International Journal of Chemical and Physical Sciences, ISSN:2319-6602
IJCPS Vol. 4 Special Issue ETP – 2015
www.ijcps.org

Structural and Electrical Properties of (1-x)$Ni_{0.90}Co_{0.05}Mn_{0.05}Fe_2O_4$ + (x)$BaTiO_3$ Magnetoelectric Composites

S. A. LOKARE[1], Y. B. KHOLLAM[1]

[1]Department of Physics, Anantrao Pawar College, Pirangut, Maharashtra, India
e-mail: lokaresmita@gmail.com, ykhollam@yahoo.co.in

Abstract

The (1-x)$Ni_{0.90}Co_{0.05}Mn_{0.05}Fe_2O_4$+(x)$BaTiO_3$ Magnetoelectric (ME) composites were prepared by using conventional double sintering ceramic process, where x varies as 1.00, 0.85,0.70, 0.55 and 0.00. The presence of both the phases was confirmed by X - ray diffraction. The grain size was determined by using scanning electron micrograph. The dc resistivities of the samples were studied with variation in temperature. The variation of dielectric constant (ε') and loss tangent (tan δ) were measured in the frequency range of 100 Hz - 1 MHz. The ac conductivity is derived from dielectric constant (ε') and loss tangent (tan δ). The characterization results indicated that the drop in dc resistivity uin case of ME composite id due the addition of ferrite phase. Further, the polarization of ME composites is similar to the conduction in the ferrite via, electron exchange between Fe^{2+} and Fe^{3+}. Furthermore, the conduction phenomena in ME composites are due to the small polaron hopping as is seen from the linear part of ac conductivity plots.

Keywords: Magnetoelectric composite; XRD; SEM; dc resistivity, ac conductivity.

Introduction

Magnetoelectric (ME) conversion is predicted as a product property in some two phase materials. The property would be exhibited when piezoelectric and piezomagnetic materials are combined in proper proportion to form a ME composite. The coupling between magnetic and electric subsystem results in ME effect, i.e. the electric field induced magnetization and magnetic field induced an electric polarization. The ME effect obtained in composites is more than hundred times of single phase ME materials such as Cr_2O_3. These materials are used as transducer, actuators, and magnetic sensors for ac and dc magnetic fields measurements and also used in microwave field, magnetic field probed, radio electronics, current measurements, integral optics and fiber communicating technology [1 - 4]. To realize high output of ME conversion in composite materials, the following guidelines are to be kept in mind [5].

i)) The two phases must be in chemical equilibrium.

ii)) The values of magnetostriction coefficient of piezomagnetic phase and piezoelectric coefficient of piezoelectric phase must be high.

iii) Mechanical contact between the grains of the two phases must be good.

iv) The resistivities of two the phases should be high in order to avoid the leakage of accumulated charges through the magnetostrictive phase.

As reported earlier, manganese, cobalt doped nickel ferrite has highly resistive and magnetostrictive [6] and $BaTiO_3$ has high dielectric permittivity. If the two compounds can be successfully incorporated into composite, it is expected that the composites might have interesting electrical as well as magnetoelectric properties. Hence, $Ni_{0.90}Co_{0.05}Mn_{0.05}Fe_2O_4$ and $BaTiO_3$ are chosen as a ferrite phase and as a ferroelectric phase respectively to form the ME composites in present work. The dc resistivity, ac conductivity and dielectric constant at room temperature of these ME composites are presented in current communication.

Experimental Work

Synthesis of powders

The composites were prepared with the general formula, $(1-x)Ni_{0.90}Co_{0.05}Mn_{0.05}Fe_2O_4 + (x)BaTiO_3$. The component ferrite phases were prepared by using AR grade $NiCO_3$, $CoCO_3$, and $MnCO_3$ and Fe_2O_4 powders, whereas the ferroelectric phase was prepared by using $BaCO_3$ and TiO_2 as starting materials in stoichiometric proportions. The composites were prepared by milling presintered $BaTiO_3$ and $Ni_{0.90}Co_{0.05}Mn_{0.05}Fe_2O_4$ in different molar proportions. These mixtures were presintered at 1000 ^oC for 12 hrs. The presintered powders were uniaxially pressed in stainless steel die to form pellets having 15 mm diameter and 2-3 mm thickness using hydraulic press and polyvinyl alcohol as a binder. They were finally sintered at 1200 ^oC for 12 hr and furnace cooled to room temperature.

