International Journal of Advanced Research in Physical Science (IJARPS)
Volume 2, Issue 8, August 2015, PP 21-27
ISSN 2349-7874 (Print) & ISSN 2349-7882 (Online)
www.arcjournals.org

Structural, Dielectric and Magnetic Studies in (X)$Mn_{0.5}Zn_{0.5}Fe_2O_4$ +(1-X)$Batio_3$ Magnetoelectric Nano-Composites

S.Abdul Khader, T.Sankarappa [*]

Department of Physics, Gulbarga University, Gulbarga, Karnataka, India
* *sankarappa@rediffmail.com*

Abstract: *The Magneto-electric nano-composites, (x)$Mn_{0.5}Zn_{0.5}Fe_2O_4$+(1-x)$BaTiO_3$ (x=15%,30%,45%) were synthesized by sintering the mixtures of highly ferroelectric BaTiO3 (BT) and highly magnetostrictive magnetic component $Mn_{0.5}Zn_{0.5}Fe_2O_4$ (MZF). The presence of magnetic and ferroelectric phases were probed by X-ray diffraction (XRD) studies. The peaks observed in the XRD spectrum indicated spinel cubic structure for MZF ferrite and tetragonal perovskite structure for BT and, both spinel and pervoskite structures for nanocomposites. Surface morphology of the samples has been investigated using Field Emission Scanning Electron Microscope (FESEM), which reveals a homogeneous microstructure with uniform dispersion of BT grains. The variation of dielectric constant and dissipation factor as a function of frequency from 100 Hz to 1 MHz at room temperature were carried out using a Hioki LCR Hi-Tester. The dielectric dispersion is observed at lower frequencies which may due to interfacial polarization arising from the interface of the two phases. At higher frequencies, the dielectric constant is almost constant and that was due to inability of electric dipoles to follow the quick variation of applied electric field. The electrical conductivity deduced from the measured dielectric properties has been analyzed and found that the conduction mechanism in these composites is in conformity with electron hopping model. Magnetic ordering in the composites was studied by acquiring M-H hysteresis loops at room temperature.*

Keywords: *combustion; dielectric; ferroelectric; magneto electric (ME); composites.*

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1. INTRODUCTION

The magneto electric (ME) property of the ferroelectric-ferromagnetic composites arises from the interaction between the two phases [1]. That is, ME effect is a product of the piezomagnetic effect of ferrite phase and piezoelectric effect of ferroelectric phase. ME composites are exploited as sensors for different types, wave guides, modulators, phase inverters, rectifiers, transducers etc [2].Manganese zinc ferrites (MZF) 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]. These materials are extensively used in electronic applications to make transformer choke coils, recording heads, magnetic amplifiers etc [5]. The most widely studied magneto electric composite systems for structural, dielectric and magnetic studies include (x) $BaTiO_3$ + (1-x) $Ni_{0.94}Co_{0.01}Cu_{0.05}Fe_2O_4$ [6]. It was found that with increasing ferroelectric content the dielectric constant increases and curie temperature decreases. The ME composites, $Ni_{0.5}Zn_{0.5}Fe_2O_4$+BPZT [7] were studied for ac susceptibility. ME coefficient in these systems was maximum for composites containing 30% of ferrite. Lithium nickel ferrite composites, y[$Li_{0.5}Ni_{0.6}Zn_{0.15}Fe_2O_4$]+(1-y)$Ba_{0.5}Sr_{0.5}TiO_3$ [8] were studied for conductivity and dielectric properties over a wide range of frequency and temperature. Conductivity was analyzed using small poloron hopping model in these systems. The cobalt doped nickel manganese ferrite composites [9,10], (x)$Ni_{0.93}Co_{0.02}Mn_{0.05}Fe_{1.95}O_4$ +(1-x)$Na_{0.5}Bi_{0.5}TiO_3$ and $Ni_{0.75}Zn_{0.25}Fe_2O_4$-$Ba(Ti_{0.85}Zr_{0.15})O_3$ were prepared by a solid state reaction method and investigated for magnetoelectric effect and dielectric behavior. Cobalt ferrites doped with barium titanate, $CoFe_2O_4$-$BaTiO_3$ [11], were probed for dielectric properties. It was noticed that at higher frequencies, the dielectric constant was constant and decreases at lower frequencies. As per our survey of the literature, no research results have been reported on (x)$Mn_{0.5}Zn_{0.5}Fe_2O_4$+(1-x)$BaTiO_3$ (x=15%,30%,45%) composites.

