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# $\begin{array}{c} Dielectric \ Properties \ and \ Magnetoelectric \ Effect \ of \ BaTiO_3 - \\ Ni_{0.94}Co_{0.01}Mn_{0.05}Fe_2O_4 \ Composites \end{array}$

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## Abstract

The ME composites with a general formula  $(x)BaTiO_3+(1-x) Ni_{0.94}Co_{0.01}Mn_{0.05}Fe_2O_4$ where, x varies as 0, 0.55, 0.70, 0.85 and 1 were prepared by standard double sintering ceramic method. The phase formation of magnetoelectric composites was confirmed by X-ray diffraction technique. The variation of dielectric constant ( $\hat{\epsilon}$ ) and loss tangent (tan  $\delta$ ) in the frequency range 100 Hz - 1 MHz and also with change in temperature at constant frequency was studied. The static value of ME conversion factor i.e. dc (ME)<sub>H</sub> was studied as function of intensity of magnetic field. The changes were observed in dielectric properties as well as ME effect as molar ratio of the components was varied. A maximum value of ME conversion factor of 610  $\mu$ V/cm Oe was observed in the case of a composite containing 15 mol % ferrite phase.

Keywords: Magnetoelectric composites, X-ray diffraction, SEM and dielectric properties.

#### Introduction

The magnetoelectric (ME) effect is defined as a variation of dielectric polarization in a system as a response to an applied magnetic field or induced magnetization by an external electric field. Magnetoelectric composites consist of two phases: piezoelectric phase and piezomagnetic phase. The ME effect is a property exhibited by composite materials and is absent in their constituent phases [1]. A much stronger magnetoelectric effect could be realized in a composite of ferromagnetic and ferroelectric phases in which the ME coupling is mediated by mechanical stress. The ME effect is characterized by the fact that materials becomes magnetized after applying an electric field and electrically polarized by applying magnetic field [2] and is exhibited as a result of interaction between the magnetic and electric dipoles. The ME composites have been used as sensors, waveguides, phase shifters, switches, modulators etc [3]. ME effect obtained in composites is > 100 times than that of single phase ME materials, such as  $Cr_2O_3$ .

To achieve better ME effect, the piezomagnetic coefficient of a ferrite phase and the piezoelectric coefficient of ferroelectric phase must be high, the resistivity of the phases should be comparable and mechanical coupling between the two phases should be good. In the present work, we have chosen as magnetostrictive phase  $Ni_{0.94}Co_{0.01}Mn_{0.05}Fe_2O_4$  because of the fact that nickel cobalt ferrite and cobalt ferrite are highly magnetostrictive and resistive [2]. It is also well known that  $BaTiO_3$  has high dielectric permittivity. Hence it is expected that composites of these two phases might possess good electrical and





magnetic properties. Here we report dielectric polarization in present composites, which helps to explain ME effect

## **Materials and Methods**

The composite samples in the present case were prepared by standard double sintering ceramic method. The ferrite phase chosen was cobalt and magnese substituted nickel ferrite and the ferroelectric phase was barium titanate. The ferrite phase (Ni<sub>0.94</sub>Co<sub>0.01</sub>Mn<sub>0.05</sub>Fe<sub>2</sub>O<sub>4</sub>) was prepared through normal solid state reaction between NiCO<sub>3</sub>, CoCO<sub>3</sub>, MnCO<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> in molar proportions and was presintered at 800 °C for 8 h. Similarly, the ferroelectric phase (BaTiO<sub>3</sub>) was prepared with BaCO<sub>3</sub> and TiO<sub>2</sub> in molar proportions and presintered at 900 °C for 10 h. The ME composites with compositions (x) BaTiO<sub>3</sub> + (1-x) Ni<sub>0.94</sub>Co<sub>0.01</sub>Mn<sub>0.05</sub>Fe<sub>2</sub>O<sub>4</sub> were prepared by mixing 85, 70 and 55 mole % of ferroelectric material with 15, 30 and 45 mole % of ferrite material respectively. The mixture was presintered again at 1000 °C for 10 h. These compositions were then mixed with polyvinyl alcohol as a binder and pressed into pellets of thickness 2-3 mm and diameter 15 mm using the hydraulic press applying a pressure of about 7 tons per sq. in. The pelletized samples were finally sintered at 1150 °C for 12 h and furnace cooled to room temperature.

