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# ELECTRICAL CONDUCTION, dielectric BEHAVIOR AND MAGNETOELECTRIC EFFECT IN (1-x) $Co_{1.2}Mn_{0.2}Fe_{1.6}O_4$ + (x) $BaTiO_3$ ME Composites

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## ABSTRACT

**Objective:** Electrical and magnetoelectric properties of magnetoelectric (ME) composites ferroelectric as electric component and a mixed ferrite as magnetic component are reported. The (1-x) $Co_{1.2}Mn_{0.2}Fe_{1.6}O_4$ + (x) $BaTiO_3$ magnetoelectric (ME) composite have been prepared using conventional double sintering ceramic process where x varies as 0.00, 0.25, 0.50, 0.75 and 1.00. The X-ray diffraction pattern of the composites reveals the formation of spinel structure for the piezomagnatic phase and tetragonal perovskite structure for the piezoelectric phase without any other phase formation. The dc resistivity was measured as a function of temperature. The variation of dielectric constant ε' dielectric loss ε'' and dielectric loss tangent δ with frequency in the range 1kHz-1MHz was studied. The dielectric constant shows dispersion in the lower frequency region, with almost a constant value at higher frequencies. The magnetoelectric voltage coefficient $(dE/dH)_H$ was studied as a function of intensity of the magnetic field. The measured magnetoelectric (ME) response demonstrated strong dependence on the volume fraction of $CoMnFe_2O_4$ and the applied magnetic field. A large ME voltage coefficient of about 647 $Vcm^{-1}Oe^{-1}$ was observed for 25% $CoMnFe_2O_4$ + 75% $BaTiO_3$composite.

**Materials and Methods:** The piezoelectric phase Barium Titanate ($BaTiO_3$) was prepared by standard doubling sintering ceramic method using AR grade oxides/carbonate. Barium carbonate ($BaCO_3$) and Titanium-dioxide ($TiO_2$) were taken in molar proportion.

**Results:** The electrical resistivity of ferrite phase is less as compared to the resistivity of ferroelectric material. The resistivity of composites is found to be in between ferrite and ferroelectric.

**Conclusion:** Magneto-electric conversion factor with varying magnetic field shows maxima in the curve at a lower magnetic field and then decreases continuously at higher magnetic field. As ferroelectric content increases both the resistivity and magnetoelectric conversion factor also increases.

**Keywords**: Piezoelectric; Piezomagnatic; Electric, Dielectric Properties.

## INTRODUCTION

The ME composite materials consist of piezomagnatic and piezoelectric phases mechanically coupled in equilibrium. Magnetoelectricity is a product properties in which the material gets magnetized after applying electric field and electrically polarized in a magnetic field. The two phase must be equilibrium, the mechanical coupling between the two phases must be perfect, the value of magnetostriction coefficient of piezomagnatic phase and piezoelectric coefficient of piezoelectric phase must be high, the resistivity of the constituent phases must high to avoid the leakage current during poling are required to be satisfied to get good ME output [1,2]. Such magnetoelectric composites find many applications in ME data storage and switching, radio electronic device, Modulation of amplitudes, optoelectronic, microelectronic, Spin wave generation, frequency conversion, amplification, transducers, etc. The ME effect occurs due to the interaction between the magnetic and electric dipoles.

Higher ME effect has been identified in specially designed composites in which the piezomagnetic phase is combined with the piezoelectric one so that an efficient magneto mechanical piezoelectric coupling between the two phases is observed [3, 4]. In the present communication, we have chosen $Co_{1.2}Mn_{0.2}Fe_{1.6}O_4$ as a piezomagnatic phase and $BaTiO_3$ as the piezoelectric phase. Such composite to show high magnetoelectric effect, which in turn suggests that, the magnetoelectric interaction in these composites may lead to interesting results in their dc electric conductivity dielectric and magnetic properties is reported [5, 6].

