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Electrical conduction and magnetoelectric effect in ferroelectric rich $(x)\text{Ni}_{0.9}\text{Zn}_{0.1}\text{Fe}_2\text{O}_4 + (1-x)\text{PZT}$ ME composites

S.S. Chougule, D.R. Patil, B.K. Chougule *

Composites Materials Laboratory, Department of Physics, Shivaji University, Kolhapur 416004, India

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Abstract

Magnetoelectric composites with ferrite–ferroelectric compositions $(x)\text{Ni}_{0.9}\text{Zn}_{0.1}\text{Fe}_2\text{O}_4 + (1-x)\text{PZT}$ in which x varies as 0, 0.15, 0.30, 0.45 and 1 mol% were prepared by using a conventional ceramic double-sintering method. The phase analysis was carried out using X-ray diffraction technique, which confirms that there is no any intermediate phases present in the composites. The variation of dielectric constant ($\acute{\varepsilon}$) and loss tangent ($\tan\delta$) in the frequency range 20 Hz to 1 MHz was studied. The conduction phenomenon was explained on the basis of a small polaron hopping model. The confirmation of this phenomenon was made with the help of ac conductivity measurements. The dc resistivity was measured as a function of temperature in the temperature range from 300 to 800 °C. Static magnetoelectric conversion factor $(\mathrm{d}E/\mathrm{d}H)_\mathrm{H}$ was measured as a function of magnetic field. All composites show linear decrease of magnetoelectric conversion in the presence of static magnetic field.

Keywords: ME voltage coefficient; Electrical and dielectric properties; X-ray diffraction

1. Introduction

There has been renewed interest in recent years in the phenomenon of magnetoelectric (ME) effect in ferromagnetic–ferroelectric heterostructures.

Magnetoelectric (ME) effect is defined as a variation of dielectric polarization in a system as a response to an applied magnetic field, or an induced magnetization by an external electric field [1]. With this effect, an effective conversion between electric energy and magnetic energy is possible. The ME effect was first observed in antiferromagnetic Cr_2O_3 compound, i.e. the single-phase materials [3]. ME effect could be accomplished in composites which are of interest for the engineering of materials either with desired properties or new characteristics that are absent in single-phase materials. Many ME materials and structures have been discovered and developed.

The magnetoelectric (ME) effect in composite materials of ferrite and ferroelectric phases originates from the elastic interaction between the ferrite and ferroelectric subsystems. In a magnetic field, the magnetostriction in the ferrite phase gives rise to mechanical stresses that are transferred the ferroelectric phase, owing to the piezoelectric effect, resulting in an electric polarization of the ferroelectric phase [4].

The ME materials thus represent a kind of smart structures which have received continuous attentions as potential sensors for magnetic field measurements and transducers for magnetoelectric conversion [2]. ME composites are also of interest for a variety of device applications including electrically controlled microwave phase shifters, magnetically controlled electro-optic or piezoelectric devices, actuators, and magnetoelectric memory devices.

However, a much higher ME effect has been identified in specially designed composites in which the ferrite phase is combined with the ferroelectric one so that an efficient magnetomechanical piezoelectric coupling between the two phases is achieved [5]. Since then, much effort has been made along this line, which was in excellent agreement with the theoretical prediction [6,7]. The earlier studies allow us to emphasize the essential role of two issues in fabricating magnetoelectric composites with enhanced ME effect. On one hand, the two phases chosen must have, large magnetostrictive and piezoelectric effects in ferrite and ferroelectric phases respectively and the other hand, an effective coupling between

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* Corresponding author. Tel.: +91 231 2690571; fax: +91 231 2691533.
E-mail addresses: bkchougule@yahoo.com, sucomposites@yahoo.co.in (B.K. Chougule).

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the magnetomechanical transfer and piezoelectric transfer is the key factor for an enhanced ME effect [8,23].

