

Electrical properties of $\text{Ni}_{0.93}\text{Co}_{0.02}\text{Mn}_{0.05}\text{Fe}_2\text{O}_4 + \text{BaTiO}_3$ ME composites

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Abstract Polycrystalline samples of mixed composites of $\text{Ni}_{0.93}\text{Co}_{0.02}\text{Mn}_{0.05}\text{Fe}_2\text{O}_4 + \text{BaTiO}_3$ were prepared by conventional double sintering ceramic method. The phase analysis was carried out by using X-ray diffraction technique. Variation of dc resistivity and thermo emf was studied as a function of temperature. AC conductivity (σ_{ac}) was investigated in the frequency range 100 Hz–1 MHz. The loss tangent ($\tan \delta$) measurements conclude that the conduction mechanism in these samples is due to small polaron hopping. The magnetoelectric conversion factor, i.e. $\text{dc}(\text{ME})_H$ was studied as a function of intensity of magnetic field and the maximum value 407 $\mu\text{V}/\text{cm}/\text{Oe}$ was observed at a field of 0.8 kOe in a composite with 85% BaTiO_3 and 15% $\text{Ni}_{0.93}\text{Co}_{0.02}\text{Mn}_{0.05}\text{Fe}_2\text{O}_4$ phase.

Introduction

Magnetoelectric composites consist of two phases such as piezoelectric and piezomagnetic. The deformation of ferrite phase causes polarization of piezoelectric phase in the composites and the electrical polarization of piezoelectric phase causes change in magnetization of ferrite phase due to strong mechanical coupling between the piezomagnetic (ferrite) and piezoelectric (ferroelectric) phases [1]. The ME effect is a property of ME composites, which is absent in their constituent phases [2]. Such magnetoelectric

composites find many applications in radioelectronic device, optoelectronic, microelectronic, transducers, etc. [3, 4]. The ME effect occurs due to the interaction between the magnetic and electric dipoles [2, 5, 6]. In the present communication, we have chosen $\text{Ni}_{0.93}\text{Co}_{0.02}\text{Mn}_{0.05}\text{Fe}_2\text{O}_4$ as a piezomagnetic phase and BaTiO_3 as the piezoelectric phase. Such composite to show high magnetoelectric effect, which in turn suggests that the magnetoelectric interaction in these composites may lead to interesting results in their electric and magnetic properties [7, 8]. No attempts have been made to study the electric and magnetic properties in detail for these particular composites. Hence in the present work the measurement of dc conductivity, thermoelectric power, and ac conductivity are under taken on composites of $\text{Ni}_{0.93}\text{Co}_{0.02}\text{Mn}_{0.05}\text{Fe}_2\text{O}_4 + \text{BaTiO}_3$. A conductivity in wide range of frequencies combined with dc resistivity and thermo emf measurement helps to understand the conduction mechanism and identify the charge carriers responsible for conduction.

Experimental details

Preparation of ME composites

The ferrite phase ($\text{Ni}_{0.93}\text{Co}_{0.02}\text{Mn}_{0.05}\text{Fe}_2\text{O}_4$) was prepared by using the AR grade NiCO_3 , CoCO_3 , MnCO_3 and Fe_2O_3 in the required stoichiometric proportions. These oxides and carbonates were mixed using agate mortar. The mixture was presintered at 800 °C for 16 h. The ferroelectric phase (BaTiO_3) was prepared using BaCO_3 and TiO_2 in molar ratios and was presintered at 1000 °C for 20 h. After presintering the raw materials were ground to fine powders.

The magnetoelectric composites were prepared by dispersing 15, 30 and 45 mol% of $\text{Ni}_{0.93}\text{Co}_{0.02}\text{Mn}_{0.05}\text{Fe}_2\text{O}_4$

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phase in the 85, 70 and 55 mol% of BaTiO₃ phase, respectively.

The compositions were mixed thoroughly and presintered at 1000 °C for 24 h. The presintered powder was pressed into disc shaped pellets having 15 mm diameter and 3–4 mm thickness.

Characterization

The samples were characterized by X-ray diffractometer (Phillips Model PW-1710) using Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$). The electrical measurements were made by two-probe method in the temperature range from room temperature to 800 K. The ohmic electrical contacts were established by applying silver paste on both the surfaces of the pellets.

A constant voltage was applied to the sample and current through the sample was measured as a function of temperature.

The thermoelectric power (α) was calculated by relation

$$\alpha = \Delta V / \Delta T$$

where ΔV is the voltage measured across the sample and ΔT is the temperature gradient.

A temperature difference $\Delta T = 25 \text{ }^\circ\text{C}$ was mentioned across the pellet using laboratory designed sample holder. Temperature of both the surface of pellets was measured with Alumel Chromel thermocouple. Seebeck coefficient was measured as a function of temperature.

