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Structural analysis and Studies on Dielectric Behavior of (x) $Ni_{0.6}Zn_{0.4}Fe_2O_4$ + (1-x)PZT ME Composites

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Abstract

The Magnetoelectric (ME) composites consisting of ferrite and ferroelectric phases viz. (x) $Ni_{0.6}Zn_{0.4}Fe_2O_4$ + (1-x) $PbZr_{0.52}Ti_{0.48}O_3$ (PZT) in which x varies as 0, 0.15, 0.30, 0.45 and 1 mol % were prepared by a conventional double sintering ceramic method. The presence of two phases in composites was confirmed by XRD technique. The dielectric measurements were carried out as a function of frequency in the range 20 Hz to 1 MHz and with temperature at fixed frequencies of 1 kHz, 10 kHz, 100 kHz, and 1 MHz. The detailed studies on the dielectric properties were done presuming that the magnetoelectric interaction between the constituent phases may result in various anomalies in the dielectric behavior of the ME composites. The conduction is explained on the basis of small polaron hopping model. The confirmation of this phenomenon was made with the help of ac conductivity measurements.

Keywords: XRD, ME composites, dielectric properties, AC conductivity etc.

Introduction

ME effect is nothing but dielectric polarization of a material under magnetic field or an induced magnetization under an electric field. The ME effect requires simultaneous presence of long-range ordering of magnetic moments and electric dipoles [1]. The literature survey suggests that very few single phase materials are ME in nature [2]. However, due to weak ME output and temperature constraint they do not find any technological applications [3]. The ME output obtained in ferrite – ferroelectric ME composites is much larger than that of single phase materials [2].

Composite materials are best suited for particular application which could not be achieved by any one component acting on its own. Ferrite-ferroelectric composites consist of two phases viz. piezomagnetic and piezoelectric. The ME composite can be prepared by solid state reaction and when placed in an external magnetic field generates an electrical response. These materials are used as transducers, actuators, magnetic sensors for ac and dc magnetic fields measurements. Also they are used in microwaves, magnetic field probes, radio electronics, current measurements, integral optics and fiber communicating technology [1].

In the present work we report the electrical properties and ME effect in (x) $Ni_{0.6}Zn_{0.4}Fe_2O_4$ + (1-x) PZT composites, which offer valuable information about the behavior of localized electric charge carriers. This can also lead to better understanding of the mechanism of electrical conduction and dielectric polarization in such systems. The zinc doped nickel ferrite is selected due to its high resistivity, high magnetostriction coefficient and low eddy current loss [4]. PZT having high piezoelectric constant, high dielectric permittivity and superior coupling factor is selected as a ferroelectric phase [5, 6].

Experimental

Preparation of Samples

ME composites with the general formula (x) $Ni_{0.6}Zn_{0.4}Fe_2O_4$ + (1-x) $PbZr_{0.52}Ti_{0.48}O_3$ (PZT) in which y varies as 0, 0.15, 0.30, 0.45 and 1 mol % were prepared by the conventional double-sintering ceramic method. The ferrite phase was prepared by taking AR grade NiO, ZnO and Fe_2O_3 in required molar proportions. These oxides were mixed and ground in agate mortar for couple of hrs. The powder mixture was presintered at 800 ^{O}C for 8 h and final sintered at 1000 ^{O}C for 10 h.

The ferroelectric phase was prepared using AR grade $PbCO_3$, ZrO_2 and TiO_2 as starting materials and presintered at 600 ^{O}C for 3 h. while final sintered at 1200 ^{O}C for 4 h. The ME composites were prepared by mixing 15, 30 and 45 mole % of ferrite phase with 85, 70 and 55 mole % of ferroelectric phase respectively. The powder mixture was pressed into pellets of diameter of 10-15 mm and 2-4 mm thickness using a hydraulic press. The pellet samples were final sintered at 1200 ^{O}C for 5 h. in a programmable furnace and slow cooled to room temperature to yield the final product.

Characterization and Property Measurement

The structural characterization of the samples was carried out by using x-ray diffractometer (Phillips Model PW 1710) using CuKα radiation (λ =1.5418Å).

The dielectric measurements were carried out as a function of frequency in the range 20 Hz to 1 MHz and with temperature at fixed frequencies of 1 kHz, 10 kHz, 100 kHz, and 1 MHz by using a LCR Meter Bridge (Model HP 4284 A). The dielectric constant (έ) was calculated using the relation-

$$\acute{\varepsilon} = c\, d / \varepsilon_o A \qquad (1)$$

Were, c is capacitance of pellet in Farad, d is the thickness of pellet, A is the cross-sectional area of the flat surface of the pellet and ε_o is permittivity of free space ($\varepsilon_o = 8.85\times10^{-12}$ F/m).

