Magnetoelectric Effect in Composites of Magnetostrictive and Piezoelectric Materials

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Abstract. In the past few decades, extensive research has been conducted on the magnetoelectric (ME) effect in single phase and composite materials. Dielectric polarization of a material under a magnetic field or an induced magnetization under an electric field requires the simultaneous presence of long-range ordering of magnetic moments and electric dipoles. Single phase materials suffer from the drawback that the ME effect is considerably weak even at low temperatures, limiting their applicability in practical devices. Better alternatives are ME composites that have large magnitudes of the ME voltage coefficient. The composites exploit the product property of the materials. The ME effect can be realized using composites consisting of individual piezomagnetic and piezoelectric phases or individual magnetostrictive and piezoelectric phases. In the past few years, our group has done extensive research on ME materials for magnetic field sensing applications and current measurement probes for high-power electric transmission systems. In this review article, we mainly emphasize our investigations of ME particulate composites and laminate composites and summarize the important results. The data reported in the literature are also compared for clarity. Based on these results, we establish the fact that magnetoelectric laminate composites (MLCs) made from the giant magnetostrictive material, Terfenol-D, and relaxor-based piezocrystals are far superior to the other contenders. The large ME voltage coefficient in MLCs was obtained because of the high piezoelectric voltage coefficient of the piezocrystals and large elastic compliances. In addition, an optimized thickness ratio between the piezoelectric and magnetostrictive phases and the direction of the magnetostriction also influence the magnitude of the ME coefficient.

Keywords: magnetoelectric, piezoelectric, magnetostrictive, composite, Terfenol-D, PZT

1. Introduction

Magnetoelectricity is a product property and needs biphasic surrounding to exhibit the complex behavior. The primary magnetoelectric (ME) materials become magnetized when placed in an electric field and electrically polarized when placed in a magnetic field. In the secondary effect, the permeability or permittivity change is expected. The history of the ME effect dates back to as early as 1894, when Curie stated that it would be possible for an asymmetric molecular body to polarize directionally under the influence of a magnetic field [1]. Later, Landau and Lifshitz [2] showed from symmetry considerations that a linear ME can occur in magnetically ordered crystals. Subsequently, Dzyaloshinskii [3], on the basis of theoretical analysis, predicted the existence of the ME effect in antiferromagnetic Cr_2O_3. This was confirmed by Astrov [4] by measuring the electric field induced magnetization and later by Rado and Folen [5] by detection of the magnetic field-induced polarization.

The primary requirement for the observance of this effect is the coexistence of magnetic and electric dipoles. Materials exhibiting the ME effect can be classified into two classes: single phase and composites. Single phase materials exhibiting the ME effect have an ordered structure and require the presence of a ferroelectric/ferrielectric/antiferroelectric state. These

materials should show two transitions—one from a ferroelectric to a paraelectric state and the other from a ferromagnetic/ferrimagnetic/antiferromagnetic to a paramagnetic state. The ME effect arises due to the local interaction between the ordered magnetic and ferroelectric sublattices. The conditions for the occurrence of ferroelectricity and magnetic order in the same material often accompanied by ferroelasticity implies (a) the presence of adequate structural building blocks permitting ferroelectric-type ionic movements, (b) magnetic-interaction pathways, usually of the superexchange type, and (c) the fulfillment of symmetry conditions [6]. One simple inference from this is that it is possible to synthesize the ferroelectric ferromagnets by replacing diamagnetic ions by paramagnetic ones on the B-site of oxyoctahedral ferroelectric perovskites. Smolensky and Ioffe [7] in 1958 synthesized the antiferromagnetic ferroelectric perovskite ceramic $Pb(Fe_{1/2}Nb_{1/2})O_3$ (PFN). Later single crystals of PFN were grown and the presence of a weak spontaneous moment in the ferroelectric phase below 9K was confirmed [8]. In the last few decades, the ME effect has been found in numerous compounds [3, 9–25]. The ME effect has been reported in materials with the perovskite structure, RE magnates, pseudo-ilmenites, $BaMeF_4$ (Me = Mn, Fe, Co, Ni), Cr_2BeO_4 and inverted spinels [26]. In 1980, Ismailzade et al. [27] reported the presence of linear ME effect in $BiFeO_3$, a compound of antiferromagnetic-ferroelectric nature. Its combination with bismuth titanate and barium titanate forms a family with the general formula $Bi_4Bi_{m-3}Ti_3Fe_{m-3}O_{3m+3}$ (m = 4, 5 and 8) in which the coexistence of ferroelectric and magnetic nature exists up to high temperatures [28]. Schmid [6] has extensively worked on boracites belonging to the large crystal structure family with the general formula $M_3B_7O_{13}X$, where M stands for a bivalent cation of Mg^{2+}, Cr^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, etc. and X stands for a monovalent anion like OH^-, F^-, Cl^-, Br^-, I^- or NO_3^-. The simultaneous presence of ferroelectricity and ferromagnetism in coexistence with ferroelasticity in materials such as nickel boracite $Ni_3B_7O_{13}I$, activates coupling between the spontaneous polarization, spontaneous magnetization and spontaneous deformation. It has been found that an electric field-induced 180° reversal of the spontaneous polarization causes a symmetry-conditioned 90° reorientation of the spontaneous magnetization, and a magnetic field-induced 90° reorientation of the spontaneous magnetization causes a 180° reversal of the spontaneous polarization.

The realizable magnitude of the magnetoelectric voltage coefficient in the single phase materials is of the order of ∼1–20 mV/cm · Oe, which is not sufficient for practical applications. Another limitation on the usage of these materials is the working range of temperature. Most of the single phase materials can be used only at very low temperatures, involve expensive materials and processing technique and suffer from degradation under cyclic conditions. The solution to these limitations was offered by shifting to composites.

