

High Magnetoelectric Properties in $0.68\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - 0.32PbTiO_3 Single Crystal and Terfenol-D Laminate Composites

Jungho Ryu[†], Shashank Priya, Kenji Uchino, Hyoun-Ee Kim* and Dwight Viehland**

*International Center for Actuators and Transducers, Materials Research Institute,
The Pennsylvania State University, University Park, PA 16802, U.S.A.*

**School of Materials Science and Engineering, Seoul National University, Seoul 151-742, Korea*

***Department of Materials Science and Engineering, Virginia Polytechnic Institute and State University,
Blacksburg, VA 24061, U.S.A.*

(Received May 22, 2002; Accepted July 8, 2002)

ABSTRACT

Magnetoelectric (ME) laminate composites of $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - PbTiO_3 (PMN-PT) and Terfenol-D were prepared by sandwiching single crystals of PMN-PT between Terfenol-D disks. The magnetoelectric voltage coefficient (dE/dH) of the composite was determined to be $10.30 \text{ V/cm} \cdot \text{Oe}$, at 1 kHz and under a dc magnetic bias of 0.4 T. The value of dE/dH is ~80 times higher than either that of naturally occurring magnetoelectrics or artificially-grown magnetoelectric composites. This superior magnetoelectric voltage coefficient is attributed to the high piezoelectric voltage constant as well as the high elastic compliance of PMN-PT single crystal and the large magnetostrictive response of Terfenol-D.

Key words : Magnetoelectric composite, PMN-PT single crystal, Terfenol-D, Piezoelectric, Magnetostrictive

1. Introduction

Magnetoelectricity (ME) is a product property and needs biphasic surrounding to exhibit the complex behavior.^{1,2)} The primary Magnetoelectric (ME) is represented as the material becomes magnetized after applying an electric field and electrically polarized when placed in a magnetic field. In the secondary effect, the permeability or permittivity change is expected.^{2,3)}

The ME effect obtained in composites is more than a hundred times that of single phase ME materials such as Cr_2O_3 . In 1978, Boomgaard *et al.*,⁴⁾ outlined the conceptual points inherent to the ME effect in composites. These can be summarized as (i) two individual phases should be in chemical equilibrium (ii) mismatching between grains should not be present (iii) magnitude of the magnetostriction coefficient of the piezomagnetic or magnetostrictive phase and magnitude of the piezoelectric coefficient of the piezoelectric phase must be high (iv) accumulated charge must not leak through the piezomagnetic or magnetostrictive phase and (v) deterministic strategy for poling of the composites. At present various ME composites have been reported such as $\text{Ni}(\text{Co},\text{Mn})\text{Fe}_2\text{O}_4$ - BaTiO_3 , CoFe_2O_4 - BaTiO_3 , NiFe_2O_4 - BaTiO_3 , LiFe_5O_8 - BaTiO_3 , CoFe_2O_4 - $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, CuFeCrO_4 - BaPbTiO_3 and NiFe_2O_4 - $\text{Pb}(\text{ZrTi})\text{O}_3$,³⁻¹⁵⁾ but none of them meet the requirement

for practical devices.

ME laminate composites of piezoelectric and magnetostrictive materials have gained considerable importance in recent times due to the large ME effect found in these composites and are very promising for multitude of practical applications.^{14,16,17)} The selection of piezoelectric and magnetostrictive material depends on various factors including transverse piezoelectric voltage coefficient (g_{31}), longitudinal and transverse piezoelectric coefficient (d_{33} and d_{31}), magnetostrictive coefficient, optimum thickness ratio between piezoelectric and magnetostrictive layer and the direction of magnetostriction in the Terfenol-D disks.^{16,17)} In addition to these properties, there are additional constraints on the choice of materials. Materials should have high poling strength, excellent aging characteristics and high vibrational amplitude. Based on these factors, previously, Lead Zirconate Titanate (PZT) and Terfenol-D were selected as the piezoelectric and magnetostrictive materials, respectively. The composites were fabricated by sandwiching and then bonding a PZT disk between two Terfenol-D disks. These composites demonstrated an extremely high ME voltage coefficient ($dE/dH = 5.90 \text{ V/cm} \cdot \text{Oe}$, The SI unit for ME voltage coefficient, $(\text{V/m})/(\text{A/m}) = 0.8 \text{ V/cm} \cdot \text{Oe}$), in comparison to previously reported naturally occurring or *in-situ* grown ME composites as well as other co-fired laminate composites.¹⁷⁾

