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# Magnetoelectric effect in metal–PZT laminates

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**Abstract. Magnetoelectric (ME) composites are two-phase composites consisting of piezoelectric and piezomagnetic materials as the participating constituents. These magnetoelectric composites when placed under external magnetic field, show electrical polarization (magnetoelectric output). The ME coupling is mediated by mechanical stress. In the present study, we have synthesized Ni/PZT/Ni and Fe/PZT/Fe layered composites for studying their ME output by dynamic magnetoelectric set up in which both d.c. and a.c. magnetic fields can be varied. The ME output obtained in these composites are higher than those obtained in 40% $Ni_{0\cdot97}Co_{0\cdot03}Mn_{0\cdot01}Fe_{1\cdot9}O_4$ + 60%$BaTi_{1\cdot02}O_{3\cdot04}$. The results with varying d.c. and a.c. magnetic fields are presented.**

**Keywords. Magnetoelectric effect; composite; laminate; PZT.**

## 1. Introduction

The magnetoelectric (ME) effect, the appearance of an electric polarization (ME output) on applying a magnetic field (or) by appearance of magnetization on applying an electric field, is a predominant property observed in two phase composites consisting of piezoelectric and piezomagnetic materials which is absent in either of the phases (Suryanarayana 1994). The deformation of piezomagnetic phase causes polarization of piezoelectric phase in the composite. On the other hand the electrical polarization of piezoelectric material causes change in magnetization of piezomagnetic phase due to the mechanical coupling of the piezomagnetic and piezoelectric phases (Lopatin *et al* 1994). Magnetoelectric composites are exploited as sensors, waveguides, modulators, switches and phase inverters (Brache and Van Vliet 1981).

In the literature, various composites have been reported. These are Ni (Co, Mn) $Fe_2O_4$–$BaTiO_3$, $CoFe_2O_4$–$BaTiO_3$, $NiFe_2O_4$–$BaTiO_3$, $LiFe_5O_8$–$BaTiO_3$, $CoFe_2O$–$Bi_4Ti_3O_{12}$, PZT–$CoFe_2O_4$ NCF–PZT (Vanden Boomgaard *et al* 1974, 1976; Van Run *et al* 1974; Lupeiko *et al* 1994, 1995; Yu *et al* 1996; Srinivas 2001; Srinivas *et al* 2002). Srinivas *et al* (2002) evaluated the electromechanical coupling coefficients in 50% PZT and 50% $CoFe_2O_4$ composite.

Srinivas (2001) investigated the microstructures, piezoelectric and ME properties of $Ni_{0\cdot98}Co_{0\cdot02}Fe_{1\cdot9}Mn_{0\cdot02}O_4$ (NCF) and PZT matrix and reported a ME voltage of 160 mV/cm in 60% NCF–40% PZT composite which was 62% higher than the previously reported value for the ME particulate composite (Vanden Boomgaard *et al* 1976).

According to Jungho Ryu and co-workers (2001a), the fabrication technique of the laminate composites (2–0 composite) on a macroscopic scale can have advantages in tailoring design patterns for magnetic noise sensing. They reported a high ME coefficient of 4·68 V/cm-Oe at room temperature for a laminate consisting of Terfenol-D–PZT. They also observed ME output dependence on the direction of an a.c. magnetic field under a d.c. bias field and reported a very high ME coefficient ($dE/dH$) at 1 kHz for the composite as 5·90 V/cm-Oe (Jungho Ryu *et al* 2001b).

Kiyotakemori and Wuttig (2002) reported an $ME_H$ coefficient of 1·43 V/cm-Oe in the Terfenol-D–PVDF composite. In laminate composites of PMN–PT single crystal and Terfenol-D, Jungho Ryu *et al* (2002) reported an ME coefficient of 10·30 V/cm-Oe.

