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Dielectric Behavior and Magnetoelectric Effect in $Ni_{0.75}Co_{0.25}Fe_2O_4 + Ba_{0.8}Pb_{0.2}TiO_3$ ME Composites

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Abstract. Magnetoelectric composites with ferrite + ferroelectric compositions $x Ba_{0.8}Pb_{0.2}TiO_3 + (1 - x)$ $Ni_{0.75}Co_{0.25}Fe_2O_4$ in which x varies as 0, 0.55, 0.70, 0.85 and 1.0 were prepared by ceramic method. X-ray analysis confirms single-phase formation in $x = 0$ and $x = 1$ compositions, whereas the presence of both phases is shown in $x = 0.55$, 0.70 and 0.85 compositions. Variation of dielectric constant (ε') with temperature and frequency has been studied. All the samples have show linear magnetoelectric conversion in the presence of static magnetic field. Static magnetoelectric conversion factor, (dE/dH), was measured as a function of magnetic field in the samples with $x = 0.55$, 0.70 and 0.85 compositions. The maximum value of dE/dH was found to be 140 μV/cm/Oe for $x = 0.85$ composition.

Keywords: magnetoelectric composites, dielectric behavior, ferroelectromagnet and ME effect

Introduction

Composite materials consisting of piezoelectric and piezomagnetic phases are known as magneto-electric composites. These composites have magnetoelectric (ME) property which is absent in their constituent phases [1]. Magnetoelectric property in a ferroelectromagnet is the electric polarization on applying dc or ac magnetic field $(ME)_H$ or the magnetic polarization on the application of dc or ac electric field $(ME)_E$. It occurs due to the interaction between the magnetic and electric dipoles [2–4]. Magnetoelectric composites are used as sensors, isolators, phase shifters, modulators, wave-guides, transducers etc. Materials showing ME conversion can also be used as thin film wave-guides in integral optics and fiber communication technology [5]. Inspite of these, literature survey indicates that not much detailed work has been done on the composites so far.

Patankar et al. [6] have reported ME conversion of the order of 190 μV/cm/Oe in Cu(Fe, Cr) $Fe_2O_4 + Ba_{0.8}Pb_{0.2}TiO_3$ composites prepared by ceramic method. Though the ferrites chosen were less magnetostrictive, due to larger Jahn-Teller distortion the sample showed higher ME effect. Suryanarayana et al. [7] have studied $NiFe_2O_4$-$BaTiO_3$ and $CoFe_2O_4$-$BaTiO_3$ composites and reported ME signal of the order of 160 μV/cm/Oe. They have also studied the dependence of dE/dH on composition and magnetic field. The highest value of magnetoelectric conversion (*dE/dH*) viz. 160 μV/cm/Oe has been observed in case of 60% $BaTiO_3 + 40\%$ $CoFe_2O_4$ composite.

In the present communication we report the dependence of dE/dH on composition and magnetic field of $Ni_{0.75}Co_{0.25}Fe_2O_4 + Ba_{0.8}Pb_{0.2}TiO_3$ composites. The high resistivity ferrite phase has been selected since it is one of the important requirements of getting ME signal in composites. Here, we also report variation of dielectric constant and loss tangent with frequency and temperature.

Experimental

The ME composites consist of two individual phases, one ferroelectric and the other ferrite. The ferroelectric phase $Ba_{0.8}Pb_{0.2}TiO_3$ was prepared from the basic oxides viz. BaO, PbO and TiO_2 after thorough mixing and then presintering them at 900°C for 12 hrs in molar proportions. Similarly the ferrite phase viz. $Ni_{0.75}Co_{0.25}Fe_2O_4$ was prepared using NiO, CoO and

Fe_2O_3 as starting materials. It was presintered at 700°C for 12 hrs. The individual phases were ground to fine powders and ME composites were prepared by thoroughly mixing 85, 70 and 55 mole% of ferroelectric material with 15, 30 and 45 mole% of ferrite material respectively. The mixture was presintered again at 800°C for 12 hrs. The composites were mixed with 2% polyvinyl alcohol (PVA) as a binder and pressed into pellets using the hydraulic press applying a pressure of about 5 tonnes/sq.inch. The pellets were kept for final sintering at 1100°C for 24 hrs in a programmable furnace and they were cooled at the rate of 60°C/hr. The X-ray diffraction patterns of the samples were taken on Philips X-ray diffractometer (Model PW 1710) using Cu K_α radiation ($\lambda = 1.5418$ Å). The AC parameters such as capacitance (C) and dissipation factor (D) of the samples were measured in the frequency range 100 Hz to 1 MHz using LCR Meter Bridge (Model HP 4284 A). The variation of dielectric constant and loss tangent with temperature was studied by recording these parameters at different frequencies. The real dielectric constant was calculated using the relation [8]