The structural analysis of the composites was done by X-ray diffraction studies using Phillips Xray diffractometer (Model PW-1710) using Cu K<sub> $\alpha$ </sub> radiation ( $\lambda = 1.5418$  Å). The particle morphological features were imaged by scanning electron microscopy (SEM, JEOL - JSM6360) with an accelerating voltage of 25 kV. The AC parameters such as capacitance (c) and dissipation factor (tan  $\delta$ ) of the samples were measured in the frequency range: 100 Hz - 1 MHz using LCR meter bridge (HP Model 4284 A). Silver paste was applied on the flat surfaces of the pellets for good electrical contacts. The variation of dielectric constant and loss tangent with temperature at different frequencies was also measured. The dielectric constant was calculated by using relation,

# $\acute{\epsilon} = c \ d \ / \ \epsilon_o \ A$

where, c is a capacitance of the pellet in Farad, d is the thickness of the pellet and A is the area of cross section of the pellet. To obtain the ME signal, the pelletized samples were poled electrically and magnetically. The poling procedure adopted in present work is similar to the one described elsewhere [4].

The electric poling was carried out by heating the samples at 500 °C above the ferroelectric Curie temperature and thereafter cooled to room temperature in the presence of an electric field (2 kV/cm). The composite was magnetically poled by applying external dc magnetic field of 6 kOe at room temperature. The electric field (E) developed at different dc magnetic fields (H) was measured. From these measurements the ME conversion factor (dE/dH)<sub>H</sub> for different values of dc magnetic field was calculated.





### **Results and Discussion**

Fig. 1 shows the X-ray diffraction (XRD) patterns of composites with x = 0.55, 0.70 and 0.85. The patterns show well defined peaks and there is no any intermediate phase formed. The occurrence of peaks with specific indices characteristic of spinel and perovskite structure confirms the formation of cubic spinel structure in Ni<sub>0.94</sub>Co<sub>0.01</sub>Mn<sub>0.05</sub>Fe<sub>2</sub>O<sub>4</sub> ferrite phase and tetragonal perovskite structure in the BaTiO<sub>3</sub> ferroelectric phase. The composites of NiFe<sub>2</sub>O<sub>4</sub> - BaTiO<sub>3</sub>, CoFe<sub>2</sub>O<sub>4</sub> - BaTiO<sub>3</sub> and MnFe<sub>2</sub>O<sub>4</sub> - BaTiO<sub>3</sub> crystallize in cubic spinel structure for ferrite phase and tetragonal perovskite structure for ferroelectric phase as reported earlier [2, 5].



Fig. 1. XRD patterns for (1-x)  $Ni_{0.94}Co_{0.01}Mn_{0.05}Fe_2O_4 + (x) BaTiO_3 ME$  composites



Fig. 2 SEM Micrographs of (1-x)  $Ni_{0.94}Co_{0.01}Mn_{0.05}Fe_2O_4 + (x) BaTiO_3 ME$ composites with x = 0.85 and x = 0.70

The intensities of ferrite peaks and number of peaks increase with increase in ferrite percentage. The lattice parameter calculated for two phases in all composites varies with composition, as given in Table - I. The lattice parameters fairly match in all three composites. This means that there are no structural



distortions observed even though the variation in composition of composites is done deliberately [8]. Fig. 2 shows the SEM micrographs of the ME composites with x = 0.85 and 0.55. The average grain size is found to be decreasing with increase in ferrite content.



Fig. 4. Variation of loss tangent with frequency (1-x)  $Ni_{0.94}Co_{0.01}Mn_{0.05}Fe_2O_4 + (x) BaTiO_3 ME$  composites The variation of dielectric constant ( $\dot{\epsilon}$ ) and loss tangent (tan $\delta$ ) with frequency for the composites at room temperature is shown in Fig. 3 and Fig 4 respectively. The dielectric constant and loss tangent decrease





rapidly at lower frequency and remains constant at higher frequency. The large value of dielectric constant or dispersion at lower frequencies is due to dislocations and other defects [11]. The samples show dispersion due to Maxwell Wagner type interfacial polarization in agreement with Koops phenomenological theory [10].



Fig. 5. Variation of dielectric constant with temperature 15%  $Ni_{0.94}Co_{0.01}Mn_{0.05}Fe_2O_4 + 85\% BaTiO_3 ME$  composite at different frequencies

The large value of dielectric constant in case of ferrite and ferroelectric phases is explained on the basis of space charge polarization and is attributed to the effect of heterogeneity of the samples. The response time  $\tau = 1/\omega_{max}$  of the interfacial polarization compared with other mechanism is relatively long. The dielectric relaxation can be observed at lower frequencies. However, in case of composites the high value of dielectric constant ( $\hat{\epsilon}$ ) is ascribed to the fact that ferroelectric regions are surrounded by non ferroelectric (ferrite) regions similar to that in case relaxor ferroelectric materials [13]. Polaron hopping mechanism resulting in electronic polarization also contributes to lower frequency dispersion [11]. The variation of dielectric constant with temperature at different frequencies: 1 kHz, 10 kHz, 100 kHz and 1 MHz for composites with x = 0.85 and 0.55 is shown in Figs. 6 and 7 respectively. The dielectric constant increases with increase in temperature up to Curie temperature and decreases thereafter. It is observed from the figure that the region around dielectric peak is broadened at all frequencies in all the





composites. The broadening of the peak may be due to the microscopic heterogeneity in the composites [4].



