J Mater Sci (2008) 43:2708–2712
DOI 10.1007/s10853-008-2456-x

Magnetoelectric properties of ME particulate composites

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Received: 21 July 2007 / Accepted: 8 January 2008 / Published online: 21 February 2008

Abstract Magnetoelectric (ME) composites are biphasic materials consisting of piezoelectric and piezomagnetic materials as the participating constituents. These ME composites when placed under external magnetic field show electrical polarization (ME output). This ME coupling is mediated by mechanical stress. In the present study, we have synthesized particulate composites of $Ni_{0.8}Cu_{0.2}Fe_2O_4$ and $Ba_{0.8}Sr_{0.2}TiO_3$ using conventional ceramic method. The XRD identifications showed that the sintered ceramics retained the presence of distinct ferroelectric and ferrite phases. The dielectric constant was determined as a function of temperature (room temperature to 650 °C) at different test frequencies. The DC resistivity was studied as a function of temperature. The measured ME response, dielectric constant, and resistivity demonstrated strong dependence on the volume fraction of $Ni_{0.8}Cu_{0.2}Fe_2O_4$ in the composite. The ME voltage coefficient strongly depends on the resistivity of the composites.

Introduction

Ferroelectric materials have wide applications such as non-volatile memories, capacitors, transducers, actuators, etc. Likewise, magnetic materials are also used in data storage and a variety of other applications. There is great technological promise and fundamental interest if ferroelectricity and ferromagnetism co-exist at room temperature. Further, if there is a coupling between the two order parameters, it should be possible to cause electric polarization by applying either an electric or a magnetic field. Thus writing of a data bit with an electric field and reading it with a magnetic field, and vice-versa, will be possible. This certainly offers additional degree of freedom in device designing [1].

The materials with magnetoelectric (ME) effect are named as magnetoelectric materials, and they are considered to be a kind of promising new materials for sensors, processors, actuators, and memory systems [2]. The ME effect was first observed in single crystals where ME effect arises due to the local interaction between the ordered magnetic and ferroelectric sublattices [3]. A lot of ME single-phase materials have been discovered in the last three decades [4]. While, the use of single-phase materials on device applications has not been successful because of the fact that these single-phase materials normally have weak ME effect. Moreover, most of them have Neel or Curie temperature far below the room temperature; hence, they merely exhibit the ME effect at very low temperature [5]. One way to overcome these limitations is to use the composite materials. A composite is a combination of at least two chemically distinct materials with an interface separating the components; the combination has its own distinctive properties. Following the concept of product property, Suchtelen [6] suggested the realization of composites of piezoelectric and magnetostrictive phases that could be electromagnetically coupled via stress mediation. ME effect in these composites entails the combined deformation of the matrix of the piezoelectric and magnetostrictive components. A primary deformation of the magnetostrictive phase causes polarization of the piezoelectric particles of composite; on the other hand, electric polarization of piezoelectric materials causes change in magnetization of the ferrite phase due to mechanical coupling of piezomagnetic (ferrite) and piezoelectric

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(ferroelectric) phases. Various groups have, therefore, focused their efforts on realization of bulk composites or heterostructure layers [2].

We report here the electrical, dielectric properties, and ME effect in composites having $Ni_{0.8}Cu_{0.2}Fe_2O_4$ and $Ba_{0.8}Sr_{0.2}TiO_3$ phases. The soft ferrite $NiFe_2O_4$ with low anisotropy and high initial permeability is a promising candidate. Furthermore, a larger net magnetic moment caused by the ion rearrangement, which favors the ME effect, can be obtained by putting some additional amounts of copper oxide as one of the bivalent components into nickel ferrite. The Cu^{2+} ion being a Jahn–Teller ion induces more mechanical coupling, which is one of the prerequisites for increasing the efficiency of ME conversion factors [7]. In addition, Sr-doped $BaTiO_3$ has a large figure of merit and superior dielectric and piezoelectric properties [8]. Hence this system offers the detailed investigation of electric properties and ME effect of the composites.