In composite materials, the ME effect is realized by using the concept of product properties introduced by Van Suchetelene [29]. A suitable combination of two phases can yield the desirable property such as a combination of piezomagnetic and piezoelectric phases or a combination of magnetostrictive and piezoelectric phases. The ME effect can also be realized by coupling the thermal interaction in pyroelectric–pyromagnetic composites. Most ferromagnetic materials show the magnetostrictive effect, however, piezomagnetic effect in these materials has not been observed. This means that the strain caused by a magnetic field in these materials is not linearly proportional to the field strength but is related to the square of the magnetic field strength. This makes the product property, the magnetoelectric effect in the piezoelectric-magnetostrictive composites, a non-linear effect unlike the single phase materials where the magnetoelectric effect is a linear effect over a wide range of the values of the magnetic or electric field. Also the magnetoelectric effect in these composites shows a hysteretic behavior. This makes the applications of such composites difficult in linear devices. Linearity in such composites is achieved by applying a bias magnetic field across them so that the magnetoelectric effect over a short range around this bias can be approximated as a linear effect. The hysteretic nature of this effect can be made use of in memory devices, for which there is no necessity of a bias magnetic field.

The ME effect obtained in composites is more than a hundred times that of single-phase ME materials such as Co_2O_3. In 1978, Boomgaard [30] outlined the conceptual points inherent to the ME effect in composites. These can be summarized as (i) two individual phases should be in equilibrium (ii) mismatching between grains should not be present (iii) magnitude of the magnetostriction coefficient of piezomagnetic or magnetostrictive phase and magnitude of the

piezoelectric coefficient of the piezoelectric phase must be greater (iv) accumulated charge must not leak through the piezomagnetic or magnetostrictive phase and (v) deterministic strategy for poling of the composites. At present various composites have been reported such as $Ni(Co,Mn)Fe_2O_4$–$BaTiO_3$, $CoFe_2O_4$–$BaTiO_3$, $NiFe_2O_4$–$BaTiO_3$, $LiFe_5O_8$–$BaTiO_3$, $CoFe_2O_4$–$Bi_4Ti_3O_{12}$ etc. [29–38].

The basic ideas underlying composite electroceramics can be classified into three categories: (1) sum properties, (2) product properties, (3) combination properties [29, 39, 40]. Figure 1 shows a schematic representation of these properties of a composite [40].

Depending on the application, the appropriate properties of the individual phases can be invoked to design a composite which will have a sum property or a product property. These concepts are of fundamental importance and will be very briefly discussed here. A sum property of a composite is a weighted sum of the contributions from the individual component phases, proportional to the volume of weight fractions of these phases in the composite. Physical quantities like density and resistivity are sum properties. A more interesting result of a composite structure is the product property, which is reflected in the composite structure but is absent in the individual phases. In a biphasic composite material,
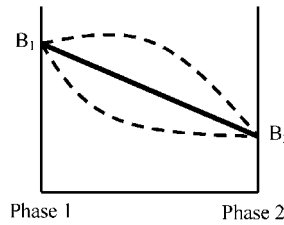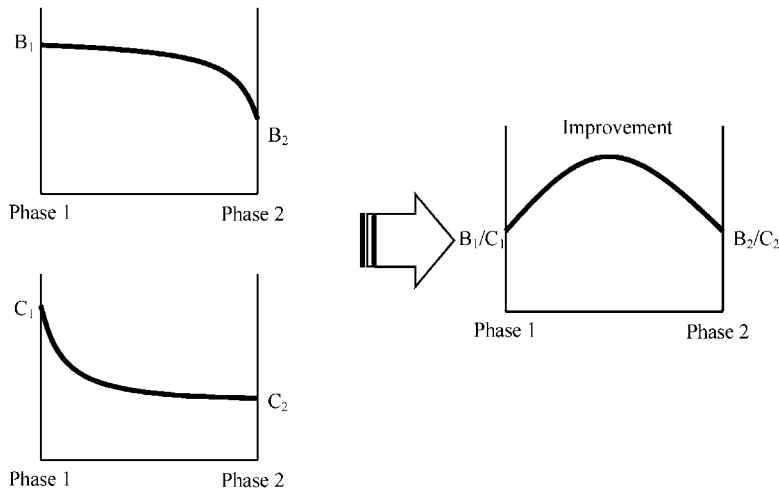

Fig. 1. Composite properties; (a) sum properties, (b) product properties, and (c) combination properties [30].

if one phase exhibits a property $A \rightarrow B$ (application of an independent variable A resulting in an effect B) with a proportionality tensor $dB/dA = X$ (may be a constant or dependent on A or B) and the second phase exhibits a property $B \rightarrow C$ with a proportionality tensor $dC/dB = Y$, then the composite will exhibit a property $A \rightarrow C$ which is absent in either of the initial phases. The property $A \rightarrow C$ is called a product property of the composite. The proportionality tensor dC/dA is the product of the proportionality tensor of the phases, i.e. $dC/dA = (dC/dB)(dB/dA) = YX$. In certain cases, the averaged value of the output, B^*, of a composite does exceed the magnitude of end components B_1 and B_2. This enhanced output refers to an effect B/C which depends on the two parameters B and C. Suppose that A and C follow convex and concave type sum effects, respectively, as illustrated in Fig. 1(c). The combination value B/C will exhibit a maximum at an intermediate ratio of the phases. This is called a "combination property". All these properties can be exploited to yield the requisite effect for the desired application.

Recently, we discovered an exceptionally high ME effect in magnetoelectric laminate composites (MLCs) of piezoelectric and magnetostrictive material [41, 42]. The ME voltage coefficient (dE/dH) in MLCs of $Pb(Mg_{1/3}Nb_{2/3})O_3$–$PbTiO_3$ single crystal and Terfenol-D was found to be 10.30 V/cm · Oe at 1 kHz when under a d.c. magnetic bias of 0.4 T. This value of dE/dH is $\sim$80 times higher than either that of naturally occurring magnetoelectrics or artificially-grown magnetoelectric composites. The specimens had the dimensions of 5 mm diameter and 2.4 mm thickness. In this article, we review the progress made in the area of the ME effect in composites and describe the advances and contributions of our group.