In the present work we report the electrical properties and ME effect in $(x)\mathrm{Ni}_{0.9}\mathrm{Zn}_{0.1}\mathrm{Fe}_2\mathrm{O}_4 + (1-x)\mathrm{PZT}$ composites, which offer valuable information about the behaviour of localized electric charge carriers. This can also lead to better understanding of the mechanism of electrical conduction and dielectric polarization in such systems. In present case zinc doped nickel ferrite having high resistivity high magnetostriction coefficient and low eddy current losses [10] is selected as a ferrite phase and PZT having high piezoelectric constant, high dielectric permittivity and superior coupling factor as a ferroelectric phase [11].

2. Experimental

2.1. Preparation of ME composites

A conventional double-sintered ceramic method was used to prepare $(x)\mathrm{Ni}_{0.9}\mathrm{Zn}_{0.1}\mathrm{Fe}_2\mathrm{O}_4 + (1-x)\mathrm{PbZr}_{0.52}\mathrm{Ti}_{0.48}\mathrm{O}_3$ ME composites consisting of two individual phases, ferrite and a ferroelectric. The ferrite phase was prepared by normal solid-state reaction using AR grade NiO, ZnO and $\mathrm{Fe}_2\mathrm{O}_3$ powder. These oxides were weighted in required molar proportions and mixed thoroughly in agate mortar for couple of hours. The mixture was presintered at 800 °C for 8 h and finally sintered at 1000 °C for 10 h. Similarly the ferroelectric phase was prepared by using AR grade PbCO_3, ZrO_2 and TiO_2 as starting materials and presintered at 600 °C for 3 h while finally sintering at 1200 °C for 4 h.

ME composite containing ferrite and ferroelectric phases with the general formula $(x)\mathrm{Ni}_{0.9}\mathrm{Zn}_{0.1}\mathrm{Fe}_2\mathrm{O}_4 + (1-x)\mathrm{PbZr}_{0.52}\mathrm{Ti}_{0.48}\mathrm{O}_3$, where x varies as 0, 0.15, 0.30, 0.45 and 1 mol% were prepared. The powder mixture was mixed with 2% polyvinyl alcohol as a binder and was pressed into pellets of 10 mm diameter and 2–3 mm thickness using hydraulic press. The pelletized samples were finally sintered at 1200 °C for 5 h in a programmable furnace and slow cooled to room temperature to yield the final product.

2.2. Characterization

Structural characterization of the samples was carried out by using X-ray diffractometer (Phillips Model PW 1710) using Cu Kα radiation ($\lambda = 1.541$ Å).

The dielectric constant was measured in the frequency range from 20 Hz to 1 MHz at room temperature by using the LCR Meter Bridge (Model HP 4284A). The samples were painted on either side with silver paste to ensure good electric contacts. The dielectric constant ($\acute{\varepsilon}$) was calculated by using the formula.

$$\acute{\varepsilon} = \frac{Cd}{\varepsilon_0 A}$$

where C is capacitance of pellet, d the thickness of pellet, A the cross-sectional area of the flat surface of the pellet and ε_0 is the permittivity of free space ($\varepsilon_0 = 8.85 \times 10^{-12}$ F/m).

The electrical resistivity measurement was performed by means of a two-probe method. A low value of constant voltage was applied across the sample and the current through the sample was measured as a function of temperature in the range 300–800 °C

To get better ME signal, the samples have to be poled both electrically and magnetically. For electrical poling, the samples were heated approximate 50 °C above the ferroelectric Curie temperature and then allowed to cool slowly in presence of an electric field about 2 kV/cm. The magnetic field of 6 kOe was applied across the sample in the direction of electric field. All the traces of space charges in ME output developed by the poling are removed by proper grounding. The ME output was measured by varying applied dc magnetic field at room temperature.