Physical characterization

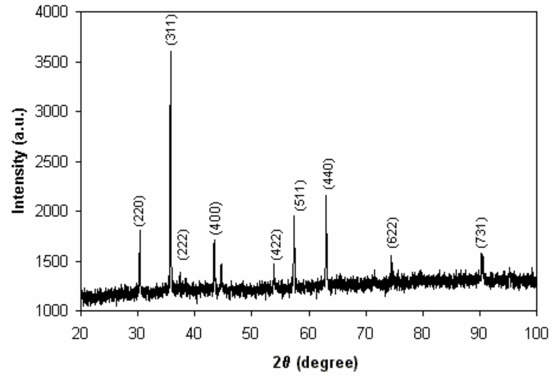
The phase analysis of samples was done by using Phillips X-ray diffractometer (Model PW 1710, CuK_α radiation λ = 1.5418 Å). The average particle size was calculated using Scherrer's formula. The particle morphological analysis was done by scanning electron microscopy (SEM, JEOL JSM 6360) with an accelerating voltage of 25 kV.

Electric measurements

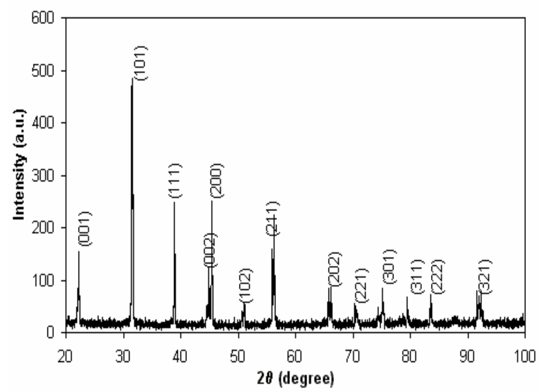
The dc resistivity was measured by using two-probe method. The pellet samples were coated with silver paste to ensure good ohmic contacts. The silver paste coated samples were cured at temperature of 200 ^0C. The ac parameters such as capacitance (C) and dissipation factor (tan δ**)** of the samples were measured in the frequency range of 100 Hz - 1 MHz by using LCR meter bridge (Hewlett Packard, Model HP 4284).

Results and Discussions

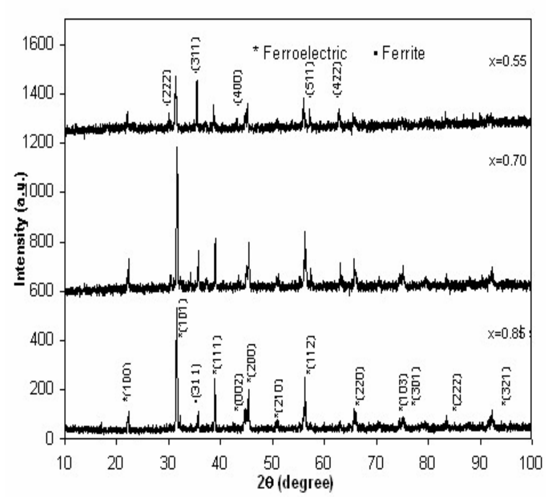
Figure 1 (a), (b) and (c) show the X - ray diffraction (XRD) patterns of ferrite, ferroelectric and ME composites with composition $(1-x)Ni_{0.90}Co_{0.05}Mn_{0.05}Fe_2O_4 + (x)BaTiO_3$ as x = 0.85, 0.70 and 0.55. The results obtained from XRD data corresponding to $BaTiO_3$, $Ni_{0.90}Co_{0.05}Mn_{0.05}Fe_2O_4$ ferrite and ME composites are well indexed. The $BaTiO_3$ and $Ni_{0.90}Co_{0.05}Mn_{0.05}Fe_2O_4$ were identified as tetragonal perovskite structure and spinel cubic structure respectively. In case of ME composites there was no any intermediate phases other than those belonging to a cubic spinel structure of ferrite phase and tetragonal perovskite structure of ferroelectric phase.