Experimental

Preparation

The composites containing the two individual phases viz. $Ni_{0.8}Cu_{0.2}Fe_2O_4$ and $Ba_{0.8}Sr_{0.2}TiO_3$ having the general formula $(x)Ni_{0.8}Cu_{0.2}Fe_2O_4 + (1-x)Ba_{0.8}Sr_{0.2}TiO_3$ ($x = 0$, 0.15, 0.30, 0.45, and 1) were prepared by conventional double-sintering ceramic method. The ferrite phase was prepared through solid-state reaction using NiO, CuO, and Fe_2O_3 in appropriate molar proportions. The component oxides were mixed and ground in agate mortar for a couple of hours and presintered at 900 °C for 9 h. The ferroelectric phase was also prepared following the same route by mixing $BaCO_3$, $SrCO_3$, and TiO_2 in appropriate molar proportions and presintered at 1000 °C for 10 h. The ME composites were prepared by mixing 15, 30, and 45 mole% of $Ni_{0.8}Cu_{0.2}Fe_2O_4$ phase with 85, 70, and 55 mole% of $Ba_{0.8}Sr_{0.2}TiO_3$, respectively. The composite mixtures were presintered again at 1100 °C for 11 h. The pellets having 3–4 mm thickness and 10 mm diameter were prepared using the hydraulic press. The pellets were final sintered at 1200 °C for 12 h to yield the final products.

Characterization

The crystalline phases of the prepared samples were identified with the help of X-ray diffractometer (Philips Model PW 1710) using CuKα(radiation ($\lambda = 1.5418$ Å).

The dielectric constant was evaluated as a function of temperature at selected frequencies (1 kHz, 10 kHz, 100 kHz, and 1 MHz) using LCR meter bridge (Model HP 4284 A). The dc resistivity was measured in the temperature range (300–800 k) by two-probe method.

The ME coefficient of the composites was measured as a function of dc magnetic field. The composites had to be poled electrically and magnetically before measuring the ME effect. The electric poling enhances the piezoelectric coefficient of the ferroelectric phase whereas the magnetic poling enhances the magnetostriction of the ferrite phase, both being helpful for observing the ME effect in the composites [9]. The electric poling was carried out in a dc field of 2 kV/cm during cooling of the samples from 130 °C to room temperature. The samples were magnetically poled by applying dc magnetic field of 5 kOe at room temperature. The static ME voltage coefficient $(dE/dH)_H$ was measured using Keithley Electrometer (Model 2000) in dc magnetic field using the same set up.

Results and discussion

XRD analysis

As shown in Fig. 1, the coexistence of $Ni_{0.8}Cu_{0.2}Fe_2O_4$ and $Ba_{0.8}Sr_{0.2}TiO_3$ is confirmed by the XRD patterns, and no mutual solubility between the two phases is observed, i.e., the two phases are compatible with each other. The intensity of their diffraction peaks depends on the amount of the corresponding phase. A comparison between the XRD patterns of composites revels that the number of peaks of ferrite phase and intensity of ferrite peaks increase with increasing percentage of ferrite in the composites. The lattice parameters match well with the lattice parameters of the components when present as single phases. The peaks were identified to be characteristics of both $Ba_{0.8}Sr_{0.2}TiO_3$ and $Ni_{0.8}Cu_{0.2}Fe_2O_4$ phases. The $Ni_{0.8}Cu_{0.2}Fe_2O_4$ ferrite phase has a cubic spinel structure with $a = 8.32$ Å. The ferroelectric phase has a tetragonal perovskite structure with lattice parameters $a = 3.97$ Å and $c = 3.99$ Å. The lattice parameters for all the compositions are given in Table 1.