In addition to a high ME voltage coefficient, the laminated ME composites have a simple design and are easy to fabricate.^{16,17)} The laminated ME composites can be easily applied in practical applications, such as magnetic field

[†]Corresponding author : Jungho Ryu

E-mail : jor4@psu.edu

Tel : +1-814-863-2927 Fax : +1-814-865-2326

sensing devices for a quasi dc ~100 kHz apparatus and current measurement probes for high-power electric transmission systems. The objective of this study was to obtain higher values for dE/dH , which can fulfill the need for a wide range of applications. To achieve this goal, a proper substitute for the PZT ceramic layer is needed.

In recent years, the relaxor based single crystals have emerged as a group of promising materials for various applications like ultrasonic medical imaging transducers and sonars due to their extremely high piezoelectric constant and electromechanical coupling coefficient.¹⁸⁻²⁵⁾ $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN) is an important member of the relaxor ferroelectric material family.^{20,23-25)} Compared to other relaxor-based piezoelectric materials, PMN and its solid solution with $PbTiO_3$ (PT) have been extensively investigated because of ease in growing large crystals using the Bridgeman method.²¹⁾ The high electromechanical properties of these materials are dependent on many factors such as composition, orientation, temperature and electric field. Single crystals of PMN-PT oriented along $\langle 001 \rangle$ at the Morphotropic Phase Boundary (MPB) composition have been reported to possess high electromechanical coupling coefficients, k_{33} (> 0.9), high actual piezoelectric coefficient, d_{33} (> 2000 pC/N) and high dielectric constant, ϵ_3^T/ϵ_0 (> 4000), at room temperature.^{20,22)} Enhanced performance in these crystal is expected due to the coexistence of an intermediate metastable ferroelectric and monoclinic phase between the ferroelectric rhombohedral and tetragonal phases.^{26,27)} Thus, PMN-PT has all the desired characteristics for use as a piezoelectric material in ME laminate composites. Basic analysis in terms of stress and strain showed a much improved magnitude of magnetoelectric voltage coefficient. Motivated by these results, single crystal PMN-PT/Terfenol-D laminate composites were fabricated and the ME properties were investigated. Experimental results on these composites are essential for transducer engineers to deterministically design magneto-sensing devices. Moreover, these composites offer a new vista for application of the piezocrystals.

2. Experimental Procedure

PMN-PT single crystals of Morphotropic Phase Boundary (MPB) compositions were grown directly from the melt. $\langle 001 \rangle$ -oriented seed crystals were used to initiate the crystal growth. Crystals were cut and oriented along the $\langle 001 \rangle$ direction. PMN-PT ceramic specimens were made by the columbite precursor method.²⁴⁾ Specimens were made with compositions close to Morphotropic Phase Boundary (MPB) with PT content around 32% (i.e. $0.68Pb(Mg_{1/3}Nb_{2/3})O_3$ - $32PbTiO_3$). All specimens were cut and polished to the dimensions of 5 mm diameter and 0.4 mm thickness. Specimens were electroded on the radial surface by gold sputtering and subsequently poled along thickness direction in silicone oil. The $\langle 001 \rangle$ -oriented crystals were poled on cooling from $\sim 160^\circ\text{C}$ under an electric field of 1 MV/m, whereas

Table 1. Materials Characteristics of Piezoelectric Disks

Materials	ϵ_3^T/ϵ_0	d_{33} (pC/N)	\bar{g}_{33} (mVm/N)	S_{33}^E (10^{-12} m ² /N)
PMN-PT single crystal	4340	1710	44.5	56.4
PMN-PT ceramic	5610	570	11.5	9.5
PZT ceramic	1080	250	26.1	17.4