Results and Discussion

Phase Determination

The x-ray diffraction patterns show well-defined peaks of $Ni_{0.6}Zn_{0.4}Fe_2O_4$ and $PbZr_{0.52}Ti_{0.48}O_3$ as shown in Figure1. All the indexed peaks are characteristics of the ferrite and ferroelectric phases with no any additional impurity phases. For the spinel ferrite a (311) peak where as for a tetragonal perovskite ferroelectric phase (110) peak are more intense peaks respectively.

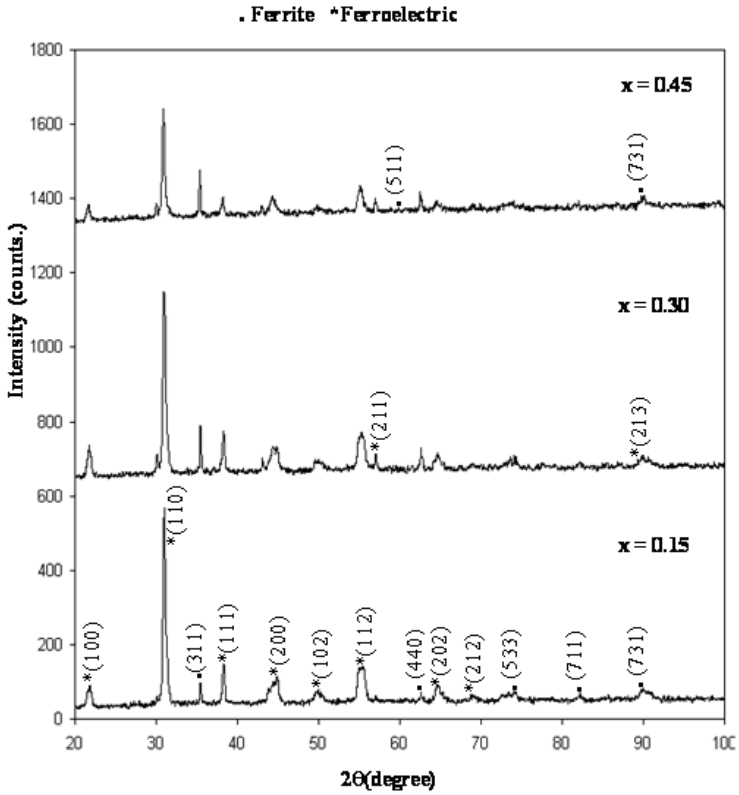

Figure 1: XRD pattern of (x)$Ni_{0.6}Zn_{0.4}Fe_2O_4$ + (1-x) $PbZr_{0.52}Ti_{0.48}O_3$ ME composites.

The number and intensity of ferrite peaks increases with increase in mole % of ferrite content [7].

The ferrite phase has a cubic Spinel structure with lattice parameter a = 8.35 Å and the ferroelectric phase has a structure with a = 4.05 Å, c = 4.08 Å and c/a = 1.00. The lattice parameters for the phases in different compositions of the composite are nearly equal [table – 1]; indicating that no any structural change has takes place in composites [8, 9]

Table 1: Data on lattice parameter, dielectric constant and ME output for the (x) $Ni_{0.6}Zn_{0.4}Fe_2O_4$ + (1-x) PZT ME composites.

Composition (X)	Lattice parameters (Å)			Curie temperature at 1kHz	
	Ferrite	Ferroelectric	c/a	Ferrite	Ferroelectric
0	-	a = 4.05 c = 4.08	1.00		400
0.15	a =8.34	a = 4.04 c = 4.06	1.01	490	400
0.30	a =8.33	a = 4.03 c = 4.08	1.00	490	390
0.45	a =8.35	a = 4.05 c = 4.08	1.00	495	385
1	a=8.35	-	-	495	

Dielectric Behavior

A. With Frequency

Variation of dielectric constant of composites as a function of frequency at room temperature is shown in Figure 2. The dielectric constant decreases with increase in frequency showing dispersion in a certain lower frequency range and remains constant at higher frequencies indicating the large dispersion in composition with large values of ε' in comparison with those having small values of ε'. This dispersion is explained with the help of Koop's two layer model [10]. The dielectric constant decreases with an increase in frequency, showing dispersion in certain lower frequency thereafter. All samples reveal dispersion due to Maxwell- Wagner type interfacial polarization, in agreement with Koop's phenomenological theory [11, 12].

