

Effect of Polaron Hopping on Electrical Properties of Magneto Electric Composites

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Research Article

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Abstract

$\text{Co}_{0.7-x}\text{Ni}_x\text{Mn}_{0.3}\text{Fe}_2\text{O}_4$ (CNMFO) ferrites with $x = 0.00, 0.05, 0.10$ and 0.15 , $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ (PZT) ferroelectric and 30% CNMFO – 70% PZT magneto electric (ME) composites were synthesized by double sintering ceramic method. XRD confirms pure phase formation for all compositions of ferrite, ferroelectric and ME composites. All compositions of ferrites, ferroelectric and ME composites show negative temperature coefficient of resistance (NTCR) confirming the semiconducting behavior, though the conduction mechanism is quite different than known semiconductors such as, silicon and germanium. The conduction, due to electron hopping in semiconductors against polaron hopping in ferrites is explained. The effect of cation distribution on resistivity of ferrite phase is also discussed. Thus, effect of polaron hopping and cation distribution on resistivity and dielectric constant of ferroelectric and ME composites has been discussed. Effective resistance of ME composites due to combined resistance of the constituent phases has also been studied.

Introduction

Development of two-phase ME composites consisting of magnetostrictive ferrite and piezoelectric ferroelectric has become a revolutionary trend for multiple state memory device in which data is stored both in electric and magnetic polarizations [1]. Apart from this several other applications of ME composites have emerged including power harvesting, current transformer, phase shifters, waveguides, sensors and resonators [2]. According to Boomgard, higher ME coefficient necessary for device application is obtained by high and comparable resistivity of the constituent phases [3]. Ferroelectrics are insulating materials with high resistivity being their inherent property. Ferrites show lower resistivity as compared to ferroelectrics. Now a day's research is being focused on higher resistivity of ferrite phase. Attempts are begin made to increase resistivity of ferrite phase, so that, the charges developed during ME coefficient measurement should not leak through the lower resistive ferrite phase [4]. Change in cation distribution also affects the resistivity of ferrite phase [5]. Increase or decrease in resistivity of ferrite phase affects ME coefficient drastically [6]. Also, development and discharge of charges during ME coefficient measurement is still unrevealed. Thus, aim of the present work is to understand conduction mechanism in ferrite and ferroelectric phase and its effect on electric properties of ME composites.

$\text{Co}_{0.7-x}\text{Ni}_x\text{Mn}_{0.3}\text{Fe}_2\text{O}_4$ (CNMFO) ferrites with $x = 0.00, 0.05, 0.10$ and 0.15 is selected as a ferrite phase. Cobalt ferrite is well known for its highest magnetostriction among all known cubic spinel ferrites; thus, it is selected as a parental ferrite [7]. Addition of small amount of Mn enhances magnetostriction of cobalt ferrite. Addition of 0.3 concentration of Mn shows highest magnetization and magnetostriction in Co-Mn series [8]. Attempt has been made to increase resistivity of Co-Mn ferrite by addition of nickel in step of 0.05, as nickel ferrite is well known for its higher resistivity [9]. Amount of nickel has kept very low ($x = 0.00, 0.05, 0.10$ and 0.15) as magnetic moment of Ni^{2+} ($2\mu\text{B}$) is lower than Mn^{2+} ($4\mu\text{B}$) and Co^{2+} ($3\mu\text{B}$) and it may affect magnetic properties adversely [10]. $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ (PZT) is selected as ferroelectric phase which shows highest value of dielectric and piezoelectric constant at morphotropic phase

boundary (MPB) [11]. Also, it shows good coupling coefficient with cobalt ferrite [12]. ME coefficient with 30% of ferrite phase and 70% of ferroelectric phase have been synthesized and characterized to understand effect of polaron hopping on resistivity.

Synthesis And Characterization

Magneto electric composites with (30%) $\text{Co}_{0.7-x}\text{Ni}_x\text{Mn}_{0.3}\text{Fe}_2\text{O}_4$ and (70%) $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ with $x = 0.00, 0.05, 0.10, 0.15$ were synthesized by double sintering ceramic method. For the preparation of $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ (PZT), equimolar amounts of lead oxide (PbO), titanium oxide (TiO_2) and zirconium oxide (ZrO_2) were mixed thoroughly using acetone as mixing medium so that stoichiometry is maintained. The mixed powder was pre-sintered at 1000°C for 6 h in PbO atmosphere. The calcinated powder was then grounded for 1 hr and final sintering was carried out at 1100°C for 12 hr again in PbO atmosphere. For the synthesis of $\text{Co}_{0.7-x}\text{Ni}_x\text{Mn}_{0.3}\text{Fe}_2\text{O}_4$ with "x" varying from 0.00 to 0.15 with an increment of 0.05, equimolar amounts of CoO, NiO, Mn_2O_3 , and Fe_2O_3 were mixed thoroughly using acetone medium so as to maintain stoichiometry. The obtained powder was then pre-sintered at 1050°C for 10 hr and ferrites were obtained at final sintering temperature of 1100°C for 11 hr. For both pre-sintering and final sintering of ferrites oxygen atmosphere was maintained. After preparing the individual components, for the preparation of the composites, obtained PZT and CNMFO powders were ground in molecular ratio of 70:30, respectively, in acetone medium. The mixed powders were pressed into pellets and finally sintered at 900°C for 9 hr. Samples were accordingly designated as K, L, M and N for $x = 0.00, 0.05, 0.10$ and 0.15 (representing the content of Ni in the CNMFO phase), respectively. X-ray diffraction patterns were recorded on X1 PHILIPS, Holland and Bruker D8 Advance X-ray diffractometer with CuK α radiation ($k = 1.5407 \text{ \AA}$). Surface morphology of samples was recorded by scanning electron microscope (JEOL, Model JSM-6360A). Variation of dielectric constant with frequency was measured using LCR meter, HP4248A. Resistivity measurements were carried out from room temperature to 500°C .

