Study of Structural and Dielectric properties of $BaTiO_3$ Doped with Mg-Cu-Zn Ferrites

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Abstract— The magnetoelectric (ME) composites having the general formula, (x) $Mg_{0.25}Cu_{0.25}Zn_{0.5}Fe_2O_4$ + (1-x) $BaTiO_3$ (x=15%, 30%, 45%) were synthesized by sintering mixtures of highly ferroelectric $BaTiO_3$ and highly magnetostrictive magnetic component Mg0.25Cu0.25Zn0.5Fe_2O_4. The presence of constituent phases of ferrite, ferroelectric and their composites were confirmed by X-ray diffraction (XRD) studies. Surface morphology of the samples has been investigated using Field Emission Scanning Electron Microscope (FESEM), which revealed uniform mixing of two phases. The variations in dielectric constant and dissipation factor as a function of frequency from 100 Hz to 1 MHz were measured in a Hioki LCR Hi-Tester. The dielectric constant and dielectric loss were found to decrease rapidly in the low frequency region and became almost constant in the high frequency region. The electrical conductivity deduced from the measured dielectric parameters has been analyzed and found that the conduction mechanism in these composites is in conformity with small polaron hopping model.

Key words: Dielectric, Ferroelectric, Magneto Electric (ME), Composites

I. INTRODUCTION

Piezomagnetic-piezoelectric composites exhibit unique magneto-electric phenomena which are facilitated by mechanical deformations [1–3]. Upon application of a magnetic field to ME composites, the ferromagnetic component produces a deformation due to magneto-striction that is transferred to the ferroelectric component via interfacial bonding, in turn this induces an electric charge across the piezoelectric phase due to piezoelectricity. ME materials evolve from single phase compounds to particulate composites, to laminated composites. The difficulties associated with uniting electric and magnetic orderings in a single phase material have been circumvented by forming multi-phase ME composites consisting of ferromagnetic and ferroelectric components that can be electromagnetically coupled by stress mediation [4]. ME effect in composites is a product tensor property and that first proposed by van Suchtelen [5]. The ME composites have applications field as sensors, waveguides, switches, phase invertors, etc. [7].

$Mg_{0.25}Cu_{0.25}Zn_{0.5}Fe_2O_4$ (MCZF) are considered to be the important soft magnetic materials because of their high initial magnetic permeability, saturation magnetization, high electrical resistivity and low core losses [3,4].

The selection of a suitable combination of magnetic and electric materials to achieve better ME effect is a difficult task. For the present work, MCZF as piezomagnetic material and $BaTiO_3$ (BT) as a piezoelectric material were choosen and the composites were prepared and studied the effect of composition and frequency on the dielectric properties. The study offered a valuable information on the behavior of localized electric charge carriers which is useful in understanding magneto electric effect [10, 11].

II. EXPERIMENTAL

The nano ferrite $Mg_{0.25}Cu_{0.25}Zn_{0.5}Fe_2O_4$ (MCZF) in the powder form has been prepared by solution combustion method using stoichiometric compositions of corresponding metallic nitrates as oxidizers and citric acid as fuel. Barium titanate (BT) powder of size 100 nm procured from Sigma Aldrich. The ME composites were prepared by thoroughly mixing MCZF and BT powders in required molar proportions and sintered at 1000^0C for 4 hrs and were cooled slowly to room temperature. These sintered powders were pressed into pellets of 10 mm diameter and 1-2 mm thickness. The pellets were again sintered at 1000 ^{0}C for 2 hrs and cooled to room temperature. The synthesized ME composites, $(MCZF)_x(BT)_{1-x}$ with x = 15%, 30% & 45% have been labeled as MBT1, MBT2 and MBT3 respectively. The composites were prepared in ferroelectric-rich regions [8, 13].

The presence of constituent phases in the composites and the crystal structure of constituent phases and their composites were determined by XRD studies using Bruker AXS D8 Advance X-ray diffractometer (λ=1.5406 A^0). Surface morphology has been investigated using Field Emission Scanning Electron Microscope (FESEM, JEOL JSM 6700).