The selection of a suitable combination of piezomagnetic and electric materials to achieve better ME effect is a challenging task. In the present work, MZF as piezomagnetic material and $BaTiO_3$ (BT) as a piezoelectric material were choosen and composites were prepared and studied the effect of composition and frequency on dielectric and magnetic properties of these composites. The study also offered valuable information on the behavior of localized electric charge carriers which in turn helps in understanding magneto electric effect [12].

2. EXPERIMENTAL

The $Mn_{0.5}Zn_{0.5}Fe_2O_4$ nano ferrite (MZF) powder has been prepared by solution combustion method using stoichiometric compositions of corresponding metallic nitrates as oxidizers and citric acid as fuel. Sigma Aldrich make 100nm size nanoparticles of BT were procured. The ME composites were prepared by thoroughly mixing MZF 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 grinded and pressed in the form of 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, $(MZF)_x(BT)_{1-x}$ with x = 15%, 30% & 45% have been labeled as ME1, ME2 and ME3 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 of the samples has been investigated using Field Emission Scanning Electron Microscope (FESEM, JEOL JSM 6700).

The Capacitance and dissipation factor, tanδ as a function of frequency in the range 100 Hz-1 MHz 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 [14,26]

$$\varepsilon' = Ct/\varepsilon_0 A \tag{1}$$

$$\varepsilon'' = \varepsilon' \tan \delta \tag{2}$$

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

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

$$\sigma_{ac} = \omega\, \varepsilon_0\, \varepsilon'' \tag{3}$$

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

3. RESULTS AND DISCUSSION

3.1. Phase

The XRD patterns of pure MZF, BT, ME1, ME2 and ME3 are shown in Fig.1. The diffraction patterns of composites showed the presence of the both ferrite and ferroelectric phases. The ferrite phase showed a cubic spinel structure with a=8.33 A^0 and ferroelectric phase exhibited perovskite tetragonal structure with a=3.99 A^0, c=4.04 A^0 (c/a=1.01). The lattice parameters of the constituent phases are described to be same for ME1, ME2 and ME3. It is also found that the intensity of the ferrite peaks increases with its content. The scanning electron micrographs of pure MZF, BT and composites are shown in Fig.2 (a-e). From the figures, a dense microstructure for each sample can be observed. The grains of two different phases distributed in homogeneously in the micrographs of composites. Addition of MZF to BTO produced irregular grain shapes. This may be attributed to the filling of pores between the ferroelectric grains by the MZF particles and their segregation at the grain boundaries.

3.2. 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 Fig.3 (a), it is clear that ε' decreases steeply at lower frequencies and remains constant at higher frequencies. The variation of dielectric constant with applied frequency is due to charge transport relaxation. This dielectric dispersion can be attributed to Maxwell [15] and Wagner [16,17] type of interfacial polarization. The dielectric constant is known to be the 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. These in homogeneties arise from impurities, grain structure and pores [18]. In case of composites, the high values of dielectric constant are ascribed to the fact that ferroelectric grains are surrounded by non-ferroelectric grains similar to that observed in relaxor ferroelectric materials [19].

According to Rabinkin et al. [20], the polarization in ferrites follows a mechanism similar to the 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 [21]. The increase in ferrite concentration beyond the percolation limit leads to the formation of conducting paths between the ferrite particles. This results in increase of conductivity 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.

