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Synthesis and property measurement of three phase ME composites

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Abstract

The y ($Ni_{0.5}Cu_{0.2}Zn_{0.3}Fe_2O_4$) + (1-y) (50% $BaTiO_3$ + 50% PZT) magnetoelectric composites were prepared by using standard ceramic method. The presence of component phases in the composites was confirmed by XRD. The dc resistivity was studied as a function of temperature. The decrease in dc resistivity with increase in temperature shows semiconducting behavior of samples. The variation of ac conductivity with frequency shows that the conduction in composites is of small polarons type. The variation of dielectric constant (έ) and tan δ with frequency in the range 20 Hz - 1 MHz was studied. The magnetoelectric effect $(dE/dH)_H$ was measured as a function of intensity of dc magnetic field. The maximum value of ME coefficient was measured to be 975 μV $Oe^{-1}Cm^{-1}$.

Keywords– X ray diffraction, ME composite materials, electrical properties, magnetoelectric effect

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Introduction

Composite materials containing piezomagnetic and piezoelectric phases are known as magnetoelectric composites. When composites are placed in magnetic field, they undergo deformation due to magnetostrictive effect and generate electrical charge due to piezoelectric effect [1].

Dielectric polarization of a material under the magnetic field or an induced magnetization under an electric field requires simultaneous presence of long range ordering of magnetic moments and electric dipoles. The particulate ME composites materials show higher ME properties compared to single phase ME materials such as Cr_2O_3. Hence, extensive work has been carried out in the field of particulate composites that have importance in number of applications such as memory devices proposed by O'Dell, transducers and filter applications, recording heads and electromagnetic pick ups [2].

Ni-Zn ferrite is considered as one of the most versatile ferrites due to its high resistivity and low eddy current losses at higher frequencies [3]. The electrical conductivity of Ni ferrite changes with Zn content and it was found to be minimum for the composition $Ni_{0.7}Zn_{0.3}Fe_2O_4$ [4]. Also, Cu^{2+} being Jahn- Teller ion has high mechanical coupling leading to high magnetostriction [5]. The PZT also has great piezoelectric properties. It is well known that $BaTiO_3$ exhibits high dielectric constant, high piezoelectric coefficient and better mechanical properties [6, 7]. It is expected that the composites of these three may trigger better ME output.

Materials and Methods

2. Experimental

2.1 Preparation

The ME composites having the general formula y ($Ni_{0.5}Cu_{0.2}Zn_{0.3}Fe_2O_4$) + (1-y) (50% $BaTiO_3$+ 50 % PZT) where y varies as 0.15, 0.30, 0.45 were prepared using standard ceramic method. The $Ni_{0.5}Cu_{0.2}Zn_{0.3}Fe_2O_4$ ferrite phase was prepared by using NiO, CuO, ZnO and Fe_2O_3 as starting materials in required molar proportions by solid state reaction method. This powder was presintered at 900^0C for 9 h. The ferroelectric $BaTiO_3$ was prepared by using $BaCO_3$ and TiO_2 in molar proportions and sintered at 1100^0C for 11 h. The other ferroelectric phase PZT was prepared by using PbO, ZrO_2 and TiO_2 as starting materials taken in required molar proportions and sintered at 1100^0C for 2 and half h. The ME composites were prepared by mixing 15, 30 and 45% ferrite phase with 85, 70 and 55 % of ferroelectric phase respectively. These composite powders were then mixed with 2% polyvinyl alcohol as a binder and pressed uniaxially to form pellets of thickness of 2-3 mm and diameter 10 mm using hydraulic press. The pelletized samples were finally sintered at 1100^0C for 11 h in furnace and later furnace cooled.

2.2 Characterization

The samples were characterized by using x-ray diffractometer (Philips Model PW 3710). The XRD patterns show the presence of both ferrite and ferroelectric phases. It can be also seen that no any chemical reaction has taken place between the component phases during sintering. The dc resistivity measurements were carried out by two probe method in the temperature range 30^0C to 500^0C. The variation of dielectric constant (ε) and loss tangent were measured at room temperature in the frequency range 20 Hz to 1 MHz using LCR meter- bridge (Modem HP 4284). The ac conductivity (σ_{ac}) was calculated from dielectric data using the relation,

$$\sigma_{ac} = \varepsilon \, \varepsilon_0 \, \omega \tan\delta \qquad \ldots\ldots\ldots\ldots (1)$$

where ε is dielectric constant, ε_0 is permittivity of free space, tan δ is the loss tangent and ω is the angular frequency.

The ME output of the samples was measured as a function of dc magnetic field. The electric poling was carried in an electric field of 2 KV/cm during cooling of the sample from 30 to 40^0 C above the Tc of ferroelectric phase to room temperature. The composites were magnetically poled by applying dc magnetic field of 1KOe at room temperature. The static ME voltage coefficient was calculated by the change in ME output with respect to dc bias magnetic field.