So far the reported work on magnetoelectric composites has been on mostly involving ceramic oxides or a combination of an intermetallic and a ferroelectric oxide. The samples were prepared either as bulk by solid state sintering or as laminates or recently as thin films (Chang *et al* 2004). Magnetoelectric coefficients, $a_E$, of the bulk particulate composites of ferrite–piezoelectric ceramics were 2 or 3 orders of magnitude smaller than theoretical predictions. Such low values are primarily due to low resistivity for ferrites, which (i) limits the electric field used for poling the composite and consequently a poor piezoelectric coupling and (ii) produces a leakage current that results in the loss of induced voltage. However, higher ME output values were reported in layered laminates (Srinivasan *et al* 2001; Jungho Ryu *et al* 2002). While studying the frequency dependence of ME interactions in Permendur and PZT laminates, Laletsin *et al* (2004) reported the maximum ME coefficient of 90 V/cm-Oe at the resonant frequency of PZT.

In this present work, we report the fabrication of laminate composite with a metal (i.e. Ni and Fe) and PZT.

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The magnetostriction value of Ni varies between $-32 \times 10^{-6}$ and $-35 \times 10^{-6}$ while that for Fe it varies from $-8 \times 10^{-6}$ to $-10 \times 10^{-6}$. The ME properties of metal–PZT laminates with varying thickness of PZT from 0·1–1 mm, at a constant thickness (1 mm) of metal are being reported in this paper.

## 2. Experimental

### 2.1 *Materials*

The magnetic phases chosen were Ni and Fe. The desired dimensions of Ni and Fe specimens were cut from spec pure (99·9 + %) metals obtained from Chempure. The PZT disks were cut from the samples (C-52) obtained from M/s Concord Electroceramics Ltd, New Delhi. PZT was chosen as the piezoelectric phase to prepare the laminates, in view of its high piezoelectric constants.

### 2.2 *Sample preparation*

PZT pellets were obtained with different thicknesses of 1 mm, 0·5 mm and 0·4 mm with a diameter of 5 mm and 12 mm. Ni discs were machined to dimensions of Φ5 mm × 1 mm and Fe discs were machined to dimensions of Φ12 mm × 1 mm. Ni/Fe and PZT discs were stacked using conducting epoxy and cured at 80°C for 1 h and 100°C for 30 min. The schematic geometry of a laminar composite sample is shown in figure 1. The dimensions of the prepared samples are given in table 1. PZT pellets were electroded by silver paint and electrically polarized under an electric field of 30 kV/cm for 10 min.

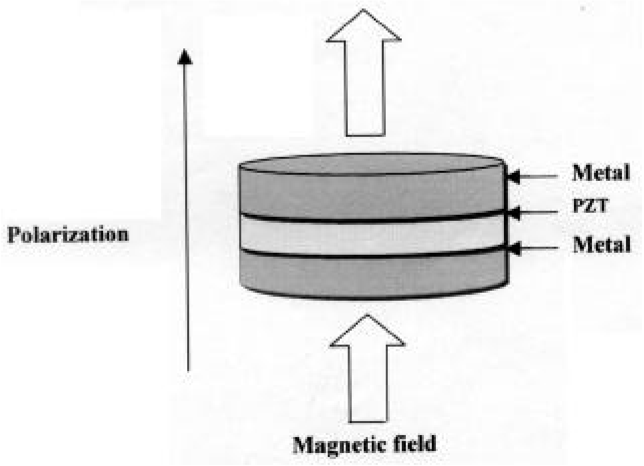

**Figure 1.** The schematic structure of a laminate composite.

## 3. Measurements

An indigenous experimental set up (Mahesh Kumar *et al* 1998) for the measurement of dynamic magnetoelectric effect has been used. The samples are kept between the pole pieces of a d.c. magnet, which can generate the d.c. magnetic field up to 5 kOe. The magnetoelectric voltage coefficient is determined by measuring the electric field generated across the sample when an a.c. magnetic field and a d.c. bias are applied to it.

In the dynamic method, the ME output is measured at a constant a.c. magnetic field of 64 Oe ($f = 1{\cdot}008$ kHz) superimposed on a varying d.c. field in the range of 1–4·5 kOe. ME conversion in these laminate composites were recorded as a function of d.c. bias field at an a.c. field of 64 Oe ($f = 1{\cdot}008$ kHz).