Variation of dielectric constant with temperature

The temperature dependence of dielectric constant at four different frequencies (viz. 1 kHz, 10 kHz, 100 kHz, and 1 MHz) for all studied samples is illustrated in Figs. 2, 3 and 4. Dielectric constant is found to increase with increase in temperature, reaches a maximum value at Curie temperature and follows a decreasing trend indicating phase transition. With increase in temperature the mobility of charge carriers increases that leads to increase in the conductivity and polarization of the samples and hence increase in dielectric constant [10]. The huge increase in

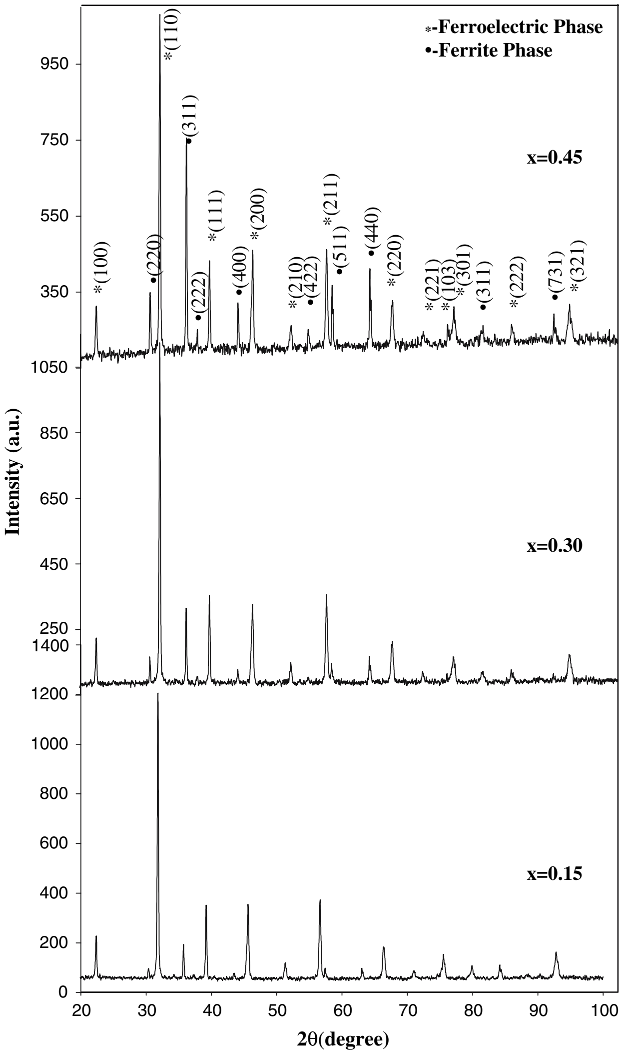

Fig. 1 XRD patterns of $(x)\mathrm{Ni_{0.8}Cu_{0.2}Fe_2O_4} + (1-x)\mathrm{Ba_{0.8}Sr_{0.2}TiO_3}$ composites with $x = 0.15, 0.30, 0.45$

dielectric constant near transition temperature (Tc) can be explained by the temperature-dependent characteristics of domain wall motion. At lower temperatures it is difficult for the domains to move so that the extrinsic contribution of domain walls to the dielectric response is small. At temperatures above Tc the ferroelectric phase has been translated to the paraelectric phase wherein all the domains disappear causing decrease in dielectric constant [11]. Variation in the ferrite Curie temperature is observed as the ferrite content increases. The Curie temperature is found to decrease with increasing ferrite content. This is because the electric field-induced magnetic phase transition depends on the strength of interaction between electric and magnetic ordering, which in turn depends on the molar ratio of the phases [12]. The decrease in dielectric constant is also attributed to the doping effect of ferrite addition in these composites. It is reported that difference in behavior of permittivity as a function composition is a result of superposition of two effects, modification of the piezoelectric material with ferrite components and change in grain size of piezoelectric materials. Also the increase of ferrite content has a result of decrease in polarization efficiency leading to increased conductivity [13].