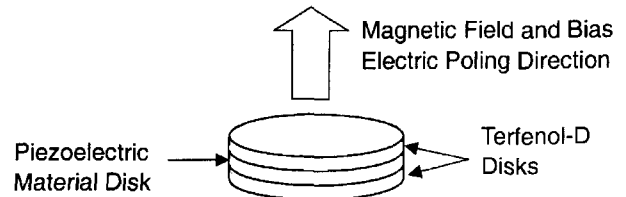


Fig. 1. Schematic structure of ME laminate composite.

the ceramics were poled at 100°C under a field of 2.5 MV/m. PZT (APC 840, American Piezoceramics Inc., PA, USA) and PMN-PT ceramic disks of 5 mm diameter and 0.4 mm thickness were obtained by conventional ceramic processing. Table 1 shows the material characteristics of the piezoelectric materials used in this study. Electromechanical properties were measured and calculated from impedance spectra (HP4194A, Hewlett Packard Co. USA) and d_{33} was measured from the unipolar strain-electric field curve. A $TbDyFe_2$ (Terfenol-D) magnetostrictive alloy of 5 mm in diameter and 1.0 mm in thickness was obtained from Etrema Products (Ames, IA, USA). This alloy has an exceptionally high magnetostrictive effect ($\epsilon_{\text{max}} = 1600 \times 10^{-6}$) and coupling constant ($k=0.70$)²⁸⁾ and is easily fabricated as a thick disk which can produce enough stress to generate electric charge from PZT disk. Piezoelectric/Terfenol-D laminate ME composite samples were prepared by stacking and then bonding the piezoelectric disks and Terfenol-D disks with silver epoxy (E-Solder No. 3021, ACME Division of Allied Products Co., CONN, USA) and cured at 80°C for 4 h for good mechanical coupling. Fig. 1 shows the schematic structure of the composites. The poling direction of the piezoelectric disk and the direction of the applied magnetic dc bias and the ac field are the same as the thickness direction.

Fig. 2 shows the schematic diagram of the experimental setup used for measuring the ME coefficient. The ME coefficient was determined by measuring the electric field generated across the composite when an ac magnetic field and a dc bias were applied to it. An electromagnet (GMW 5403 Magnet, Power and Buckley Inc., New Zealand) was used to apply the dc bias field up to 0.45 T (4.5 kOe). The coefficient was measured directly as the response of the sample on the digital oscilloscope to an applied ac magnetic input signal of 1 kHz and 1×10^{-4} T (1 Oe) amplitude (Helmholtz coils were used to give a uniform ac field in the space between the coils) superimposed on the dc bias field, both parallel to the sample axis. The voltage generated in the piezoelectric layer

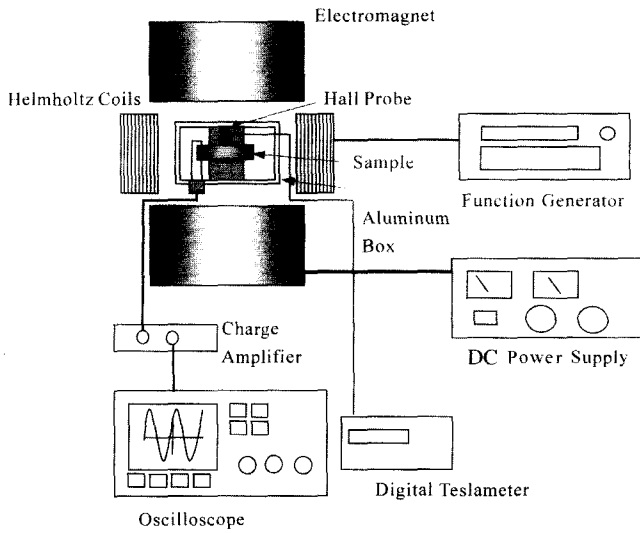


Fig. 2. Schematic diagram of ME measurement system.

was measured under an open circuit condition by using charge amplifier (5010B Dual Mode Amplifier, Kistler Instrument Co. NY, USA). This amplifier was designed for converting a charge signal from the piezoelectric transducer into a proportional output voltage. The output voltage from the amplifier was measured with an oscilloscope (54645A, Hewlett Packard Co. USA). The output voltage was obtained from charge and the capacitance of the piezoelectric disk of the composite, using $V=Q/C$ (1 kHz). The output voltage divided by the thickness of the sample and the ac magnetic field gives the magnetolectric voltage coefficient of the samples.