3. Results and Discussion

3.1 Structural analysis

Fig. 1 shows X ray diffraction patterns of composites with compositions y= 0.15, 0.30 and 0.45. All the peaks can be easily identified. There is no intermediate phase formed. The number of ferrite peaks increases with increase in ferrite content, also its intensity increases with increase in ferrite percent in the composites. The ferrite phase has cubic spinel structure whereas the ferroelectric phase has tetragonal perovskite structure. No structural change is observed for both the phases in composites. The lattice parameters of the composites are given in Table-1.

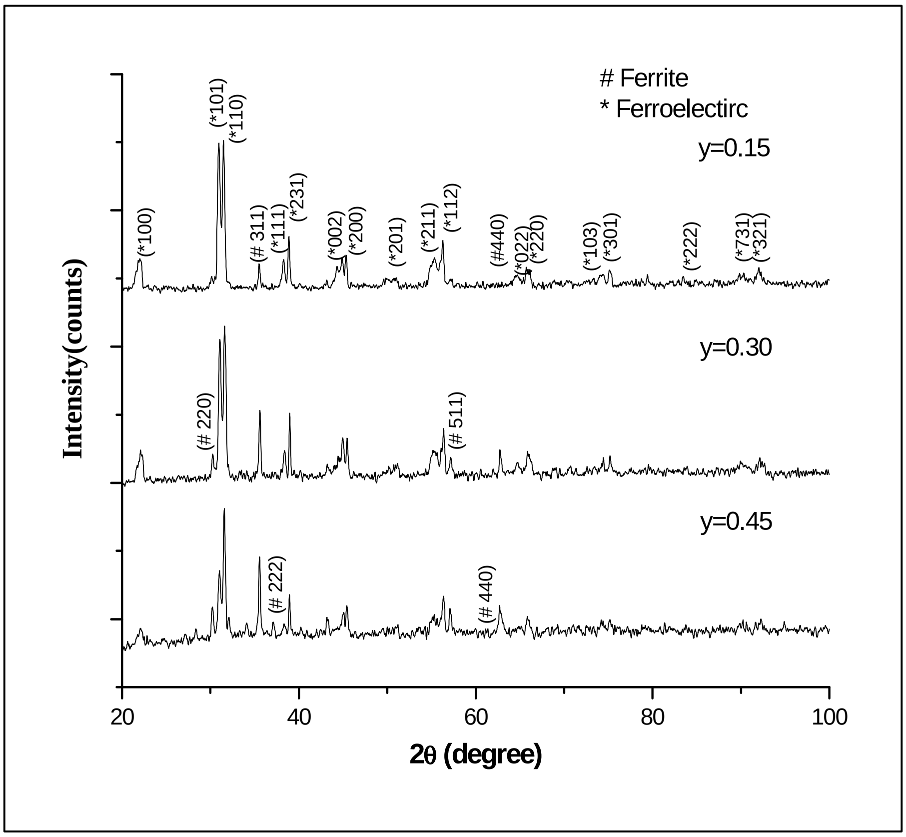

Fig. 1. X-ray diffraction patterns of y(Ni$_{0.5}$Cu$_{0.2}$Zn$_{0.3}$Fe$_2$O$_4$) + (1-y) (50% BaTiO$_3$+ 50% PZT) ME composites

Table-1. Lattice parameters of y [$Ni_{0.5}Cu_{0.2}Zn_{0.3}Fe_2O_4$] + (1-y) [50% $BaTiO_3$ + 50% PZT] ME composites

Composition	Lattice parameter (Å)						
	Ferrite	Ferroelectric					
		$BaTiO_3$			PZT		
y	a	a	c	c/a	a	c	c/a
0.15	8. 37	3.99	4.05	1.01	4.03	4.13	1.02
0.30	8. 36	3.99	4.01	1.005	4.04	4.15	1.02
0.45	8. 36	3.99	4.04	1.01	4.01	4.11	1.02

3.2 DC resistivity

Fig. 2 shows variation of dc resistivity with temperature for the composites. Linear decrease in resistivity with temperature shows semiconducting nature of the samples. Also, the change in slope occurs in ferroelectric and composite samples while crossing the ferroelectric curie temperature. But, for ferrite phase no much marked change in slope is observed due to transition of sample from ferri to para state.