Results And Discussion

1. X- ray diffraction studies

X- ray diffraction patterns of $\text{Co}_{0.7-x}\text{Ni}_x\text{Mn}_{0.3}\text{Fe}_2\text{O}_4$ (CNMFO) ferrites with $x = 0.00, 0.05, 0.10$ and 0.15 , $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ (PZT) ferroelectric and 30% CNMFO – 70% PZT magneto electric (ME) composites are shown in Fig. 1 (a), (b), and (c) respectively. Figure 1 confirms pure phase formation without any impurity for all compositions of ferrite, ferroelectric and ME composites. From Fig. 1 (a), presence of particular characteristic peaks at certain 2θ positions confirms cubic spinel structure for all four compositions of ferrites. Lattice parameter decreases from 8.40 \AA to 8.37 \AA with addition of Ni content. This decrease in lattice parameter is due to the replacement of larger Co^{2+} (0.78 \AA) ions by smaller Ni^{2+} (0.74 \AA) ions. Lattice contraction obeys Vegard's law which states that, cell volume decreases with addition of smaller cation and vice-versa [13]. Figure 1 (b) shows well defined peaks as well as splitting of peaks which

confirms tetragonal perovskite structure for ferroelectric phase. Lattice parameters ($c = 4.14$ c and $a = 4.03$ Å) are in good agreement with reported values [14].

X-ray diffraction patterns of ME composites in Fig. 1 (c) show characteristic peaks of both ferrite and ferroelectric phases. Absence of any unidentified peak confirms that, there is no any chemical reaction between two constituent phases. Two distinct phases are maintained as the final sintering temperature of ME composites is kept lower than that of final sintering temperature of pure phases.

2. Scanning electron microscopy

Figure 2 (a), (b), (c) and (d) shows scanning electron micrographs of $\text{Co}_{0.7-x}\text{Ni}_x\text{Mn}_{0.3}\text{Fe}_2\text{O}_4$ (CNMFO) ferrites with $x = 0.00, 0.05, 0.10$ and 0.15 . From SEM it is clearly observed that, grain size decreases with increase in Ni content. This decrease in grain size is due to substitution of Ni^{2+} (0.74 Å) ions in place of Co^{2+} (0.78 Å) ions. The results obtained from SEM are in good agreement with results obtained from XRD in which lattice parameter decreases with increase in Ni content. Also, the number of grain boundaries and pores was found to increase with addition of Ni content which may increase the resistivity of ferrite phase and may serve our purpose to increase the resistivity of ferrite phase. With the addition of Ni content grain size was decreased from 4.9 μm to 3.8 μm. Figure 3 shows SEM of $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ (PZT) ferroelectric phase. The grains are grown and well connected with grain size of nearly 5.1 μm are observed.

Two different regions of large sized well grown grains and smaller sized grains are observed in Fig. 4 (a), (b), (c) and (d) confirming co-existence of two constituent phases in ME composites. In the present work ME composites are synthesized in ferroelectric rich (with 70% PZT) region. Obviously, the grains of major component would grow rapidly and vice-versa, as a result, microstructure becomes heterogeneous. Variation of grain size with Ni content is random as ferrite and ferroelectric are mixed randomly.

3. Resistivity

Temperature dependent variation of dc resistivity for $\text{Co}_{0.7-x}\text{Ni}_x\text{Mn}_{0.3}\text{Fe}_2\text{O}_4$ (CNMFO) ferrites with $x = 0.00, 0.05, 0.10$ and 0.15 is shown in Fig. 5 (a). All compositions of ferrites show semiconducting behavior but the conduction mechanism is quite different than that of known semiconductors such as silicon and germanium. In semiconductors, carrier concentration increases with increase in temperature and results into decrease of resistivity. Here electron jumps from lower energy state to higher energy state of same ion and then it is available for conduction. Thus, conduction in semiconductors is due to electron hopping and ΔE in Arrhenius equation is the activation energy. In case of ferrites, carrier concentration is almost constant but, mobility of charge carriers increases with increasing temperature. In ferrites electron jumps from one ion to another ion situated at different crystallographic sites, thus ΔE is migration energy. As ferrites are resistive materials, electrons apply strain on the lattice while moving through it. Thus, electron coupled with strain field is called as polaron. If this strain field extends beyond the lattice parameter, polaron is called as large polaron and if the strain field is smaller than lattice parameter, polaron is called as small polaron. Many reports are available on conduction in ferrites due to small polaron [15]. Spatial