(a)



(b)



(c)

Figure 1. XRD patterns of (a) $Ni_{0.90}Co_{0.05}Mn_{0.05}Fe_2O_4$, (b) $BaTiO_3$ and (c) (1-x) $Ni_{0.90}Co_{0.05}Mn_{0.05}Fe_2O_4$ + (x) $BaTiO_3$ ME composites with x = 0.85, 0.70 and 0.55.

Thus, it is confirmed that there is no any chemical reaction between the two phases of composites after sintering. The lattice parameters of the two phases in the ME composites with the composition as given in Table 1.

Table 1. Structural data for (1-x) $Ni_{0.90}Co_{0.05}Mn_{0.05}Fe_2O_4$ + (x) $BaTiO_3$ ME composites

x	Phase		
	Ferrite	Ferroelectric	
	Lattice parameter (A°)	lattice parameters (A°)	c/a ratio
1.00	-	a = 3.99, c = 4.08	1.02
0.85	a = 8.34	a = 3.99, c = 4.08	1.02
0.70	a = 8.34	a = 3.99, c = 4.08	1.02
0.55	a = 8.34	a = 3.99, c = 4.08	1.02
0.00	a = 8.33	-	-

The intensity of (101) reflection decreases while intensity of (311) reflection increases with increasing the ferrite content in the composites. The number of ferrite peaks are found to be increasing with increasing the ferrite content in composites, which specifies the presence of scattering components from both the participating phases. The composites of $Ni_{0.90}Co_{0.05}Mn_{0.05}Fe_2O_4$ + $BaTiO_3$ crystallize in cubic spinel structure for ferrite phase and tetragonal perovskite structure for ferroelectric phase as reported earlier [4].

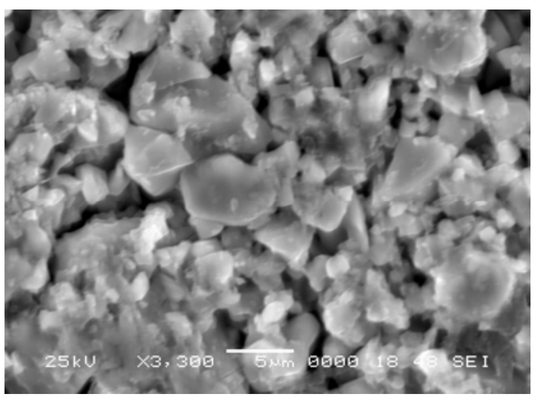


Figure 2. SEM microphotograph of $0.85BaTiO_3 + 0.15Ni_{0.90}Co_{0.05}Mn_{0.05}Fe_2O_4$ ME composite

Figure 2 shows the SEM microphotograph of the $0.85BaTiO_3 + 0.15Ni_{0.90}Co_{0.05}Mn_{0.05}Fe_2O_4$ ME composites. It shows dense microstructure with proper grain growth after sintering. The presence of two phases in the composite indicates that a grain of the other phase as its neighbor. The average grain size was calculated by using line intercept method. In the present investigation, the composites were prepared in ferroelectric rich regions. The average grain size of the composites varies with their contents (not shown here). The average grain size of the composites goes on decreasing with ferrite content. The large grain size of ferroelectric phase as compared to ferrite phase can effectively reduce the effective charges induced by the chain formation of ferrite phase particle. Increase in grain size results into reduction in grain boundary area and as a consequence conductivity decreases. The variation of dc resistivity with reciprocal of temperature is shown in Figure 3. It is found to obey the Arrhenius relation

$$\rho = \rho_0 e^{\Delta E / kT} \quad \text{.... (1)}$$

where, ΔE is activation energy required to cause an electron jump from one ion to another, ρ is the resistivity at temperature T, ρ_0 is the temperature independent constant and k is Boltzmann constant.