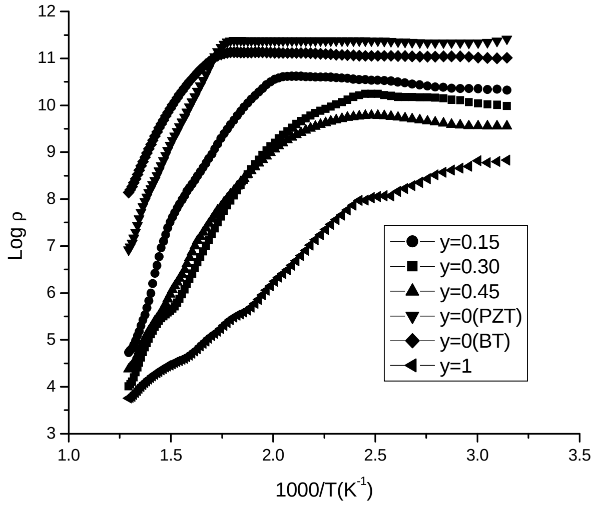

Fig.2 Variation of dc resistivity with temperature for $y(Ni_{0.5}Cu_{0.2}Zn_{0.3}Fe_2O_4)$ + (1-y)(50% PZT+ 50 % $BaTiO_3$) ME composites samples

The conduction mechanism can be explained by electron exchange between ions of same elements which are present in different valance state. The conduction mechanism can be explained with hopping of electrons between Fe^{2+}/Fe^{3+} and Ti^{3+}/Ti^{4+}. There is also contribution from p type charge carriers by hole hopping between Ni^{2+}/Ni^{3+}, Cu^{2+}/Cu^{3+} etc. But, this contribution is lower as compared electronic contribution [8].

The activation energies calculated by using Arrhenius relation are 0.53, 0.52, 0.51 eV with composition y = 0.15, 0.30, 0.45 suggesting temperature dependence of charge mobility. From, the graph it can be seen that the dc resistivity is found to be decreased with increasing ferrite content in composites. The variation of dc resistivity with content of constituent phases is attributed to the difference in their resistivity. As the resistivity of ferrite phase is lower than ferroelectric phase, the maximum resistivity is observed for ferrite with composition y = 0.15, with minimum ferrite content in composite**.**

3.3 AC conductivity

To know the conduction mechanism in these composites, ac conductivity was studied. The variation of ac conductivity with frequency is as shown in Fig.3. The plots are observed to be almost linear confirming small polaron type conduction in composites. In ionic solids, the electrical conduction is due to migration of ions and this ionic transport depends on the angular frequency. Thus, ac conductivity is proportional to angular frequency confirming linear nature [14].

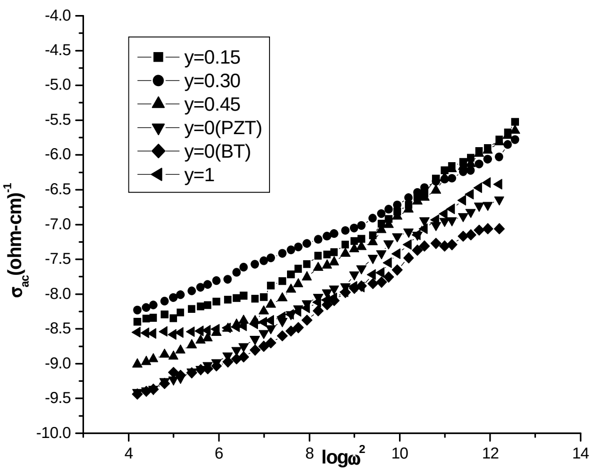

Fig.3 Variation of ac conductivity with frequency for $y(Ni_{0.5}Cu_{0.2}Zn_{0.3}Fe_2O_4)$+ (1-y) (50% $BaTiO_3$+ 50% PZT) ME composite samples

3.4 Dielectric properties

The variation of dielectric constant with frequency is as shown in Fig. 4. The dielectric constant decreases with increase in frequency showing dispersion in the lower frequency region. It attains a constant value and remains independent of frequency later on. All the samples reveals dispersion due to Maxwell – Wagner [9, 10] type interfacial polarization in agreement with Koop's phenomenological theory [11]. At higher frequencies dielectric constant reaches a constant value because beyond a certain frequency of electric field the electron exchange does not follow the alternating field. The high value of dielectric constant at lower frequencies is observed due to heterogeneous conduction in composites [12]. At higher frequencies, this does not contribute to the polarization mechanism. There is only electronic polarization contribution at higher frequency, which results in decrease in dielectric constant.