extent of polaron will be the appropriate term to show size of polaron rather than “polaron radius”. The term polaron radius is quite misleading and confusing, as strain field is not having exactly round shape. The conduction mechanism in ferrites is explained on the basis of Vervy de Bhor theory, which involves electron exchange between ions of the same element present in more than one valance state and randomly distributed over equivalent crystallographic sites. In cubic spinel ferrites iron ions are present in Fe^{2+} and Fe^{3+} states. This cubic spinel structure has 64 tetrahedral (A) and 32 octahedral (B) sites out of which iron ions have strong preference for B site. The distance between cation in B-site (0.292) is much smaller than the distance between cation at A-site (0.357). Thus, polaron hoping between Fe^{2+} and Fe^{3+} ions present at B-site controls conduction in ferrites. This polaron hoping is thermally activated and with increase in temperature, conductivity increases showing NTCR. Careful observation of Fig. 3 (a) shows increases in resistivity with addition of Ni content. This is obviously due to the fact that, Ni^{2+} ions have strong preference for B-site [16]. This will displace Fe^{2+} or Fe^{3+} ions from B-site reducing conduction at B-site. Thus, it can be said that, inverse spinel structures have higher resistivity than normal spinel structures. As observed from SEM grain size decreases with Ni content. Increased number of grain boundaries and pores will act as opposing walls for conduction and will cause resistivity increase. Spatial extent of polaron can roughly calculated by the formula

$$R_p = \frac{1}{2} \left[\frac{\pi}{6N} \right]^{1/3} \text{-----1}$$

Where, N is number of sites per unit volume = $64 (A) + 32 (B) / (a)^3 = 96/a^3$, where ‘a’ is lattice parameter.

Values of polaron field extent (Table 1.1) are smaller than lattice parameter. Thus, conduction due to small polaron hoping is confirmed. At certain higher temperature there is change in slope of graphs indicating phase transition from ferromagnetic to paramagnetic state. Figure 5 (b) shows variation of dc resistivity with temperature for $PbZr_{0.52}Ti_{0.48}O_3$ (PZT) ferroelectric phase. In resemblance with the ferrites conduction in ferroelectric can also be explained with the help of Vervy de Bhor mechanism. With increase in temperature polaron hoping between $Zr^{3+}-Zr^{4+}$, $Pb^{2+}-Pb^{3+}$ and $Ti^{3+}-Ti^{4+}$. Polaron extent is calculated by using Eq. 1.

Where, N = number of sites per unit volume = $(1 B + 8 A) / a^3 = 9 / a^3$ from the Table 1.1 it can be seen that for PZT also charge carriers are small polaron. But polaron extent is much bigger than ferrites as ferroelectrics are more resistive.

Variation of dc resistivity with temperature for ME composites with 30% CNMFO and 70% PZT is shown in Fig. 5 (c). All compositions of ME composites show semiconducting behavior due to polaron hoping between $Zr^{3+}-Zr^{4+}$, $Pb^{2+}-Pb^{3+}$ and $Ti^{3+}-Ti^{4+}$ and $Fe^{2+}-Fe^{3+}$.

Table 1.1
 Values of polaron radius of $\text{Co}_{0.7-x}\text{Ni}_x\text{Mn}_{0.3}\text{Fe}_2\text{O}_4$ pellets with X = 0.00,0.05,0.10
 and 0.15

$\text{Co}_{0.7-x}\text{Ni}_x\text{Mn}_{0.3}\text{Fe}_2\text{O}_4$ x	Polaron Radius (Rp) (Å)
0.00	0.55
0.05	0.54
0.10	0.53
0.15	0.52

4. Dielectric Constant

Dielectric constant decreases with increase in frequency showing regular dielectric dispersion behavior for all compositions of ferrites, ferroelectrics and ME composites as shown in Fig. 6 (a), (b), and (c) respectively. High values of dielectric constants at lower frequencies are sum of four types of polarizations; electronic, ionic, orientational and space charge polarization. Each polarization has different dimensions e. g. electronic polarization is smallest and its dimensions are nearly 10^{19} Å. Ionic polarization is slightly sluggish and has dimensions of nearly 10^{15} Å. whereas dimensions of orientational polarization are approximately 10^9 Å and so on. Due to different dimensions, they are active in different frequency regions. At lower frequency all polarizations are present but with increase infrequency contribution of each polarization decreases and dielectric constant also decreases [17]. Thus, all compositions show dielectric dispersion behavior. With the present instrument we can measure dielectric constant up to 10^7 Hz. Thus, only space charge and orientational polarizations are reduced and observed due to limitations of instrument. Resultant value due to sum of electronic and ionic polarization is called as static value of dielectric constant.

Figure6 (a) shows variation of dielectric constant with frequency for all compositions of ferrites. According to Maxwell Wanger theory and Koops phenomenological theory inhomogeneous dielectric is made up of conducting grains, less conducting grain boundaries and non-conducting cracks, pores and defects [18]. Polarization in ferrites is similar process to the conduction. Conduction of polaron in Fe^{2+} - Fe^{3+} ions present at B-site leads to local displacement of charges responsible for polarization. Due to higher resistivity of grain boundaries these charges pile up at grain boundaries and contribute for higher dielectric constant. As observed from resistivity section, resistivity increases with addition of Ni content in ferrites. Due to increased resistivity of grains, charges reaching the grain boundaries are reduced and as a result dielectric constant decrease. Thus, with increase in resistivity dielectric constant decreases and it can be said that, resistivity and dielectric have inverse proportion [19].