$$\varepsilon' = Cd/\varepsilon_0 A$$

where $C =$ capacitance, $d =$ thickness of the pellet, $A =$ area of the surface of the pellet and $\varepsilon_0 =$ permittivity of free space $= (8.854 \times 10^{-12}$ F/m). The samples were coated with silver paste to ensure good ohmic contacts. To realize ME signal in the composites, samples have to be poled electrically and magnetically. The electric poling was carried out by heating the samples at 220°C, which is 30°C above the ferroelectric Curie temperature (T_c), in an external field of about 2.5 kV/cm. The composite samples were subsequently cooled to room temperature. The samples were poled magnetically by applying an external DC magnetic field of 6 kOe at room temperature [9]. The *dE/dH* was measured using Keithley Multimeter (Model 2000) in DC magnetic bias field using the same set up. The experimental arrangement for measurement of ME output is described elsewhere [6].

Results and Discussion

The ME effect is structure sensitive property. It is adversely affected if the composite results with an intermediate or impurity or unidentified phase apart from the ferrite and ferroelectric phases. Hence, the preparation itself becomes a challenging task. Since in the ceramic method, there are slim chances of forming the impurity phases in the composite, this method of preparation was used in the present case. Moreover, the ceramic method provides us with a free choice of the mole ratio of component phases and also it is economical.

The XRD-patterns of one of the representative composite is shown in Fig. 1. It is clear from the figure that all the peaks could be indexed, as the peaks obtained are characteristic of both $Ba_{0.8}Pb_{0.2}TiO_3$ (ferroelectric) and $Ni_{0.75}Co_{0.25}Fe_2O_4$ (ferrite) phases. Thus it is

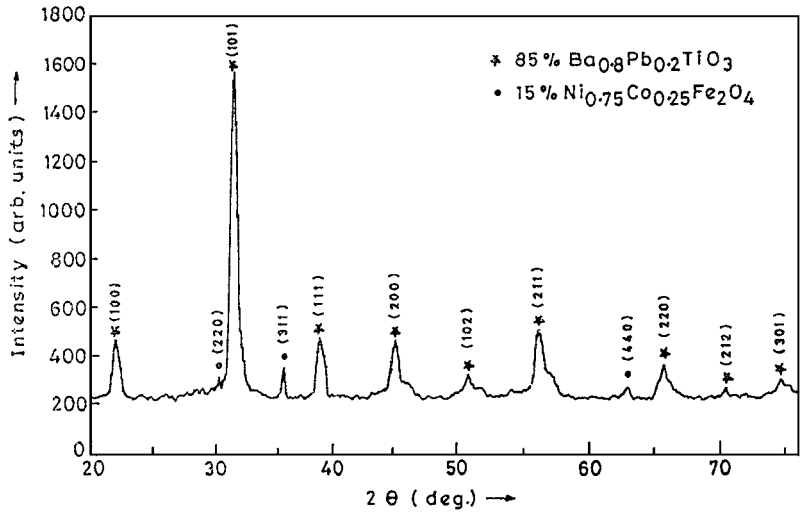

Fig. 1. XRD of 85% $Ba_{0.8}Pb_{0.2}TiO_3 + 15\%$ $Ni_{0.75}Co_{0.25}Fe_2O_4$.

