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# Magnetic properties and magnetoelectric effect in $Ni_{0.8}Co_{0.1}Cu_{0.1}Fe_2O_4$ + $PbZr_{0.2}Ti_{0.8}O_3$ composites

S. R. KULKARNI, C. M. KANAMADI, K. K. PATANKAR, B. K. CHOUGULE*
*Composite Materials Laboratory,Department of Physics, Shivaji University, Kolhapur,*
*416004, Maharashtra India*
*E-mail: bkc_phy@unishivaji.ac.in*

Composites with compositions $x\,(Ni_{0.8}Co_{0.1}Cu_{0.1}Fe_2O_4) + (1-x)\,PbZr_{0.2}Ti_{0.8}O_3$ ($x$-mole fraction varies as 0.15, 0.25, 0.35 and 0.45) were prepared by standard ceramic method. The presence of constituent phases, namely ferrite and the ferroelectric were confirmed by X-ray diffraction. The structural analyses were carried out using the obtained powder pattern X-ray data. The porosity of the samples was calculated and the values obtained lie between 10% to 19%. To date, the variations in the magnetic properties with variation in ferrite phase in composites and thereby its influence on magnetoelectric effect is not yet reported. The saturation magnetization ($M$s) and magnetic moment ($\eta_B$) in Bohr magneton were calculated for all the composites. The static value of magnetoelectric voltage coefficient ($dE/dH$) was measured as a function of intensity of magnetic field. The maximum value of ME coefficient was observed for a composite with 35% ferrite + 65% ferroelectric phase. © *2005 Springer Science + Business Media, Inc.*

## 1. Introduction

The composite material consists of piezomagnetic (ferrite) and piezoelectric (ferroelectric) phases mechanically coupled in equilibrium. Magnetoelectricity (ME) is a product property in which the material gets magnetized after applying an electric field and electrically polarized when placed in a magnetic field.

In the nineteenth century, Pierre Curie presumed the existence of ME effect in some materials on the basis of symmetry conditions [1]. However, it would be possible for asymmetric molecules to polarize directionally. Initially, the ME effect was observed experimentally in 1961 in single phase material such as $Cr_2O_3$. The ME effect obtained in composites is very large than that of single phase ME material [2, 3]. The requirements of obtaining good ME effect in composites can be summarized as follows:

1. The mechanical coupling between two phases in equilibrium.
2. The porosity of the sample should be as low as possible to ensure good mechanical coupling.
3. There should not be chemical reaction between the constituent phases.
4. The resistivity of magnetostrictive phase should be as high as possible to avoid the leakage current during electric poling.
5. The magnetostriction coefficient of piezomagnetic phase and piezoelectric coefficient of piezoelectric phase must be high.
6. The proper poling strategy should be adopted to get high ME effect in composites.

The selection of piezomagnetic and piezoelectric material depends on various factors like high magnetostrictive coefficient, high piezoelectric coupling constant, high dielectric permeability and high poling strength [4]. Ni ferrite doped with cobalt and copper having high magnetostriction coefficient was selected as magnetostrictive material and Lead Zirconate Titanate as piezoelectric material having high piezoelectric coefficient [5]. The Jahn-Teller ion like $Cu^{+2}$ has high coupling coefficient and therefore the corresponding contribution to the magnetostriction is high. The large value of magnetostriction is the basic requirement for composites to exhibit large ME effect. This is the reason for selecting the copper substituted ferrite as a piezomagnetic phase in the composites.

In the present work, the standard ceramic method was used to prepare the composites having the general formula $x\ (Ni_{0.8}Co_{0.1}Cu_{0.1}Fe_2O_4) + (1-x)\ PbZr_{0.2}Ti_{0.8}O_3$ where $x$ is a mole fraction and varies as 0.15, 0.25, 0.35 and 0.45. The sintered materials have many advantages as these are easier and cheaper in fabrication, the grain size and sintering temperature is easily controllable [6–16].

In the present work, the measurement of porosity, saturation magnetization, magnetic moment and static magnetoelectric voltage coefficient $(dE/dH)_H$ is done.

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[*] Author to whom all correspondence should be addressed.