## EXPERIMENTAL TECHNIQUES

### Preparation of ME composites

The piezomagnatic material chosen as a ferromagnetic phase $Co_{1.2}Mn_{0.2}Fe_{1.6}O_4$ has been prepared by standard double sintering ceramic method using AR grade oxides. The oxides were mixed in stiochiometric proportion and wet ground for about 2-3 hours in an agate mortar and pestle. The mixed fine powder is pre-sintered at 925⁰C for 9 hours. The sintered powder is again reground and finally sintered at 1080⁰C for 16 hours followed by slow cooling to room temperature to obtain pure single phase piezomagnatic samples. The single phase cubic spinel structure formation of piezomagnatic was confirmed by X- ray diffraction technique. The piezoelectric phase Barium Titanate ($BaTiO_3$) was prepared by standard doubling sintering ceramic method using AR grade oxides/carbonate. Barium carbonate ($BaCO_3$) and Titanium-dioxide ($TiO_2$) were taken in molar proportion. The mixed powder of Barium carbonate ($BaCO_3$) and Titanium-dioxide ($TiO_2$) was ground using agate in mortar and pestle and pre-sintered at 900⁰C for 12 hours. In the final sintering the material was held at 1050⁰C for 16 hours. The sintered samples were allowed to cool to room temperature. Analysis of XRD pattern of $BaTiO_3$ revealed the formation of single phase tetragonal perovskite structure. The composite of piezomagnatic and piezoelectric phase (1-x) $CoMnFe_2O_4$+(x) $BaTiO_3$ with (x= 0.25, 0.50 and 0.75 mole %) was prepared by standard doubling sintering ceramic method using prepared piezomagnatic and piezoelectric phases. The fine powders of piezomagnatic ($CoMnFe_2O_4$) and piezoelectric phase ($BaTiO_3$) were mixed thoroughly in molar proportion and ground for above 3 hours. The composite phase of piezomagnatic and piezoelectric was pre-sintered at 925⁰C for 12 hours and is cooled at room temperature. The composite powder is then reground again and finally sintered at 1080⁰C for 24 hours. The magnetoelectric composites of piezomagnatic and piezoelectric prepared by mixing the constituent phase were ground for 2-3 hours and mixed with 2-3 drops of polyvinyl alcohol as a binder. The composite powder is then pressed into pellets of thickness around 2-3 mm and diameter 10mm using a hydraulic press. A pressure of 6 ton /cm$^2$ was applied for 10 to 15 minute. The pellets are finally heated up to $600^0C$ for 6 hours to remove the binder and cooled at room temperature. The prepared composite of piezomagnatic $Co_{1.2}Mn_{0.2}Fe_{1.6}O_4$ and piezoelectric $BaTio_3$ was characterized by X- ray diffraction technique and was used for further investigations of structural electrical and, dielectric properties of piezomagnatic, piezoelectric and their composites.

### Characterization

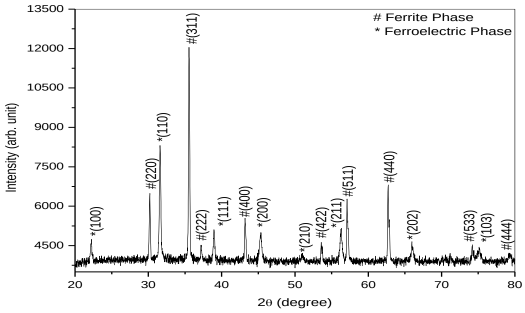
The presence of constituent phases in the composites as well as the crystal structure of constituent phases and their composites was determined by X-ray diffraction using a Rigaku Miniflux-II and λ=1.5406Å.

## RESULT AND DISCUSSION

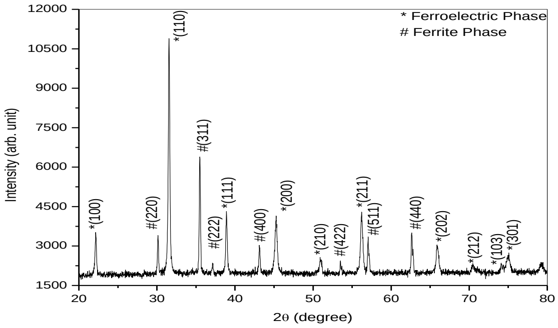
### Structural analysis

The XRD pattern of the representative composite is shown in figure 1. The pattern revels the presence of both ferroelectric as well as ferrite phases. All the peaks are indexed and no additional peaks were observed. This indicates the absence of impurities or intermediate phases in the composite. Ferroelectric phase has tetragonal perovskite structure and ferrite phase has a cubic spinel structure. The lattice parameters of ferroelectric phase are a=4.001 and c=4.005 and c/a ratio is 1.001 the lattice parameter for ferrite phase is a=8.366Å.