2. Particulate or in situ ME Composites

The first work on ME composites was done at Philips Laboratories in the Netherlands [29–33]. The ME composites were prepared by unidirectional solidification of a eutectic composition of the quinary system Fe-Co-Ti-Ba-O [29, 31]. The unidirectional solidification helps in the decomposition of the eutectic liquid into alternate layers of the constituent phase—a piezoelectric perovskite phase (P) and a piezomagnetic spinel phase (S) ($L \rightarrow P + S$). The unidirectional solidification process requires a critical control over the composition especially when one of the components (oxygen) is a gas. Their results showed that an ex-
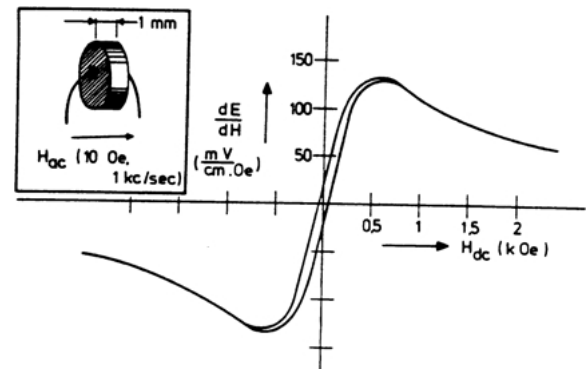

Fig. 2. ME properties of $BaTiO_3$-$CoFe_2O_4$ in situ composites as a function of applied magnetic bias field (insert: specimen shape) [31]. (Permission obtained from Taylor & Francis Ltd.)

cess of TiO_2 (1.5 wt%) gives a high ME voltage coefficient $dE/dH = 50$ mV/cm · Oe [31]. However, other compositions showed a lower dE/dH in the range 1–4 mV/cm · Oe. In a subsequent work, they reported to have obtained a ME voltage coefficient $dE/dH = 130$ mV/cm · Oe in a eutectic composition of $BaTiO_3$-$CoFe_2O_4$ by unidirectional solidification [32]. Figure 2 shows the best result from the Philips Lab [31]. This value is about an order of magnitude higher than that of the single crystal Cr_2O_3 for which $dE/dH = 20$ mV/cm · Oe. A more relevant parameter is the ME coefficient $\alpha = dP/dH$ (in the Gaussian system $\alpha = 4\pi(dP/dH)$ is a dimensionless quantity). Comparison of these values using the relation $\alpha = dP/dH = \varepsilon \, dE/dH$, where ε is the dielectric permittivity of the material, and using the values of the dielectric constants ε_r, 500 for the composite and 11.9 for Cr_2O_3, shows $\alpha = 7.22 \times 10^{-10}$ (s/m) for the composite. This is about 270 timesmore than $\alpha = 2.67 \times 10^{-12}$ (s/m) for Cr_2O_3. In 1978, they reported about their work on sintered ME composites of the same system with excess TiO_2, the particle size effect, the cooling rate and the mole ratios of both the phases [30]. They reported a maximum value of the ME voltage coefficient of 80 mV/cm · Oe in sintered ME composites of $BaTiO_3$-$Ni(Co,Mn)Fe_2O_4$.

Bunget and Raetchi have reported observation of the ME effect in Ni-Zn ferrite-PZT composites and its dependence on the applied magnetic field [43]. There is no published work about the applications of such composites except the work of Bracke and Reatchi who have reported an application of an ME sintered composite of $BaTiO_3$ and Ni-ferrite doped with Co and Mn as a

broadband transducer up to 650 kHz frequency. The ME voltage coefficient value is about 3 mV/cm · Oe.

Theoretical models are available in the literature to account for the large ME effect of composites [31, 44, 45]. In the past, studies on ME composites have concentrated on estimation of the effective properties of the composite as a function of microstructure variables such as physical properties of individual phases, volume fraction, shape and connectivity. These models have their own advantages and disadvantages. Van den Boomgaard et al. [31] assumed that if (1) the dielectric constant of $BaTiO_3 \gg$ dielectric constant of the ferrite, (2) Young's moduli for both the phases are equal and (3) there is perfect coupling between the phases, then the ME voltage coefficient is given by

$$(dE/dH)_{comp} = (dx/dH)_{comp}(dE/dx)_{comp}$$
$$= m_v(dx/dH)_{ferrite}(dE/dx)_{BaTiO_3}$$

Where (dx/dH) is the change in dimension per unit magnetic field and (dE/dx) is the change in dimension per unit electric field. The subscript 'comp' stands for composite and m_v is the volume fraction of the ferrite. Using the maximum optimistic value of the parameters, $(dx/x)/dH = 6.28 \times 10^{-9}$ (m/A) (= 5×10^{-7} Oe^{-1}), $dE/(dx/x) = 2 \times 10^9$ (V/m) and $m_v = 0.5$. The estimated maximum value of the ME voltage coefficient comes out to be $dE/dH = 6.28$ (V/m)/ (A/m) (= 5 V/cm · Oe). Zubkov has modified the expression as follows [44]:

$$(dE/dH)_{comp}$$
$$= m_v(dS/dH)_{ferrite}(1 - m_v)(dE/dS)_{piezo}$$

Since $dE = dE_3 = g_{33}dT_3$ and $dS = (dT_3)/C_{33}$ where g_{33} and C_{33} are the piezoelectric voltage and stiffness coefficients respectively of the piezoelectric phase, T is the stress and S is the strain.

$$\alpha E = m_v(dS/dH)_{ferrite}(1 - m_v)(g_{33}C_{33})_{piezo}$$

The value of the ME voltage coefficient dE/dH is estimated to be 1.15 (V/m)/(A/m) (= 0.92 V/cm · Oe).