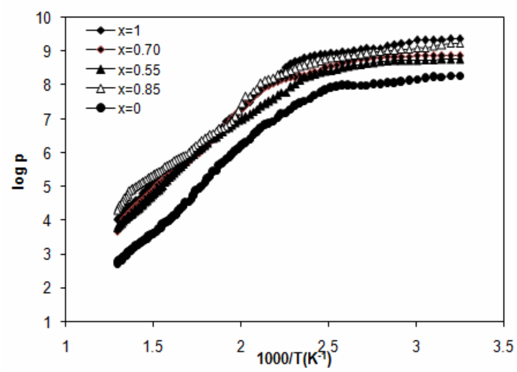


Figure 3. Variation of dc resistivity with reciprocal of temperature for (1-x) $Ni_{0.90}Co_{0.05}Mn_{0.05}Fe_2O_4$ + $xBaTiO_3$ ME composites with x = 1, 0.85, 0.70, 0.55 and 0

The plots show a semiconducting nature of the samples. The resistivity is maximum for $BaTiO_3$ and minimum for $Ni_{0.90}Co_{0.05}Mn_{0.05}Fe_2O_4$. The resistivities of composites decreases with increase in ferrite content [5]. The values of activation energy are given in Table 2. There are two regions in the resistivity plots and plots are linear in certain temperature range. The first region at low temperature (less than 400 K) is due to impurities may be attributed to ordered state of the ferroelectric phase, while the second region (greater than 400 K) is due to polaron hopping may be attributed to paraelectric state of the composites. The calculated values of activation energies are greater than 0.2 eV, which clearly suggest the conduction due to hopping of electrons or ions. The activation energy increases with increase in ferroelectric content. The result of conduction by hopping process is due to large effective mass and low mobility of current carriers [7]. There is a change in activation energy, when transition from ferroelectric to paraelectric state takes place.

Table 2. Electrical data for (1-x) $Ni_{0.90}Co_{0.05}Mn_{0.05}Fe_2O_4$ + (x)$BaTiO_3$ ME composites

x	$\rho_{RT}\times10^8$ (Ω/cm)	ΔE (eV)	ε_{RT}
1.00	23.9	0.34	222.5
0.85	17.6	0.33	1756.0
0.70	7.73	0.33	1569.0
0.55	5.85	0.32	772.0
0.00	1.96	0.28	132.5

The room temperature resistivity variation with mole % of ferroelectric phase for the composites is as shown in Figure 4.

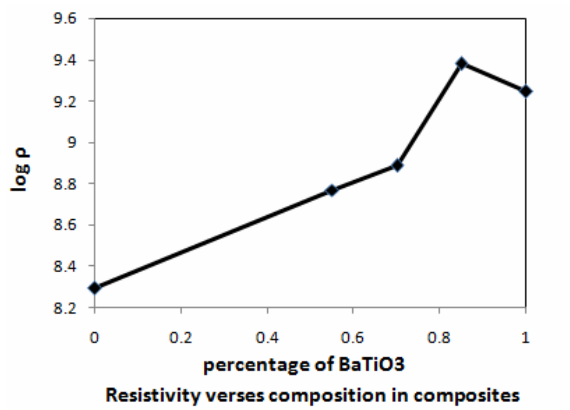


Figure 4. Variation of dc resistivity with percentage of $BaTiO_3$ in ME composites

The constituent phases give an effective value of resistivity in its composites. The maximum value of resistivity in composites helps in obtaining the highest magnetoelectric voltage coefficient [5, 6]. The variation of dielectric constant (ε') with frequency is shown in Figure 4. All the samples reveal dispersion due to Maxwell-Wagner type interfacial polarization in agreement with Koops phenomenological theory [9]. The dielectric constant (ε') decreases with increase in frequency and reaches a constant value due to the fact that beyond certain frequency of electric field the electron exchange does not follow the alternating field. The space charge polarization is governed by number of space charge carriers and resistivity of sample.

The charge carriers, which take part in exchange, can be produced during sintering process [10, 11]. The pattern at lower frequencies may be attributed to different types of polarizations. The high value of dielectric constant observed at lower frequencies is explained on the basis of space charge polarization due to inhomogeneous dielectric structure. The inhomogenities in the ferrite and ferroelectric composites are impurities, porosity and grain structure. Further at higher frequencies it arises due to the contribution of electronic polarization.