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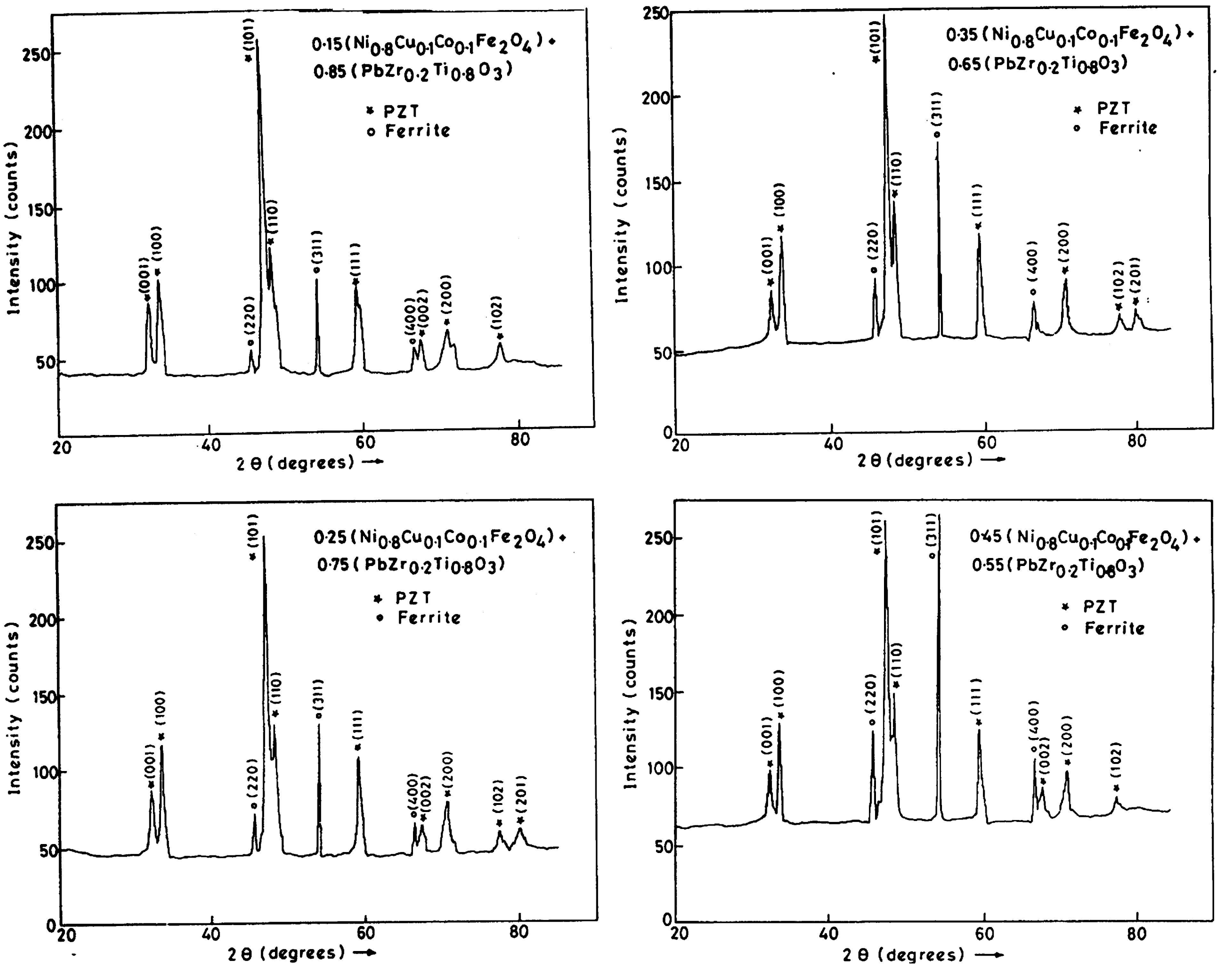

*Figure 1* XRD of composites with $x = 0.15, 0.25, 0.35$ and $0.45$.

An attempt is done to correlate the magnetic properties with the observed ME effect in the composites.

