Studies on Electrical Properties and Magnetoelectric Effect of $(x)\text{Ni}_{0.8}\text{Cu}_{0.2}\text{Fe}_2\text{O}_4 + (1 − x)\text{Ba}_{0.8}\text{Pb}_{0.2}\text{Ti}_{0.8}\text{Zr}_{0.2}\text{O}_3$ Composites

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Abstract. Materials consisting of piezomagnetic and piezoelectric phases viz. $\text{Ni}_{0.8}\text{Cu}_{0.2}\text{Fe}_2\text{O}_4$ and $\text{Ba}_{0.8}\text{Pb}_{0.2}\text{Ti}_{0.8}\text{Zr}_{0.2}\text{O}_3$ have been prepared by standard ceramic method. The presence of two phases in the composites has been confirmed by XRD. Variation of the dielectric constant with frequency in the range 100–1 MHz has been studied at room temperature and the variation of dielectric constant with temperature at set frequencies (1 kHz, 10 kHz, 100 kHz and 1 MHz) has been studied. The dielectric relaxation was observed for the compositions with tetragonal structure whereas normal behaviour was observed for cubic structure. All the samples have shown linear magnetoelectric conversion in the presence of a static magnetic field. The dc resistivity (ρ_{DC}) was studied as a function of temperature in the range 300–773°K. The variation of resistivity with temperature shows metal/seconductor behaviour.

Keywords: dielectric properties, magnetoelectric composites, polaron hopping

Introduction

Composite materials consisting of piezomagnetic and piezoelectric phases are known as magnetoelectric (ME) composites. These composites are used in microwave applications and radio electronics. Such magnetoelectric composites can be prepared by sintering together powders of piezomagnetic and piezoelectric phases by using the standard ceramic method. Moreover sintered composites are much cheaper and easier to prepare. A literature survey indicates that not much detailed work on the electrical properties has been done in these magnetoelectric composites. The ME effect was first observed in antiferromagnetic Cr_2O_3 in 1961 [1, 2] and later some single phase crystal families were found to show the ME effect [3]. Alternativeily, piezomagnetic/piezoelectric composite ceramics were reported to exhibit a larger ME effect than those of the single phase materials [4]. The work available in the literature is confined to the measurement of magnetoelectric effect only. Schmid [5] has mentioned important applications of the magnetoelectric effect. According to his analysis, the ME coefficient of composites largely depends on the equilibrium of two phases, perfect mechanical coupling between grains and the resistivity of composites. The selection of suitable combination of piezomagnetic and piezoelectric materials to achieve better ME effect is, however, a challenging task. In order to achieve better ME output, the piezomagnetic coefficient of ferrite and piezoelectric coefficient of ferroelectric phase must be high [6]. In the present work nickel copper mixed ferrite has been chosen to introduce large Jahn—Teller distortion in the ferrite lattice with lead and zirconium doped barium titanate which may yield maximum ME signal. Here, we report our results on the measurements of dielectric constant, dielectric loss, dc resistivity and ME effect for these composites. Electrical resistivity has been used to suggest the conduction phenomenon and identify the charge carriers responsible for conduction.

Experimental

ME composites contain ferromagnetic and ferroelectric phases. The ferromagnetic phase chosen was copper doped nickel ferrite i.e. $\text{Ni}_{0.8}\text{Cu}_{0.2}\text{Fe}_2\text{O}_4$ and the

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ferroelectric phase chosen was lead and zirconium doped barium titanate i.e. $Ba_{0.8}Pb_{0.2}Ti_{0.8}Zr_{0.2}O_3$. The conventional solid state route using analytical reagent grade NiO, CuO and Fe_2O_3 was used to prepare the ferrite phase. Similarly, the ferroelectric phase was prepared from $BaCO_3$, $PbCO_3$, TiO_2 and ZrO_2. These raw materials were mixed thoroughly. The ferrite phase was presintered at 800°C for 10 h. and the ferroelectric phase was presintered at 1000°C for 10 h. After presintering the raw material was ground to fine powder. The following composites were prepared by taking $Ni_{0.8}Cu_{0.2}Fe_2O_4$ and $Ba_{0.8}Pb_{0.2}Ti_{0.8}Zr_{0.2}O_3$ in molar proportions and presintered at 1100°C for 12 h. The samples in the form of pellets were finally sintered at 1200°C for 12 h.