3. Results and Discussions

Magnetolectricity (ME) is due to the interaction of the magnetic and electric dipoles in the material. In a single phase material exhibiting ME, the change in Gibbs energy can be written in terms of the applied magnetic field dH and the resultant electric field dE , neglecting the higher order ME coefficient, as:

$$\Delta G = -1/2\chi_{ij}E_iE_j - 1/2\zeta_{ij}H_iH_j - \alpha_{ij}H_iE_j \quad (1)$$

where χ_{ij} and ζ_{ij} are the electric and magnetic susceptibility tensors and α_{ij} is the ME tensor. Differentiating eq.(1), with respect to E and H , the expressions for the magnetic moments and electrical polarization can be obtained as:

$$M_i = (-\partial(\Delta G)/\partial H_i) = \zeta_{ij}H_j + \alpha_{ij}E_j \quad (2)$$

$$P_i = (-\partial(\Delta G)/\partial E_i) = \chi_{ij}E_j + \alpha_{ij}H_j \quad (3)$$

Eq.(2) and (3) are the constitutive relations for the general single phase material exhibiting magnetolectric effect. Similar analysis was performed on the composite structure with piezoelectric and magnetostrictive phases and it was shown that for the composite sandwich structure, the out-

put voltage is given as:¹⁶

$$V_{out} = 2g_{31}t_p\sigma_{31}^E \quad (4)$$

and the ME coefficient is then obtained by:

$$\frac{dE}{dH} = \frac{V_{out}}{H_{ac}t_p} = \frac{2g_{31}\sigma_{31}^E}{H_{ac}} (\text{V/cm} \cdot \text{Oe}) \quad (5)$$

where t_p is the thickness of the piezoelectric disks, σ_{31}^E is the stress placed on the piezoelectric disk and H_{ac} is an applied ac magnetic field. The generated stress on the magnetostrictive material is dependent on the elastic stiffness and thickness of the piezoelectric and magnetostrictive materials and is given as:^{16,29}

$$\sigma_{31}^E = -\frac{2c_m c_p t_m \Delta \epsilon_0}{(1-\nu)(2c_m t_m + c_p t_p)}$$

$$\sigma_{31}^E = \frac{c_m c_p t_m \Delta \epsilon_0}{(1-\nu)(2c_m t_m + c_p t_p)} \quad (6)$$

where c , t , $\Delta \epsilon_0$ and ν are the elastic stiffness, thickness, the linear strain of the magnetostrictive layer and Poissons

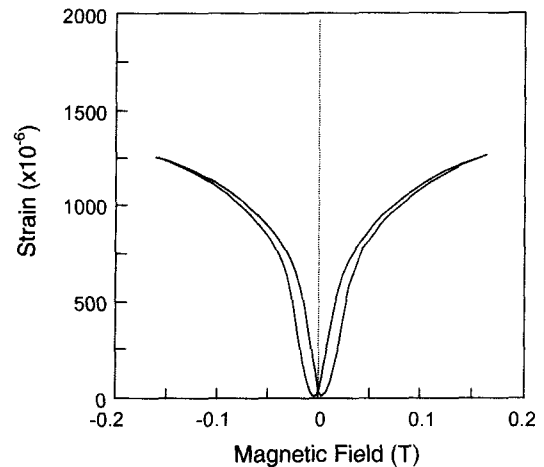


Fig. 3. Magnetostrictive response of Terfenol-D disk as a function of applied magnetic field.