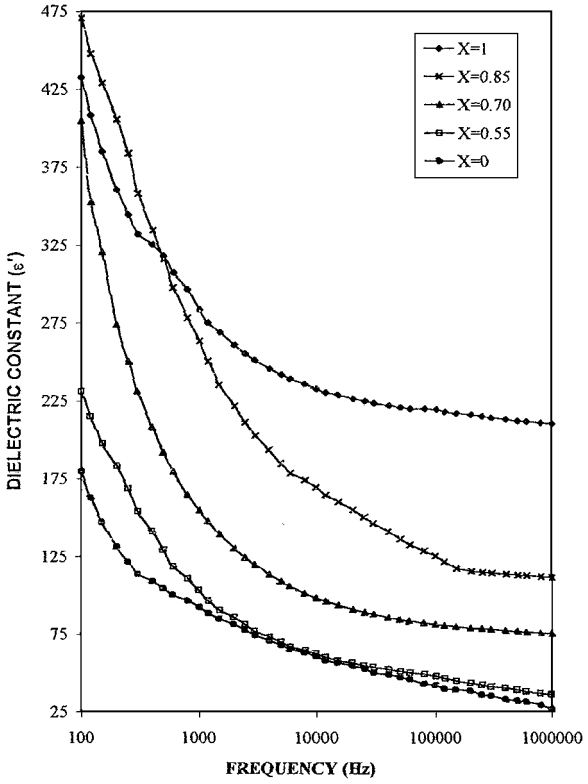

Fig. 2. Variation of dielectric constant with frequency for $x\mathrm{Ba}_{0.8}\mathrm{Pb}_{0.2}\mathrm{TiO}_3 + (1-x)\mathrm{Ni}_{0.75}\mathrm{Co}_{0.25}\mathrm{Fe}_2\mathrm{O}_4$.

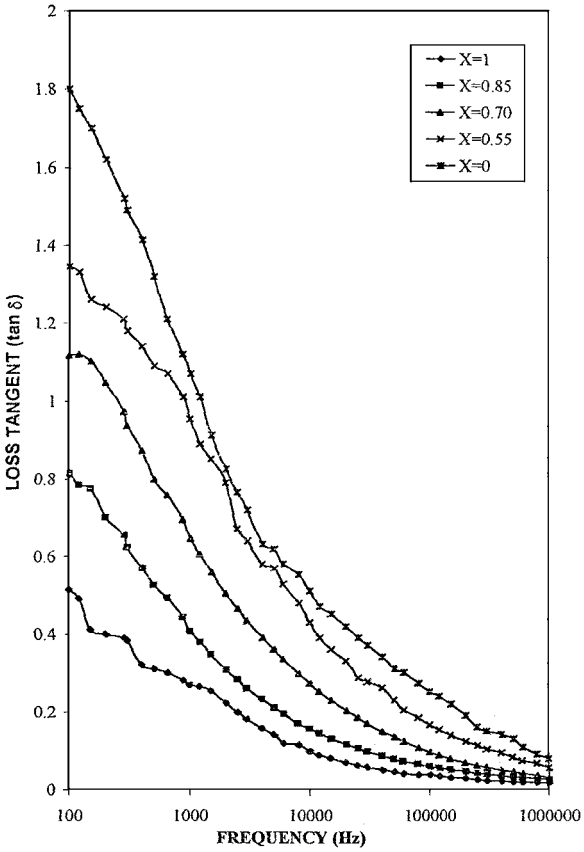

Fig. 3. Variation of loss tangent with frequency for $x\mathrm{Ba}_{0.8}\mathrm{Pb}_{0.2}\mathrm{TiO}_3 + (1-x)\mathrm{Ni}_{0.75}\mathrm{Co}_{0.25}\mathrm{Fe}_2\mathrm{O}_4$.

clear that the composite have only $\mathrm{Ba}_{0.8}\mathrm{Pb}_{0.2}\mathrm{TiO}_3$ and $\mathrm{Ni}_{0.75}\mathrm{Co}_{0.25}\mathrm{Fe}_2\mathrm{O}_4$ phases present in the composite. A comparison between the XRD patterns obtained for all the composites in the present study reveal the following observations:

1. The intensity of ferrite peaks increases with its increasing percentage in the composites.
2. The number of peaks also increases with increase in ferrite percentage.
3. The $\mathrm{Ba}_{0.8}\mathrm{Pb}_{0.2}\mathrm{TiO}_3$—ferroelectric phase has a tetragonal perovskite structure and $\mathrm{Ni}_{0.75}\mathrm{Co}_{0.25}\mathrm{Fe}_2\mathrm{O}_4$—ferrite phase has a cubic spinel structure. These same structures are retained by the components in the composite irrespective of the variation in mole percent of either phase.
4. The lattice parameters calculated for two phases in all the three composites fairly match with the lattice parameters of the components when present separately as single phases inspite of the variation of volume fraction of either phase. The lattice parameter for ferrite phase in composite is $a = 8.335$ Å. For the ferroelectric phase in the composite the parameters are $a = 3.997$ Å and $c = 4.035$ Å. This means that there are no structural distortion observed though the variation in the composition of composite is done deliberately.