Variation of dielectric constant with frequency for PZT is shown in Fig. 6 (b). Polaron hopping between Zr^{3+} - Zr^{4+} , Pb^{2+} - Pb^{3+} and Ti^{3+} - Ti^{4+} is responsible for displacement of charges [20]. PZT shows much higher dielectric constant as compared to ferrites. Figure 6 (c) shows variation of dielectric constant with frequency for all compositions of ME composites. Random variation of dielectric constant with Ni content was observed as ferrite and ferroelectric grains are randomly mixed.

Conclusion

$Co_{0.7-x}Ni_xMn_{0.3}Fe_2O_4$ (CNMFO) ferrites with $x = 0.00, 0.05, 0.10$ and 0.15 , $PbZr_{0.52}Ti_{0.48}O_3$ (PZT) ferroelectric and 30% CNMFO – 70% PZT magneto electric (ME) composites were synthesized by double sintering ceramic method. Presence of both phases in ME composites without any chemical reaction was achieved by keeping final sintering temperature of ME composites lower than that of final sintering temperature of constituent phases. Addition of smaller cation decreased lattice parameter and grain size in ferrites. In ferrites conduction is due to polaron hopping between Fe^{2+} and Fe^{3+} ions situated at B-site whereas polaron hopping between Zr^{3+} - Zr^{4+} , Pb^{2+} - Pb^{3+} and Ti^{3+} - Ti^{4+} is responsible for conduction in PZT. Mixed type of conduction was observed in ME composites. Change in cation distribution changes resistivity. Thus, inverse spinel structures have higher resistivity than normal spinel structures. Resistivity affects dielectric constant adversely. Further it will be interesting to observe the effect of change in resistivity and dielectric constant on ME coefficient.

Declarations

Acknowledgement

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Figures

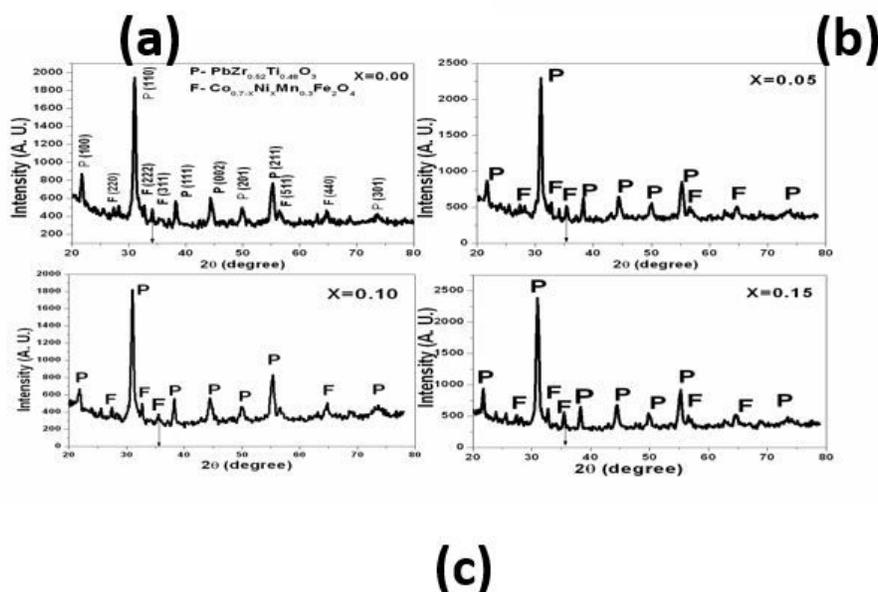
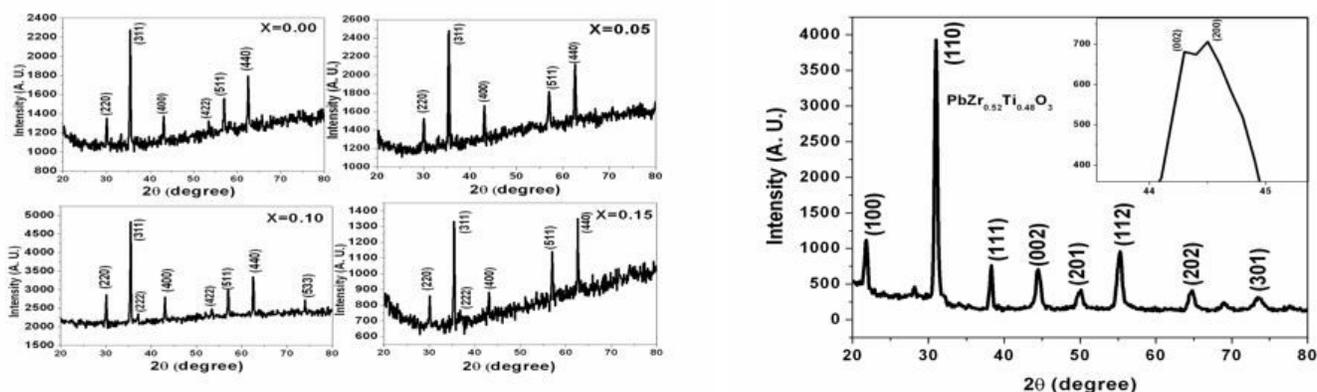