The ME measurements have also been carried out as function of varying a.c. field. A varying a.c. magnetic field ($f = 1{\cdot}008$ kHz) is superimposed over constant d.c. magnetic fields of 1 kOe to 4·5 kOe in steps of 0·5 kOe for measuring magnetoelectric output.

## 4. Results and discussion

In the dynamic method the ME output is observed at a fixed a.c. magnetic field range of 2 Oe to 64 Oe. At all these a.c. magnetic fields, the ME output is constant with varying d.c. magnetic field. Figure 2 depicts the variation of magnetoelectric (ME) output with d.c. magnetic field bias. The ME output of sample $S_1$ (please refer to table 1 for the nomenclature) is higher than that of samples $S_2$ and $S_3$. The ME output of Ni/PZT/Ni samples is almost constant with the d.c. magnetic field in the range 1 kOe–4·5 kOe.

The maximum ME output obtained for sample $S_1$ is 169·5 mV/cm at a fixed 64 Oe a.c. magnetic field (1·008 kHz frequency) and 1 kOe d.c. magnetic field (table 2). The value of ME output is higher than that reported in literature for 40% $Ni_{0.97}Co_{0.03}Mn_{0.01}Fe_{1.9}O_4$ + 60%$BaTi_{1.02}O_{3.04}$ (Brache and Van Vliet 1981). The ME output values of

**Table 1.** Dimensions of Ni/PZT/Ni and Fe/PZT/Fe layered composites.

| Metal | Sample | $t_{metal}$ | $t_{PZT}$ | $t_{total}$ | $t_{metal}/t_{PZT}$ |
|---|---|---|---|---|---|
| Ni | $S_1$ | 1 mm | 1 mm | 3 mm | 1 |
|  | $S_2$ | 1 mm | 0·5 mm | 2·5 mm | 2 |
|  | $S_3$ | 1 mm | 0·4 mm | 2·4 mm | 2·5 |
| Fe | $S_4$ | 1 mm | 1 mm | 3 mm | 1 |

samples $S_2$ and $S_3$ are even though smaller than sample $S_1$ they are higher than the ME output value reported for ferrite–piezoelectric composite (Srinivas *et al* 2002).

Figure 2 also depicts the variation of magnetoelectric (ME) output with d.c. magnetic field bias for the samples $S_1$ (Ni/PZT/Ni) and $S_4$ (Fe/PZT/Fe). The ME output of Ni/PZT/Ni is higher than Fe/PZT/Fe (table 2). The maximum ME output value obtained for Ni/PZT/Ni sample is 169·5 mV/cm at a fixed 64 Oe a.c. magnetic field (1·008 kHz frequency) and 1 kOe d.c. magnetic field, whereas 91·1 mV/cm was obtained at a fixed 64 Oe a.c. magnetic field (1·008 kHz frequency) and 1 kOe d.c. magnetic field for the sample $S_4$ (Fe–PZT–Fe). The ME output of Ni–PZT–Ni laminate is evidently higher than Fe–PZT–Fe laminate, as the magnetostriction of Ni is greater than that of Fe.

The ME voltage coefficient ($a$) is calculated using the formula (Jungho Ryu *et al* 2001a)

$$a = \frac{1}{t}\left(\frac{dV}{dH}\right), \tag{1}$$

where, $dH$ is an a.c. magnetic field applied to a biased composite, $dV$ the induced voltage and $t$ the thickness of the piezoelectric phase.