The Capacitance and dissipation factor, $\tan\delta$ as a function of frequency in the range 100 Hz-1MHz was studied using a precision LCR meter (Hioki make LCR Hi-Tester 3250). The dielectric constants (ε') and dielectric loss factor (ε'') were determined using the formulae [14,18]

$$\varepsilon' = Ct/\varepsilon_0 A \quad (1)$$

$$\varepsilon''=\varepsilon'\tan\delta \quad (2)$$

Where, t is the thickness and A the area of the pellet.

The ac conductivity, σ_{ac} was determined from the dielectric properties using a relation,

$$\sigma_{ac}= \omega\, \varepsilon_0\, \varepsilon'' \quad (3)$$

Where, ε_0 is the vacuum permittivity and ω =2Πf with f being frequency.

III. RESULTS AND DISCUSSION

A. *Phase*

The XRD patterns of pure MCZF, BT and composites MBT1, MBT2 and MBT3 are shown in Fig.1. The diffraction patterns of composites showed the presence of both ferrite and ferroelectric phases. The ferrite phase showed a cubic spinel structure with a=8.4 A^0 and the average crystallite size of 60.15 nm. Ferroelectric phase exhibited perovskite tetragonal structure with a=4.022 A^0, c=4.025 A^0 (c/a=1.0007). The lattice parameters of the constituent phases are found to be same for MBT1, MBT2 and MBT3. The intensity of the ferrite peaks increased with its content.

The scanning electron micrographs of pure MCZF, BT and MBT1, MBT2 and MBT3 are shown in Fig.2. Each sample exhibits a dense microstructure. The inhomogeneous morphology is because of different growth rate of individual phases in the composites. Addition of MCZF in BTO results into irregular grain shape. This may be attributed to the filling of pores between the ferroelectric grains by the MCZF particles and their segregation at the grain boundaries.

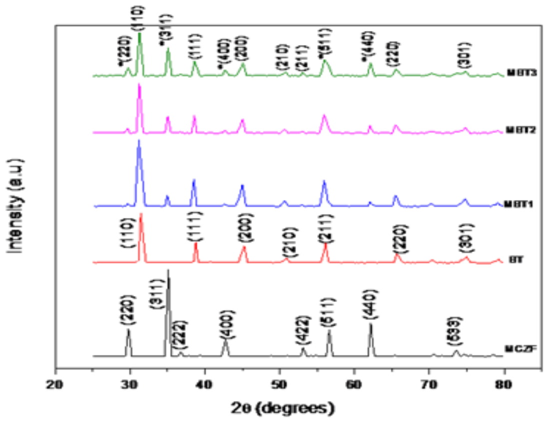
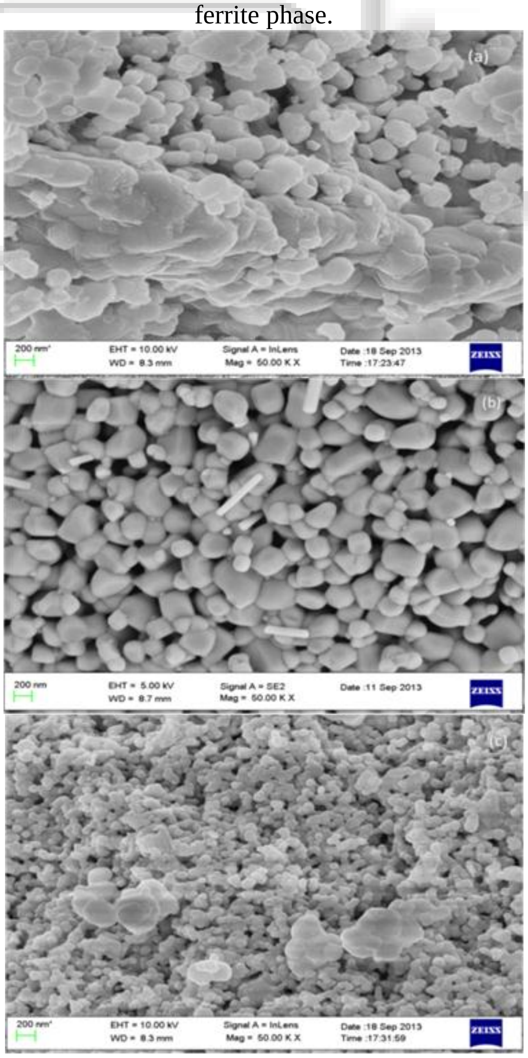