3. Results and discussions

3.1. Phase determination

The X-ray diffraction patterns of $(x)\mathrm{Ni}_{0.9}\mathrm{Zn}_{0.1}\mathrm{Fe}_2\mathrm{O}_4 + (1-x)\mathrm{PbZr}_{0.52}\mathrm{Ti}_{0.48}\mathrm{O}_3$ composites are shown in Fig. 1. The patterns show well-defined peaks, which are characteristics of $\mathrm{Ni}_{0.9}\mathrm{Zn}_{0.1}\mathrm{Fe}_2\mathrm{O}_4$ ferrite and $\mathrm{PbZr}_{0.52}\mathrm{Ti}_{0.48}\mathrm{O}_3$ ferroelectric. All the peaks have been identified. There is no intermediate phase formed in the composites. The occurrence of peaks with specific indices characteristics of spinel and perovskite structure confirms cubic spinel structure in ferrite phase and tetragonal perovskite structure in ferroelectric phase of the composites. There are no structural changes observed for both the phases in composites as reported earlier [11,12]. The lattice parameters for both phases in these composites vary with the composition as given in Table 1.

The ferrite phase has a cubic spinel structure with lattice parameter $a = 8.34$ Å and the ferroelectric phase has a tetragonal perovskite structure with $a = 4.05$ Å and $c = 4.08$ Å, $c/a = 1.007$.

The intensity of (1 0 1) peak in the ferroelectric phase decreases where as intensity of (3 1 1) peak in ferrite phase increase with increases in ferrite content in the composites. It may due to small percentage of ferrite in the composite and the probable dispersal of tiny particles in the composites. The num-

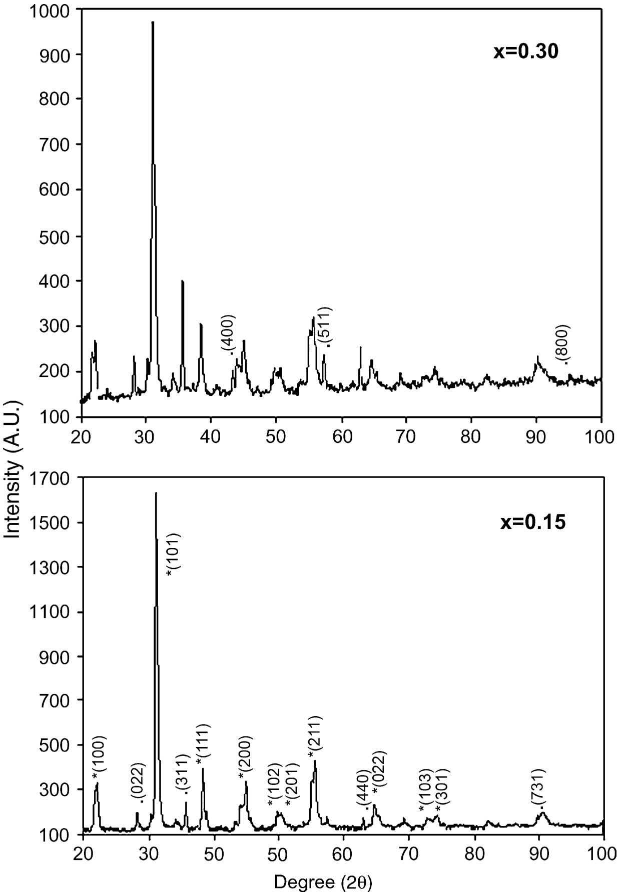

Fig. 1. XRD patterns of $(x)\mathrm{Ni}_{0.9}\mathrm{Zn}_{0.1}\mathrm{Fe}_2\mathrm{O}_4 + (1-x)\mathrm{PbZr}_{0.52}\mathrm{Ti}_{0.48}\mathrm{O}_3$ ME composites. (*) indicates ferroelectric peaks and (.) indicates ferrite peaks.