## 2. Experimental

### 2.1. Preparation of ME composites

Piezomagnetic phase (ferrite) was prepared by solid state reaction by using NiO, CoO, CuO and $Fe_2O_3$ in molar proportions as starting materials. Similarly, the piezoelectric phase (ferroelectric) was prepared by using PbO, $ZrO_2$ and $TiO_2$ in molar proportions. The constituent phases were presintered at 900°C for 10 h separately. After presintering, the constituent phases were ground to fine powder. The composites were prepared with compositions $x$ ($Ni_{0.8}Co_{0.1}Cu_{0.1}Fe_2O_4$) + $(1 - x)$ $PbZr_{0.2}Ti_{0.8}O_3$ where $x = 0.15, 0.25, 0.35$ and $0.45$. These composites were again ground for 3 h to mix them thoroughly. The powder was then pressed into pellets and final sintering was carried at 1000°C for 12 h.

### 2.2. Characterization

The presence and determination of crystal structure of the constituent phases was done by X-ray diffraction technique using X-ray diffractometer (Philips Model PW 1710). The XRD patterns show the presence of constituent phases. The patterns do not indicate any

TABLE I Data on lattice parameters and porosity of ($x$) $Ni_{0.8}Co_{0.1}Cu_{0.1}Fe_2O_4$) + $(1-x)$ $PbZr_{0.2}Ti_{0.8}O_3$ ME composites

| Composition $x$ (mol %) | Lattice Constant Ferrite (Å) | Lattice Constant Ferroele. (Å) | c/a | X-ray density (g/cc) | Actual density (g/cc) | Porosity (%) |
|---|---|---|---|---|---|---|
| 0.00 | – | $a = 3.909$<br>$c = 4.145$ | 1.06 | 6.74 | 8.17 | 17 |
| 0.15 | $a = 8.339$ | $a = 3.942$<br>$c = 4.133$ | 1.04 | 6.66 | 7.69 | 13 |
| 0.25 | $a = 8.349$ | $a = 3.954$<br>$c = 4.134$ | 1.04 | 5.99 | 7.39 | 18 |
| 0.35 | $a = 8.308$ | $a = 3.937$<br>$c = 4.107$ | 1.04 | 5.71 | 7.10 | 19 |
| 0.45 | $a = 8.345$ | $a = 3.952$<br>$c = 4.122$ | 1.04 | 6.12 | 6.81 | 10 |
| 1.00 | $a = 8.346$ | – | | 4.52 | 5.37 | 15 |

TABLE II Data on magnetization and static ME voltage coefficient (dE/dH) for $(x)\mathrm{Ni}_{0.8}\mathrm{Co}_{0.1}\mathrm{Cu}_{0.1}\mathrm{Fe}_2\mathrm{O}_4) + (1-x)\mathrm{PbZr}_{0.2}\mathrm{Ti}_{0.8}\mathrm{O}_3$ ME composites

| Composition in mole fraction | $\sigma_s$ (emu/g) | $M_s$ (emu) | $\eta_B$ (observed in Bohr Magneton) | $\eta_B$ (theoretical) | $\rho_{RT}$ ($\Omega$−m) | $dE/dH$ ($\mu$V/cm/Oe) |
|---|---|---|---|---|---|---|
| $x = 0.15$ | 5.92 | 39.44 | 0.31 | 0.32 | 2132 | 319 |
| $x = 0.25$ | 12.11 | 72.59 | 0.63 | 0.65 | 1888 | 370 |
| $x = 0.35$ | 14.10 | 97.62 | 0.72 | 0.76 | 2075 | 397 |
| $x = 0.45$ | 18.39 | 112.63 | 0.91 | 0.97 | 2010 | 378 |
| $x = 1.00$ | 51.70 | 233.76 | 2.17 | – | 2303 | – |
| $x = 0.00$ | – | – | – | – | 3268 | – |

chemical reaction between the components during sintering. The porosity of the samples was calculated by Hendrick and Adams method [7].