Harshe et al. calculated the ME voltage coefficient theoretically by using a cubes model with 3–0 or 0–3 connectivity of phases [45]. According to their results, for the best ME effect, both the phases should have comparable elastic and dielectric properties. The maximum theoretical effect for the composites studied was found to be in a $CoFe_2O_3$ (80%) and PZT-4 (20%)
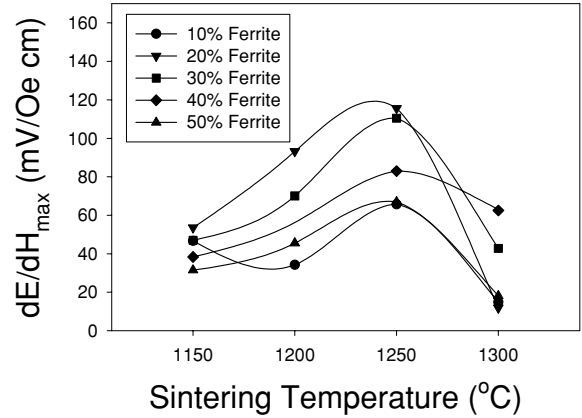

Fig. 3. Maximum ME voltage coefficient of the PZT and Ni-ferrite particulate composites as functions of sintering temperature and Ni-ferrite particle content.

composite. The magnitude of the ME voltage coefficient was 4.5 (V/m)/(A/m).

In our group, we investigated the effect of the sintering temperature on the sintering behavior, microstructures, piezoelectric and ME properties of this ME particulate composite with Ni-ferrite doped with Co, Cu, Mn particles and PZT matrix [42, 46]. Not only the connectivity of the ferrite phase, but also the sintering temperature are the important parameters for higher ME voltage coefficient dE/dH. The chemical reaction of the PZT with ferrite, and connection of ferrite particles make it difficult to get high ME effects. Figure 3 shows the maximum ME voltage coefficient of each composite as a function of sintering temperature which is reported from our group [46]. We obtained the highest ME voltage coefficient from the composite with 20% ferrite added and sintered at 1250°C. A homogeneous and well dispersed microstructure, no chemical reaction between the two phases, and large grain size of the matrix PZT phase [47] were the most important factors to get a high ME voltage coefficient. The value was 115 mV/cm · Oe, which is 44% higher than the previously reported value for the ME particulate composite from Philips Lab [31].

3. Experimental

The measurement of the non-linear ME effect in composites requires a d.c. bias along with an a.c. magnetic field. A permanent magnet or a d.c. electromagnet can provide the d.c. bias. Bunget and Raetchi have proposed and used a different experimental configuration [43].

Since in the ME composites the electric polarization is a function of the applied electric and magnetic fields, one can apply them simultaneously and measure polarization. They have measured the polarization by keeping the electric field constant and varying the magnetic field. Thus the ratio of the increase in polarization per unit increase in magnetic field gives the ME coefficient.

The results reported in this paper were obtained using a similar method. The ME property was measured in terms of the variation of the coefficient dE/dH as a function of d.c. magnetic bias field. An electromagnet (GMW 5403 Magnet, Power and Buckley Inc., New Zealand) was used for the bias field up to 0.45 T (4.5 kOe). The coefficient was measured directly as response of the sample to an a.c. magnetic input signal at 1 kHz and 1 Oe amplitude superimposed on the d.c. bias field, both parallel to the sample axis. A signal generator (DS340, Stanford Research Systems) was used to drive the Helmholtz coils and generate the a.c. magnetic field. The electric charge generated from the piezoelectric layer was measured through a charge amplifier (5010B Dual Mode Amplifier, Kistler Instrument Co, NY). 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.). The measured voltage represented an electric charge from the piezoelectric PZT layer under a short-circuit condition [48]. The output voltage was obtained from charge and the capacitance of the PZT layer of the composite, using $V = Q/C$ (1 kHz). The output voltage divided by the thickness of the PZT layer and the a.c. magnetic field gives the ME voltage coefficient of the samples. Figure 4(a) and (b) show the schematic diagram and picture respectively of the measurement setup for the ME property measurement.

4. Applications

The ME effect is a tool for the conversion of energy from magnetic to electric form or vice versa. Tellegen proposed a gyrator using a ME material before the discovery of any ME material [49]. The ME coupling factor is an important indication of the usefulness of these materials for any devices. Unfortunately, many ME materials have very low ME coupling factors. Nevertheless, many applications have been already proposed by various researchers.
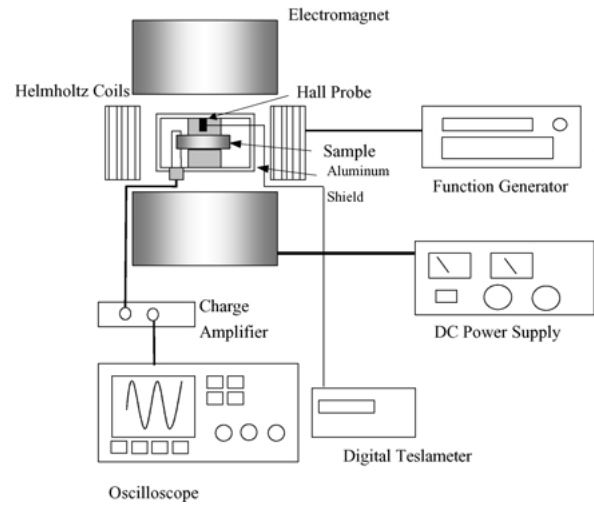
(a)
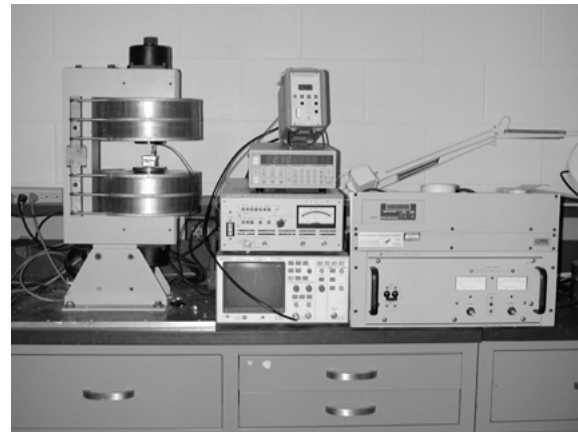
(b)

Fig. 4. (a) Schematic diagram of ME measurement system, (b) Photograph of ME measurement system.

