperature. When the sintering temperature was 775°C, PYN-PTx ceramics could not be sintered because the PbO liquid phase was insufficient for densification. For PYN-PTx ceramics sintered at 800°C, a dense microstructure was developed with ~96.5% of the theoretical density; this might be because of excess PbO in a liquid phase, which would result in the densification of PYN-PTx ceramics. The PYN-PTx was found that the dielectric permittivity with the phase transition temperature exhibited strongly compositional dependence. In addition, it was found that the temperature dependence of the inverse relative permittivity of PYN-PTx followed a Curie-Weiss Law above the deviation temperature (T_D), providing that there was not a space— charge polarization contribution at high temperatures. The optimized piezoelectric properties of $d_{33} = 510$ pC/N, $\varepsilon_r = 2800$ at RT, $k_p = 0.57$, and $k_t = 0.42$ were obtained from PYN-PT49.5 sintered at 800°C for 8 h. Therefore, the low sintering temperature and excellent piezoelectric properties of the obtained PYN-PT49.5 ceramic make it an attractive candidate as a multilayer actuator material for LTCC applications(<900°C).

Table 2 Detailed dielectric and piezoelectric properties of PYN-PT49.5 sintered at 800°C for 8h

Material	T_{r-t}/Tc (°C)	P_r (uC/cm^2)	E_c (kV/cm)	d_{33} (pC/N)	d_{31} (pC/N)	ε_r @R.T.	$tan\delta$
PYN-PT49.5	163/373	33	16.2	510	−110	2800	0.038
PZT5A	−/369	34	15.5	374	−171	1700	0.020
Material	k_p	k_t	k_{33}	k_{31}	s_{33}^E	s_{33}^D	s_{11}^E	s_{11}^D
PYN-PT49.5	0.57	0.42	0.60	0.32	16.6	10.5	12.3	11.0
PZT5A	0.60	0.49	0.71	0.34	18.8	9.5	16.4	14.4

References

1. T. Okawa, H. Utaki, Sumitomo Search **47**, 117 (1991)
2. T. Takada, S.F. Wang, S. Yoshikawa, S.J. Jang, R.E. Newham, J Am Ceram Soc **77**, 2485 (1994)
3. P. Muralt, J Micromech Microeng **10**, 136 (1994)
4. R.E. Newnham, G.R. Ruschau, J Am Ceram Soc **74**, 463 (1991)
5. E.P. Smirnova, O.V. Rubinshtein, V.A. Isupov, Ferroelectrics **143**, 263 (1993)
6. C.A. Randall, A. Kelnberger, G.Y. Yang, R.E. Eitel, T.R. Shrout, J Electroceram **14**, 177 (2005)
7. H. Lim, H.J. Kim, W.K. Choo, Jpn J Appl Phys **34**, 5449 (1995)
8. T. Yamamoto, S. Ohashi, Jpn J Appl Phys **34**, 5349 (1995)
9. C. Duran, S.T. Mckinstry, G.L. Messing, J Electroceram **10**, 47 (2003)
10. J.H. Kim, *Master Thesis* Korea Advanced Institute of Science and Technology. (2004)
11. S.L. Swartz, T.R. Shrout, Mater Res Bull **17**, 1245 (1982)
12. Y. Yu, Y.J. Oh, C. Feng, Application of Ferroelectrics, ISAF-2007, 16th IEEE int. Symposium NM **626** (2007)
13. M. Nevriva, K. Fischer, Mater Res Bull **21**, 1285 (1986)
14. M. Villegas, J.F. Fernández, A.C. Caballero, Z. Samardija, G. Drazic, M. Kosec, J Mater Res **14**, 898 (1999)
15. S.M. Gupta, A.R. Kulkarni, J Mater Res **10**, 953 (1995)
16. G.A. Smolenskii, J Phys Soc Jpn Suppl **28**, 26 (1970)
17. V.V. Kirillov, V.A. Isupov, Ferroelectrics **5**, 3 (1973)
18. K. Uchino, S. Nomura, Ferroelectric Lett **44**, 55 (1982)
19. C.J. Stringer, T.R. Shout, C.A. Randall, J Appl Phys **101**, 054107-6 (2007)
20. M.E. Lines, A.M. Glass, (Claredon Press Oxford, New York, 1977)
21. E.F. Alberta, (Thesis for Ph.D in Pennsylvania State University, 2003)
22. IEEE Standard, Institute of Electrical and Electronic Engineers, New York, **176** (1978)