The variation of ME coefficient, $a_{\max}$, with d.c. magnetic field for the samples of Ni/PZT/Ni with different thicknesses of PZT and Fe/PZT/Fe is shown in figure 3. The ME coefficient of sample $S_1$ is higher than the ME coefficients of samples $S_2$, $S_3$ and $S_4$. The maximum magnetoelectric coefficient $(\mathrm{d}E/\mathrm{d}H)_{\max} = 8{\cdot}5$ mV/cm-Oe is obtained for $S_1$ sample at fixed 3 Oe a.c. magnetic field (1·008 kHz frequency) and 1 kOe d.c. magnetic field. Magnetoelectric coefficient $(\mathrm{d}E/\mathrm{d}H)_{\max} = 4{\cdot}5$ mV/cm-Oe is obtained at fixed 3 Oe a.c. magnetic field (1·008 kHz frequency) and 1 kOe d.c. magnetic field for the sample $S_4$ (Fe–PZT–Fe). The magnetoelectric coefficients of samples $S_2$ and $S_3$ vary between 5 and 8 mV/cm-Oe.

Figure 4 depicts the variation of magnetoelectric (ME) output with a.c. magnetic field (1·008 kHz) at fixed d.c. magnetic bias for Ni/PZT/Ni and Fe/PZT/Fe samples. In this measurement the d.c. magnetic field is fixed in the range 1–4·5 kOe in steps of 0·5 kOe d.c. magnetic field. Magnetoelectric output values of the Ni/PZT/Ni samples with variation of a.c. magnetic field at fixed 1 kOe d.c. magnetic field are shown in figure 4. The ME output