Table 1
Data on lattice parameter, resistivity, dielectric constant, saturation magnetization and ME voltage coefficient of $(x)Ni_{0.9}Zn_{0.1}Fe_2O_4 + (1-x)PZT$ ME composites

Composition	Lattice parameter (Å)		c/a	ρ_{RT} (Ω cm)	Activation energy (eV)		$(dE/dH)_H$ (μV/cm Oe)
	Ferrite phase	Ferroelectric phase			Para region	Ferro region	
$x=1$	$a=8.34$			0.29×10^8	0.25	0.090	–
$x=0.15$	$a=8.33$	$a=4.07$, $c=4.09$	1.01	1.35×10^8	0.28	0.083	748
$x=0.30$	$a=8.35$	$a=4.03$, $c=4.09$	1.01	0.89×10^8	0.27	0.082	680
$x=0.45$	$a=8.35$	$a=4.06$, $c=4.07$	1.00	0.47×10^8	0.25	0.080	643
$x=0$		$a=4.08$, $c=4.05$	1.00	2.28×10^9	0.30	0.079	–

ber of ferrite peaks increases with increase in mol% of ferrite [5].

3.2. Dielectric behaviour

Fig. 2 shows variation of dielectric constant as a function of frequency for the composites at room temperature. The dielectric constant decreases rapidly with increase in frequency. At lower frequencies the dispersion of dielectric constant is large. As the frequency increases ionic and orientation sources of polarizability decrease and finally disappear due to inertia of the molecules and ions. In practice, there is relaxation time for charge transport.

The mechanism of this dielectric polarization is similar to that of conduction in ferrites. It is concluded that the electron exchange interaction Fe^{2+} to Fe^{3+} in ferrites results in local displacement of electrons in the direction of electric field, which determine the polarization in ferrites. In normal dielectric behaviour $\dot{\varepsilon}$ decreases with frequency and reaches a constant value beyond a certain frequency, which indicate that beyond that frequency the electron exchange does not fall by alternating field. The entire samples show dispersion due to Maxwell–Wagner type interfacial polarization in agreement with Koop's phenomenological theory [14,15].

In case of composites the high value of dielectric constant is ascribed to the fact that ferroelectric regions are surrounded by non-ferroelectric (ferrite) regions similar to that in case of relaxor ferroelectric materials [16]. This gives rise to interface polarization. From this figure it is observed that the dielectric constant is decreased with increase in ferrite content. This is because the dielectric constant of ferrite is lower as compared to the ferroelectric phase.

Fig. 3 shows variation in tan δ with frequency for the composites, which shows a similar dispersion as that of dielectric constant with frequency.

3.3. ac conductivity

To study the mechanism of conduction ac conductivity was determined at room temperature in the frequency range 20 Hz to 1 MHz. Fig. 4 shows frequency dependent ac conductivity plot. The conductivity is observed to increases with increases in frequency for all the composites under study. Linear variation of ac conductivity indicates that the conduction occurs by hopping of charge carriers among localized states. Adler and Feinleib [17] have shown that for conduction by small polarons, ac conductivity increases with frequency. Hence the present results indicate that the conduction is due to small polarons in the composite.

3.4. dc resistivity

Variation of resistivity (log ρ) with temperature is shown in Fig. 5. The plots show two regions of conductivity with changing slope at different temperatures. The first region at low temperature is attributed to the ordered state of the ferroelectric phase

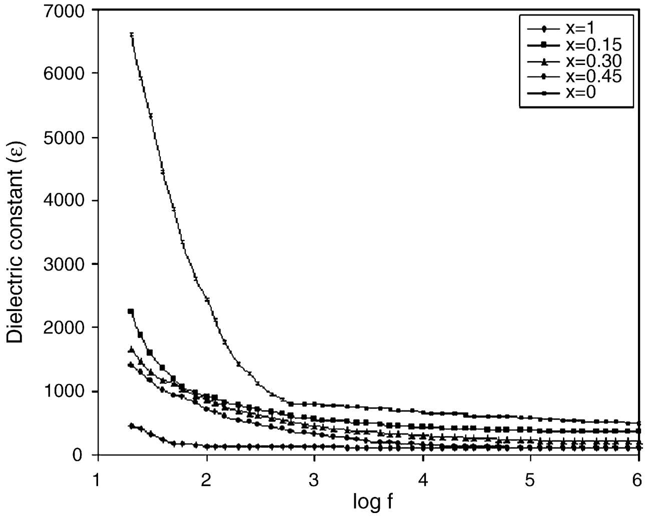

Fig. 2. Variation of dielectric constant with frequency for $(x)Ni_{0.9}Zn_{0.1}Fe_2O_4 + (1-x)PbZr_{0.52}Ti_{0.48}O_3$ ME composites.