Figure 1

(a) X - ray diffraction patterns of $\text{Co}_{0.7-x}\text{Ni}_x\text{Mn}_{0.3}\text{Fe}_2\text{O}_4$ (CNMFO) ferrites with $x = 0.00, 0.05, 0.10$ and 0.15 (b) X - ray diffraction patterns of $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ (PZT) (c) X - ray diffraction patterns of 30% CNMFO – 70% PZT magnetoelectric (ME) composites with $x = 0.00, 0.05, 0.10$ and 0.15

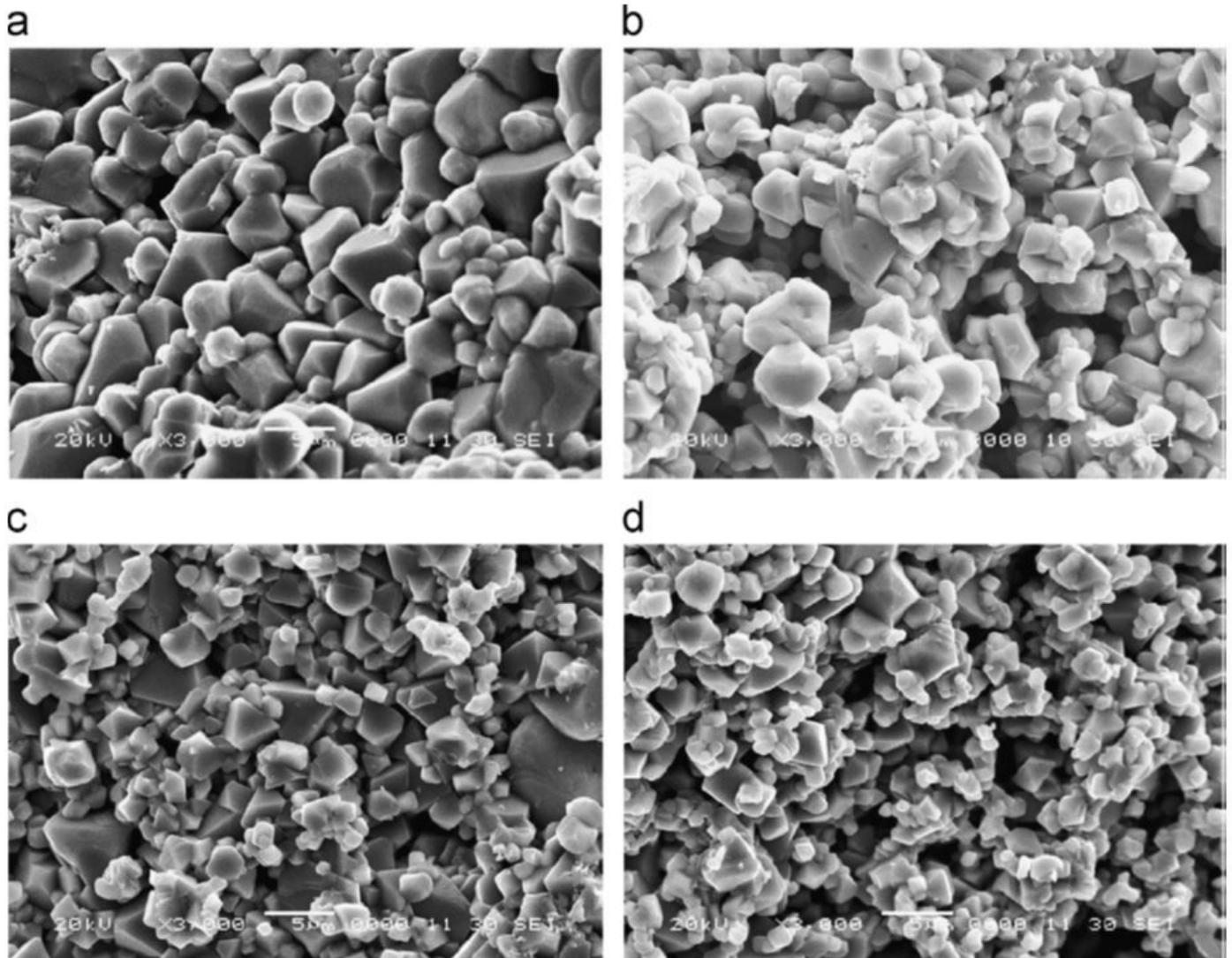


Figure 2

(a), (b), (c), (d) SEM of $\text{Co}_{0.7-x}\text{Ni}_x\text{Mn}_{0.3}\text{Fe}_2\text{O}_4$ (CNMFO) ferrites with $x = 0.00, 0.05, 0.10$ and 0.15