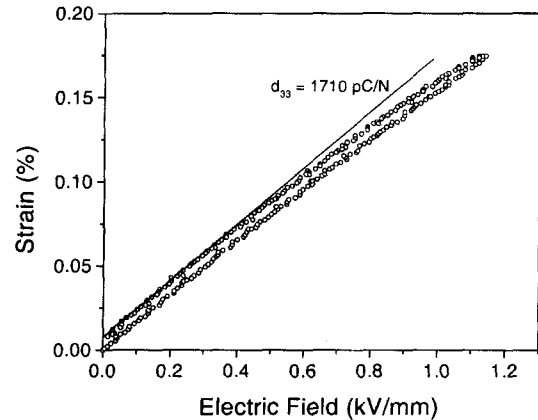


Fig. 4. Unipolar field induced strain behavior of PMN-PT single crystal.

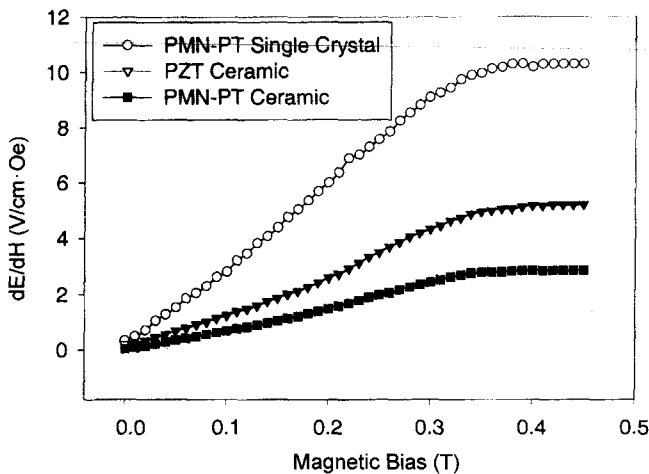


Fig. 5. ME voltage coefficient for laminate composites as a function of an applied dc magnetic bias field with different piezoelectric disks. Data are shown for PZT, PMN-PT ceramic and PMN-PT single crystal disks.

ratio, respectively. The subscript m or p means magnetostrictive or piezoelectric, respectively.

Fig. 3 shows the magnetostriction behaviors of Terfenol-D disk as a function of applied magnetic field. The maximum strain along the thickness direction of Terfenol-D used in this article was 1250 ppm. The electrically induced strain was measured using a LVDT method. Fig. 4 shows the strain-electric field response of PMN-PT single crystal disk. The unipolar field induced strain response was nearly linear and had a very low hysteresis. From the slope of the curve, piezoelectric constant d_{33} was 1710 pC/N.

Fig. 5 shows the ME voltage coefficient (dE/dH) as a function of applied dc magnetic bias for three kinds of specimens, i.e., with PMN-PT single crystal, PMN-PT ceramic and PZT ceramic. The magnetic and electric polarization directions were along the thickness of the disks. The magnetic bias dependence of dE/dH was similar for all three types of piezoelectric specimens. As evident in the figure, the ME voltage coefficient increased with increasing magnetic bias, saturating at a bias level of ~ 0.4 T. This saturation field corresponds to the field at which magnetization saturation is reached in Terfenol-D disks.

The ME laminate composite made using a PMN-PT single crystal had the highest ME voltage coefficient. The maximum dE/dH was 10.30 V/cm·Oe, which is ~ 80 times higher than that previously reported in either naturally occurring magnetoelectrics or artificially-designed composites.⁴⁻¹⁵ This high value of dE/dH for PMN-PT single crystals is due to the high piezoelectric voltage constant (g_{33}), as well as high elastic compliance (S_{33}^E). The piezoelectric voltage constant (g_j) is the most important factor to obtain a superior ME voltage coefficient^{16,17} as mentioned earlier. In eq.(4), it can be seen that the output voltage from the composite is directly proportional to the piezoelectric voltage constant g_{31} .

As is evident from eq.(6), generated stress in the piezoelectric layer is in direct correspondence with the stiffness (or compliance) of piezoelectric layer and small stiffness (or large compliance) of piezoelectric layer results in effective mechanical coupling. Table 1 shows the piezoelectric voltage constant and elastic compliance of the three different materials studied in this investigation. From the table, it is clear that both the piezoelectric voltage coefficient and elastic compliance are higher for specimens with PMN-PT single crystal compared to specimens with PZT ceramic or PMN-PT ceramics. This difference is responsible for the higher ME properties of the PMN-PT laminate composites. These results indicate that a better ME response can be obtained if the elastic and piezoelectric properties of the materials are improved.