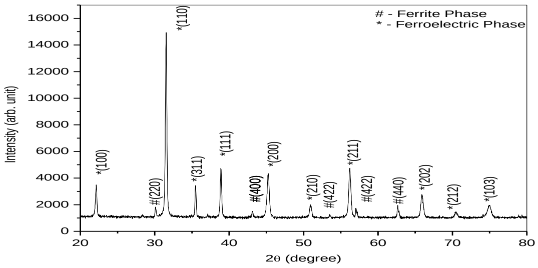
As all the peaks of the composites are identified it conforms the formation of composites with two distinct phases. Increased molar percentage of ferroelectric in composites leads to increase in the intensity of (110) ferroelectric peaks. From XRD pattern it observed that with increase in ferroelectric percent in composite, number of ferroelectric peaks increases also the intensity of most intense ferroelectric peak (110) also increases. The XRD pattern shows the presence of two phases i.e. piezomagnetic and piezoelectric, no single phase formation of composite material is observed, further it can be observed from figure that the intensity of all the reflections of piezomagnetic and piezoelectric phases decreases as compared to their individual phases.



**(x=0.25)**



**(x=0.50)**



**(x=0.75)**

**Fig 1: X-Ray Diffraction pattern of (1-x) $Co_{1.2}Mn_{0.2}Fe_{1.6}O_4$ + (x) $BaTiO_3$ composite**

### Electrical measurements

The resistivity of the sample was measured using two-probe method in the temperature range 300-800K.Silver paste was applied on the flat surfaces of the pellet for good ohmic contacts.

### Electrical resistivity

The variation of dc resistivity with temperature is shown in Fig.2. The variation of log of resistivity versus reciprocal of temperature is shown in Fig 2. It is found that the resistivity versus temperature plot obeys the relation

$$\rho = \rho_0 \exp(\Delta E/kT) \quad (3.3)$$

where, ρ is resistivity at temperature T,
$\rho_0$ is temperature independent constant
ΔE is activation energy
T is temperature
k is Boltzmann constant

**Table 1: Lattice constant of ferrites, ferroelectric phase, Resistivity and Activation energy in region I and II of (1-x) $Co_{1.2}Mn_{0.2}Fe_{1.6}O_4$ + (x) $BaTiO_3$. (x= 0.00 - 1.00) composite.**

| Comp 'x' | Lattice parameters (Å) Ferrite | Ferroelectric | | | Resistivity $\rho_{RT}$ (Ω cm) | Activation energy (eV) | | $[dE/dH]_H$ (μV/cm/O$_e$) |
|---|---|---|---|---|---|---|---|---|
| | a | a | c | c/a | | Region I | Region II | |
| 0.00 | 8.366 | --- | --- | --- | 1.22x10$^8$ | 0.0910 | 0.0218 | --- |
| 0.25 | 8.376 | 4.000 | 4.000 | 1.000 | 3.30x10$^8$ | 0.0618 | 0.0252 | 254 |
| 0.50 | 8.387 | 4.000 | 4.006 | 1.002 | 4.55x10$^8$ | 0.0213 | 0.0272 | 351 |
| 0.75 | 8.389 | 4.001 | 4.005 | 1.001 | 6.25x10$^8$ | 0.0142 | 0.0320 | 647 |
| 1.00 | --- | 4.002 | 4.003 | 1.003 | --- | --- | --- | --- |