The variation of dielectric constant (ε') with frequency is shown in Fig. 2. The dielectric constant decreases with increase in frequency showing dispersion in the lower frequency range. It attains a constant value independent of frequency thereafter. Dielectric constant falls rapidly in the beginning for the compositions having higher values of dielectric constant indicating that dispersion is large in compositions with large values of ε' in comparison with those having smaller values of ε'. All the samples reveal dispersion due to Maxwell-Wagner [10, 11] type interfacial polarization in agreement with Koops phenomenological theory [12]. The high values of dielectric constant observed at lower frequencies are explained on the basis

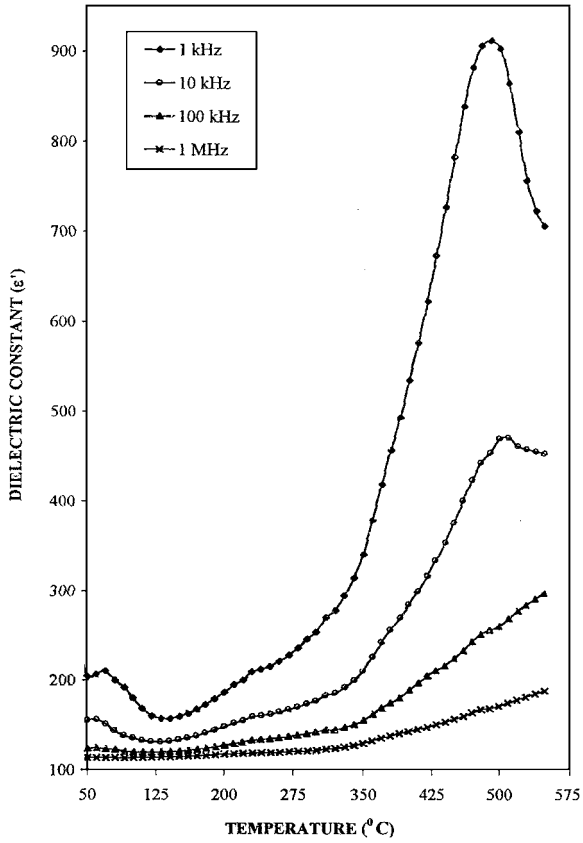

Fig. 4. Variation of dielectric constant with temperature for 15% $Ni_{0.75}Co_{0.25}Fe_2O_4 + 85\%$ $Ba_{0.8}Pb_{0.2}TiO_3$.

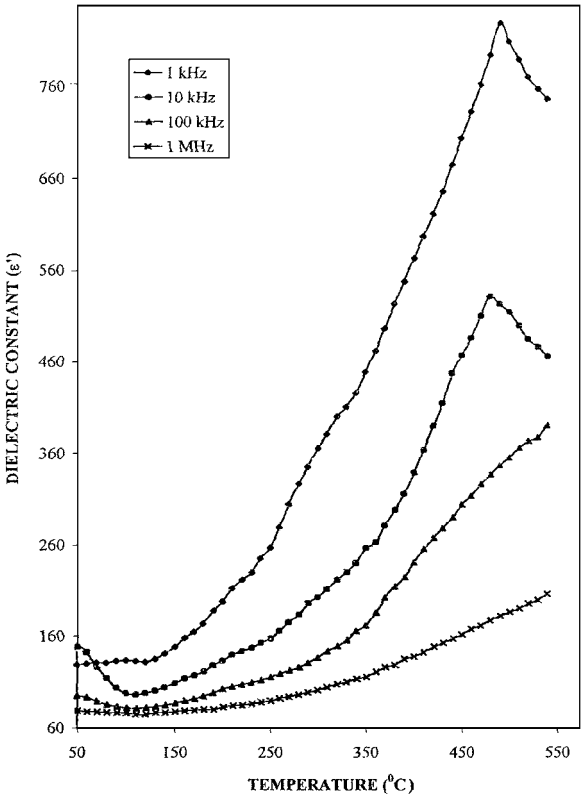

Fig. 5. Variation of dielectric constant with temperature for 30% $Ni_{0.75}Co_{0.25}Fe_2O_4 + 70\%$ $Ba_{0.8}Pb_{0.2}TiO_3$.

of space charge polarization due to inhomogeneous dielectric structure. The inhomogenities in the present system are impurities, porosity and grain structure. However in case of composites, the high values of ε' is ascribed to the fact that ferroelectric regions are surrounded by non-ferroelectric regions similar to that in case of relaxor ferroelectric materials [13]. This again gives rise to interfacial polarization. Figure 3 shows the variation of tan δ with frequency for all the composites, which shows a similar dispersion as that of ε'.