Fig. 6. Variation of dielectric constant with temperature for 45 %  $Ni_{0.94}Co_{0.01}Mn_{0.05}Fe_2O_4 + 55$  % BaTiO<sub>3</sub> ME composite at different frequencies



Fig. 7. Variation of magnetoelectric conversion factor  $(dE/dH)_H$  with magnetic field for (1-x)  $Ni_{0.94}Co_{0.01}Mn_{0.05}Fe_2O_4+$  (x) BaTiO<sub>3</sub> ME composites

The value of transition temperature and dielectric constant at  $T_c$  for the samples is given in Table - I. The transition temperature for given composite is independent of test frequency. The transition temperature in the present case shifts towards lower temperature side as the ferrite content decreases. The dielectric



constant also decreases with increase in ferrite content. It is reported that different behavior of permittivity as a function of 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 [2, 4]. This is due to Verway type electron exchange interaction in ferrite on one hand and the polarization being an inherent property of ferroelectric on the other. The conduction in ferrites which is due to electron hopping also causes local displacement in the direction of the external field, influencing dielectric polarization in ferrites. Increase in dielectric polarization in turn causes an increase in dielectric constant and it starts decreasing after passing through the transition temperature [9].

Composition	Lattice parameters			Grain	$\epsilon$ at T <sub>c</sub>	$(dE/dH)_{H}$
(x)	Ferrite phase	Ferroelectric phase	c/a	Size (µm)	(10 kHz)	V/cmOe
	(Å)	(Å)				
0.00	a = 8.36	-		0.98	934	
0.55	a = 8.35	a = 3.99, c = 4.04	1.01		2079	376
0.70	a = 8.35	a = 4.00, c = 4.02	1.00	1.91	2093	463
0.85	a = 8.35	a = 3.99, c = 4.03	1.01	1.57	2354	610
1.00		a = 3.98, c = 4.04	1.01	2.71	576	

 $Table - I \ Electrical \ and \ magnetic \ data \ of (1-x) \ Ni_{0.94}Co_{0.01}Mn_{0.05}Fe_2O_4 + (x) \ BaTiO_3 \ ME \ composites$ 

The ME effect in composite materials is determined by the magnetostrictional deformation of one phase and piezoelectric effect of the other phase, and for this reason the magnitude of magnetoelectric sensitivity  $(dE/dH)_H$  should depend in a complicated way on the composition of the composite material [5]. The variation of magnetoelectric output  $(dE/dH)_H$  versus magnetic field (H) is shown in Fig. 8. It is clear that  $(dE/dH)_H$  decreases with increase in magnetic field for all the composites. The value of  $(dE/dH)_H$  obtained for the composites is given in Table - I. The maximum value of ME voltage coefficient observed for the composite with the x = 0.85 and the  $(dE/dH)_H$  decreases with increase in ferrite content in the composites. It is attributed to low resistivity of ferrite phase as compared to that of ferroelectric phase resulting in the leakage of the charges developed in piezoelectric grains through the low resistance path of the surrounding ferrite phase [3]. The ME conversion factor is also influenced by the strain induced by lattice distortion on ferrite phase by John Teller ion like Mn, Ni. Hence John Teller effect in the ferrite can lead to polarization in the piezoelectric phase [8, 13]. Due to this as ferrite content increases the ME output decreases. Decrease in  $(dE/dH)_H$  with increase in de magnetic field may due to the fact that magnetostiction coefficient reaches saturation at a certain value of magnetic field.





# Conclusions

The X-ray analysis confirms the single phase formation of the component phases. The presence of both ferrite and ferroelectric phases is confirmed in case of x = 0.85, x = 0.70, x = 0.55 composites. There are no changes in the crystal structure of constituent phases. The number of ferrite peaks increases with increase in ferrite content. The ac conductivity increases with increase in frequency. This confirms that the conduction in the composites is due to small polaron hopping. The variation of dielectric constant ( $\hat{\epsilon}$ ) and loss tangent (tan  $\delta$ ) with frequency show a normal behavior. There is dielectric dispersion at lower frequencies due to the interfacial polarization and heterogeneity of the samples. The variation of dielectric constant with temperature indicates broad peaks that show relaxor type of behavior, which is obvious in the present case due to the microscopic in-homogeneities. The magnetoelectric conversion factor (dE/dH)<sub>H</sub> for all three composites is due to the strain induced by lattice distortion in ferrite phase and also magnetstriction produced due to applied magnetic field.

## Acknowledgment

Authors are thankful to BCUD, University of Pune for the financial support to present research work. Author is also grateful to Principal, Dr. B. N. Zaware, Anantrao Pawar College, Pirangut for giving the research facilities to present work.

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