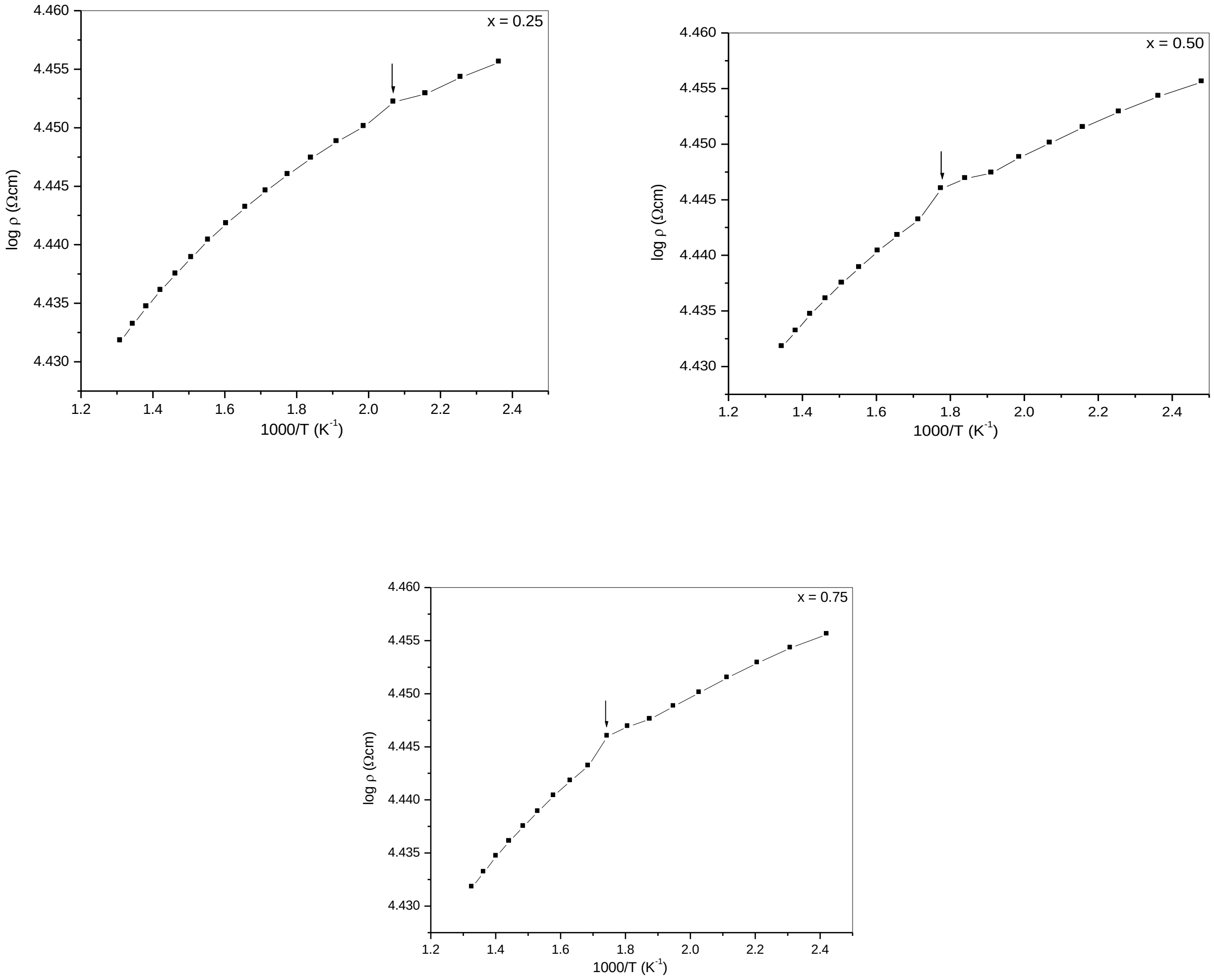


**Fig 2 Variation of dc resistivity (log ρ) with temperature (1000/T) for (1-x) $Co_{1.2}Mn_{0.2}Fe_{1.6}O_4$ + (x) $BaTiO_3$.**

The plot of logρ versus 1000/T indicates two regions in all the cases. The temperature at which plot shows two regions may correspond to Curie temperature of the sample. Using these plots and from above relation the activation energy of ferrite, ferroelectric and their composites was calculated and the values are listed in Table1. The activation energy found to decrease as ferroelectric content 'x' increases. The activation energy for x = 1 i. e. for ferroelectric phase no activation energy is found because it has very high resistivity. Similar results were repeated for other ferroelectric phase. At room temperature resistivity found to increase as ferroelectric content 'x' increases. The value of resistivity measured at room temperature is shown in Table 1. It is evident from Table 1 that the resistivity of ferrite phase is less as compared to the resistivity of ferroelectric phase. The resistivity of composite (x= 0.25, 0.50, 0.75) is found to be in between ferrite and ferroelectric phase. The conduction at lower temperature is attributed to impurities and at higher temperature to polar hopping.

