

Dielectric, ferroelectric and piezoelectric properties of $(1-x)[\text{Pb}_{0.91}\text{La}_{0.09}(\text{Zr}_{0.60}\text{Ti}_{0.40})\text{O}_3]-x[\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3]$, $0 \leq x \leq 1$

Benudhar Sahoo · Prasanta Kumar Panda

Received: 18 February 2006 / Accepted: 19 July 2006 / Published online: 28 February 2007
© Springer Science+Business Media, LLC 2007

Abstract The dielectric, ferroelectric, and piezoelectric properties of ceramic materials of compositions $(1-x)[\text{Pb}_{0.91}\text{La}_{0.09}(\text{Zr}_{0.60}\text{Ti}_{0.40})\text{O}_3]-x[\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3]$, $x = (0, 0.2, 0.4, 0.6, 0.8, \text{ and } 1.0)$ were studied. The above compositions were prepared by mixing the individual $\text{Pb}_{0.91}\text{La}_{0.09}(\text{Zr}_{0.60}\text{Ti}_{0.40})\text{O}_3$ (PLZT) and $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (PMN) powders in order to design materials with different combination of piezo and dielectric properties. The powders were calcined at 850 °C for 4 h. The presence of various phases in the calcined powders was characterized by X-ray diffraction (XRD) technique. The compacts were prepared by uniaxial pressing and were sintered at 1250 °C for 2 h. The sintered compacts were electroded, poled at 2 kV/mm dc voltage and their dielectric, ferroelectric, and piezoelectric properties were measured. In general, it was observed that the dielectric constant, loss factor and the slimness of the ferroelectric curves increase with the PMN content while the remnant polarization, saturation polarization, and the coercive fields were decreased. It is now possible to design materials with a wide combination of d_{33} , K , and loss factor by varying PLZT and PMN ratio.

Introduction

Lead zirconate titanates (PZTs) $[\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3]$ have been studied extensively in the last three to four decades since the system permits to prepare large number

of compositions with varied dielectric and piezoelectric properties and these materials are widely used for various applications such as actuators and sensors [1–5], as sonar transducers [6], as accelerometers [7], as gas igniters, in drug delivery systems, in smart toilets, in inkjet printers [8], etc. Similarly, lead magnesium niobate (PMN) $[\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3]$ is a relaxor ferroelectric material with high dielectric constant and large electric field-induced strain [9–13]. Therefore, PMN is extensively used as capacitor and also as electrostrictive actuator. While PZT possesses very high piezoelectric properties such as high d_{33} , d_{31} , etc., PMN is known for its high dielectric constant ($K = 20,000$ at RT).

With the complementary features of the PZT and PMN, the solid solutions between PZT and PMN are expected to combine the properties of both normal ferroelectric PZT and relaxor ferroelectric PMN, which could exhibit better piezoelectric and dielectric properties than those of the single phase PZT and PMN. Koval et al. [14] reported that the highest values of the dielectric constants as well as the piezoelectric and ferroelectric parameters were observed in a material with a low PMN content in the composition $x\text{PMN}-(1-x)\text{Pb}(\text{Zr}_{0.53}\text{Ti}_{0.47})\text{O}_3$ at $x = 0.125$. Tsotsorin et al. [15] investigated the dielectric and electromechanical properties of $(1-x)\text{PMN}-x\text{Pb}(\text{Zr}_{0.53}\text{Ti}_{0.47})\text{O}_3$ ceramic solid solutions and reported that the dielectric peaks in temperature dependence of the relative dielectric permittivity and loss tangent are transformed from a wide diffused shape to a more sharp form with increasing of ferroelectric components PZT in the solid solution.