The variation of dielectrics constant (ϵ') and the loss tangent ($\tan \delta$) were measured at room temperature in the frequency range from 20 Hz to 1 MHz using LCR meter bridge (Model HP 4284A). The ac conductivity was calculated by the relation:

$$\sigma_{ac} = \epsilon' \epsilon_0 \omega \tan \delta$$

where ϵ' is the dielectric constant, $\tan \delta$ is loss tangent, ϵ_0 permittivity of free space ($8.85 \times 10^{-12} \text{ F/m}$) and ω is the angular frequency.

To realize ME signal in composites samples were poled both electrically and magnetically. For electric poling the sample was heated approximately 30 °C above ferroelectric Curie temperature (T_c) and thereafter cooled to room temperature in the presence of an electric field. Magnetic poling of the samples was carried out at room temperature before measuring the magnetoelectric coefficient using the procedure reported earlier workers [9, 10]. The experimental arrangement for measurement of ME output is similar to that described by Suryanarayana [5] and the magnetoelectric conversion factor was measured by varying dc magnetic field.

Results and discussion

Figures 1 and 2 show X-ray diffractometer patterns of the samples with composition $x = 0.85$ and 0.70, respectively. The patterns show well-defined peaks. There is no any intermediate phase formed in the composites. The occurrence of peak with specific indices confirms the cubic spinel structure for the ferrite phase and tetragonal perovskite structure for the ferroelectric phase. No structural changes are observed for both the phases in composites [11]. It can be noticed from the figures that the intensity of the peaks corresponding to ferrite phase increases with increase in ferrite content [8, 11]. The data on lattice parameters of both the phases is given in Table 1. The lattice constant for the two phases in composites remains almost the same.

The variation of dc resistivity for the composites with temperature in the range room temperature to 800 K is shown in Fig. 3. The plots show semiconducting behaviour

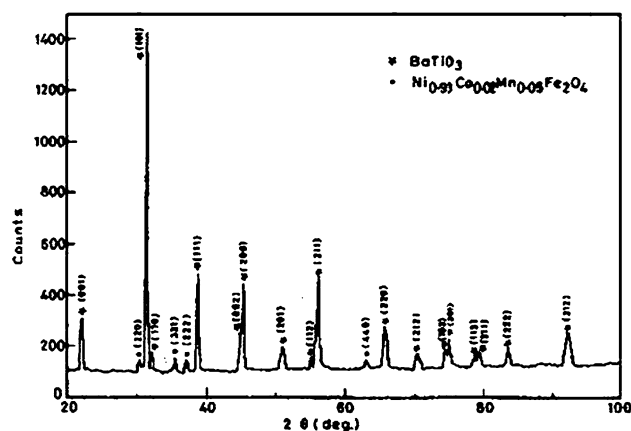


Fig. 1 XRD pattern of 15%Ni_{0.93}Co_{0.02}Mn_{0.05}Fe₂O₄ + 85%BaTiO₃ composite

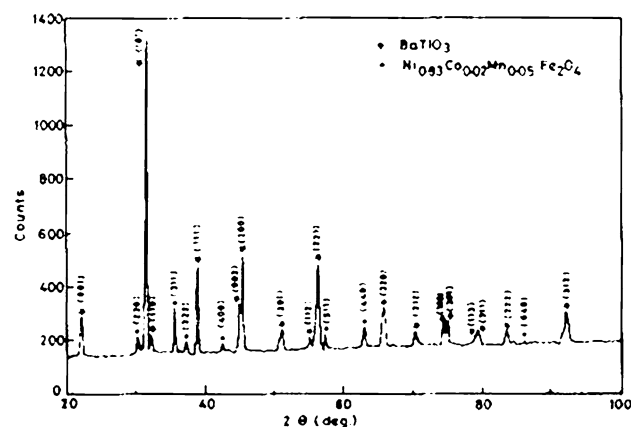
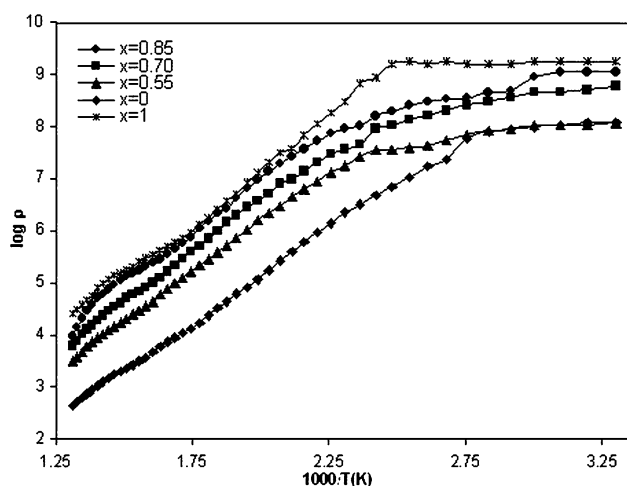