### Dielectric behavior:

The frequency dependent dielectric properties of piezomagnatic, piezoelectric and the composite were measured at room temperature using LCR-Q meter. Using the measured capacitance C, the values of dielectric constant (ε'), dielectric loss (ε'') and dielectric loss tangent (tan δ) were calculated. The variation of dielectric constant as a function of frequency for all composition 'x' is shown in Fig. 3, 4 and 5. It is observed from these figures that the dielectric constant decreases very fast at lower frequency and attains constant value at higher frequency. The decrease in dielectric constant is exponential. Further, it is also observed that the dielectric constant for piezoelectric phase is maximum and that for piezomagnatic phase is minimum. For composites, the dielectric constant ranges in between piezoelectric and piezomagnatic phase. The variation of dielectric constant as a function of frequency is attributed Maxwell-Wagner [7, 8] type interfacial polarization is good agreement with Koop's phenomenological theory [9].

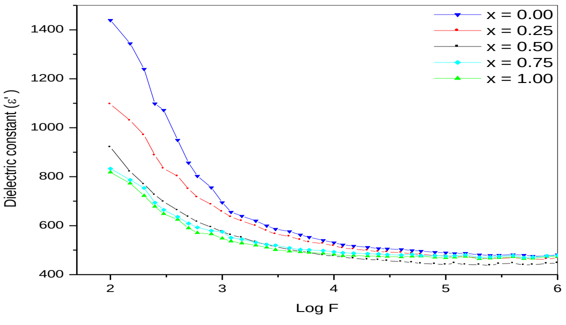


**Fig 3: Variation of dielectric constant (ε') with frequency (F) for (1-x) $Co_{1.2}Mn_{0.2}Fe_{1.6}O_4$ + (x) $BaTiO_3$**

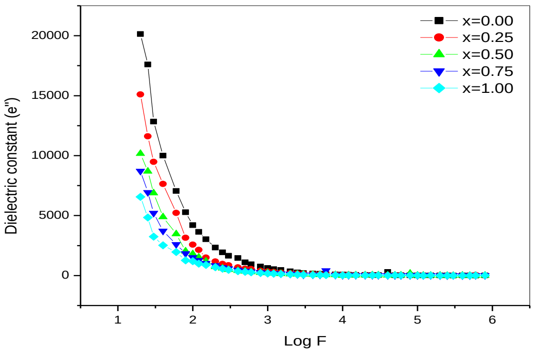


**Fig 4: Variation of dielectric loss (ε'') with frequency (F) for (1-x) $Co_{1.2}Mn_{0.2}Fe_{1.6}O_4$ + (x) $BaTiO_3$**

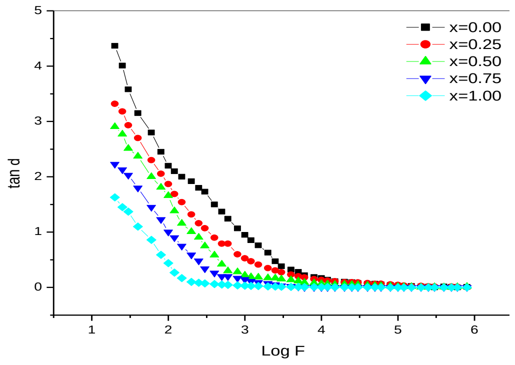


**Fig 5: Variation of dielectric loss tangent (δ) with frequency (F) for (1-x) $Co_{1.2}Mn_{0.2}Fe_{1.6}O_4$ + (x) $BaTiO_3$**