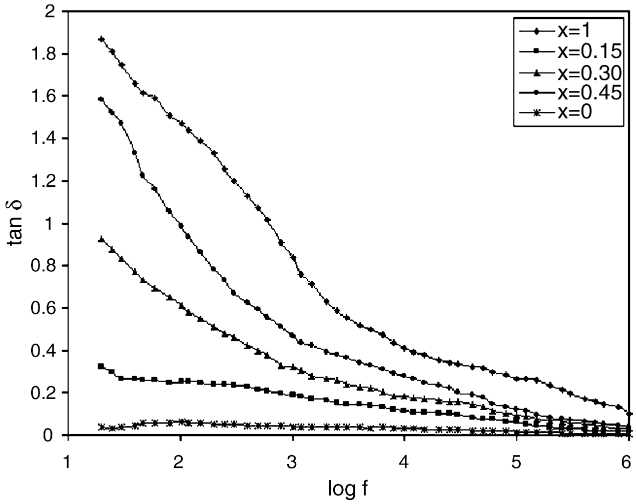

Fig. 3. Variation of dielectric loss with frequency for $(x)Ni_{0.9}Zn_{0.1}Fe_2O_4 + (1-x)PbZr_{0.52}Ti_{0.48}O_3$ ME composites.

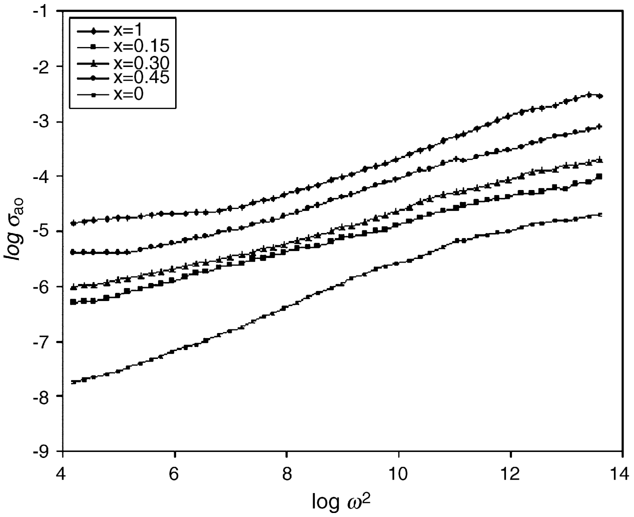

Fig. 4. Variation of ac conductivity with frequency for $(x)\mathrm{Ni}_{0.9}\mathrm{Zn}_{0.1}\mathrm{Fe}_2\mathrm{O}_4 + (1-x)\mathrm{PbZr}_{0.52}\mathrm{Ti}_{0.48}\mathrm{O}_3$ ME composites.

in the composites while the second region at higher temperature, which is due to the polaron hopping, is for the disordered paraelectric state of the ferroelectric phase [18]. It is suggested that the conduction mechanism change from one region to other region [19]. The activation energy also changes when transition from ferroelectric to paraelectric takes place. The activation energy was calculated using the relation:

$$\rho = \rho_0 \exp\left(\frac{\Delta E}{kT}\right) \tag{1}$$

where ΔE is the activation energy, ρ the resistivity at temperature T, k the Boltzmann constant and ρ_0 is the temperature independent constant.

The resistivity of the composites decreases with increase in ferrite content. The values of room temperature resistivity at room temperature are given in Table 1. There is drop in resistivity with increases in ferrite content suggesting parallel connectivity between ferrite and ferroelectric grains in the composites. Hence a control and connectivity of ferrite content is also significant while preparing the mixture of these two phases or else the two phases must have comparable values of resistivity so that one phase must not shunt the other phase [13]. The resistivity is maximum for the ferroelectric phase ($x = 0.15$) and it is minimum for the ferrite phase ($x = 0.45$).