An ME memory device application has been proposed by O'Dell [9]. The linear ME effect has a positive or a negative sign depending on the ME annealing conditions in the case of a polycrystalline material. If the magnetic and electric fields during annealing are parallel to each other then the ME effect is positive. If the magnetic and electric fields are antiparallel then the effect is negative. This shows that the material can store information in two different states '0' and '1'. Thus the ME material can be used in binary data storage devices. Such a memory will be an effective 'read only' memory, since the reading can be done at very high frequencies. The ME coefficient is practically

constant up to the antiferromagnetic resonance frequency which is around 100 GHz. The data writing is somewhat difficult since it involves annealing from above the Néel temperature in a magnetic and electric field and then cooling it below the Néel temperature. This process cannot be done fast enough to use in data writing applications. However, the data may be stored by using high magnetic fields if the material undergoes a metamagnetic transition as mentioned above.

Device applications of piezoelectric and magnetostrictive materials in a composite structure had been proposed long before the initial work on composites. Even before the discovery of the ME effect in Cr_2O_3, Katz discussed transducers and filter applications of ceramics using a composite of piezoelectric and magnetostrictive materials [50]. Besides the applications mentioned above, a few other applications might be possible because of the non-linear ME effect of composites. Since the magnetic field input is required to have two components, a d.c. bias and an a.c. signal, either of the two can be detected by providing the other component of a fixed magnitude in the input. Thus such a composite can be used as a magnetic probe for detecting a.c. as well as d.c. fields. These composites can be used as ME transducers in recording heads and electromagnetic pick-ups. The thickness of the phase in layered composites can be controlled so that the resonance frequency is increased and they can be used in high frequency transducer applications. Because of the hysteretic nature of the ME effect, the composites may find applications in memory devices.

As mentioned, the ME effect in materials can be utilzed in many applications. However, no commercial application has as yet been found for these composites. This may be due to the difficulty of achieving the product property in the composite materials with reproducibility. To achieve maximum product property, good mechanical coupling is required between the phases. At the same time, it is desired that no chemical reaction occur between the phases. In the sintered composites or the unidirectionally solidified composites of piezoelectric materials and ferrites, the temperature of processing is too high to avoid any chemical reaction of the phases. Also small deviations in compositions while sintering may cause a reasonable drop in the piezoelectric or magnetostrictive properties of the component phase. The connectivity pattern of the component phases in the composites is of importance for the electric properties such as resistivity, dielectric constant, piezoelectric coefficient and hence the ME constant.

The possible applications of the ME materials have been reviewed by Wood and Austin [51]. For such applications ME composite materials are suitable because of their wide temperature range of operation above and below room temperature and also because of their larger ME coefficients compared to the single phase ME materials.

5. ME Laminate Composites

The particulate or in situ ME composites made of piezoelectric materials and magnetostrictive ferrite materials showed higher ME properties compared with single-phase ME materials such as Cr_2O_3, as we mentioned in the previous section. However, these composites still need some important issues addressed when fabricating the sintered or in situ ME particulate composites to obtain superior ME response. First, no chemical reaction should occur between the piezoelectric and magnetostrictive materials during the sintering process. The chemical reaction may reduce the piezoelectric or magnetostrictive properties of each phase. Second, the resistivity of the magnetostrictive phase should be as high as possible. If the resistivity of the magnetostrictive phase is low, the electric poling becomes very difficult due to leakage current. Also, the leakage current reduces the ME properties of the composites. When the ferrite particles make connected chains, the electric resistivity of the composites is reduced significantly because of the low resistivity of the ferrite. Therefore, good dispersion of the ferrite particles in the matrix is required in order to sustain sufficient electric resistivity of the composite. Third, mechanical defects such as pores at the interface between the two phases should not exist in the composite for good mechanical coupling.

These difficulties may be overcome by using a laminar composite, because no chemical reactions and dispersions are involved in the fabrication process. In addition to these advantages, the laminated ME composites have a very simple structure and relatively simple fabrication method, i.e., bonding each disk [41, 42, 52, 53]. The laminated ME composites can be easily applied to practical applications, such as magnetic field sensing devices, leak detectors for microwave ovens, and current measurement of high power electric transmission systems.

Recently, the laminated ME composites made by using piezoelectric and magnetostrictive materials have been studied by our group [41, 42, 52, 53]. Lead
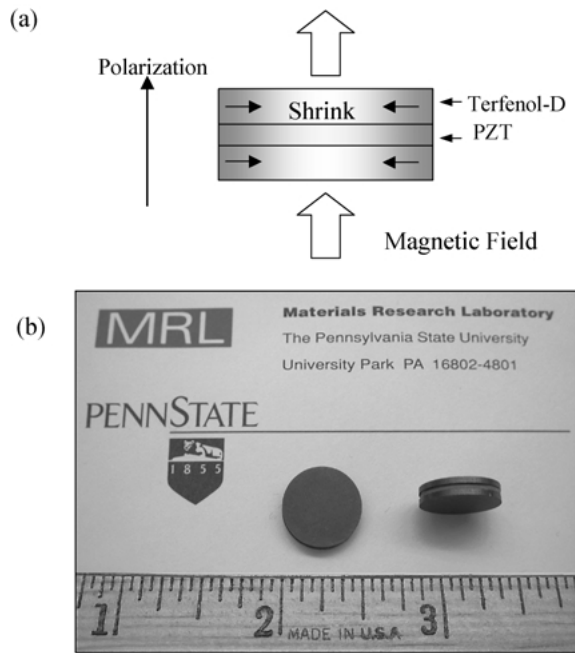
(a)

(b)

Fig. 5. ME laminate composite using Terfenol-D and PZT disks. (a) schematic structure, and (b) photograph of the device.