Figures 4–6 show variation of dielectric constant (ε') with temperature at different frequencies viz. 1 kHz, 10 kHz, 100 kHz and 1 MHz. The dielectric maxima are observed at 490°C, 495°C and 515°C for $x = 0.85$, 0.70 and 0.55 composites respectively. These transition temperatures are closer to ferrite transition temperature (525°C) rather than ferroelectric transition temperature (210°C). One of the manifestations of ME interactions in composite is shift in magnetic transition temperature due to an electric field. Obviously the magnetic transition temperature in the present composites shifts towards lower temperature as ferroelectric Curie temperature is less than that of ferrite Curie temperature and polarization is an inherent property of ferroelectrics. From these transition temperatures, it could also be inferred that the ferrite phase is dominant in the composite. Thus this anomaly in the variation of dielectric constant can be explained by saying that beyond the percolation limit of ferrite phase in the composites, it becomes dominant, suppressing the anomalies expected in ferroelectric phase [14]. However, in all three composites, the loss tangent increases with increase in temperature, irrespective of ferrite or ferroelectric transition temperature (Fig. 7). This observation is similar to that reported earlier for the other composite [15].

Comparisons between the Figs. 4–6 also reveal the following information:

1. The dielectric maxima are obtained in the variation of dielectric constant with temperature curves only at 1 kHz and 10 kHz test frequencies. For the higher

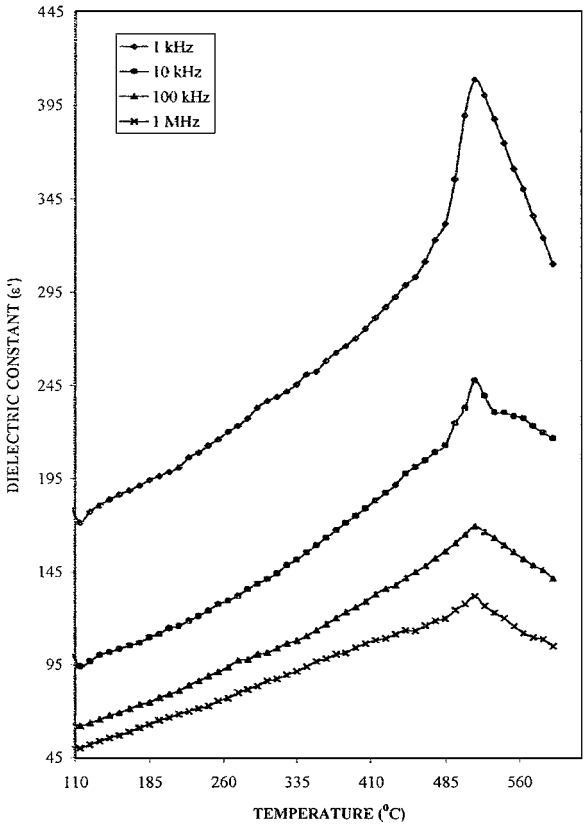

Fig. 6. Variation of dielectric constant with temperature for 45% $Ni_{0.75}Co_{0.25}Fe_2O_4 + 55\%$ $Ba_{0.8}Pb_{0.2}TiO_3$.

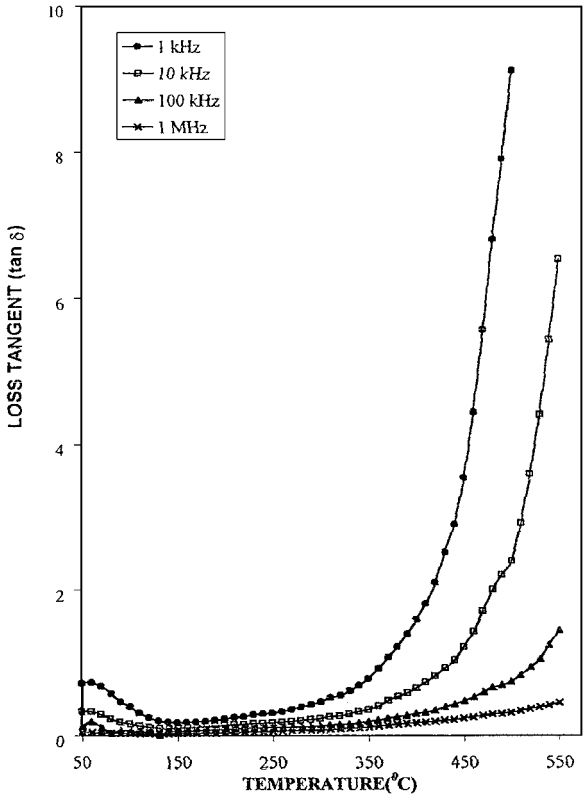

Fig. 7. Variation of loss tangent with temperature for 15% $Ni_{0.75}Co_{0.25}Fe_2O_4 + 85\%$ $Ba_{0.8}Pb_{0.2}TiO_3$.