In the previous studies, PZT compositions near MPB ($\text{Zr}/\text{Ti} = 53/47$) were used for preparation of PZT–PMN compositions. PLZT with rhombohedral Zr-rich composition ($\text{Zr}/\text{Ti} = 60/40$) is known to

B. Sahoo · P. K. Panda (✉)
Materials Science Division, National Aerospace
Laboratories, P.B. No. 1779, Kodihalli, Bangalore 560017,
India
e-mail: pkpanda@css.nal.res.in

generate high d_{33} values [16]. Therefore, we present the study on piezoelectric, dielectric and ferroelectric properties of $(1-x)\text{PLZT}-x\text{PMN}$ by taking PLZT (La/Zr/Ti = 9/60/40) and by varying PMN over a wide range of compositions ($x = 0, 0.2, 0.4, 0.6, 0.8, \text{ and } 1.0$).

Experimental

The PLZT–PMN powders of the required compositions were prepared by semi-wet chemical method. Analytical grade lead nitrate (99.5%), zirconium oxychloride (99.9%), titanium tetrachloride (99%), and lanthanum nitrate (99.9%) were used as the chemical precursors. The required amount of precursor and dopant solutions was co-precipitated in the pH range of 8.5–9.0. The mixed hydroxides thus produced were processed by repeated washings, dried and calcined at 850 °C for 4 h. Similarly, for the formation of PMN powder, analytical grade basic magnesium carbonate, niobium pentoxide and lead oxalate were used as precursors. PMN powders were prepared by a modified columbite route with 3% excess MgO to minimize the formation of pyrochlore phase. In this process, the required amount of basic MgCO_3 (including 3% excess MgO) was converted into its oxalate form with excess oxalic acid to keep the oxalate in solution form. Nb_2O_5 powder was then dispersed in this solution and the solution was evaporated to dryness to get an intimate mixture of magnesium oxalate and niobium pentoxide. This powder was calcined at 1,050 °C for 6 h to form columbite and the phase purity was confirmed by XRD. The columbite powder was dispersed in to lead nitrate solution and was precipitated as an oxalate by adding 10% oxalic acid solution. After filtration and drying, the mixture was reacted at 850 °C for 4 h for PMN phase formation. Finally, the compositions corresponding to the formula $(1-x)\text{PLZT}(9/60/40)-(x)\text{PMN}$ (where $x = 0, 0.2, 0.4, 0.6, 0.8, \text{ and } 1.0$) were

prepared by mixing appropriate amount of individual powders and sintering them at 1250 °C for 2 h. The density of the sintered samples was measured by Archimedes principle. The pellets were leveled, polished, electroded and finally poled in a dc field of 2 kV/mm. The linear piezoelectric charge constant (d_{33}) was measured using a piezometer (Model PM-35, M/s. Take control, UK) and the transverse piezoelectric constant (d_{31}) was calculated and the values are presented in Table 1. The room temperature dielectric properties of the sintered ceramics were studied at a frequency of 100 Hz. The remnant polarization (P_r), saturation polarization (P_s) and coercive field (E_c) of the samples were recorded from their hysteresis loops recorded at 50 Hz with an ac field of 30 kV/cm by a modified Sawyer-Tower circuit (M/s Digital systems, Model HLT-2, Mumbai).

Results and discussion

X-ray diffraction studies

X-ray diffraction patterns of calcined PLZT–PMN powders are shown in Fig. 1. From the XRD patterns, it is observed that PLZT–PMN is a single-phase material with perovskite structure exhibiting rhombohedral symmetry corresponding to higher Zr/Ti ratio. All compositions are reasonably pure without “pyrochlore” and any other impurity phases. The peak positions of the intermediate compositions (combination of PLZT and PMN) are also similar to PLZT or PMN except there is a minor shift of the peak position. There is no recognizable splitting of X-ray lines observed in the intermediate compositions, which indicate the absence of any other phase and confirms the formation of solid solution between them. The solid solution nature of PLZT–PMN has already been confirmed by other researchers [17, 18]. Ouchi et al. [17] established a phase diagram of ternary PMN–PZ–