Zirconate Titanate (PZT) and Terfenol-D disks were used as the piezoelectric material and magnetostrictive material, respectively, in the ME laminate composites. The composites were manufactured by sandwiching and bonding a PZT disk between two layers of Terfenol-D disks, as shown in Fig. 5. When a magnetic field is applied to this composite, the top and bottom Terfenol-D disks shrink or expand. This shrinkage or expansion generates stresses in the sandwiched piezoelectric PZT disk. Hence, electric signals can be obtained when the composite is subjected to a magnetic field. To optimize the PZT and Terfenol-D ME laminate composites, we investigated the effect of the piezoelectric properties of the piezoelectric PZT layer, thickness ratio between the PZT and Terfenol-D disks, the directional dependence of the magnetostriction of the Terfenol-D disks, and of the a.c. magnetic field on the ME response of the PZT/Terfenol-D laminate composites.

5.1. *Effect of Piezoelectric Properties of PZT Disk*

The effect of the piezoelectric properties of the PZT material on the ME response of the laminate composites was studied on samples consisting of two

Table 1. Piezoelectric properties of PZT materials used in this article.

Material	$\varepsilon_{33}^T/\varepsilon_o$	Tan δ (%)	d_{33} (pC/N)	g_{33} (mVm/N)	Q_m	k_p
APC840	1250	0.4	320	**28.9**	500	0.59
PZT-5A	1730	1.5	**340**	22.2	68	0.57
APC841	1250	0.35	275	24.8	**1400**	0.60

Terfenol-D disks and one different kind of PZT materials. Table 1 shows the piezoelectric properties of the PZT materials used for this study. APC 840, PZT-5A, and APC 841 were used for their high g_{33}, high d_{33}, and high Q_m, respectively. Figure 6 shows the ME voltage coefficient variation as a function of the d.c. magnetic bias with three different PZT types. All PZT disks were machined down to the same thickness (0.5 mm) and diameter (12.7 mm). The ME voltage coefficients of all the composites were increased with increasing d.c. bias until saturated around 4 kOe. Since the sensitivity is mainly determined by the piezoelectric voltage coefficient (g_{33}), the composite with APC-840 PZT showed the most superior ME property. The maximum ME voltage coefficient for this composite was 4.68 V/cm · Oe under 4.2 kOe d.c. magnetic bias or higher.

5.2. *Thickness Ratio Effects on the ME Property*

The ME voltage coefficient was found to increase with decreasing thickness of the PZT layer as depicted in Fig. 7. This can be explained by the increase in compressive stress in the PZT layer with decreasing thickness of PZT. The compressive stress in the PZT layer
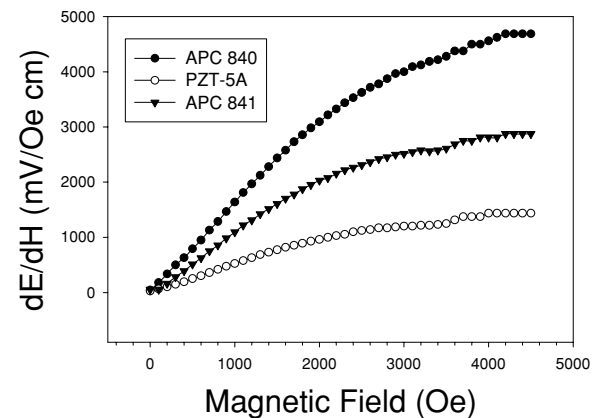

Fig. 6. ME voltage coefficient as a function of applied d.c. magnetic bias for various PZT disks (APC 840 for high g_{33}, PZT-5A for high d_{33}, APC 841 for high Q_m) at 1 kHz.
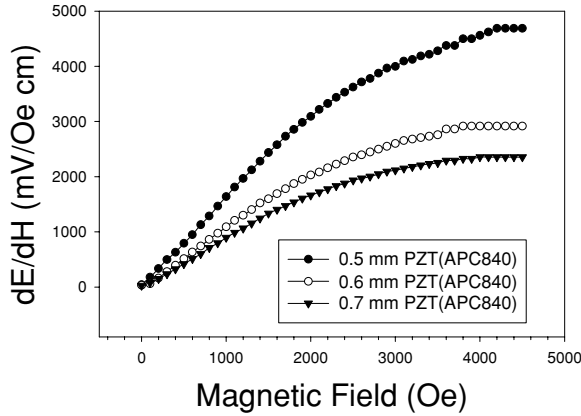
Fig. 7. ME voltage coefficient as a function of applied d.c. magnetic bias with various thickness of PZT layer 1 kHz.

Fig. 8. Theoretical expectation of the ME voltage coefficient as a function of thickness ratio(t_t/t_p) between Terfenol-D and PZT layer.

and the tensile stress in the Terfenol-D layers can be derived from simple beam theory under plane stress conditions, as indicated in Eqs. (1) and (2) [54]:

$$\sigma_{31t}^E = \frac{E_t E_p t_p \Delta\varepsilon_o}{(1-\nu)(2E_t t_t + E_p t_p)}, \quad (1)$$

$$\sigma_{31p}^E = -\frac{2E_t E_p t_p \Delta\varepsilon_o}{(1-\nu)(2E_t t_t + E_p t_p)}, \quad (2)$$

where E, t, $\Delta\varepsilon_o$, and ν are the elastic modulus, thickness, the linear strain of the Terfenol-D layer, and poisson's ratio (poisson's ratios of Terfenol-D and PZT are assumed to have the same value in these equations), respectively. The subscript 't' or 'p' means Terfenol-D or PZT, respectively. As shown in these equations, the compressive stress in the PZT layer is increased with the decreasing thickness of the PZT layer or the increasing thickness of the Terfenol-D layer. Since the thickness of the Terfenol-D is fixed at 1 mm, by decreasing the PZT layer thickness, the compressive stress in the PZT layer is increased. The output voltage from the composite can be expressed by the following equations.:

$$V_{\text{out}} = 2 \times g_{31} \times t_p \times \sigma_{31p}^E, \quad (3)$$

$$\frac{dE}{dH} = \frac{V_{\text{out}}}{H_{\text{ac}} \times t_p} = \frac{2 \times g_{31} \times \sigma_{31p}^E}{H_{\text{ac}}} (\text{V/cm} \cdot \text{Oe}). \quad (4)$$