Fig.1 XRD Pattern for pure nano powders of $Mg_{0.25}Cu_{0.25}Zn_{0.5}Fe_2O_4$ (MCZF) and $BaTiO_3$ (BT) and MBT1, MBT2, MBT3composites. Asterisk (*) indicates ferrite phase.



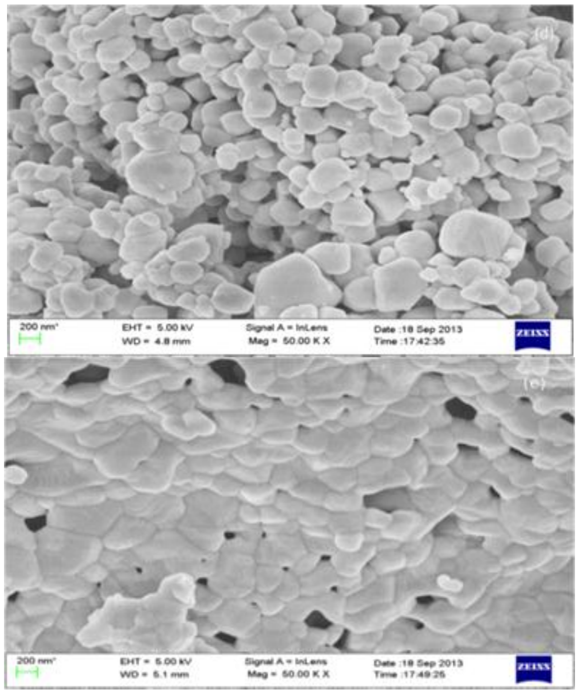


Fig. 2 (a): FESEM micrograph for pure powders of MCZF, (b): BaTiO3 and (c): MBT1 nano composite, (d): MBT2 and (e): MBT3 nano composites

B. Dielectric Properties

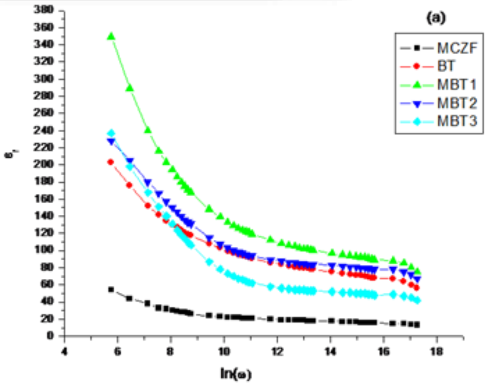
The variation of dielectric constant (ε'), dielectric loss factor (ε") and ac conductivity (σ_{ac}) with frequency at room temperature for the constituent phases and their composites is shown in Fig.3. From the figure, it is clear that ε' decreases steeply at lower frequencies and remains constant at higher frequencies. The observed variation of ε' with frequency is due to charge transport relaxation. This dielectric dispersion is attributed to Maxwell [19] and Wagner [20,21] type of interfacial polarization. The dielectric constant is a combined effect of dipolar, electronic, ionic and interfacial polarizations. Since ionic polarization is expected to decrease with frequency, the measured ε' also decreased with frequency. The large values of ε' can be associated with space charge polarization and inhomogeneous dielectric structure [17,18]. The higher ε' value for frequencies below 1 KHz is attributed to Maxwell–Wagner type interfacial polarization which arises due to the uncompensated surface charges at the dissimilar material (perovskite– spinel) interface [14]. At higher frequencies electric dipoles will be unable to follow the alternating applied electric field which results constant dielectric constant. For frequencies above 10 KHz, the dielectric behavior is due to polarization contributed by the ferroelectric region. With the addition of ferrite phase (MCZF) the real part of dielectric permittivity decreases while the dielectric loss increases.