Table 1 Piezoelectric and dielectric properties of $(1-x)\text{PLZT}-x\text{PMN}$ ceramics

| Composition x in % | d_{33} (pC/N) | d_{31} (pC/N) | g_{33} (mV/N) | g_{31} (mV/N) | Dielectric constant (K) | Tan δ | Bulk density (g/cm^3) |
|----------------------|-----------------|-----------------|-----------------|-----------------|-----------------------------|--------------|---|
| 0 | 517 | –199 | 22.8 | –8.82 | 2558 | 0.028 | 7.78 |
| 20 | 388 | –150 | 15.7 | –6.1 | 2781 | 0.0253 | 7.79 |
| 30 ^a | 330 | – | – | – | 2781 | 0.0228 | – |
| 40 | 274 | –106 | 9.2 | –3.6 | 3355 | 0.0204 | 7.85 |
| 50 ^a | 200 | – | – | – | 4400 | 0.0195 | – |
| 60 | 125 | –48.3 | 2.6 | –1.01 | 5439 | 0.0186 | 7.93 |
| 80 | 75 | –29 | 1.4 | –0.55 | 5971 | 0.0147 | 7.99 |
| 100 | 0 | 0 | 0 | 0 | 9157 | 0.0112 | 8.13 |

^a The properties for these compositions are obtained by extrapolation method

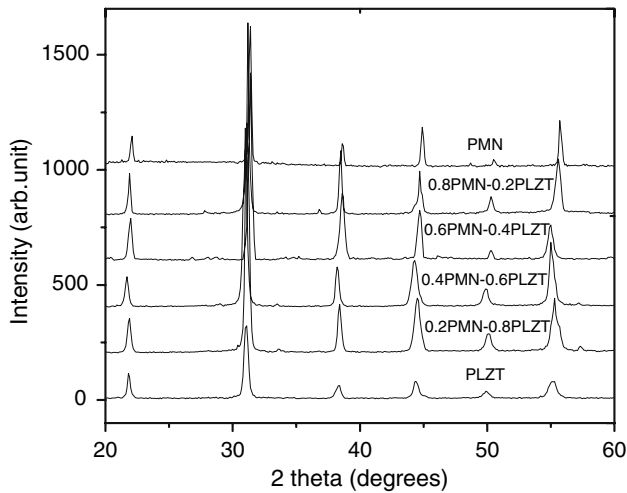


Fig. 1 XRD pattern of PLZT-PMN ceramics with 0%, 20%, 40%, 60%, 80%, and 100% PMN content

PT solid solution. Villegas et al. [18] confirmed the formation of pure single phase perovskite PMN–PZT solid solution at 800 °C by XRD and DTA/TGA analysis.

Density

The density of the sintered samples was measured by Archimedes's principle and the results are presented in Table 1 and the values are also plotted in Fig. 2. From this plot, it can be concluded that the density increases monotonically with the addition of PMN. This is due to addition of relatively high density PMN (8.13 g/cm³) compared to the density of PLZT (7.8 g/cm³) [19, 20].