Composition	Composite material
$x = 0.15$	$(x)Ni_{0.8}Cu_{0.2}Fe_2O_4 + (1 - x)Ba_{0.8}Pb_{0.2}Ti_{0.8}Zr_{0.2}O_3$
$x = 0.30$	$(x)Ni_{0.8}Cu_{0.2}Fe_2O_4 + (1 - x)Ba_{0.8}Pb_{0.2}Ti_{0.8}Zr_{0.2}O_3$
$x = 0.45$	$(x)Ni_{0.8}Cu_{0.2}Fe_2O_4 + (1 - x)Ba_{0.8}Pb_{0.2}Ti_{0.8}Zr_{0.2}O_3$

The samples were characterized by X-ray diffraction (Model Philips PW 1710) using CuKα radiation ($\lambda = 1.5418$ Å). The AC parameters such as capacitance (C) and dissipation factor (tan δ) of the samples were measured in the frequency range 100 Hz to 1 MHz using an LCR meter bridge (Model HP 4284 A). The variation of dielectric constant and loss tangent with temperature were studied by recording these parameters at different frequencies.

Resistivity of these samples was measured by applying a constant voltage of 2 V across the sample and measuring the current at different temperatures. The magnetoelectric effect was calculated experimentally by the magnetoelectric voltage coefficient *dE/dH*, where *E* and *H* are the electric and magnetic field, respectively. In order to measure the magnetoelectric conversion factor, the composites have to be poled electrically and magnetically. A suitable strategy of poling has to be employed for each material, judged on pragmatic considerations. The electrical poling involved heating the sample at 50°C above the ferroelectric Curie temperature. Then in an external field of about 2 to 3 kV/cm, the composite samples were subsequently cooled fast to room temperature. The domains in the ferroelectric phase of these composites are switched directly by the external applied field. The samples were poled magnetically by applying an external DC magnetic field of about 6 kOe at room temperature. The poling was carried out in the set up in which the DC $(ME)_H$ was measured using the DC magnetic field.

Results and Discussion

The diffraction patterns for $(x)Ni_{0.8}Cu_{0.2}Fe_2O_4 + (1 - x)Ba_{0.8}Pb_{0.2}Ti_{0.8}Zr_{0.2}O_3$ samples contained two sets of well defined and narrow peaks as shown in Fig. 1. The first set corresponds to the magnetic phase ($Ni_{0.8}Cu_{0.2}Fe_2O_4$) while the second set was identified with the piezoelectric phase ($Ba_{0.8}Pb_{0.2}Ti_{0.8}Zr_{0.2}O_3$). It is seen that the intensity of ferrite peaks increases with its increasing percentage in the composites. The number of peaks also increases with increase in ferrite percentage. The $Ba_{0.8}Pb_{0.2}Ti_{0.8}Zr_{0.2}O_3$ ferroelectric phase has a tetragonal perovskite structure with lattice parameters $a = 3.983$ Å, $c = 3.986$ Å and $c/a \approx 1$ and $Ni_{0.8}Cu_{0.2}Fe_2O_4$ has a cubic spinel structure with lattice parameter $a = 8.322$ Å.

The variation of dielectric constant with frequency at room temperature is shown in Fig. 2. The dielectric constant decreases with increase in frequency and remains constant for higher frequencies. At lower frequencies the dispersion of dielectric constant is large while it is independent of frequency beyond 10 kHz. As the frequency increases, ionic and orientation sources of polarizability decreases and finally disappear due to the inertia of the molecules and ions. In practice, there is a relaxation time for charge transport, and therefore, the dielectric constant depends on the applied frequency. All the samples reveal dispersion due to Maxwell–Wagner interfacial polarization [7, 8] in agreement with Koop's phenomenological theory [9]. The observed variation in dielectric intensity can be explained on the basis of space charge polarization and is governed by the number of space charge carriers and resistivity of the sample. The charge carriers, which take part in the ion exchange, can be produced during the sintering process.