Initially, the resistivity and dielectric constants of ferroelectric phase is high as compared to the ferrite phase and according to the rule of mixture as the ferrite content increases both resistivity and dielectric constant decrease [9]. Variation of resistivity with temperatures for all the samples indicates their semiconducting nature. The decrease in resistivity with increase in temperature is due to the increase in the thermally activated electron drift mobility of charge carriers according to the hopping conduction mechanism.

3.5. ME output

The variation of magnetoeletric output $(\mathrm{d}E/\mathrm{d}H)_\mathrm{H}$ versus magnetic field H is shown in Fig. 6.

The magnetoelectric effect in composite materials is determined by magnetostrictive deformation of one phase and piezoelectric effect in the other phase. For this reason the magnitude of magnetoelectric sensitivity $(\mathrm{d}E/\mathrm{d}H)_\mathrm{H}$ should depend in a complicated way on the composition of the composite materials [12]. The ME out put depends on the mechanical coupling and mole fraction of these two phases. Stress transfer through the interface between these phases achieves the magnetoelectric coupling. Hence magnetomechanical and electromechanical resonance in ferrite and ferroelectric phases are the possible origins of ME peaks.

It is well known fact that, in the spinel ferrite, the magnetostrictive coefficient having its saturation value initially with magnetization at a certain value of the magnetic field [21]. Hence, the strain produced in the ferrite phase would produce a constant electric field in the piezoelectric phase. Hence

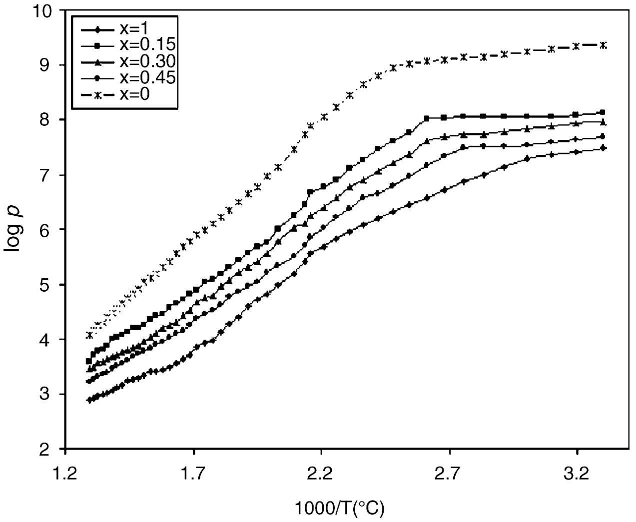

Fig. 5. Variation of dc resistivity with temperature for $(x)\mathrm{Ni}_{0.9}\mathrm{Zn}_{0.1}\mathrm{Fe}_2\mathrm{O}_4 + (1-x)\mathrm{PbZr}_{0.52}\mathrm{Ti}_{0.48}\mathrm{O}_3$ ME composites.

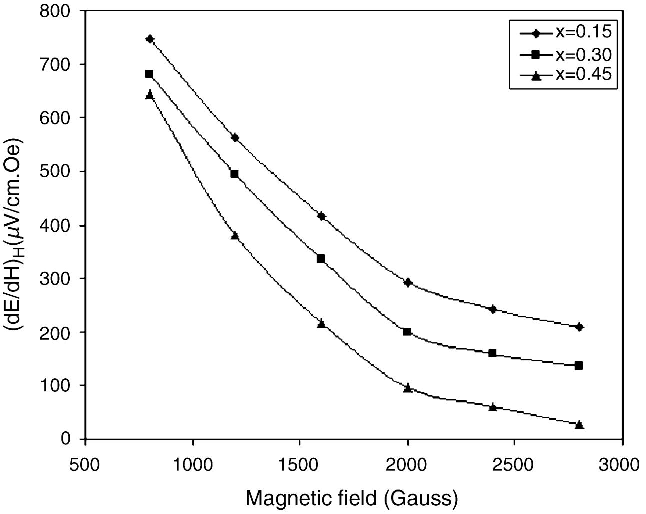

Fig. 6. Variation of ME effect of $(x)\mathrm{Ni}_{0.9}\mathrm{Zn}_{0.1}\mathrm{Fe}_2\mathrm{O}_4 + (1-x)\mathrm{PbZr}_{0.52}\mathrm{Ti}_{0.48}\mathrm{O}_3$ ME composites.