4. Conclusion

In summary, ME laminate composites have been fabricated. This was done by stacking and then bonding piezoelectric materials to Terfenol-D. Laminates were made using PZT, PMN-PT ceramics and a $\langle 001 \rangle$ -oriented PMN-PT single crystal. The highest ME voltage coefficient was found for the PMN-PT single crystal. The value of dE/dH for the laminate with the piezoelectric single crystal was 10.30 V/cm·Oe, under a dc magnetic bias of 0.4 T. This value of dE/dH is ~ 80 times higher than either that of naturally occurring magnetoelectrics or artificially-grown ME composites.

REFERENCES

1. T. H. Odell, "Magnetoelectrics- A New Class of Materials," *Electronics and Power*, **11** 266-68 (1965).
2. V. Suchtelen, "Product Properties: A New Application of Composite Materials," *Philips Research Report*, **27** 28-37 (1972).
3. K. Uchino, *Comprehensive Composite Materials: Piezoelectric Composites*; Vol. 5, chap. 5.24, pp. 523, Elsevier, Amsterdam, The Netherlands, 2000.
4. J. van den Boomgaard and R. A. J. Born, "A Sintered Magnetoelectric Composite Material $BaTiO_3$ - $Ni(Co,Mn)Fe_3O_4$," *J. Mater. Sci.*, **13** 1538-48 (1978).
5. J. van den Boomgaard, A. M. J. G. Van Run and J. Van Suchtelen, "Magnetoelectricity in Piezoelectric-magnetostrictive Composites," *Ferroelectrics*, **10** 295-98 (1976).
6. J. van den Boomgaard, D. R. Terrell, R. A. J. Born and H. F. J. I. Giller, "An in situ Grown eutectic Magnetoelectric Composite Material: Part I Composition and Unidirectional Solidification," *J. Mater. Sci.*, **9** 1705-09 (1974).
7. A. M. J. G. Van Run, D. R. Terrell and J. H. Scholing, "An in situ Grown eutectic Magnetoelectric Composite Material: Part II Physical Properties," *J. Mater. Sci.*, **9** 1710-14 (1974).
8. L. P. M. Bracke and R. G. van Vliet, "A Broadband Magnetoelectric Transducer Using a Composite Material," *Int. J. Electronics*, **51** [3] 255-62 (1981).