The variation of dielectric constant with temperature at 1 kHz, 10 kHz, 100 kHz and 1 MHz frequencies was studied for the present samples. The variation of dielectric constant with temperature for the sample with $x = 0.15$ is shown in Fig. 3. From the plot it is clear that the dielectric constant decreases with increase in temperature up to 100°C due to its high resistivity, impurities and defects in the materials. Further
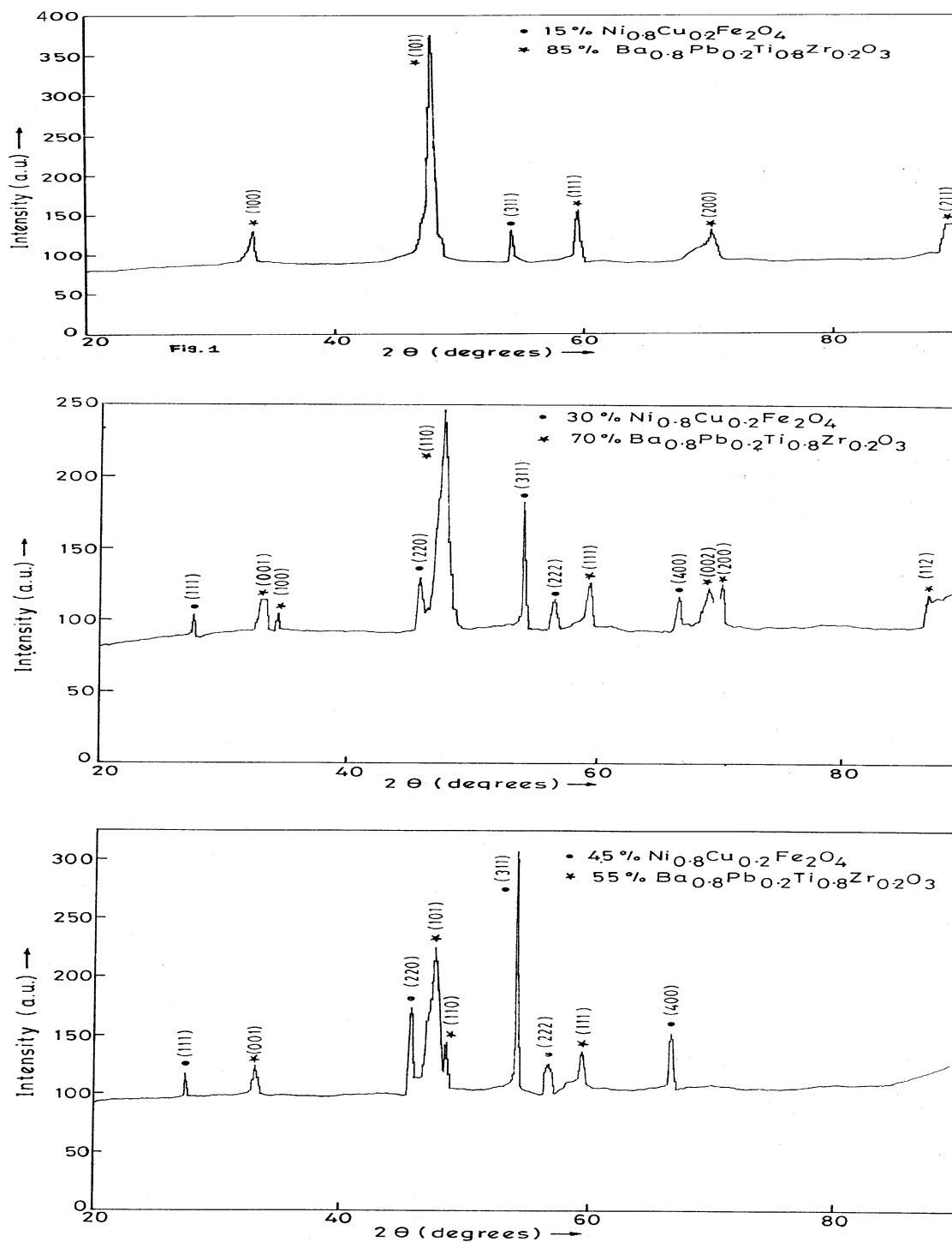
Fig. 1. XRD pattern of $(x)\mathrm{Ni}_{0.8}\mathrm{Cu}_{0.2}\mathrm{Fe}_2\mathrm{O}_4 + (1-x)\mathrm{Ba}_{0.8}\mathrm{Pb}_{0.2}\mathrm{Ti}_{0.8}\mathrm{Zr}_{0.2}\mathrm{O}_3$ ME composites.
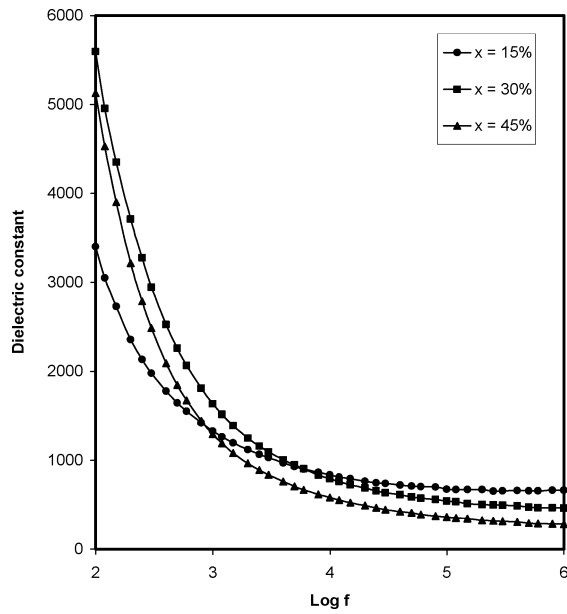
Fig. 2. Variation of dielectric constant with frequency for $(x)Ni_{0.8}Cu_{0.2}Fe_2O_4 + (1-x)Ba_{0.8}Pb_{0.2}Ti_{0.8}Zr_{0.2}O_3$ composites.