frequencies like 100 kHz and 1 MHz, no dielectric maxima are obtained even after crossing the ferrite transition temperature (525°C) against our expectation. This can be interpreted as beyond a certain frequency of an electric field, the rapidly changing electric field becomes less effective to bring about the interactions between electric and magnetic ordering in composites.

2. At a given test frequency (1 kHz/10 kHz) the maximum value of dielectric constant obtained decreases with decrease in ferroelectric content in these three composites and it is obvious.
3. For a given composite the temperature at which dielectric maxima are obtained is approximately same at both 1 kHz and 10 kHz frequencies.

The magnetoelectric effect in composite material having magnetostrictive and piezoelectric phases as constituent phases depends on the electrical resistivity of the sample and mechanical coupling between the two phases. A magnetic field induces a change in shape of the magnetostrictive phase, which in turn distorts the piezoelectric phase producing an electric field. The variation of magnetoelectric conversion factor with applied magnetic field for $x = 0.85$, 0.70 and 0.55 is shown in Fig. 8. From this it is clear that dE/dH decreases with increase in magnetic field gradually. It also decreases with increase in ferrite content in the composites. Similar variation is observed by other workers [4, 7, 16]. The decrease in dE/dH with ferrite content is attributed to lower resistivity of ferrite phase as compared to the ferroelectric phase resuiting in the leakage of charges developed in the piezoelectric grain through the low resistance path of the surrounding ferrite grains [4, 7, 17]. Though the ferrite content lowers the effective resistance of the composite it is still added in appreciable amount in the composite. It is because earlier studies on variation of ME signal with ferrite content have suggested that there is an enhancement in elastic interaction with increase in ferrite content [18]. The observed maximum values of *dE/dH* for $x = 0.85$, 0.70 and 0.55 composites are 140, 120

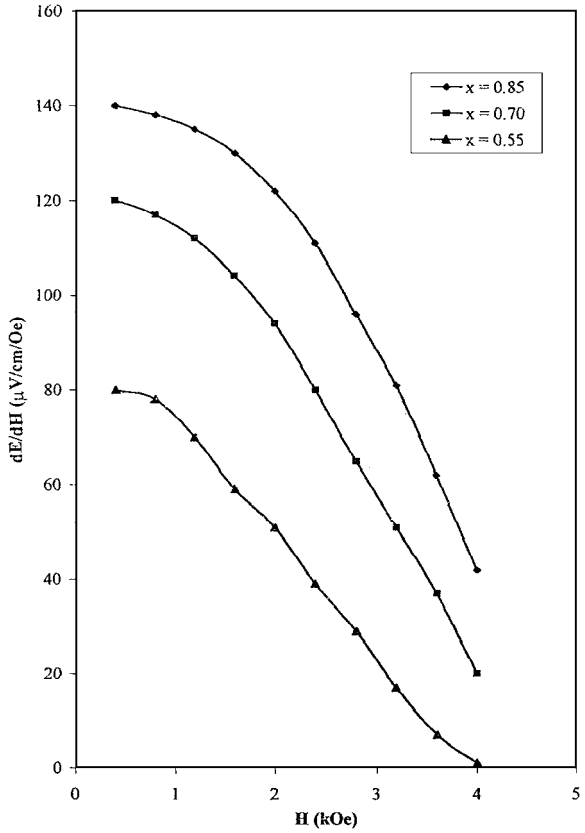

Fig. 8. Variation of magnetoelectric conversion factor with magnetic field for $x\mathrm{Ba}_{0.8}\mathrm{Pb}_{0.2}\mathrm{TiO}_3 + (1-x)\mathrm{Ni}_{0.75}\mathrm{Co}_{0.25}\mathrm{Fe}_2\mathrm{O}_4$.

and 80 μV/cm/Oe respectively. The decrease in magnitude of ME signal (*dE/dH*) with increase in magnetic field observed in all the three composites is attributed to saturation of magnetostriction concomitant with the magnetization beyond a certain value of magnetic field there by producing very small variations in electric polarization in the ferroelectric phase leading to decrease in dE/dH with further increase in magnetic field.

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