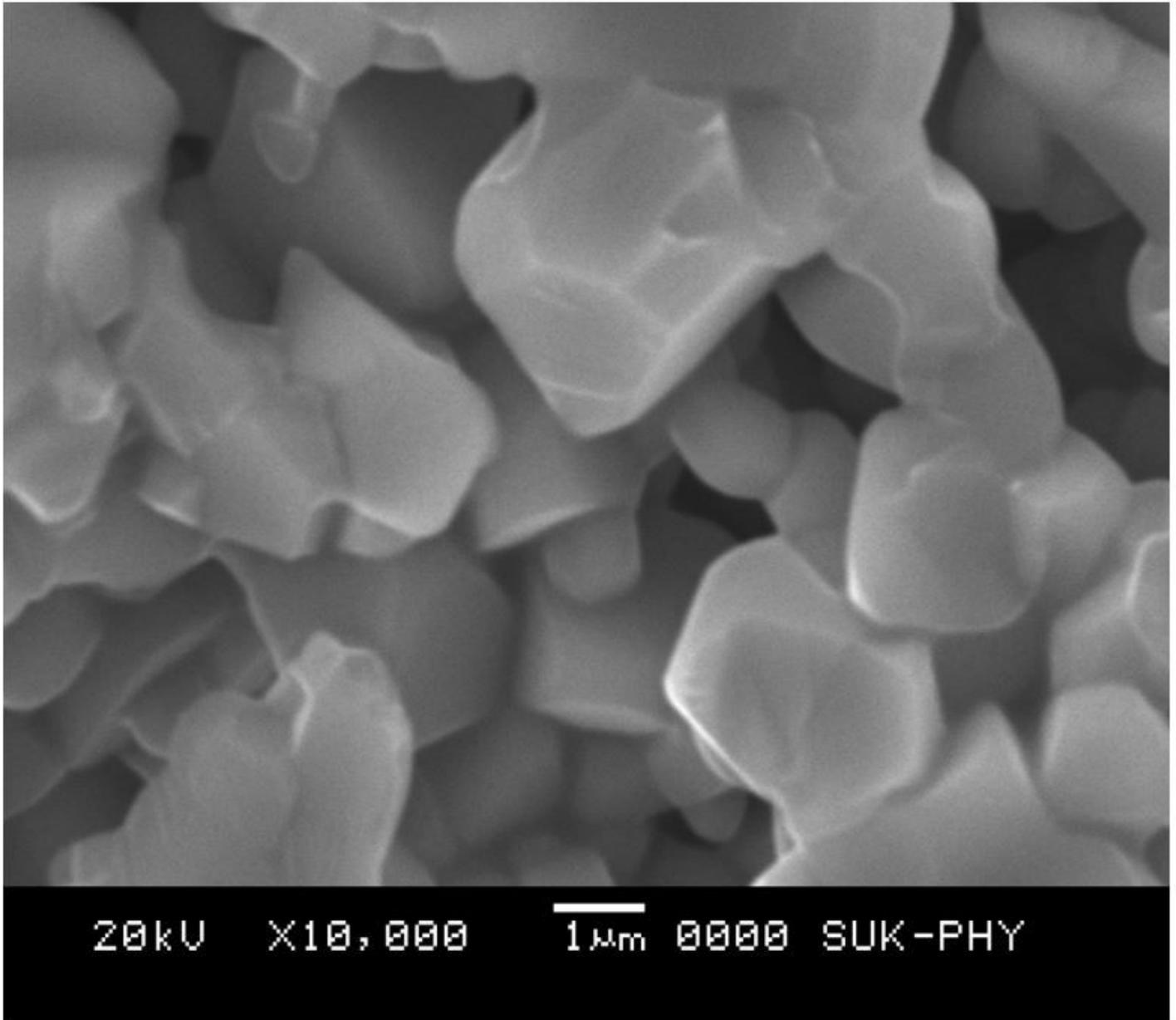


Figure 3

SEM of $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ (PZT)