Fig. 4. Variation of dielectric constant with temperature for $30\%Ni_{0.8}Cu_{0.2}Fe_2O_4 + 70\% Ba_{0.8}Pb_{0.2}Ti_{0.8}Zr_{0.2}O_3$ composites.

Fig. 3. Variation of dielectric constant with temperature for $15\%Ni_{0.8}Cu_{0.2}Fe_2O_4 + 85\% Ba_{0.8}Pb_{0.2}Ti_{0.8}Zr_{0.2}O_3$ composites.
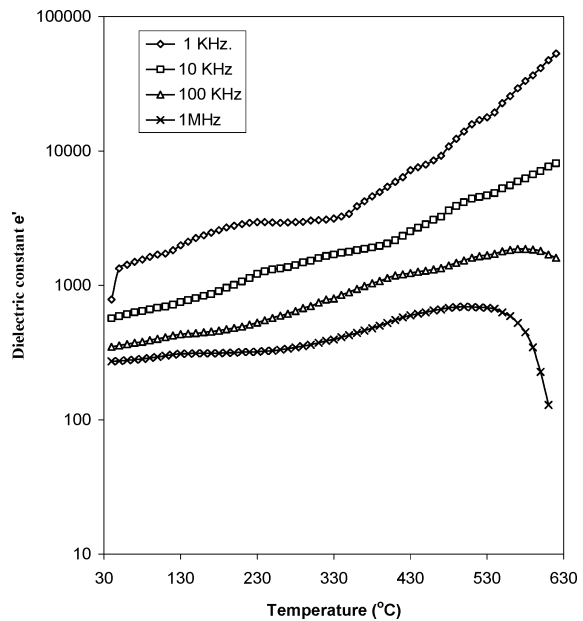
Fig. 5. Variation of dielectric constant with temperature for $45\%Ni_{0.8}Cu_{0.2}Fe_2O_4 + 55\% Ba_{0.8}Pb_{0.2}Ti_{0.8}Zr_{0.2}O_3$ composites.