Therefore, a higher output voltage can be obtained when the compressive stress in the PZT layer is higher, i.e., a thinner PZT layer. From these equations, it can be seen that the output voltage from the composite is also directly proportional to the piezoelectric voltage
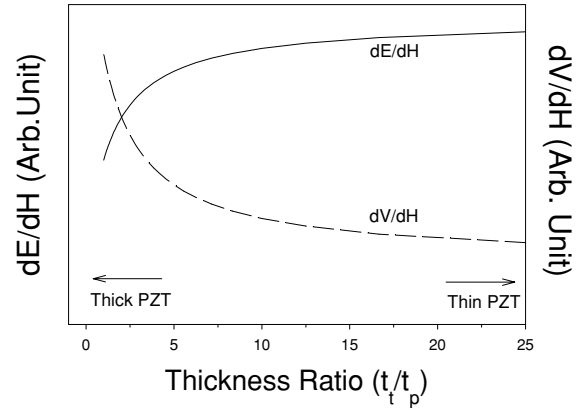
constant g_{31}. Generally in PZT ceramics, the piezoelectric voltage constant g_{31} is around 1/3 that of g_{33}. In this regard, the laminate composite made with APC-840, which has the highest g_{33}, exhibits the highest ME voltage coefficient, as shown in Fig. 6.

Figure 8 shows the theoretical expectation for the ME voltage coefficient (dE/dH) and the output voltage (dV/dH) as a function of the thickness ratio (t_t/t_p) between Terfenol-D and PZT. The ME voltage coefficient increases with increasing thickness ratio (t_t/t_p), but output voltage decreases with increasing thickness ratio. Both values saturate above a thickness ratio of 10. The value of the output voltage is more important than the ME voltage coefficient for practical sensor applications. Therefore, a lower thickness ratio (less than 10) is more suitable, even though the ME voltage coefficient is increasing with thickness ratio.

5.3. Magnetostriction Direction Dependence

Three kinds of laminate composite design were prepared by using two types of Terfenol-D disks to investigate this issue. These are as follows:
(1) Composite with two Terfenol-D disks that have their magnetostriction along the thickness direction (denoted as Comp.T-T).
(2) Composite with one Terfenol-D disk with thickness magnetostriction direction and the other Terfenol-D disk with radial magnetostriction direction (denoted as Comp.T-R).
(3) Composite with two disks that have their magnetostriction along the radial direction (denoted as Comp.R-R).
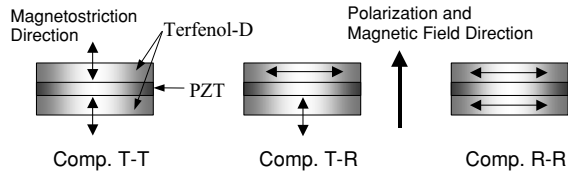
Fig. 9. Schematic illustrations for three different PZT/Terfenol-D composites.

Figure 9 shows schematic illustrations of each composite structure. The dielectric polarization direction of the PZT disk and the applied magnetic field direction were in the thickness direction for all the composites. Figure 10 illustrates the variation of the ME voltage coefficient (dE/dH) as a function of the d.c. magnetic bias for the three different composites. The ME voltage coefficients of all composites increased with increasing d.c. bias, and saturated around 4 kOe. The Comp.R-R showed the most superior ME property. Its maximum ME voltage coefficient was 5.90 V/cm · Oe when under a magnetic d.c. bias equal to or greater than 4.2 kOe. In the Terfenol-D disks, the magnitude of strain in the principal magnetostriction direction is higher than other directions [55].

5.4.   Magnetic Field Direction Dependence

In applications like magnetic field sensing devices, the dependence of the ME response on the magnetic field direction is an important factor. To examine the magnetic field direction dependence, we measured the ME
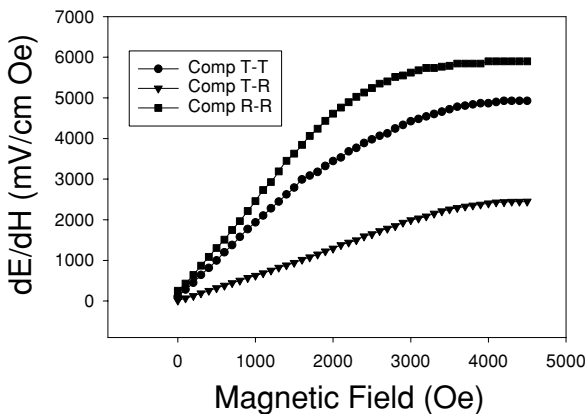

Fig. 10. ME voltage coefficient as a function of applied d.c. magnetic bias for composites with different assembly techniques.
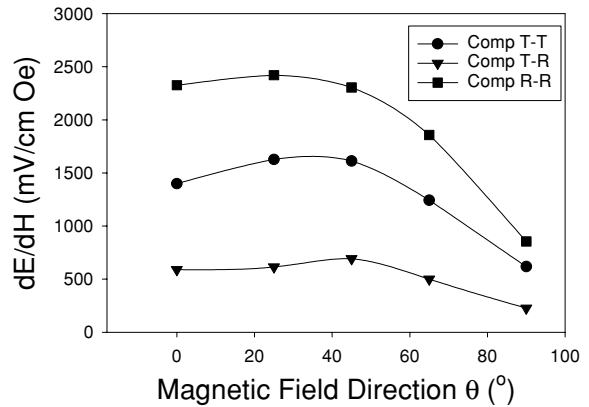

Fig. 11. ME voltage coefficient as a function of an applied a.c. magnetic field direction.

voltage coefficient by changing the applied magnetic field direction. The dependence of the ME voltage coefficient of the composites on the applied a.c magnetic field direction is shown in Fig. 11. The angle of the applied a.c. magnetic field (1 kHz) indicates the difference in angle between the a.c. magnetic field and the d.c. magnetic bias (thickness direction of the sample). The dependence of the a.c. magnetic field direction exhibited a similar behavior for all the composites, with a maxima occurring at 25–45 degrees. Beyond 45 degrees, the ME voltage coefficient decreased with an increase of the a.c. magnetic field direction. According to the theoretical calculations, these behaviors are basically related to the areal strain changing behavior of Terfenol-D with changing the applied magnetic field direction. The calculated maximum of the areal strain occurs at the orientation angle, $\theta = 51$ degree. It is expected that the ME coefficient will show a maximum around this angle. This behavior originates from the contribution of the relatively large shear mode strains, i.e., $|d_{15}| > |d_{33}|$ or $|d_{31}|$ [56].