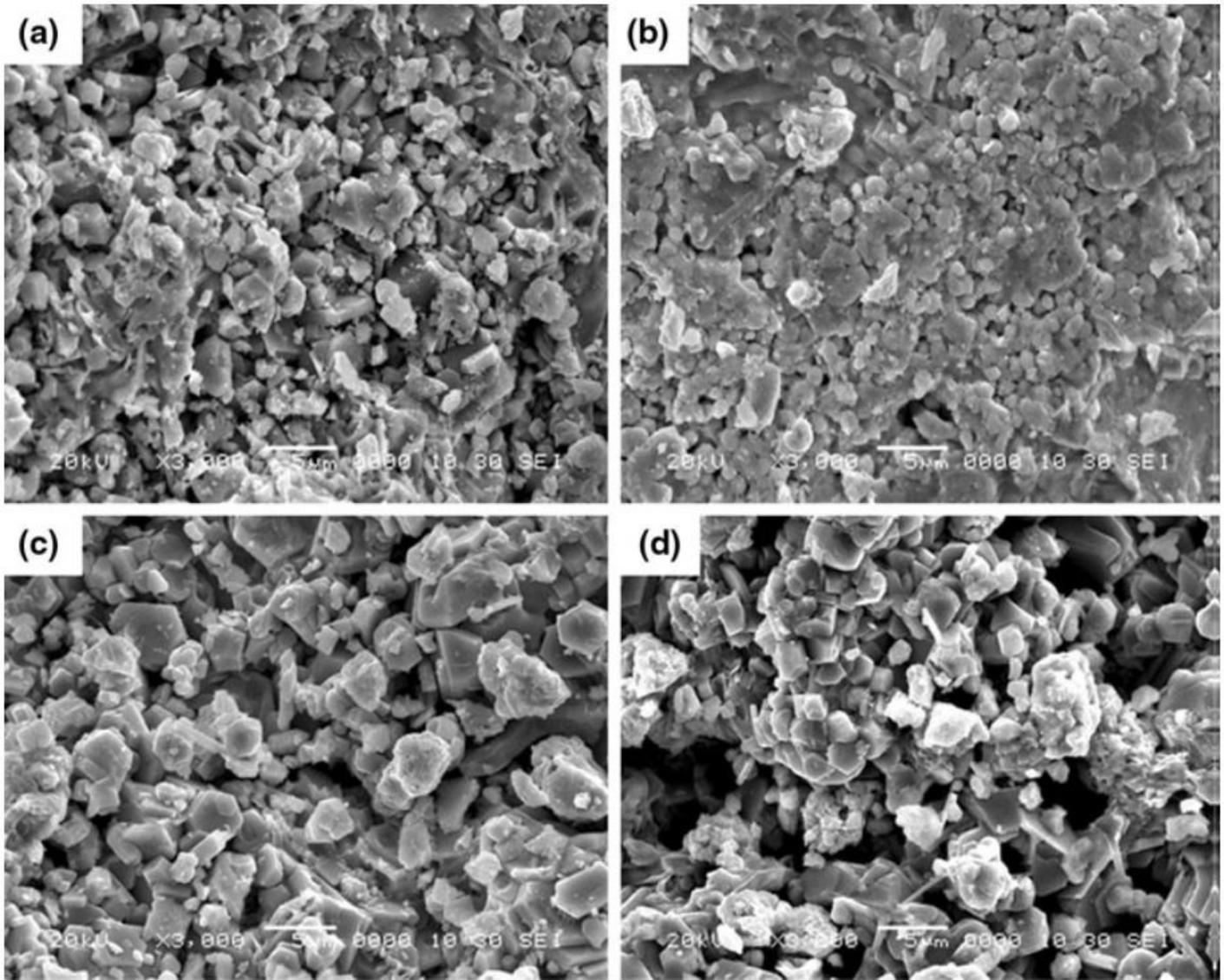
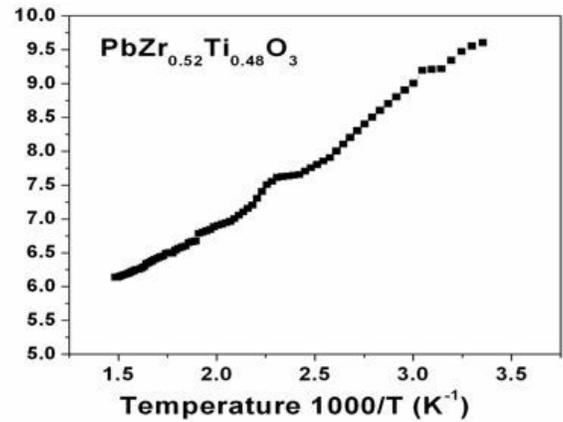
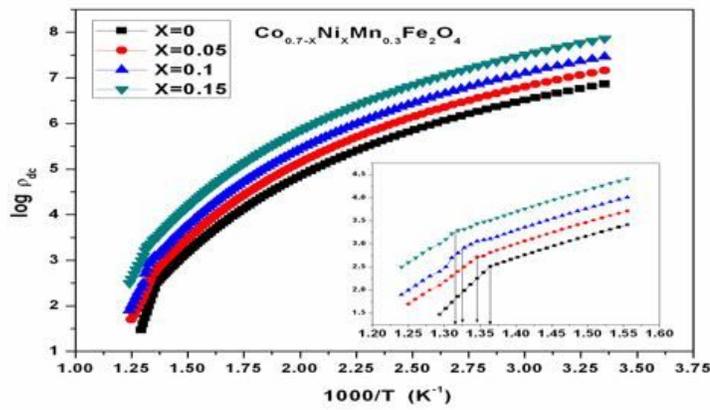


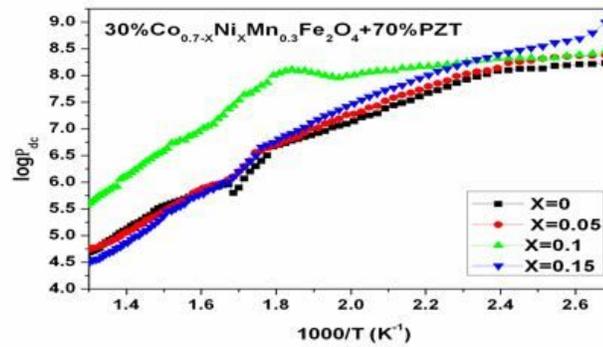
Figure 4

(a), (b), (c), (d) SEM 30% CNMFO – 70% PZT magnetoelectric (ME) composites with $x = 0.00, 0.05, 0.10$ and 0.15