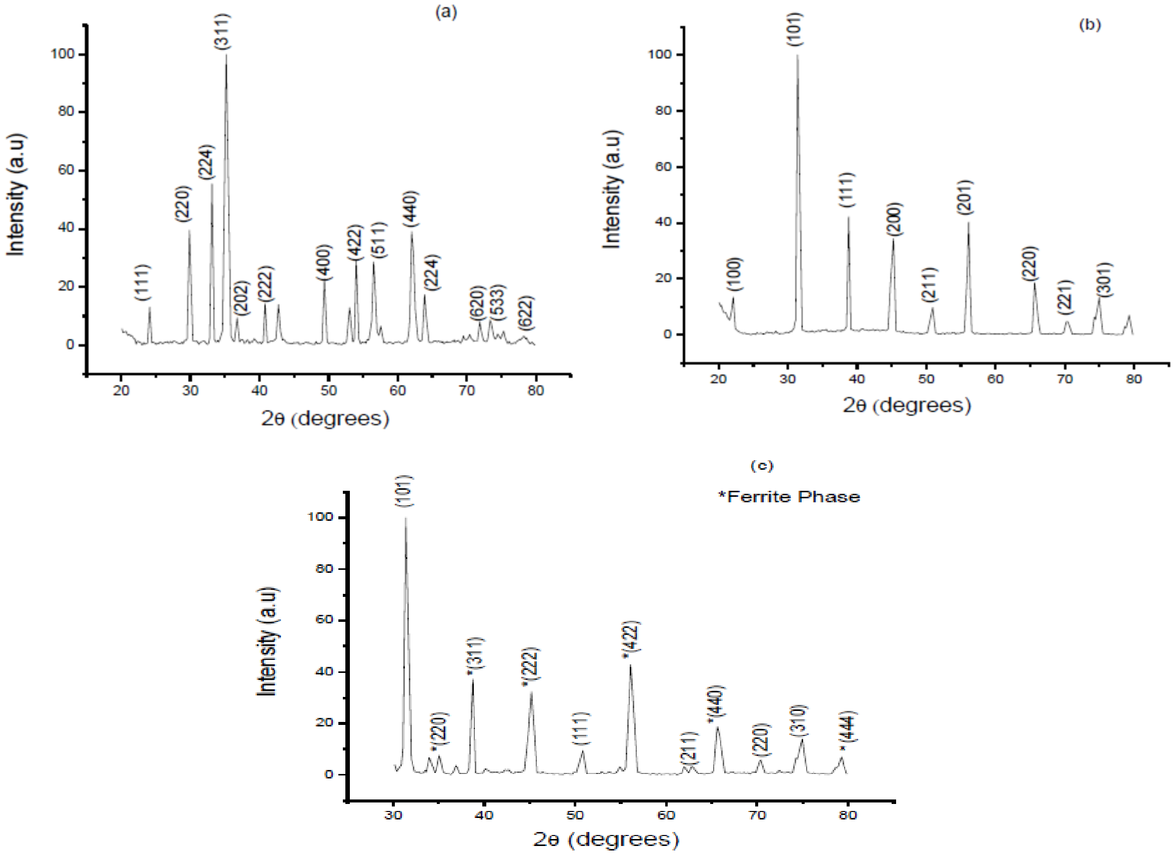
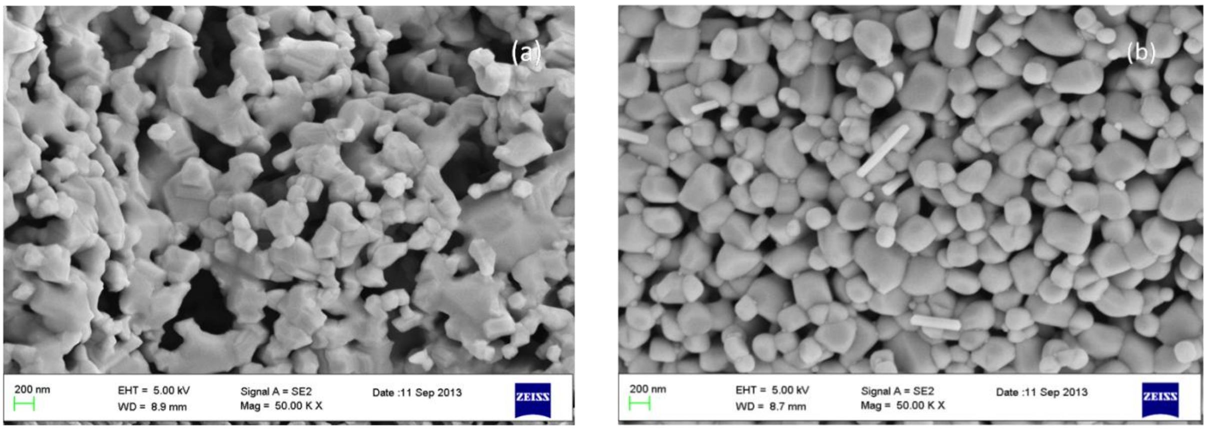