increase in temperature increases the dielectric constant up to the transition temperature and decreases thereafter [6, 10]. All the samples show dispersion in dielect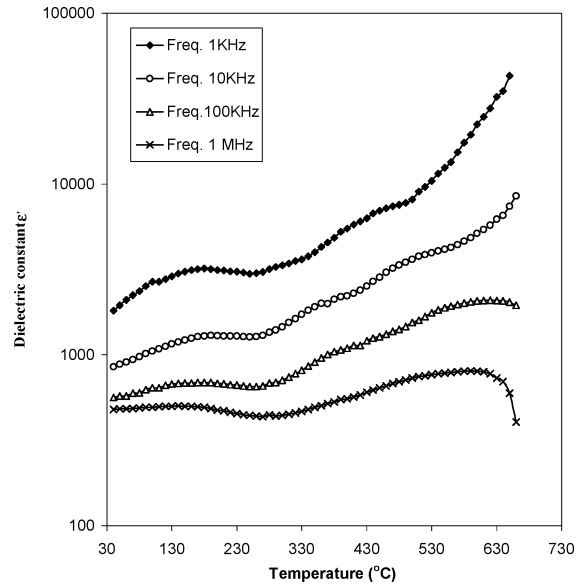ric constant with frequency i.e. the dielectric constant decreases with increasing test frequency. It is also seen that the transition temperature is independent of test frequency, obeying the Curie–Weiss law [11]. Such a behaviour is also seen in the case of other composites with $x = 0.30$ and 0.45 (Figs. 4 and 5),
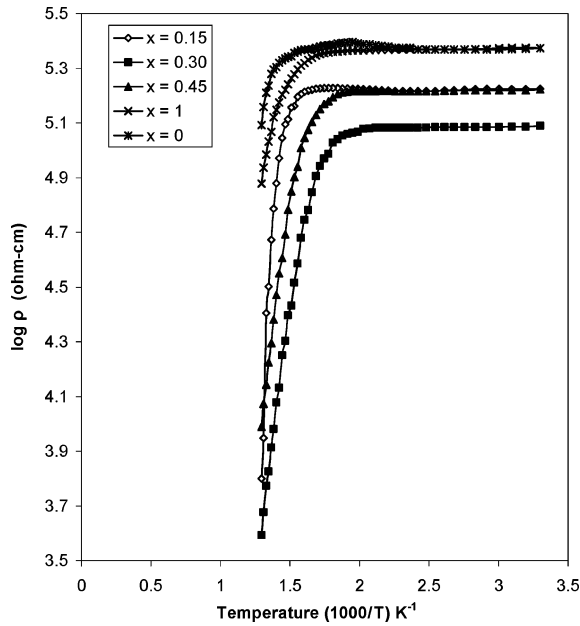
Fig. 6. Variation of dc resistivity with temperature for $(x)Ni_{0.8}Cu_{0.2}Fe_2O_4$ + $(1 - x)$ $Ba_{0.8}Pb_{0.2}Ti_{0.8}Zr_{0.2}O_3$ composites.

Fig. 7. Variation of magnetoelectric conversion factor with dc magnetic field for $(x)Ni_{0.8}Cu_{0.2}Fe_2O_4 + (1-x)Ba_{0.8}Pb_{0.2}Ti_{0.8}Zr_{0.2}O_3$ composites.

however the value of dielectric constant is found to be enhanced. The ferrite material has a dielectric dipole which is much smaller than that of the ferroelectric material [12]. The magnetic ordering should cause a dielectric change. According to Rezlescu model, the dielectric behaviour in this type of materials is due to the collective contribution of two types of carriers, p and n, to the polarization. The increase in dielectric constant with increase in ferroelectric content is also due to Verwey type electron exchange polarization in the ferrite on one hand and polarization as an inherent property of ferroelectrics on the other. The behaviour is relaxor type and the observations support the behaviour of ferrites as suggested by Rezlescu and Rezlescu [13].