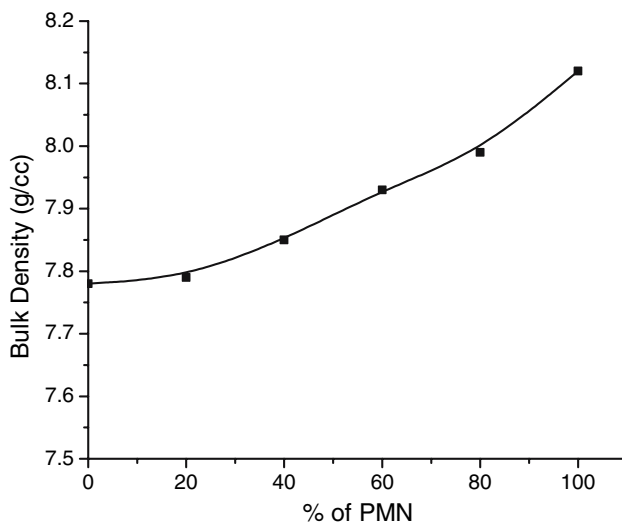


Fig. 2 Variation in density with different mol% of PMN

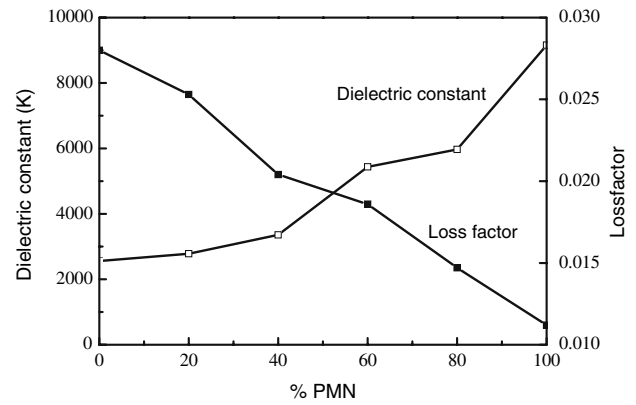


Fig. 3 Change of dielectric constant (K) and loss factor ($\tan \delta$) of PLZT ceramics with different mol% PMN

Dielectric properties

The dielectric constant (K) and loss factor ($\tan \delta$) of PLZT–PMN materials are measured for various compositions at room temperature and at a frequency of 100 Hz. The above is presented in the Table 1 and also graphically plotted (Fig. 3). It is observed that the value of “ K ” increases from 2,558 for pure PLZT to a dielectric constant of 9,157 for pure PMN, nearly four fold increase in dielectric constant. Similarly, the loss factor ($\tan \delta$) of 0.0280 for pure PLZT gradually decreases to a value of 0.0112 for pure PMN. This could be due to the high dielectric nature of PMN. Though both the components are relaxor in nature, PLZT is comparatively less relaxor than PMN. The disorderness among the “B” site cations of PMN is more compared to that of PLZT at the same time the electrostrictive properties are maximum in the case of PMN, which provides higher dielectric constant to the sample. When PMN is added to PLZT to form solid solution, the dielectric behavior of intermediate compositions shifted towards that of more relaxor materials [21] and the value increases monotonically with increase in PMN content.

Piezoelectric properties

The linear piezoelectric constant, d_{33} of the samples were measured directly using a piezometer (M/s. Take Control, UK) by using 0.1 N force. The transverse piezoelectric constant, d_{31} of the samples was obtained by using a special adaptor attached to the system wherein a sample is placed in the sample holder of the adaptor and clamped in between the force heads of the piezometer perpendicular to the poling direction. The charge coefficient known as rough d_{33} was measured

along the poled direction and d_{31} was calculated using the equation given below:

$$d_{31} = d_{33} (\text{rough}) \times \text{thickness/diameter}$$

d_{33} and d_{31} are the linear and transverse piezoelectric constant of the sample, respectively.