9. T. G. Lupeiko, S. S. Lopatin, I. V. Lisnevskaya and B. I. Zvyagintsev, "Magnetoelectric Composite Materials Based on Lead Zirconate Titanate and Nickel Ferrite," *Inorg. Mater.*, **30** 1353-56 (1994).
10. T. G. Lupeiko, I. V. Lisnevskaya, M. D. Chkheidze and B. I. Zvyagintsev, "Laminated Magnetoelectric Composites Based on Nickel Ferrite and PZT Materials," *Inorg. Mater.*, **31** [9] 1139-42 (1995).
11. T. G. Lupeiko, I. B. Lopatina, S. S. Lopatin and I. P. Getman, "Porous Magnetoelectric Ceramic Based on Lead Zirconate Titanate and Nickel Ferrite," *Inorg. Mater.*, **27** [11] 2394-96 (1991).
12. T. G. Lupeiko, I. B. Lopatina, I. V. Kozyrev and L. A. Derbaremdiker, "Electrophysical and Magnetoelectric Properties of Ceramic Materials of the Type Piezoelectric-ferrite," *Inorg. Mater.*, **28** [3] 632-36 (1991).
13. Y. I. Bokhan and V. M. Laletin, "Influence of Demagnetizing Factors on the Field Dependence of Magnetoelectric Effect in Ferrite-piezoelectric Composite Ceramics," *Inorg. Mater.*, **32** [5] 634-35 (1996).
14. K. K. Patankar, V. L. Mathe, A. N. Patil, S. A. Patil, S. D. Lotke, Y. D. Kolekar and P. B. Joshi, "Electrical Conduction and Magnetoelectric Effect in $\text{CuFe}_{1.8}\text{Cr}_{0.2}\text{O}_4$ - $\text{Ba}_{0.8}\text{Pb}_{0.2}\text{TiO}_3$ Composites," *J. Electroceramics*, **6** [2] 115-22 (2001).
15. G. Srinivasan, E. T. Rasmussen, J. Gallegos, R. Srinivasan, Y. I. Bokhan and V. M. Laletin, "Magnetoelectric Bilayer and Multilayer Structures of Magnetostrictive and Piezoelectric Oxides," *Phys. Rev. B*, **64** 214-408 (2001).
16. J. Ryu, A. Vázquez Carazo, K. Uchino and H-E. Kim, "Piezoelectric and Magnetoelectric Properties of Lead Zirconate Titanate/Ni-Ferrite Particulate Composites," *J. Electroceramics*, **7** 17-24 (2001).
17. J. Ryu, A. Vázquez Carazo, K. Uchino and H-E. Kim, "Magnetoelectric Properties in Piezoelectric and Magnetostrictive Laminar Composites," *Jpn. J. Appl. Phys.*, **40** [8] 4948-51 (2001).
18. J. Ryu, S. Priya, A. Vázquez Carazo, K. Uchino and H-E. Kim, "Effect of the Magnetostrictive Layer on Magnetoelectric Properties in $\text{Pb}(\text{Zr,Ti})\text{O}_3$ /Terfenol-D Laminate Composites," *J. Am. Ceram. Soc.*, **84** [12] 2905-08 (2001).
19. L. E. Cross, "Relaxor Ferroelectrics," *Ferroelectrics*, **76** 241-67 (1987).
20. G. A. Smolensky, "Physical Phenomena in Ferroelectrics with Diffused Phase Transition," *J. Phys. Soc. Jpn. (Suppl.)*, **28** 26-37 (1970).
21. S-E. Park and T. R. Shrout, "Ultrahigh Strain and Piezoelectric Properties in Relaxor-based Ferroelectric Single Crystals," *J. Appl. Phys.*, **82** [4] 180-411 (1997).
22. J. Kuwata, K. Uchino and S. Nomura, "Phase Transition in the $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - PbTiO_3 System," *Ferroelectrics*, **37** 579-82 (1981).
23. J. Kuwata, K. Uchino and S. Nomura, "Dielectric and Piezoelectric Properties of $0.91\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - 0.09PbTiO_3 Single Crystals," *Jpn. J. Appl. Phys.*, **21** 1298-302 (1982).
24. S. L. Swartz, T. R. Shrout, W. A. Schulze and L. E. Cross, "Dielectric Properties of Lead Magnesium Niobate Ceramics," *J. Am. Ceram. Soc.*, **67** 311-15 (1984).
25. S. L. Swartz and T. R. Shrout, "Fabrication of Perovskite Lead Magnesium Niobate," *Mater. Res. Bull.*, **17**, 124-550 (1982).
26. P. Papet, J. P. Dougherty and T. R. Shrout, "Particle and Grain Size Effects on the Dielectric Behaviour of the Relaxor Ferroelectric $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$," *J. Mater. Res.*, **5** 2902-09 (1990).
27. D. Viehland, "Symmetry-adaptive Ferroelectric Mesostates in Oriented $\text{Pb}(\text{B}_{1/3}\text{B}_{1/2})\text{O}_3$ - PbTiO_3 Crystals," *J. Appl. Phys.*, **88** 4794-806 (2000).
28. S. Priya, J. Ryu, K. Uchino and D. Viehland, "Investigation of the Ferroelectric Orthorhombic phase in the $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - PbTiO_3 System," *Ferroelectrics*, in print.
29. G. Engdahl, *Handbook of Giant Magnetostrictive Materials*; pp. 127-135, Academic Press, San Diego, CA, 2000.
30. A. V. Virkar, J. L. Huang and R. A. Cutler, "Strengthening of Oxide Ceramics by Transformation-Induced Stress," *J. Am. Ceram. Soc.*, **70** [3] 164-70 (1987).