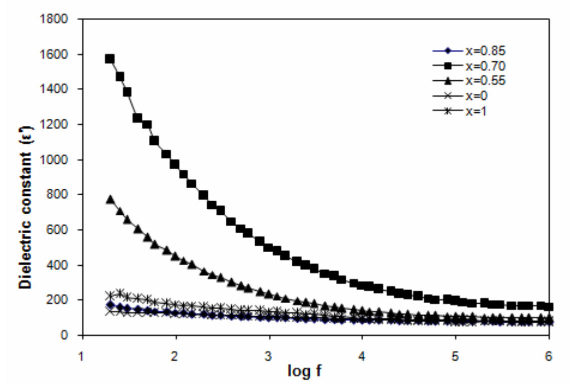


Figure 4. Variation of dielectric constant (ε') with frequency for (1-x)$Ni_{0.90}Co_{0.05}Mn_{0.05}Fe_2O_4$ + x$BaTiO_3$ ME composites with x = 1, 0.85, 0.70, 0.55 and 0.

When Ni containing ferrite is cooled from an elevated firing temperatures in an oxidizing atmosphere a considerable amount of oxygen is absorbed and Ni^{3+} ions are formed [12,14]. Fig. 5 shows variation of log σ_{ac} with log ω^2. The plots are almost linear indicating that the conductivity increases with frequency [13].

It is shown that for conduction by small polaron the following relation holds good.

$$\sigma_{ac} - \sigma_{dc} = \frac{\omega^2 \Gamma^2}{(1 + \omega^2 \Gamma^2)} \quad \text{.... (2)}$$

where, ω is the angular frequency, Γ is the staying time (10^{-10} s) and $\omega^2 \Gamma^2 < 1$. The linear nature of plots confirms the small polaron type of conduction. It has been shown that for ionic solids, the concept of small polaron is valid [14].

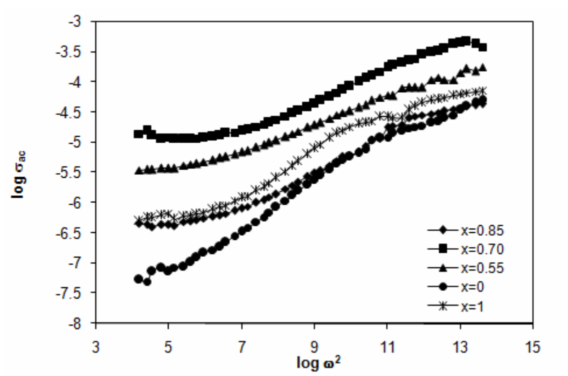


Figure 5. Variation of ac conductivity with frequency for (1-x)$Ni_{0.90}Co_{0.05}Mn_{0.05}Fe_2O_4$ + x$BaTiO_3$ ME composites with x = 1, 0.85, 0.70, 0.55 and 0.

The slight decrease in conduction at certain frequency is attributed to mixed polaron conduction. The similar results were also reported earlier by other researchers [6, 7, 15].

Conclusions

The magnetoelectric (ME) composites were prepared by the standard double sintering ceramic method. The XRD patterns of the composites exhibit both ferrite and ferroelectric phases. The number of ferrite peaks increases with increase in ferrite content. The temperature variation of resistivity shows that there is a drop in resistivity due to addition of ferrite phase in the composite. For preparing the mixtures of two phases, the two phases must have comparable values of resistivities so that one phase must not shunt the other. The dielectric behavior is explained in terms of electron exchange between Fe^{2+} and Fe^{3+}, suggesting that polarization in these compositions is similar to that of conduction in ferrite. The ac conductivity with frequency shows a linear nature. The linear behavior of ac conductivity indicates that conduction phenomena in the composites is to due to small polaron hopping.

Acknowledgement

Author is grateful to BCUD, Savitribai Phule Pune University, Pune for the financial support for present research work. Author is thankful to Prin. Dr. B. N.. Zaware, Anantrao Pawar College, Pirangut, Pune for providing the research facilities to present work.