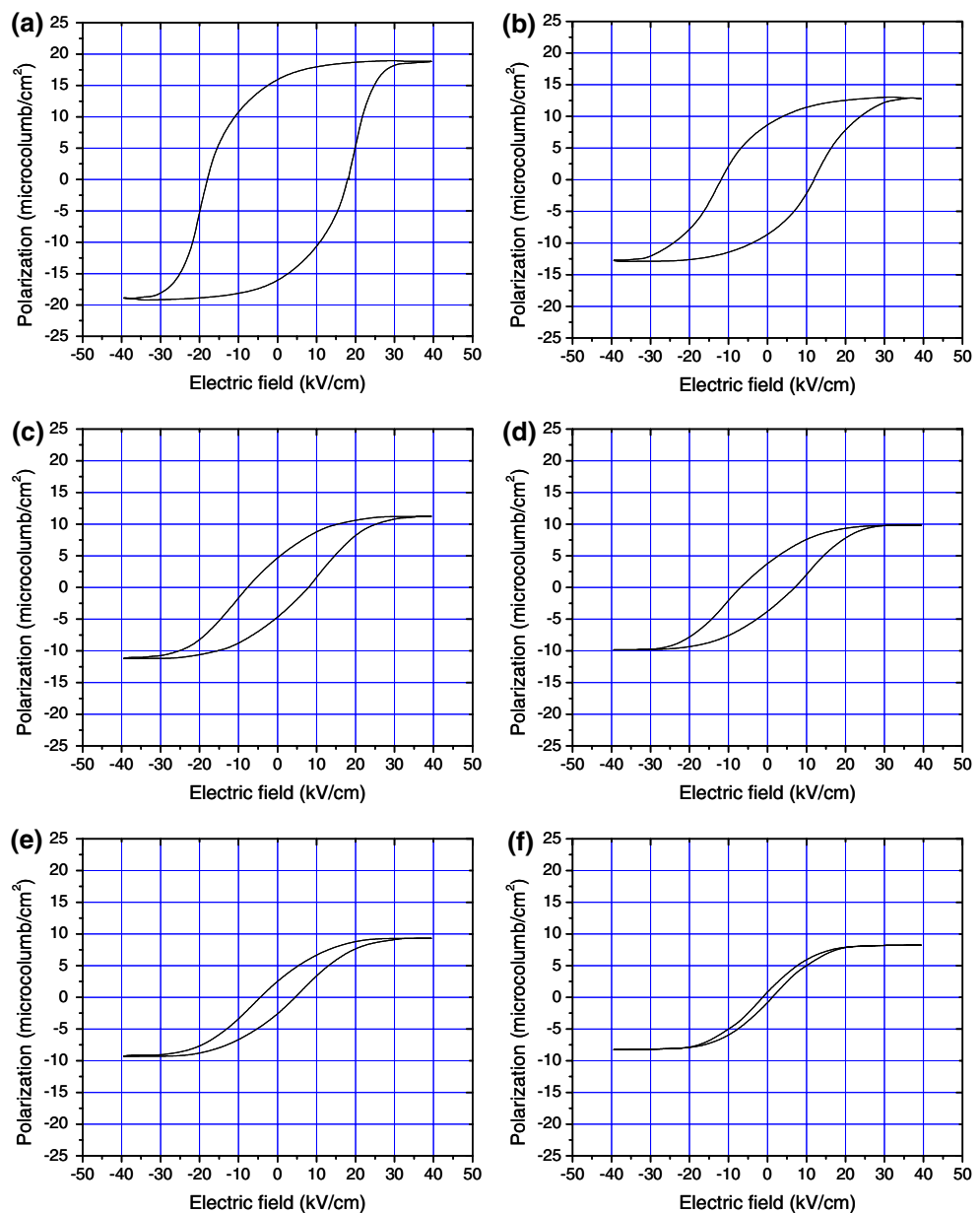
The variation in piezoelectric charge constants (d_{33} , d_{31}) of PLZT ceramics with different mole % of PMN is shown in Table 1. It is observed that the linear piezoelectric charge constant (d_{33}) decreases steadily with increase in PMN concentration. Pure PLZT exhibited the maximum, $d_{33} = 517$ pC/N and $d_{31} = -199$ pC/N at $x = 0$ and then were decreased in proportion to the

amount of PMN added. The decrease in d_{33} and d_{31} can be attributed to the lower polarization of the materials, as deduced from the ferroelectric measurements. The same trend is also observed by Koval et al. [14] in their study. The absolute d_{33} values of PLZT–PMN materials corresponding to various intermediate compositions are much higher to those obtained from PZT–PMN system [21].