Fig. 2 XRD pattern of 30%Ni_{0.93}Co_{0.02}Mn_{0.05}Fe₂O₄ + 70%BaTiO₃ composite

Table 1 Data on lattice parameters and electrical properties of the composites

Composition x	Lattice parameter (Å)		c/a	ρ_{RT} (Ω cm)	α_{RT} (mV/Oe)	$(dE/dH)_H$ (μ V/cm/Oe)	Activation energy (eV)
	Ferrite phase	Ferroelectric phase					
1.00	–	$a = 3.98$ $c = 4.04$	1.02	1.81×10^9	2.10	–	0.40
0.85	$a = 8.35$	$a = 3.98$ $c = 4.03$	1.01	1.13×10^9	1.80	407	0.37
0.70	$a = 8.35$	$a = 3.98$ $c = 4.04$	1.02	6.09×10^8	1.20	324	0.36
0.55	$a = 8.38$	$a = 4.03$ $c = 4.04$	1.00	1.33×10^8	0.75	218	0.35
0.00	$a = 8.35$			1.19×10^8	1.00	–	0.33

**Fig. 3** Variation of dc resistivity with temperature for $\text{Ni}_{0.93}\text{Co}_{0.02}\text{Mn}_{0.05}\text{Fe}_2\text{O}_4 + \text{BaTiO}_3$ composite

of the samples. The conduction of ferrite, ferroelectric and their composites results from hopping process of charge carriers. The relationship between resistivity and temperature may be expressed as

$$\rho = \rho_0 \exp(\Delta E/kT) \quad (1)$$

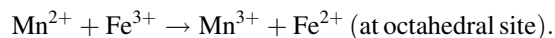
where ρ is the resistivity at temperature T , ρ_0 is the temperature independent constant, k the Boltzmann constant and ΔE is the activation energy for conduction process.

Only a fraction $\exp(-\Delta E/kT)$ of the number of charge carriers can cross the potential barriers per second [12].

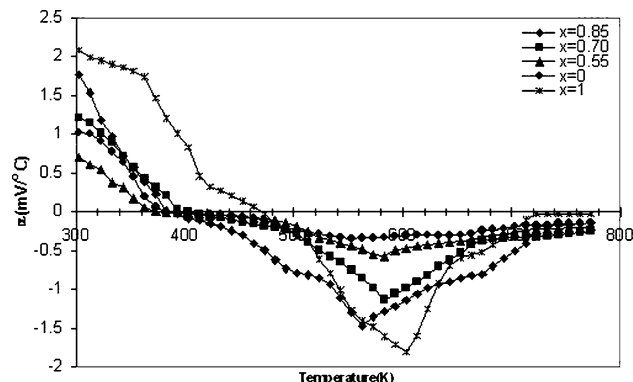
The plots show two regions of conductivity and are linear in certain temperature range. The activation energy for conduction was calculated using the above relation and are given in the Table 1. The conduction at low temperature is due to impurities whereas at higher temperature it is due to polaron hopping [13]. The first region at low temperature is attributed to the ordered state of ferroelectric

phase in the composite, while the second region is due to the paraelectric state [14]. It is observed that resistivity is maximum for BaTiO_3 ($\approx 10^9 \Omega$ cm).

The resistivity of composites decreases considerably with increase in ferrite content [10, 14]. The variation of resistivity is explained on the basis of actual location of cation in the spinel structure. Conduction in ferrite is due to electron transfer between divalent and trivalent ion. For Mn ferrite the conduction process is given by relation [7]:



The variation of Seebeck coefficient (α) for the composites with temperature is shown in Fig. 4. The plots show the type of charges responsible for conduction. A p–n transition is observed in all the compositions. The occurrence of p–n transition and Seebeck coefficient is independent on Curie temperature [15, 16]. A cusp is observed due to oxidation–reduction process [13]. At lower temperature all samples shows p type behaviour. The variation of α at low temperature (i.e. <400 K) may be attributed to impurity conduction. The observed p type

**Fig. 4** Variation of Seebeck coefficient with temperature for $\text{Ni}_{0.93}\text{Co}_{0.02}\text{Mn}_{0.05}\text{Fe}_2\text{O}_4 + \text{BaTiO}_3$ composite