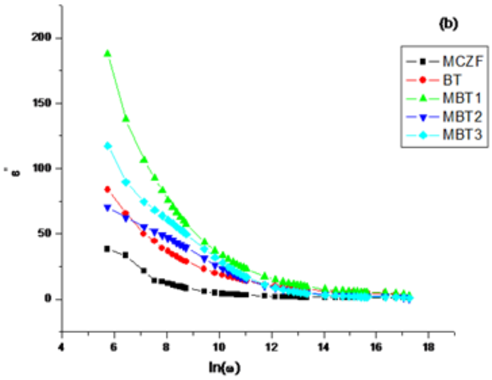
According to reference [13], the polarization in a ferrite is due to a mechanism similar to conduction process. The dielectric behavior of the composites is also similar to the conduction process because beyond the percolation limit of the ferrite phase in composites, the conduction is mainly due to the ferrite phase [16]. The increase in ferrite concentration beyond the percolation limit leads to the formation of conducting paths between the ferrite particles. This results in decrease of resistivity with increasing ferrite content. By electron exchange between Fe^{+2} and Fe^{+3}, the local displacement of electrons in the direction of the applied field occurs and these electrons determine polarization. The polarization decreases with increasing frequency and at high frequency the electron exchange between Fe^{+2} and Fe^{+3} cannot follow the alternating field hence reaches the constant value.

As per reference [17,18], the behavior of polarization in the ferrite is due to collective behavior of both n and p type carriers. In $Mg_{0.25}Cu_{0.25}Zn_{0.5}Fe_2O_4$ the presence of Mg^{+2}/Mg^{+3}, Cu^{+2}/Cu^{+3}, Zn^{+2}/Zn^{+3} gives rise to p-type carriers [18] and in $BaTiO_3$ the presence of Ba^{+2}/Ba^{+3} also contributes p-type charge carriers. The local displacement of these p-type charge carriers in the direction of external electric field adds to the net polarization. It is known that n-type carriers also contributed to polarization. However, the contribution from p-type carriers is smaller than electronic exchange between ions and their mobility is smaller than that of n-type. The contribution to polarization at lower frequencies will decreases from former to the later.

The variation of dielectric loss factor (ε") with frequency for MCZF, BT and composites can be seen in Fig.3 (b). The variation of ε" in the case of composites is similar to that of variation of ε' with frequency. The loss factors can be attributed to domain wall response. At higher frequencies, losses are less where domain wall motion is inhibited and magnetization is forced to change by rotation.

The variation of conductivity, σac with frequency, f, is shown in Fig.3 (c) for all the five samples. The plots are linear for almost entire range of frequency except at very low frequency. Linear variation of σ_{ac} with frequency indicates that the conduction occurs by the hopping of charge carriers between the localized states which confirms the small polaron type of conduction. These results are similar to that reported by other workers [14-17]. It has been shown that for ionic solids the concept of small polarons is valid [14].





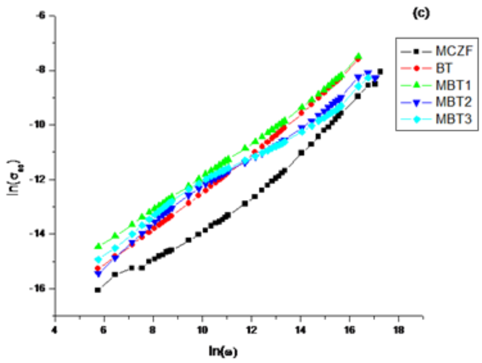


Fig. 3(a): Variation of dielectric constant, ε' (b): dissipation factor, ε" (c): (d): ac conductivity,σac with frequency, ω.

IV. CONCLUSIONS

Magnetoelectric nano composites made of MCZF and BT were prepared by solution combustion method. XRD patterns, SEM micrographs reveal the presence of both ferrite and ferroelectric phase with no other impurity phases. The frequency dependant dielectric constant showed the usual dielectric dispersion behavior for all the composites. The ac conductivity measurements suggest that the conduction is due to small polaron hopping mechanism.

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