Electrical resistivity

In order to get superior ME effect, resistivity of the composites must be high such that the accumulated charge carriers must not leak through the magnetostrictive phase. Thus electrical resistivity is an important property as far as the ME composites are concerned. The temperature dependence of electrical resistivity is shown in Fig. 5. The figure shows two trends of conductivity. The first trend observed at lower temperature is due to the impurities and is attributed to the ordered ferroelectric phase and the second trend that occurs at higher temperature is due to polaron hopping and attributed to disordered paraelectric state [14]. Initially, with increasing temperature, the resistivity decreases slowly up to transition temperature and thereafter it decreases rapidly showing semiconducting nature of the samples. The decrease in resistivity with increase in temperature is due to the increase in the

Table 1 Electrical and magnetoelectric data of $(x)\mathrm{Ni_{0.8}Cu_{0.2}Fe_2O_4} + (1-x)\mathrm{Ba_{0.8}Sr_{0.2}TiO_3}$ composites

Composition x	Lattice parameters (Å)			$\rho_{\mathrm{R.T.}}$ (Ω cm)	$(dE/dH)_H$ (μV/cm Oe)
	Ferrite phase	Ferroelectric phase	c/a		
0	–	$a = 3.97$ $c = 3.99$	1.001	3.5×10^9	–
0.15	$a = 8.31$	$a = 3.97$ $c = 4.00$	1.008	6×10^8	510
0.30	$a = 8.32$	$a = 3.97$ $c = 3.99$	1.004	3×10^8	415
0.45	$a = 8.33$	$a = 3.97$ $c = 3.99$	1.003	2×10^7	365
1	$a = 8.33$	–	–	4×10^5	–

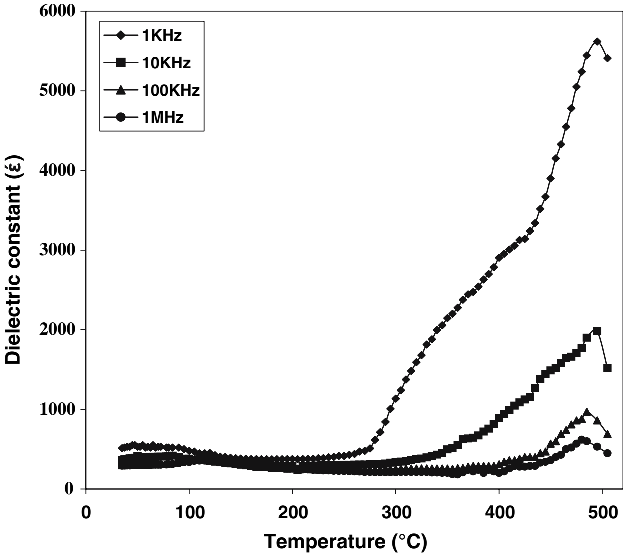

Fig. 2 Variation of dielectric constant with temperature for 15% $Ni_{0.8}Cu_{0.2}Fe_2O_4$ + 85% $Ba_{0.8}Sr_{0.2}TiO_3$ composite

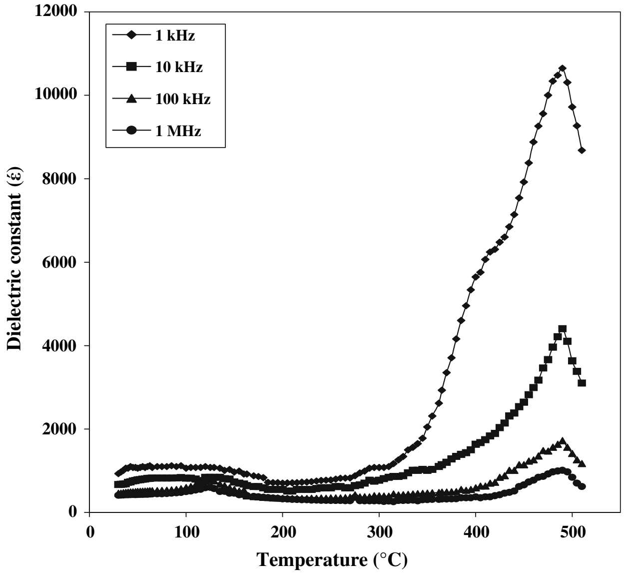

Fig. 3 Variation of dielectric constant with temperature for 30% $Ni_{0.8}Cu_{0.2}Fe_2O_4$ + 70% $Ba_{0.8}Sr_{0.2}TiO_3$ composite