5.5.   ME Laminate Composite with PMN-PT Single Crystal and Terfenol-D

As shown in the previous section, the most important factors needed in order to achieve a high ME voltage coefficient from piezoelectric-magnetostrictive composites are a high piezoelectric voltage coefficient (g_{ij}), an optimum thickness ratio between the PZT and Terfenol-D layers, and the optimized direction of magnetostriction in the Terfenol-D disks. Piezoelectric
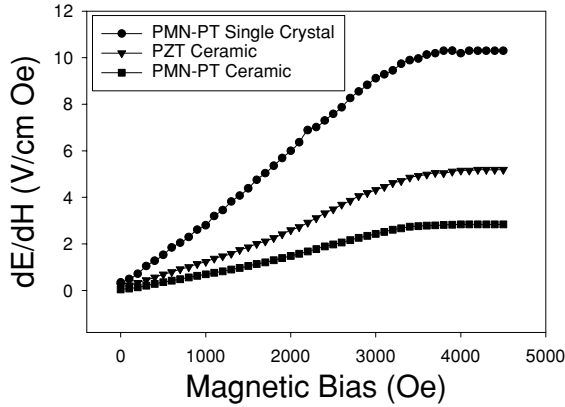
Fig. 12. ME voltage coefficient for laminate composites as a function of an applied d.c. magnetic bias field for different piezoelectric disks. Data are shown for PZT, PMN-PT ceramic, and PMN-PT single crystal disks.

Table 2. Materials characteristics of piezoelectric disks.

Materials	$\varepsilon_{33}^T/\varepsilon_o$	d_{33} (pC/N)	g_{33} (mV m/N)	S_{33}^E (10^{-12} m^2/N)
PMN-PT single crystal	4344	1710	44.45	56.4
PMN-PT ceramic	5614	570	11.47	9.5
PZT ceramic	1081	250	26.11	17.4

It is evident from the table that both the piezoelectric voltage coefficient and elastic compliance are higher for PMN-PT single crystal as compared to PZT ceramic. This difference is responsible for the higher ME properties of the PMN-PT laminate composites. These results indicate that a better ME property can be obtained if the elastic and piezoelectric properties of the materials can be improved.

5.6. Applications of MLCs

In addition to a high ME voltage coefficient, the MLCs have a simple design and are easy to fabricate. The MLCs can be easily applied in practical applications, such as magnetic field sensing devices for a quasi d.c. ~100 kHz apparatus, and current measurement probes for high-power electric transmission systems. The response speed is limited by the mechanical resonance of the MLCs. Some electric devices and high-power electric transmission systems require an accurate measurement of the electromagnetic leak signal generated from these devices from a viewpoint of human health. Also, a ME sensor will be an alternative cheap and accurate simple tool of the Hall sensor for magnetic field measurement. The MLCs can be assembled along with a simple charge amplifier and coordinated with an electric voltage meter for magnetic field sensing applications. When there is magnetic field or noise in the surroundings, electrical signals will be generated by the MLCs. These signals will be passed on to the electric voltage meter via the charge amplifier. Hence, under magnetic field or noise, we can monitor the intensity of the magnetic field in the surroundings as an electric voltage by using MLCs.

6. Conclusion

In summary, ME laminate composites have been fabricated with piezoelectric and magnetostrictive

single crystals such as $Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ (PMN-PT) and $Pb(Zn_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ (PZN-PT) are very well known to have superior piezoelectric properties [57, 58]. Extremely high ME coefficients have been achieved when the PZT ceramic layer has been replaced by *a* $\langle 001 \rangle$ oriented $Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ (PMN-PT) single crystal, which has a much higher g_{ij} coefficient. Figure 12 shows the ME voltage coefficient as a function of applied d.c. magnetic field. The magnetic field dependence of dE/dH was similar for all three types of piezoelectric specimens. As is evident in the figure, the ME voltage coefficient increased with increasing magnetic bias, saturating at a bias level of ~4 kOe. The ME laminate composite made using a PMN-PT single crystal had the highest ME voltage coefficient. The value of dE/dH was 10.30 V/cm·Oe, which is ~80 times higher than that previously reported in either naturally occurring MEs or artificially-designed composites. 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}). In Eq. (3), it can be seen that the output voltage from the composite is directly proportional to the piezoelectric voltage constant g_{31}. The stress on the piezoelectric material is dependent on the elastic compliance of the material. The higher the compliance, the higher is the generated stress, as the mechanical coupling is directly correlated with the magnitude of the compliance. Table 2 shows the piezoelectric voltage constant and elastic compliance of the three different materials studied in this investigation.

materials. This was done by stacking and then bonding piezoelectric materials to Terfenol-D. Laminates were made using several kinds of PZTs, PMN-PT ceramics and a ⟨001⟩-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 piezocrystal was 10.30 V/cm · Oe, under a d.c. magnetic bias of 0.4 T. This value of dE/dH is ∼80 times higher than either that of naturally occurring MEs or artificially-grown ME composites. To obtain excellent ME property from the ME laminate composites, a high piezoelectric voltage coefficient (g_{ij}), an optimum thickness ratio between piezoelectric layer and Terfenol-D layers, the direction of magnetostriction in the Terfenol-D disks, and higher elastic compliance of piezoelectric material were important factors.

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