Polarization measurement

The hysteresis curves of the samples under polarization study are presented in Fig. 4. It is evident that the

Fig. 4 Hysteresis loops of $(1 - x)\text{PLZT}-(x)\text{PMN}$ ceramics with different mol% of x : **(a)** 0, **(b)** 20, **(c)** 40, **(d)** 60, **(e)** 80, and **(f)** 100



shapes of P – E loops differ with the addition of PMN in PLZT structure. The polarization loop of pure PLZT is well developed showing a large remnant polarization (P_r) at zero electric field. The hysteresis loop has a typical “square” form stipulated by switching of domain structure in an electrical field, which is typical of a phase that contains long-range cooperation between dipoles. That is the characteristic of a ferroelectric micro-domain state. The same trend of P – E loop was also observed by Koval et al. [14] and Yimurin et al. [21] with higher amount of remnant polarization. This may be due to the MPB compositions in their study. The slimness of the curves increases with the increase in PMN content and a very slim curve of $E_c = 1.2$ kV/cm was obtained for 100% PMN. This is a characteristic of suppressed ferroelectric interaction with absence of long-range ferroelectric domain state. Mathan et al. [22] and Funning [23] explained the slimness of the hysteresis curve of PMN by following way. According to them, the polar domains develop during application of electric field (poling) are in nanometer scale. These nano domains grow into macro-domains in case of normal ferroelectrics like PZTs, while they do not grow in case of PMN due to disorder arrangement of ions. As a consequence, the reversal of the ferroelectric domains occurs as soon as the field is removed with very low polarization, which is reflected by its slimness. Sunder and Newnham [24] also gave a similar explanation to the lower coercive field and remnant polarization of the PMN sample. According to them, since PMN is mainly with pseudo-cubic phase with relaxor behavior, the reorientation of micro-domains cannot contribute much to E_c and P_r during the polarization, and its lower coercive field and remnant polarization may be attributed to electrostriction, induced mainly by dipolar and ionic polarization. The remnant polarization (P_r), saturation polarization (P_s), coercive field (E_c) were determined from the fully saturated loops and are tabulated in Table 2. The values of P_r and E_c for PLZT are $16.5 \mu\text{C}/\text{cm}^2$ and 18 kV/cm, respectively, whereas for PMN the P_r is only $0.9 \mu\text{C}/\text{cm}^2$, less than one tenth of that for PLZT. The P_r and E_c value of intermediate compositions are decreases with increase in PMN content, which clearly indicates the induction of disorderness in to the PLZT structure by magnesium and niobium ions of PMN.

Discussions

From the XRD study, the peak positions purely correspond to PLZT–PMN, therefore, the presence of

Table 2 Ferroelectric properties of $(1-x)$ PLZT– (x) PMN ceramics

| Compositions x in % | P_r ($\mu\text{C}/\text{cm}^2$) | P_s ($\mu\text{C}/\text{cm}^2$) | E_c (kV/cm) |
|-----------------------|-------------------------------------|-------------------------------------|---------------|
| 0 | 16.5 | 18.5 | 18 |
| 20 | 9.0 | 12.5 | 12 |
| 40 | 5.0 | 11 | 8.12 |
| 60 | 4.0 | 9.8 | 7.1 |
| 80 | 2.6 | 9.1 | 4.5 |
| 100 | 0.9 | 8.2 | 1.2 |

pyrochlore or any other phases is ruled out. The solid solution nature of PLZT–PMN has already been established by earlier researchers [17–18]. It was also concluded that the d_{33} values of PLZT–PMN materials are higher than the corresponding compositions of PZT–PMN system [21]. This is attributed to higher d_{33} values of PLZT compared to the d_{33} values of only PZT.

As a result of this study, it is possible to design materials of different PLZT–PMN compositions to generate required combination of piezo and dielectric properties for various applications. For example, the values of d_{33} , K and $\tan \delta$ are 388 pC/N, 2781 and 0.0253 , respectively for a composition of 20% PMN and 80% PLZT. Similarly, for a composition of 60% PMN and 40% PLZT, the values of d_{33} , K and $\tan \delta$ are 125 pC/N, 5439 and 0.0186 , respectively.