Fig1. *XRD Patterns for pure nano powder of (a) $Mn_{0.5}Zn_{0.5}Fe_2O_4$ (MZF), (b) pure nano powder of $BaTiO_3$ (BT) and (c) ME1 nano powder composite*



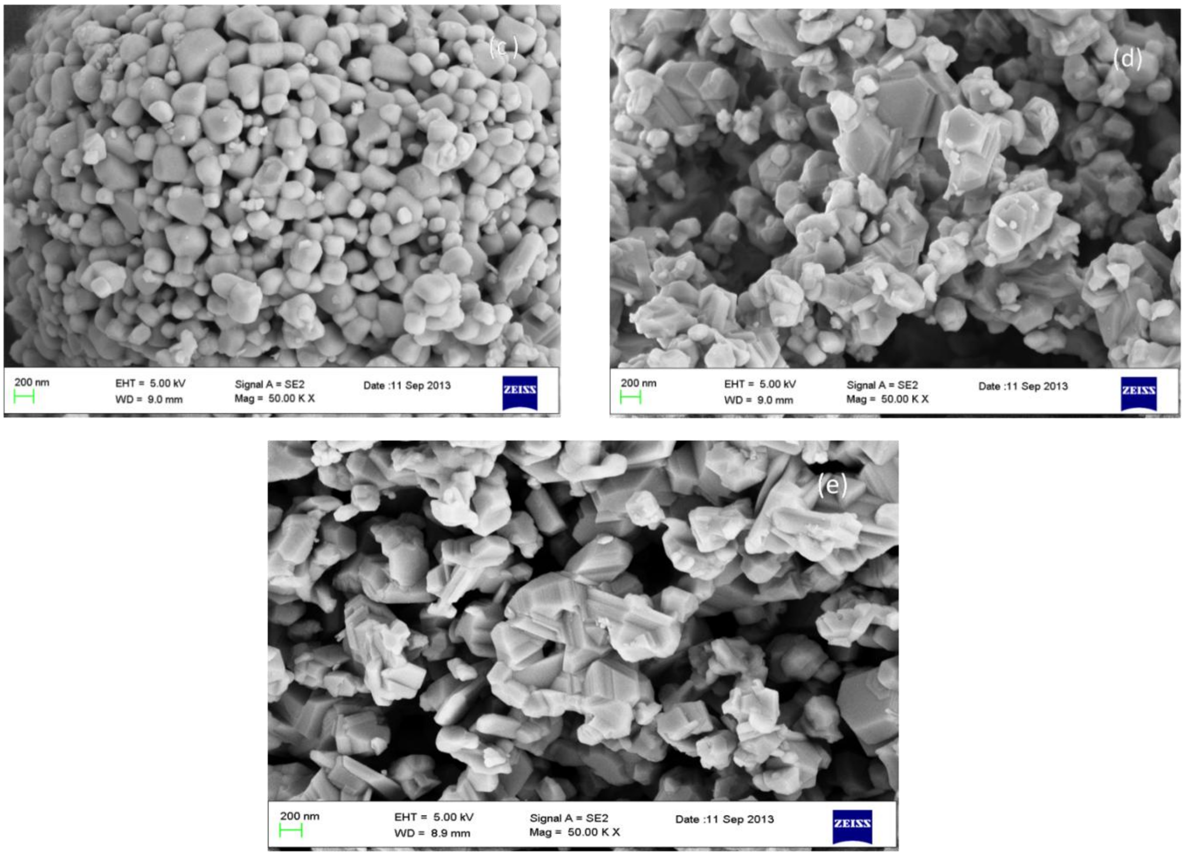
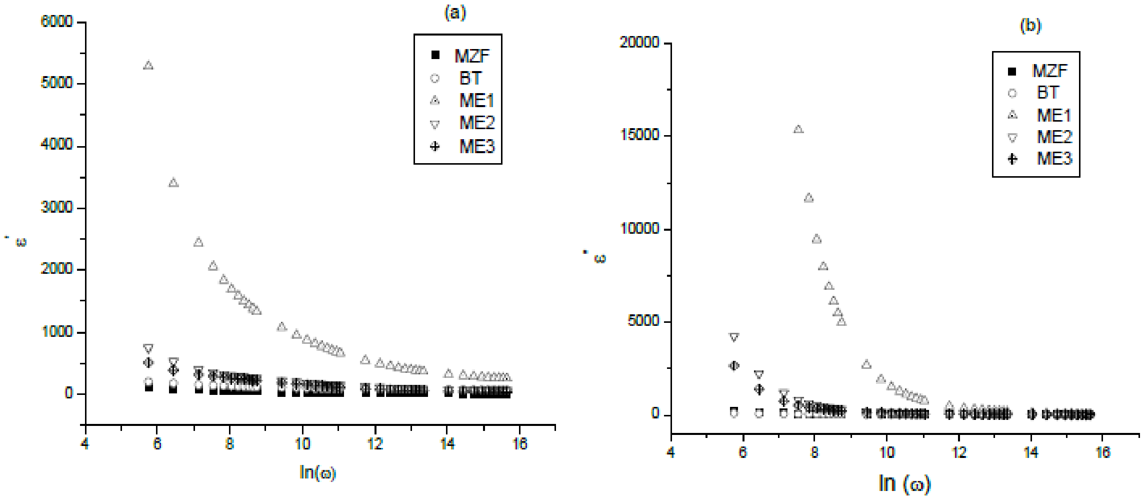