thermally activated drift mobility of charge carriers according to the hopping conduction mechanism. In such a hopping process, the carrier mobility is temperature dependent and is characterized by an activation energy that corresponds to the energy picture of the crystal lattice around the site of electrons. In case of ferrites it is well known that electron hopping between $Fe^{2+}$and Fe^{3+} and hole hopping between Ni^{3+} to Ni^{2+} and Cu^{2+} to Cu^{+} ions in B sites are responsible for electrical conduction in bulk $NiFe_2O_4$ ferrite [15]. With increase in ferrite content the resistivity is found to decrease mainly due to the fact that the resistivity of ferrite phase is less as compared to that of

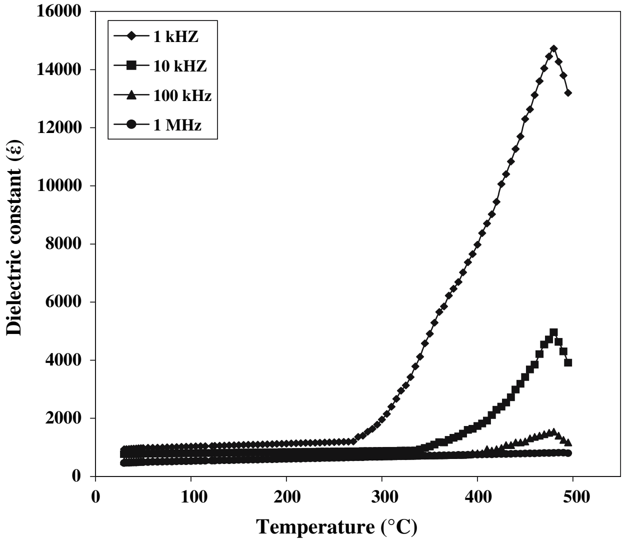

Fig. 4 Variation of dielectric constant with temperature for 45% $Ni_{0.8}Cu_{0.2}Fe_2O_4$ + 55% $Ba_{0.8}Sr_{0.2}TiO_3$ composite

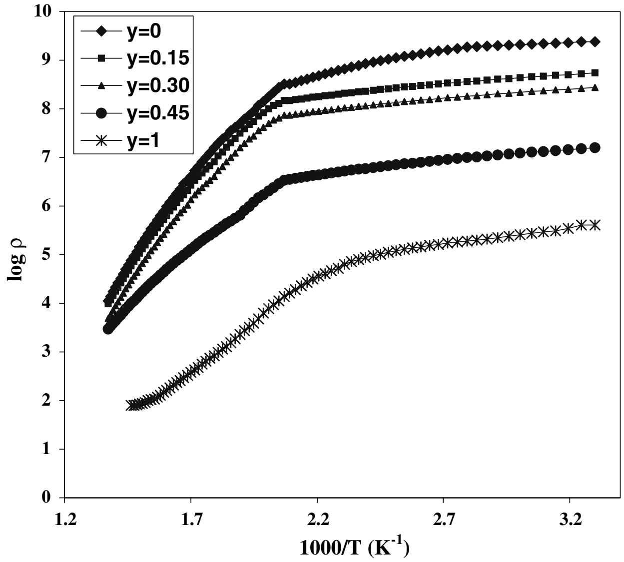

Fig. 5 Variation of dc resistivity with temperature for $(x)Ni_{0.8}Cu_{0.2}Fe_2O_4 + (1-x)Ba_{0.8}Sr_{0.2}TiO_3$ ME composites

ferroelectric phase and when the ferrite particles are dispersed throughout the composite it makes connected chains with ferroelectric particles and the resistivity is reduced significantly because of the low resistivity of the ferrite. Therefore, good dispersion of the ferrite particles in the matrix is required in order to sustain sufficient electric resistivity of the composites [5].