The saturation magnetization was measured using high field loop tracer. The magnetic moment in Bohr magneton was calculated using the following relation.

$$\eta_B = M\sigma_s/N\mu_B \quad (1)$$

where, $M$: Molecular weight of the sample, $N$: Avagadro's Number., $\mu_B$: Bohr Magneton, $\sigma_s$: Magnetization per gram of the sample.

The ME coefficient of the composites was measured as a function of dc magnetic field [8]. Prior to this it is necessary to pole the sample electrically and magnetically. The electric poling enhances the magnetostriction coefficient of the ferrite phase whereas the magnetic poling enhances the piezoelectric coefficient of the ferroelectric phase, thus both being helpful for observing the ME effect in the composites as aforesaid. The electric poling was carried in an electric field of 3 KV/cm during fast cooling of the samples from 450 to 300 K. The composite was magnetically poled by applying dc magnetic field of 5 KOe at room temperature. The static ME voltage coefficient $(dE/dH)_H$ was calculated in the same set up used for magnetic poling. Thus the magnetic field was applied perpendicular to the flat and polished faces of the pellets of composites and from the good electric contacts done on the same faces, high impedance Kiethley's Electrometer was connected in parallel to measure the developed electric voltage as a function of magnetic field.

## 3. Results and discussion

The X-ray diffractograms of the composites reveal the presence of ferrite and ferroelectric phases with no structural changes in the constituent phases (Fig. 1). Lattice parameters for both phases were calculated. Ferrite phase has a cubic spinel structure [17] and ferroelectric phase has a tetragonal perovskite structure. The lattice parameters for ferrite phase are almost same in all composites while the tetragonality or $c/a$ ratio of ferroelectric phase lies between 1.04 to 1.06 for the composites (Table I).

Porosity is inherent phase in ceramics prepared by sintering and powder pressing. High rate of sintering with small particle size reduces the porosity. In the present composites, the porosity is observed to lie between 10 to 19% (Table I).

It was seen that the saturation magnetization and magnetic moment of the composites increases with the content of ferrite (Table II). It is also known from the previous work that the saturation magnetization and hence magnetostriction increases with increase in ferrite content [10]. Thus it is likely to have high ME coefficient in composites with high saturation magnetization and one would expect the ME effect to be higher

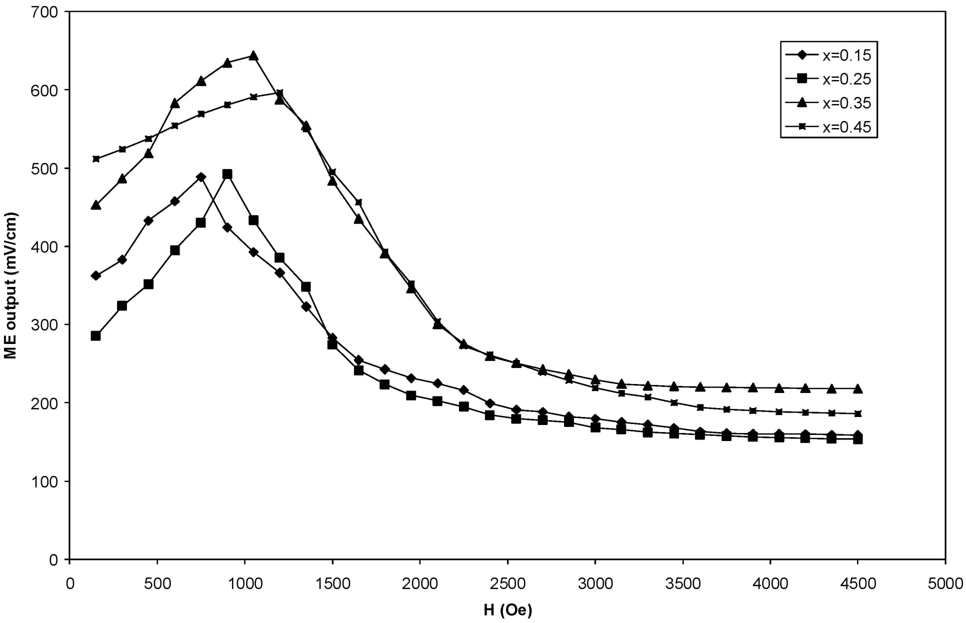

*Figure 2* ME output against dc bias magnetic field.