Fig2. *FESEM micrographs for (a) MZF, (b) BaTiO3 , (c) ME1, (d) ME2 and (e) ME3*

According to Rezlescu and Rezlescu [22], the behavior of polarization in the ferrite is due to collective behavior of two type of charge carriers i.e. n and p type. In $Mn_{0.5}Zn_{0.5}Fe_2O_4$ ferrite, the presence of Mn^{+2}/Mn^{+3}, Zn^{+2}/Zn^{+3} gives rise to p-type carriers [23] 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 should be noted that n-type carriers also contributed to polarization. However, the p-type carrier contribution is smaller than electronic exchange between ions and its mobility is smaller than that of n-type. The contribution to polarization at lower frequencies will decrease from former to the later.

The variation of ε" with frequency for MZF, BT and composites is shown 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 can be attributed to domain wall motion. At higher frequencies, losses are less where domain wall motion is inhibited and magnetization is forced to change by rotation.



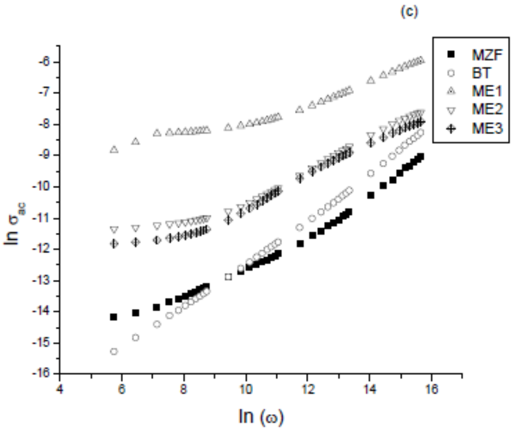


Fig3. *(a).Variation of dielectric constant,* ε' *with frequency,* ω *at RT, (b).Variation of dissipation factor,*ε'' *with frequency,* ω *at RT and (c) Variation of ac conductivity,* σ_{ac} *with frequency,* ω *at RT.*

In order to understand the conduction mechanism and type of polarons responsible for conduction, ac conductivity, σ_{ac} was estimated as per $\sigma_{ac}= \omega\ \varepsilon_0\ \varepsilon''$ [24], where ε_0 is the permittivity of free space and $\omega=2\Pi f$.