The *dc* resistivity as a function of temperature was measured in the temperature range 300 to 800 K by two probe method. The variation of *dc* resistivity with temperature i.e. ρ_{DC} vs $1/T$ is shown in Fig. 6. It is clear from the plot that the resistivity of the composites remains constant initially and decreases thereafter. Since ferrites are semiconductors, their resistivity ρ should decrease with increasing temperature according to relation $\rho = \rho o \exp(\Delta E/KT)$, where ΔE represent an
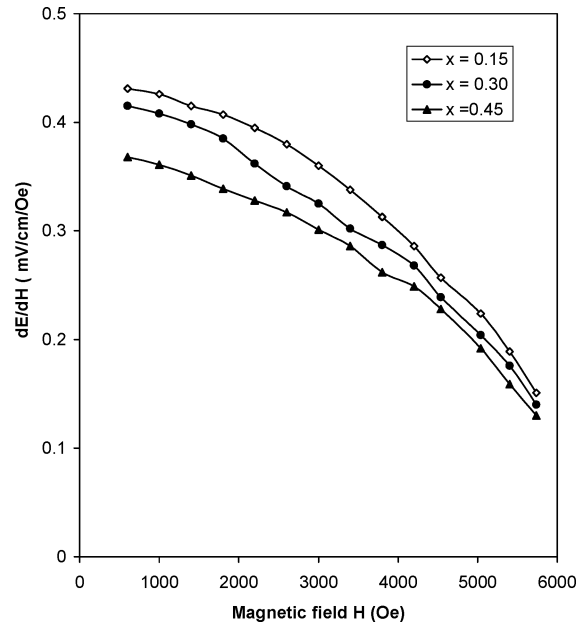
activation energy, ρo is temperature independent constant [14]. The electrical resistivity was explained on the basis of Verwey–de Boer mechanism in which electron exchange takes place between ions of the same element present in more than one valence state. Such ions are distributed randomly over crystallographically equivalent lattice sites [15]. Conduction in ferrite is due to electron transfer between divalent and trivalent ions. The conduction at higher temperature is due to polaron hopping [16].

Figure 7 shows the magnetoelectric voltage coefficient as a function of *dc* magnetic field. The composite with 15% ferrite shows highest magnetoelectric voltage coefficient among the tested compositions. The magnetoelectric conversion factor decreases with increasing percentage of ferrite in the composite. According to the product property i.e. the magnetostrictive phase is strained when a magnetic field is applied to the composite, and this strain induces stress on the piezoelectric phase. Thus the product property in such composites is the magnetoelectric effect, i.e. an applied magnetic field induces an electric field. ME coupling is achieved by electromechanical conversion in the piezoelectric phase and magnetomechanical conversion in

the magnetostrictive phase by stress transfer through the interface between the two phases. The dE/dH values decreases with increase in ferrite content in the studied composites (Fig. 7). The resistivity of $x = 0.15$ composite is higher than the others. This is the main cause for decrease in dE/dH values with increase in ferrite content. Because decrease in resistivity leads to the leakage of charges build-up in ferroelectric phase through the surrounding ferrite grains. The composite $x = 0.15$ had the highest magnetoelectric voltage coefficient of 391 μV/cm/Oe at room temperature.

Conclusions

The XRD patterns of the composites reveal the presence of both ferrite and ferroelectric phases. The intensity of ferrite peaks increases with the ferrite content. The electrical resistivity at higher temperature decreases exponentially suddenly indicating electron hopping conduction mechanism. The dielectric behaviour shows the electronic polarizability at higher frequency to be due to space charge carriers. The maximum static ME voltage coefficient of 391 μV/cm/Oe was observed for $x = 0.15$ sample. Thus it can be concluded that these composites have better ME sensitivity in the low field range.

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