(a)

(b)



(c)

Figure 5

(a) Variation of resistivity with temperature of $\text{Co}_{0.7-x}\text{Ni}_x\text{Mn}_{0.3}\text{Fe}_2\text{O}_4$ (CNMFO) ferrites with $x = 0.00, 0.05, 0.10$ and 0.15 (b) Variation of resistivity with temperature of $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ (PZT) (c) Variation of resistivity with temperature of 30% CNMFO – 70% PZT magnetoelectric (ME) composites with $x = 0.00, 0.05, 0.10$ and 0.15

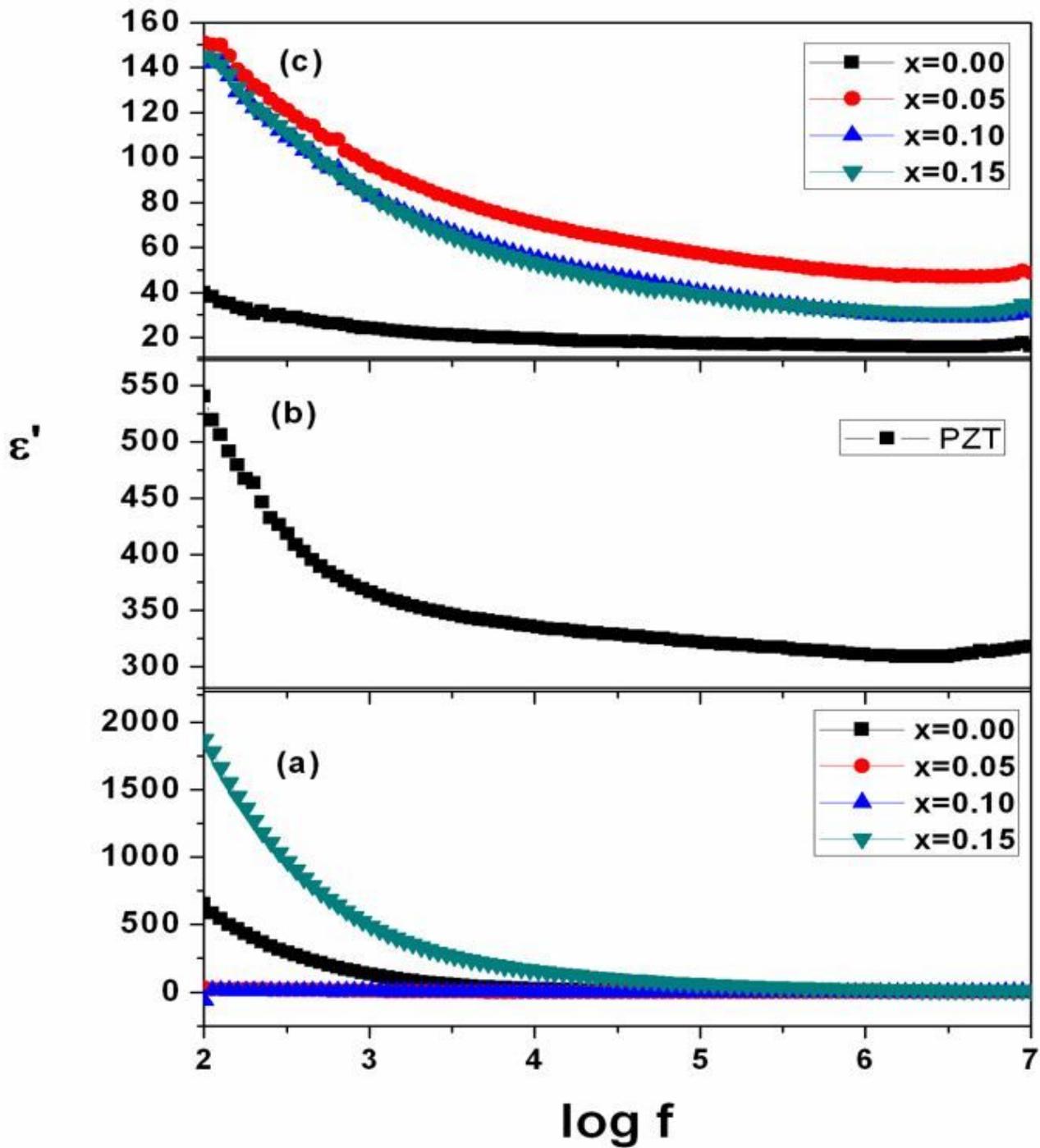


Figure 6

(a) Variation of dielectric constant with $\log f$ of $\text{Co}_{0.7-x}\text{Ni}_x\text{Mn}_{0.3}\text{Fe}_2\text{O}_4$ (CNMFO) ferrites with $x = 0.00, 0.05, 0.10$ and 0.15 (b) Variation of dielectric constant with $\log f$ of $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ (PZT) (c) Variation of dielectric constant with $\log f$ of 30% CNMFO - 70% PZT magnetoelectric (ME) composites with $x = 0.00, 0.05, 0.10$ and 0.15