The variation of σ_{ac} with frequency, f, is shown in Fig.3 (c) for all the five samples. The plots are linear for higher frequency and nonlinear at 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 [23, 24]. However, the decrease in conductivity at lower frequencies can be attributed to conduction by mixed polarons.

3.3. Magnetization

Fig.4 shows the magnetic hysteresis loops for ME1, ME2 and ME3. The hysteresis loops reveal that all composites exhibit well saturated typical ferromagnetic behavior. It can be seen from the M-H loops that the coercivity increase with the increase of BT content, which indicates that the magnetization ability becoming weak because of the presence of non-magnetic BT phase, which brings in domain wall pinning [25-28]. This pinning may increase coercivity. The saturation magnetization of the composites decreased with increase of BT phase. One expect that magnetic properties get reduced with increasing $BaTiO_3$ content. The magnetic hysteresis loops for the composites, showed the presence of ordered magnetic structure and clearly indicating this dilution effect.

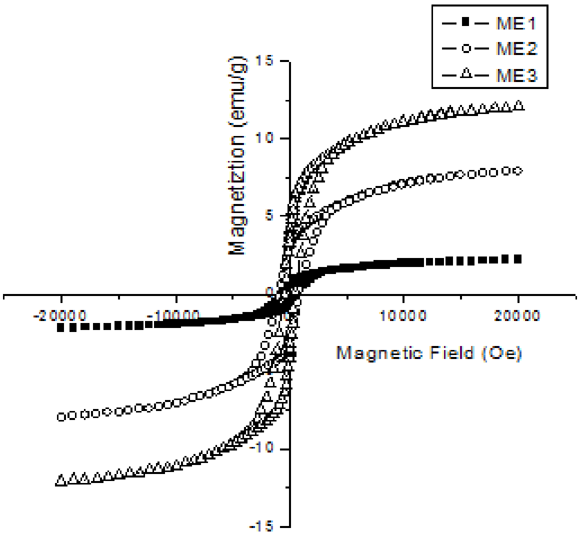


Fig4. *Hysteresis loops recorded at room temperature for ME1, ME2 and ME3.*

Table1. *Parameters derived from M-H loops at RT for ME1, ME2 and ME3 samples*

Sample	H_C(Oe)	M_S (emu/g)	M_r(emu/g)
ME1	634.02	2.19	0.6730
ME2	934.51	7.96	2.98
ME3	525.57	12.17	4.22

From the Table 1 , it can be observed that the value of saturation magnetization increasing with increasing ferrite phase due to the fact that individual ferrite grains act as centers of magnetization and the M_s of the composites is the vector sum of all these individual contributions. As the magnetic contacts increases with the ferrite content, net magnetization increases. It is observed that M_s of the composites decreases with increase of ferroelectric content. The grains of ferroelectric phase in ferrite phase acts as pores in the presence of applied magnetic field and breaks the magnetic circuit, resulting in the decrease of magnetic properties with increasing ferroelectric content. Since $BaTiO_3$ is a ferroelectric material, it has no magnetic ordering. Therefore, the magnetic nature of the composite decreases with the increase of ferroelectric content.

4. CONCLUSIONS

Magneto-electric nanocomposites consisting of MZF and BT were prepared by solution combustion method. XRD patterns and FESEM micrographs revealed the presence of both ferrite and ferroelectric phases. The present nano ME composites possess high density of nano particles and fine microstructure. The frequency dependant dielectric constant showed the usual dielectric dispersion behavior for all the composites. The ac conductivity data suggested that the conduction must be due to small polaron hopping. The composites exhibited magnetic hysteresis loops similar to a ferromagnetic sample, which indicates the presence of an ordered magnetic structure in the present mixed spinel-perovskite system. For the first time the ME nanocomposites of present composition were investigated for dielectric and magnetic properties and data analyzed thoroughly.

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