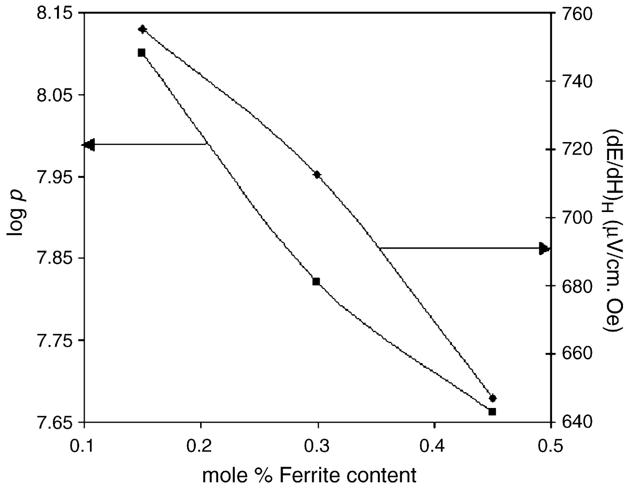

Fig. 7. Variation of resistivity and ME voltage coefficient with mol% of ferrite content in ME composites.

$(\mathrm{d}E/\mathrm{d}H)_\mathrm{H}$ decreases as the dc magnetic field is increased. Moreover for any particular value of field strength $(\mathrm{d}E/\mathrm{d}H)$ decrease with ferrite content in the composites. This is the result of decreased polarizability of the ferroelectric phase in the composites with the higher content of ferrite.

Fig. 7 shows variation of ME voltage coefficient and dc resistivity with mol% of ferrite content. The maximum values of ME voltage coefficient and dc resistivity are observed for the composite with $x = 0.15$. The $(\mathrm{d}E/\mathrm{d}H)_\mathrm{H}$ decrease with increase in mol% of ferrite phase in the composites as reported earlier [20,21]. This decrease is attributed to low resistivity of ferrite phase as compared to the ferroelectric phase resulting in the leakage of charges developed in the piezoelectric grains through the low resistance path of the surrounding ferrite grains [20–22]. Thus ME effect is resistivity dependent property.

4. Conclusions

Magnetoelectric composite with $\mathrm{Ni_{0.9}Zn_{0.1}Fe_2O_4}$ as a ferrite phase and $\mathrm{PbZr_{0.52}Ti_{0.48}O_3}$ ferroelectric phase were prepared by standard ceramic method. XRD patterns reveal the presence of the ferrite and ferroelectric phases with no any intermediate phase in the composite. XRD patterns confirm formation of cubic spinel structure and tetragonal perovskite structure of ferrite and ferroelectric phase, respectively. The number of ferrite peaks increase with increase in ferrite content in the composites.

The dielectric dispersion observed at lower frequencies is attributed to the interfacial polarization. The variation of ac conductivity with frequency is linear suggesting that the conduction is due to small polaron hopping. The resistively is higher for a composite with $x = 0.15$ and lower $x = 045$. Resistivity is mainly responsible for decrease in $(\mathrm{d}E/\mathrm{d}H)_\mathrm{H}$ with increases ferrite content. The decrease in resistivity leads to the leakage of charges built up in ferroelectric phase through the surrounding ferrite grains. The maximum ME voltage coefficient 748 μV/cm Oe was observed for the 15% $\mathrm{Ni_{0.9}Zn_{0.1}Fe_2O_4}$ + 85% $\mathrm{PbZr_{0.52}Ti_{0.48}O_3}$ composites.

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