References

[1] S. R. Kulkarni, C. M. Kanamadi, K. K. Patankar, and B. K. Chougule "Magnetic properties and magnetoelectric effect in $Ni_{0.8}Co_{0.1}Cu_{0.1}Fe_2O_4$ + $PbZr_{0.2}Ti_{0.8}O_3$ composites," J. Mater. Sci. vol. 40 pp. 5691 - 5694, 2005.

[2] M. M. Kumar, A. Srinivas, S. V. Suryanaryana, G. S. Kumar, and T. Bhimsankara, "An experimental setup for dynamic measurement of magnetoelectric effect," Bull. Mater. Sci., vol. 21, pp. 251, 1998.

[3] J. Zhai, N. Cai, Z. Shi, Y. Lin, and C. W. Nan, "Magnetic-dielectric properties of $NiFe_2O_4$/PZT particulate composites," J. Phys. D. & Appl. Phys., vol. 37, pp. 823, 2004.

[4] N. R. Reddy, E. Rajagopal, K. V. Sivakumar, K. K. Patanakar, and V. R. K. Murthy, "Effect of temperature on the elastic and inelastic behavior of magneto-ferroelectric composites $Ba_{0.8}Pb_{0.2}TiO_3$+ $Ni_{0.93}Co_{0.02}Mn_{0.05}Fe_{1.95}O_{4-\delta}$ in ferroelectric rich region," J. Electroceram., vol. 11, pp. 167 - 172, 2003.

[5] J. V. Boomgard, and R. A. J. Born, "A sintered magnetoelectric composite material $BaTiO_3$ + Ni(Co, Mn) Fe_2O_4," J. Mater. Sci. vol. 13, pp. 1538, 1978.

[6] S. L. Kadam, K. K. Patanakar, V. L. Mathe, M. B. Kothale, R. B. Kale, and B. K. Chougule, "Electrical properties and magnetoelectric effect in $Ni_{0.75}Co_{0.25}Fe_2O_4$ + $Ba_{0.8}Pb_{0.2}TiO_3$ composites," Mater. Chem. & Phys. vol. 78 pp. 684, 2003.

[7] R. P. Mahajan, K. K. Patanakar, N. M. Burange, S. C. Chaudhari, A. K. Ghatage and S. A. Patil, "Dielectric properties and electrical conduction of nickel ferrite- barium titanate composites," Indian

J. Pure & Appl. Phys., vol. 38, pp. 615, 2000.

[8] L. Sirdeshmukh, K. Krishnakumar, S. Bal. Laxman, A. Ramakrishna and G. Sathaiah, “Micro and macro properties of solids: thermal, mechanical and dielectric properties,” Bull. Mater. Sci., vol. 21, pp. 219, 1998.

[9] K. K. Patanakar, S. A. Patil, K. V. Sivakumar, R. P. Mahajan, Y. D. Kolekar, and M. B. Kothale, “AC conductivity and magnetoelectric effect in $CuFe_{1.6}Cr_{0.4}O_4$ - $BaTiO_3$ composites ceramics,” Mater. Chem. and Phys. vol. 65, issue 1, pp. 97 -102, 2000.

[10] C. G. Koops, “On the dispersion of resistivity and dielectric constant of some semiconductors at audio frequencies,” Phys. Rev. B., vol. 83, pp. 121 - 124, 1951.

[11] J. C. Maxwell, “Electricity and Magnetism” Oxford University Press, London, 1973.

[12] R. C. Kambale, Y. A. Park, and N. Hur. “Studies on the dielectric and the magnetic properties of Co-Mn ferrite and BZT ferroelectric particulate magnetoelectric composites,” J. Korean Phys. Soc., vol. 59, issue 6, pp. 3385 - 3390, 2011.

[13] B. V. Bhise, S. D. Lotake, and S. A. Patil, “Role of MnTi and MnSn substitutions on the electrical properties of Ni-Zn ferrite,” Phys. Status Solidi (a), vol. 157, pp. 411, 1996.

[14] D. Alder, and J. Feinleib, “Electrical and optical properties of narrow band materials.” Phys. Rev. B, vol. B2, pp. 3112, 1970.

[15] M. I. Klinger, “Two phase polaron model of conduction in magnetic like solids,” J. Phys. C, Solid State Phys., vol. 8., pp. 3595, 1975.