Conclusions

$(1-x)$ PLZT (9/60/40)– (x) PMN (where $x = 0, 0.2, 0.4, 0.6, 0.8,$ and 1.0) ceramic powders were prepared by mixing the individual PLZT and PMN powders. The powders were calcined at 850°C for 4 h and the phase analysis was carried out by XRD studies. Circular compacts were prepared by uniaxial pressing, sintered at $1,250^\circ\text{C}$ for 2 h and the sintered compacts were electroded, poled and the dielectric, ferroelectric, and piezoelectric properties were measured. In general, it was observed that the dielectric constant, loss factor and the slimness of the ferroelectric curves increase with the increase in PMN content while the remnant polarization, saturation polarization and the coercive field was decreased. It is also possible to design materials with a wide combination of d_{33} , K , and loss factor by varying PLZT and PMN ratio.

Acknowledgements The authors are very grateful to Dr. S. Usha Devi for XRD patterns. The authors also gratefully acknowledge Head, Materials Science Division and Director, NAL for providing necessary encouragement during the course of this study. One of the authors, Mr. B. Sahoo also thanks CSIR, New Delhi for the research fellowship.

References

1. Crawley EF, De Luis J (1987) *AIAA J* 25:1373
2. Sugawara Y, Onitsuka K, Yoshikawa S, Xu Q, Newnham RE, Uchino K (1992) *J Am Ceram Soc* 75:996
3. Newnham RE, Ruschau GR (1996) *Am Ceram Soc Bull* 75:51
4. Tressler JF, Alkoy S, Newnham RE (1998) *J Electroceram* 2:257
5. Newnham RE (1998) In: Majumdar SK, Tressler RE, Miller EW (eds) *The era of materials*. The Pennsylvania Academy of Science, p. 159
6. Newnham RE, Bowen LJ, Klicker KA, Cross LE (1980) *Mater Eng* 2:93
7. Wallaschek J (1995) *J Intell Mat Syst Struct* 6:71
8. Chang SH, Wang HC (1990) *Sens Actuators A* 24:239
9. Swartz SL, Shrout TR, Schulze WA, Cross LE (1984) *J Am Ceram Soc* 67:311
10. Nomura S, Uchino K (1982) *Ferroelectrics* 41:117
11. Uchino K (1986) *Am Ceram Soc Bull* 65:647
12. Shrout TR, Halliyal A (1987) *Am Ceram Soc Bull* 66:704
13. Chen J, Harmer MP (1990) *J Am Ceram Soc* 73:68
14. Koval V, Alemany C, Briancin J, Brunckova H, Saksl K (2003) *J Eur Ceram Soc* 23:1157
15. Tsotsorin AN, Gridnev SA, Rogova SP, Luchaninov AG (1999) *Ferroelectrics* 235:171
16. Buchanan RC (ed) (1991) *Ceramic materials for electronics, processing, properties and applications*, p 175 (2nd ed)
17. Ouchi H, Nagano K, Hayakawa S (1965) *J Am Ceram Soc* 48:T26
18. Villegas M, Jurado JR, Moure C, Duran P (1995) *J Mater Sci* 30:1391
19. Haertling GH (1999) *J Am Ceram Soc* 82:797
20. Wang HC, Schulze WA (1990) *J Am Ceram Soc* 73:825
21. Yimnirun R, Ananta S, Laoratanakul P (2005) *J Eur Ceram Soc* 25:3235
22. De Mathan N, Husson E, Calvarin G, Gavarri JR, Hewat AW, Morell A (1991) *J Phys Condens Matter* 3:8159
23. Fanning DM (2000) *Structure property relations in ferroelectric materials*. PhD Thesis, University of Illinois, Urbana-Champaign
24. Sunder V, Newnham RE (1992) *Ferroelectrics* 135:431