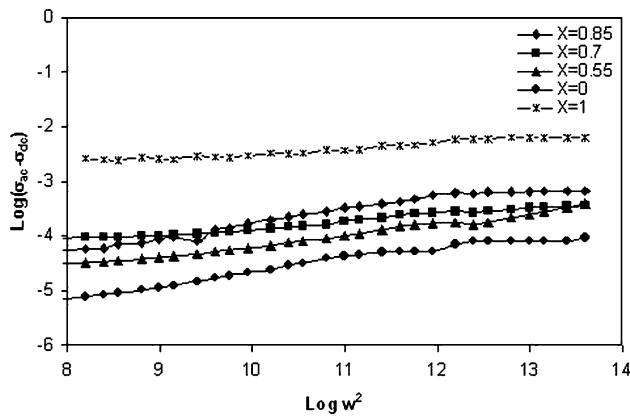


Fig. 5 Variation of ac conductivity with frequency for $\text{Ni}_{0.93}\text{Co}_{0.02}\text{Mn}_{0.05}\text{Fe}_2\text{O}_4 + \text{BaTiO}_3$ composite

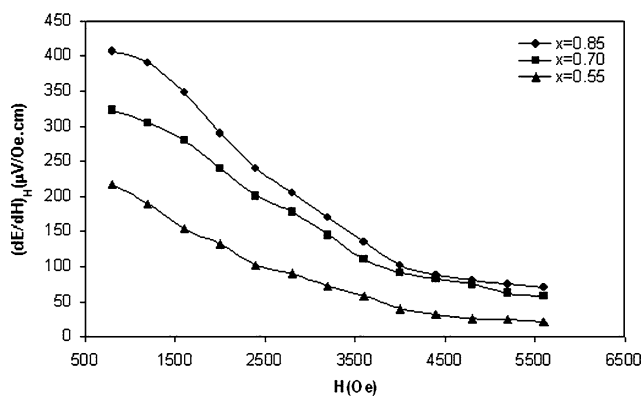


Fig. 6 Variation of ME output with variation of dc magnetic field for $\text{Ni}_{0.93}\text{Co}_{0.02}\text{Mn}_{0.05}\text{Fe}_2\text{O}_4 + \text{BaTiO}_3$ composite

conduction in BaTiO_3 is attributed to $\text{Ti}^{4+} \rightarrow \text{Ti}^{3+}$ transition [15] and p-type to n-type conduction in ferrite is attributed to $\text{Ni}^{2+} \leftrightarrow \text{Ni}^{3+}$, $\text{Mn}^{2+} \leftrightarrow \text{Mn}^{3+}$ releasing a hole and $\text{Fe}^{3+} \leftrightarrow \text{Fe}^{2+}$ releasing an electron [7, 14].

The plots of ac conductivity $\log(\sigma_{ac} - \sigma_{dc})$ with $\log \omega^2$ are shown in Fig. 5. The plots show straight line nature and ac conductivity increases with increasing frequency. Similar results are also reported by other workers [7, 14, 16]. This confirms that the conduction phenomenon in these composites is due to small polaron hopping. It has been shown that for ionic solids the concept of small polaron is valid [7, 17].

The present composite dc ME coefficient as a function of applied dc magnetic field was measured. The values of $(dE/dH)_H$ are given in Table 1. Plot of variation of magnetoelectric conversion factor with applied magnetic field is shown in Fig. 6 from this it is clear that $(dE/dH)_H$ decreases with increase in magnetic field also decreases with increase in ferrite content in the composition. As ferrite content increases, there is a leakage of charges built up in ferroelectric phase through the surrounding ferrite

grains [14]. The ME effect largely depends on electrical resistivity and the mechanical coupling between the two phases [3]. In the spinels, the magnetostriction coefficient reaches saturation at a certain value of magnetic field and conduction is of small polaron hopping type which is responsible for low ME signal in the present composites.

Conclusion

The magnetoelectric composites with composition $(1 - x)\text{Ni}_{0.93}\text{Co}_{0.02}\text{Cu}_{0.05}\text{Fe}_2\text{O}_4 + (x)\text{BaTiO}_3$ were prepared using ceramic technique with $x = 0.85, 0.70$ and 0.55 . The XRD pattern reveals the presence of both ferrite and ferroelectric phases. Since the resistivity of the composite decreases with increase in ferrite content, composites with $x = 0.85$ composition shows maximum resistivity at room temperature. The variation of Seebeck coefficient with temperature shows both the n-type and p-type charge carriers and is dependent on temperature. The frequency dependent ac conductivity measurements suggest that conduction is due to small polaron hopping. Maximum static magnetoelectric voltage coefficient of $407 \mu\text{V}/\text{cm Oe}$. is obtained for the composite with $x = 0.85$ at magnetic field of 0.8 kOe .

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