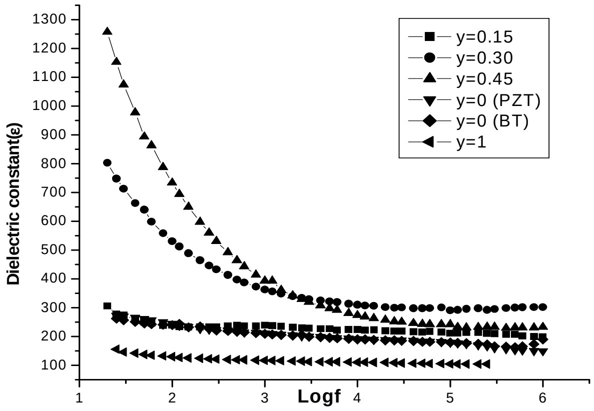

Fig.4 Variation of dielectric constant with frequency for $y(Ni_{0.5}Cu_{0.2}Zn_{0.3}Fe_2O_4)$+ (1-y) (50% $BaTiO_3$+ 50% PZT) ME composite samples

The dielectric behavior of the composites can also be explained by the fact that the mechanism of polarization process in ferrite is similar to that of their conduction process. Beyond the percolation limit of ferrite phase in composites, the conduction is mainly due to ferrite phase [13]. As, the ferrite and ferroelectric grains are randomly mixed together in parallel and series mode, it is difficult to calculate effective dielectric constant of composites and predict the rule of mixture and sum [15].

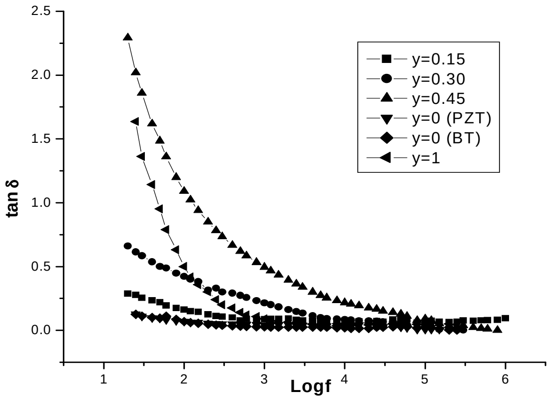

Fig.5 Variation of loss tangent with frequency for $y(Ni_{0.5}Cu_{0.2}Zn_{0.3}Fe_2O_4)$+ (1-y) (50% $BaTiO_3$+ 50% PZT) ME composite samples

Fig. 5 shows variation of loss tangent with frequency. The variation of Tan δ with frequency shows the similar nature as that of έ with frequency

3.5 Magnetoelectric effect

The variation of magnetoelectric coefficient with applied magnetic field for composites is shown in Fig. 6. The ME effect is electrical voltage obtained by the strain induced in ferroelectric phase due to magnetostrictive property of ferrite phase. The magnitude of magnetoelectric sensitivity dE/dH depends in a way on the composition of composite material [16].

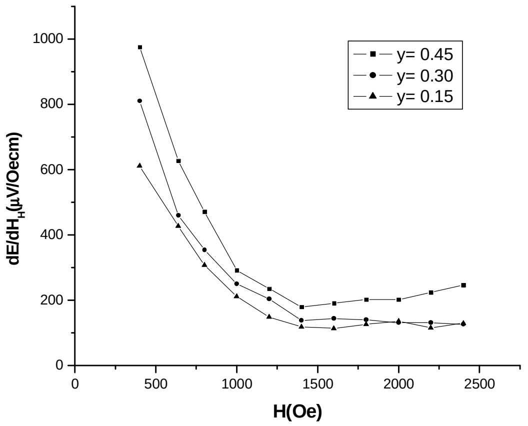

Fig. 6 Variation of magnetoelectric coefficient with magnetic field of y($Ni_{0.5}Cu_{0.2}Zn_{0.3}Fe_2O_4$)+ (1-y)(50% $BaTiO_3$ + 50% PZT) ME composite samples

From the Fig. 6, it can be seen that ME coefficient decreases gradually with increasing magnetic field. The maximum ME output about 975 μV $Oe^{-1}Cm^{-1}$ was obtained for 45% $Ni_{0.5}Cu_{0.2}Zn_{0.3}Fe_2O_4$ + 55% (50% PZT +50% $BaTiO_3$) composite. It can be concluded that as the content of ferrite increases in composite, the extent of interaction between ferrite and ferroelectric phase increases, it results in increasing value of ME coefficient [17]. The theoretical considerations show that under ideal conditions of the inherent properties of the constituent phases, the ME coefficient is maximum for equal mole percent of ferrite and ferroelectric phases [18].

Conclusion

The XRD patterns of the composites reveal presence of both ferrite and ferroelectric phases. The intensity of ferrite phase increases with ferrite content. The dc resistivity decreases with increasing temperature showing semiconducting behavior of the composites. The variation of ac conductivity with frequency is linear indicating the conduction is small polarons type. The dielectric constant shows dispersion at higher temperature and remains almost constant at lower frequencies. The variation of tan δ with frequency shows the similar nature as that of ε with frequency. The ME coefficient decreases gradually with increasing magnetic field. The maximum ME output about 975 μV $Oe^{-1}Cm^{-1}$ was obtained for 45% $Ni_{0.5}Cu_{0.2}Zn_{0.3}Fe_2O_4$ + 55% (50% PZT +50% $BaTiO_3$) composite.

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