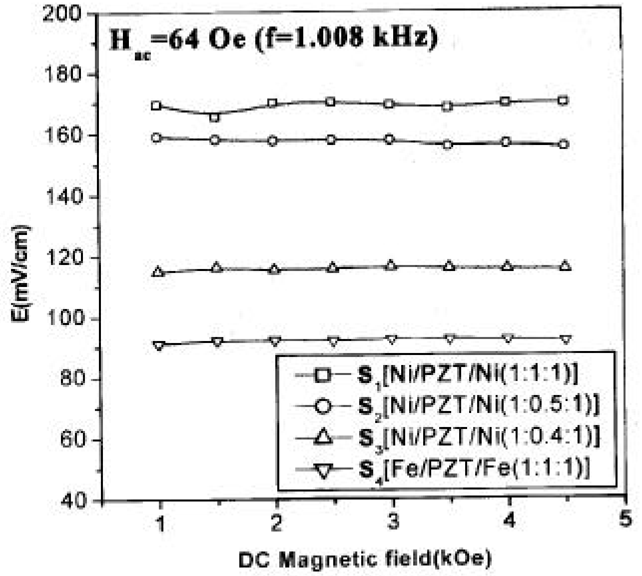

**Figure 2.** D.C. magnetic field vs magnetoelectric output of Ni–PZT–Ni and Fe–PZT–Fe samples.

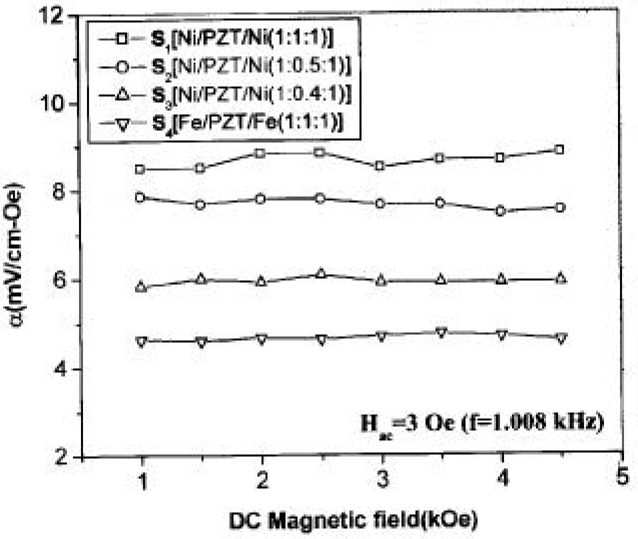

**Figure 3.** D.C. magnetic field vs magnetoelectric coefficient of Ni–PZT–Ni and Fe–PZT–Fe samples.

**Table 2.** Magnetoelectric properties of Ni/PZT/Ni and Fe/PZT/Fe layered composites.

| | | ME output, $E$ (mV/cm) | | ME coefficient, $a$ (mV/cm-Oe) | |
|---|---|---|---|---|---|
| Metal | Sample | at 3 Oe | at 64 Oe | at 3 Oe | at 64 Oe |
| | $S_1$ | 25·5 | 169·5 | 8·5 | 2·6 |
| Ni | $S_2$ | 23·4 | 159 | 7·8 | 2·4 |
| | $S_3$ | 17·4 | 115 | 5·8 | 1·7 |
| Fe | $S_4$ | 13·8 | 91·1 | 4·6 | 1·4 |

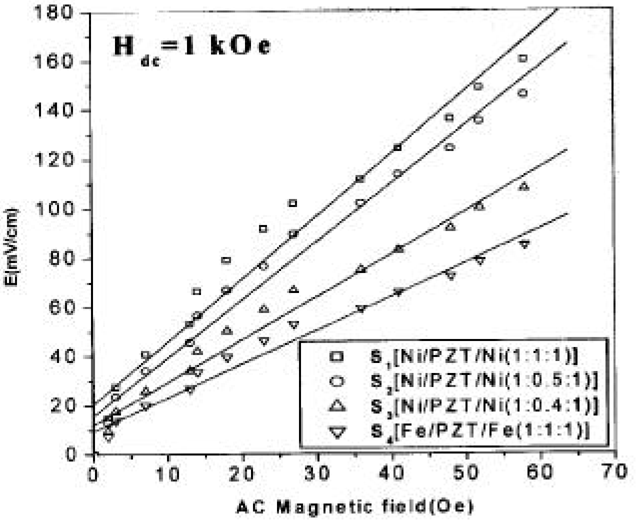

**Figure 4.** A.C. magnetic field vs magnetoelectric output of Ni–PZT–Ni and Fe–PZT–Fe samples.

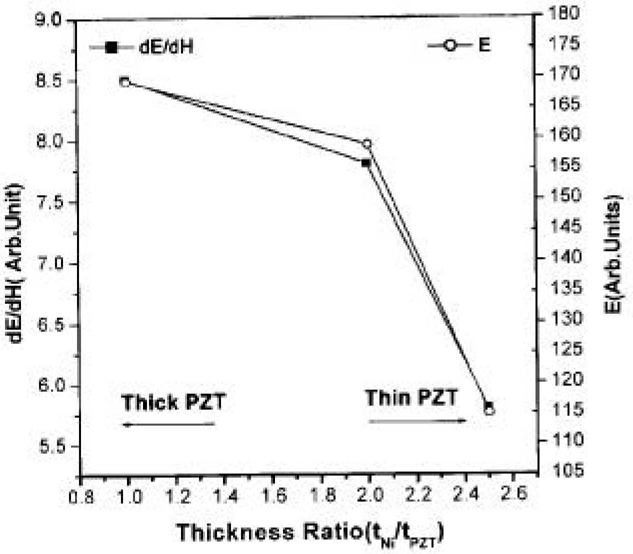

**Figure 5.** Thickness ratio vs d$E$/d$H$ & $E$ of Ni–PZT–Ni samples.

linearly increases with increase in a.c. magnetic field for all the four samples. Among $S_1$, $S_2$, $S_3$ and $S_4$ samples, $S_1$ sample exhibits higher ME output. The slope of the plot (magnetoelectric coefficient, $\Delta E/\Delta H$) is found to be 2·48 mV/cm-Oe for sample $S_1$.

The variation of ME output and magnetoelectric coefficient with thickness ratio for the samples of Ni/PZT/ Ni with different thicknesses of PZT, is shown in figure 5. It is observed that with increasing thickness ratio, both the ME output and magnetoelectric coefficient decrease. Finally, it is concluded that the ME output can be realized in the laminates of metal/ferroelectric composites. Thus a systematic search of combination of various metallic materials, intermetallics and metglasses with piezoelectrics may result in a better combination of a composite, which would show higher ME output for applications.

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