Resistivity-dependent ME effect

Although the ferroelectric and ferrite phases have no ME effect, their composites have coupled magneticelectric

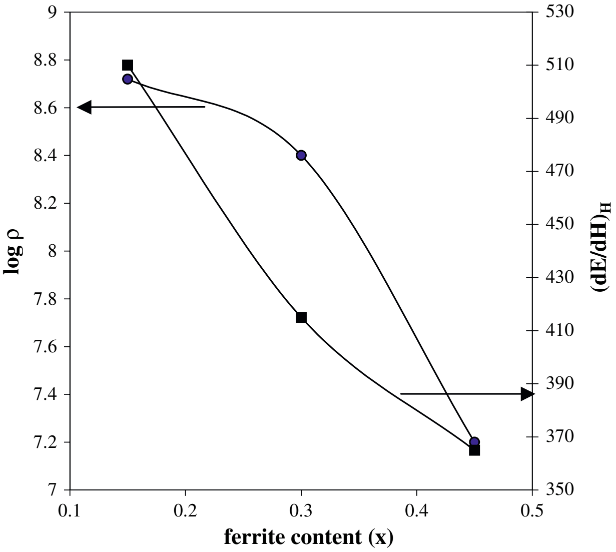

Fig. 6 Variation of dc resistivity and ME voltage coefficient with ferrite content for $(x)Ni_{0.8}Cu_{0.2}Fe_2O_4 + (1 - x)Ba_{0.8}Sr_{0.2}TiO_3$ ME composites

effect as a result of the elastic interaction between these two phases. The ME effect, which can be observed as a product property of the composites, has been strongly influenced by the connectivity between particles and the mole ratio of the two phases. Figure 6 shows the variation of dc resistivity and ME voltage coefficient with ferrite content. The ME voltage coefficient is found to be maximum for high-resistivity composites. The maximum ME voltage coefficient is observed for low mole ratio of the ferrite phase. The maximum ME voltage coefficient is observed for 15% ferrite phase and minimum for 45% ferrite phase. It is due to the fact that the resistivity of the ferrite phase is very low as compared to that of the ferroelectric phase. When composites contain too much of a ferrite, it cannot be poled at a higher voltage for its low resistance and one cannot get good piezoelectric effect due to the leakage of charges developed in the piezoelectric grains through the low resistance path of the surrounding ferrite grains. This leakage of charges reduces the ME effect of the composites. Hence there is a limit to the addition of ferrite phase. These results show the interesting behavior of the composites, which can provide a general guideline for the evaluation of more composite systems and the selection of the best combination with efficient coupling of piezoelectric and piezomagnetic properties [16]. The values of $(dE/dH)_H$ are given in Table 1.

Conclusion

The two-phase ME particulate composites were prepared by standard conventional ceramic method. The coexistence of $Ni_{0.8}Cu_{0.2}Fe_2O_4$ and $Ba_{0.8}Sr_{0.2}TiO_3$ phases in the composites is confirmed by the XRD results. The intensity of the diffraction peaks depends on the amount of the corresponding phase. The samples show negative temperature coefficient of resistivity showing semiconducting nature. The decrease in dielectric constant with frequency shows dielectric dispersion in the low-frequency region. The dielectric constant increases with increasing temperature and starts decreasing after passing through the transition temperature, indicating phase transition from ferroelectric state to paraelectric state at Curie temperature (T_c). The ME effect of the composites strongly depends on the volume fraction on the ferrite. The lower resistivity of the ferrite exerts an important influence on the ME effect of the composites, which provides the guideline for the proper selection of composition of phases.

Acknowledgement The work was carried out with financial assistance from UGC, New Delhi under UGC-DRS- II Program.

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