The high value of dielectric constant for piezoelectric phase can be explained on the basis of space charge polarization and attributed to the fact that, the piezoelectric regions are surrounded by non piezoelectric regions just as in case of relaxor piezoelectric materials [10] The polarization at lower frequency may result from electron exchange between $Fe^{3+}$ and $Fe^{2+}$ in piezomagnatic lattice [11,12]. The variation of dielectric constant (ε') with function of frequency (F) is shown in Fig. 3. From Fig. 3 it is observed that the dielectric constant (ε') decreases exponentially with increasing frequency. The dielectric constant (ε') shows high values at low frequency where as it shows minimum values at higher frequency. The dielectric constant (ε') varies with composition ‘x’ at low frequency whereas it is almost constant for all composition at higher frequency. The behaviour of dielectric constant (ε') is similar to other composites. Our results on dielectric studies are in good agreement with those reported in the literature [13, 14]. The variation of dielectric loss (ϵ'') and dielectric loss tangent (tan δ) as a function of frequency is shown in Fig. 4 and Fig. 5 Both dielectric loss and dielectric loss tangent decreases with increase in frequency and shows similar behaviour to that of variation of dielectric constant with frequency. It is observed that the dielectric constant (ε') decreases with increasing compositions ‘x’ for all the frequencies, Similar trend of the values of dielectric loss (ϵ'') and dielectric loss tangent (tan δ) was also observed.

## ME output

The magnetoelectric effect is characterized by a variation of the electrical magnetization by an external electrical field E. The ME effect is defined as an induced dielectric polarization of a material in an applied magnetic field or an induced magnetization in an external electric field. The composite, which exhibit ME effect are known as the “Magneto-electric composites”. Composite material containing piezoelectric (ferroelectric) and piezomagnetic (ferrite) phases exhibit ME effect. It is due to the strain induced in the piezomangetic (ferrite) phase by the applied magnetic field, being mechanically coupled stress induced in the piezoelectric/ ferroelectric phase, the coupling resulting in an electric voltage [15].

Fig. 5 shows the magnetoelectric effect voltage coefficient as a function of d. c. magnetic bias for all composites under investigation. The magnetoelectric (ME) effect is measured by changes in the resulting electric field in the magnetoelectric (ME) composites due to the applied external magnetic field [16]. It is observed that magnetoelectric (ME) coefficient initially increases to a certain applied magnetic field (0.5KOe) and then start decreasing as applied field increases. The magnetoelectric (ME) effect is found to be maximum for x=0.75 (i.e. for 25% $Co_{1.2}Mn_{0.2}Fe_{1.6}O_4$ + 75% $BaTiO_3$). The magnetoelectric (ME) effect in composites is due to the strain induced in ferrite phase by the applied magnetic field which being mechanically coupled to induce a stress in surrounding ferroelectric phase

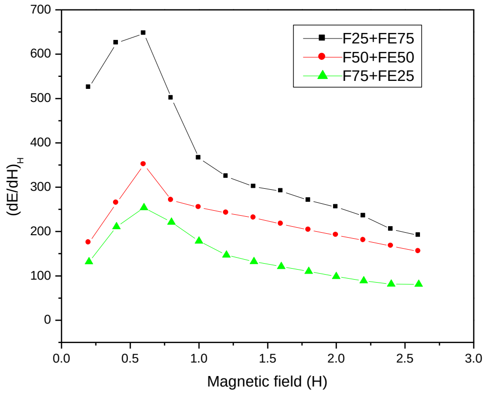


**Fig 6 Variation of magneto-electric conversion factor with magnetic field for (1-x) $Co_{1.2}Mn_{0.2}Fe_{1.6}O_4$ + (x) $BaTiO_3$.**

## CONCLUSIONS

The composites of piezomagnatic and piezoelectric with formula (1-x) $Co_{1.2}Mn_{0.2}Fe_{1.6}O_4$ + (x) $BaTiO_3$ has been successfully synthesized by ceramic technique with the presence of two distinct phases of piezomagnatic and piezoelectric as evidenced by the x-ray diffraction techniques. The electrical resistivity of ferrite phase is less as compared to the resistivity of ferroelectric material. The resistivity of composites is found to be in between ferrite and ferroelectric. The temperature dependence of resistivity shows that the resistivity decreases with increase in temperature obeying Arrhenius relation. The frequency varying dielectric studies shows that the dielectric constant decreases rapidly lower frequencies and attains a constant value at higher frequencies. Magneto-electric conversion factor with varying magnetic field shows maxima in the curve at a lower magnetic field and then decreases continuously at higher magnetic field. As ferroelectric content increases both the resistivity and magnetoelectric conversion factor also increases. The composite under investigation in the present study exhibits better values of magnetoelectric conversion factor.

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