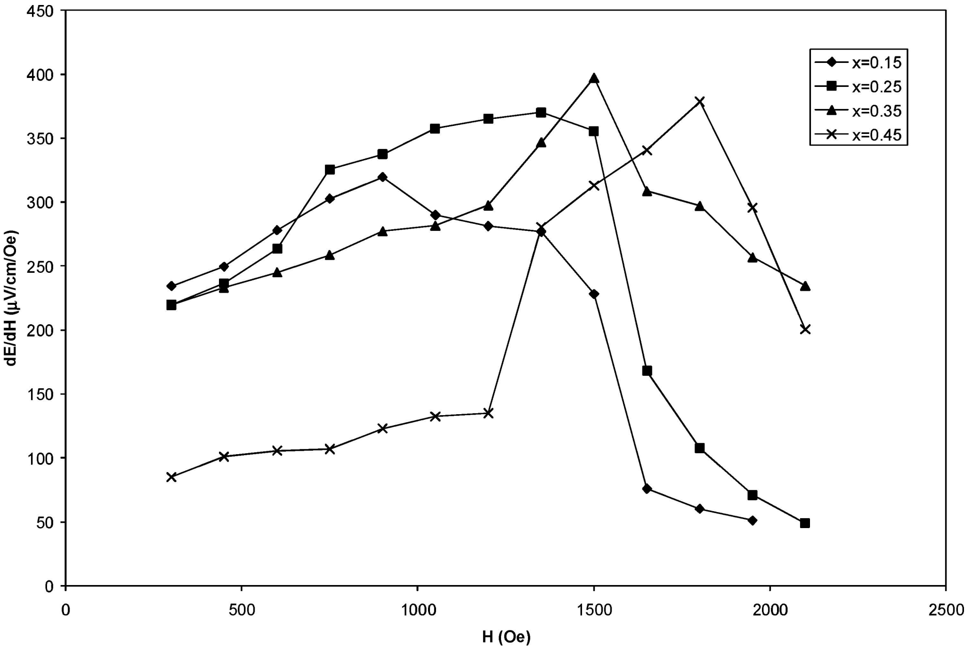

*Figure 3* Static ME voltage coefficient against dc bias magnetic field.

for composites containing relatively high mole% of ferrite phase. But one cannot rule out the possibility that several other physical parameters such as resistivity, mechanical coupling factor, mole ratio of the constituent phases etc also equally influence the observed ME effect. The theoretical considerations show that under ideal conditions of the inherent properties of constituent phases, the ME coefficient is maximum for equal mole ratio of ferrite and ferroelectric phases (50–50%) [10]. In the present series of composites, the resistivity decreases with increase in mole fraction of ferrite phase. The only exception is for $x = 0.35$ composite where the composite shows a slight increase (Table II). Thus the exceptional composite for $x = 0.35$ has result in comparatively high ME coefficient.

From the variation of ME effect with magnetic field, it was observed that the ME output increases initially with dc bias magnetic field and then decreases with further increase in the field as shown in Fig. 2. Above a certain magnetic field, the magnetostriction gets saturated and it produces a constant electric field in the ferroelectric phase thereby decreasing the ME output with increase in the field [9, 10]. The magnetic field at which the magnetostriction saturates was observed to increase with the volume fraction of ferrite.

## 4. Conclusions

Composites with Ni ferrite and PZT were prepared by standard ceramic method. The maximum ME output of 643.7 mV/cm was obtained at 1.05 KOe for composite with $x = 0.35$ and the maximum static ME voltage coefficient $(dE/dH)_H$ of 397.3 $\mu$V/cm/Oe was obtained for composite with $x = 0.35$ (Table II, Fig. 3). As a result of tailoring the composites with equally competent ferrite and ferroelectric phase, it was noted earlier [10] and also confirmed from the present work that the ME coefficient optimizes for the 30–40 mole% of ferrite phase. The composites with Ni ferrite and PZT have higher low field sensitivity and this behaviour may useful in preparing ME devices [14, 15].

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