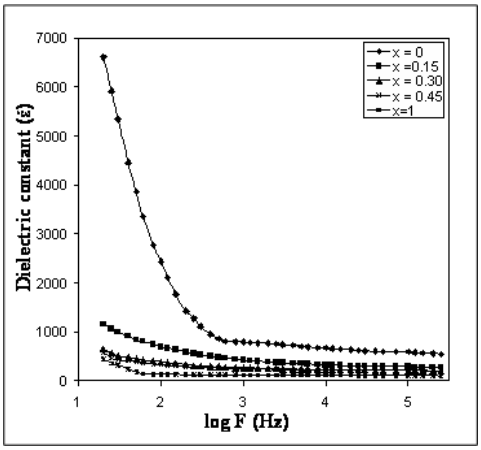

Figure 2: Variation of dielectric constant with frequency for (x) $Ni_{0.6}Zn_{0.4}Fe_2O_4$ + (1-x) $PbZr_{0.52}Ti_{0.48}O_3$ ME composites.

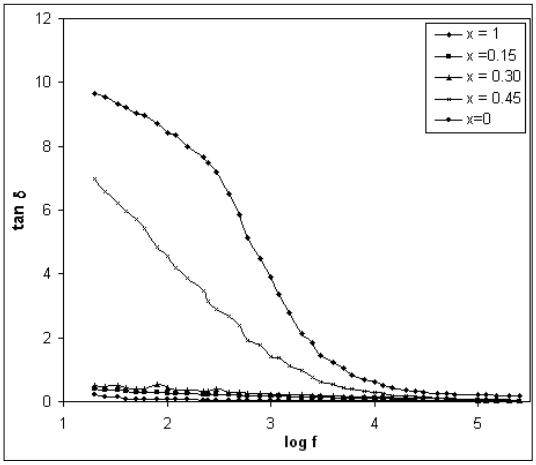

Figure 3: Variation of dielectric loss (tan δ) with frequency for (x) $Ni_{0.6}Zn_{0.4}Fe_2O_4$ + (1-x) $PbZr_{0.52}Ti_{0.48}O_3$ ME composites.

The high dielectric constant at lower frequencies is explained on the basis of space charge polarization due to inhomogeneous dielectric structure such as impurities, porosity and grain structures. It can also be attributed to dipoles resulting from the change in valence of cation, such as $Fe^{3+} \leftrightarrow Fe^{2+}$ in the ferrite lattice and space charge polarization. At higher frequencies the dielectric constant independent of frequency due to inability of electric dipoles to follow the alternating applied electric field [12].

In case of composite, the high value of the dielectric constant is ascribed to the fact that ferroelectric region is surrounded by non-ferroelectric (ferrite) regions. From the figure it can also be observed that the dielectric constant is decreased with increase in ferrite content. This is because of the fact that dielectric constant of ferrite is lower of than that of the ferroelectric phase.

The variation of loss tangent (tan δ) with frequency for all the composites shows a similar dispersion as that of dielectric constant with the frequency [13] as shown in Figure 3.

B. With Temperature

The variation of dielectric constant with temperature for the composite with X= 0.15, 0.30 and 0.45 are shown in Fig. 4 - 6 at our different fixed frequencies Viz. 1 kHz, 10 kHz, 100 kHz and 1 MHz.

The variation of dielectric constant with temperature for all the composition is normally an expected behavior that has been observed in most of the ferrites and ME composites [14, 15]. Basically the charge hopping is a thermally activated process that results in an increase of dielectric polarization proportional to temperature causing an increase in the dielectric constant. The dielectric constant is a combined effect of dipolar, electronic, ionic and interfacial polarizations contribute significantly to the dielectric constant and at higher frequency only electronic polarization becomes significant.

The change in dielectric behavior takes place on passing through the Curie temperature [16]. In present case two peaks are observed in variation. The first peak is observed near the curie temperature of ferroelectric phase and second near the curie temperature of ferrite phase. The transition temperatures in present composites viz. y = 0.15, 0.30 and 0.45 are 400, 390^0C and 385^0C for the ferroelectric and 490^0C, 490^0C and 495^0C for the ferrite phases respectively.

Figures. 4 to 6 show that the value of dielectric constant of ferrite phase is small as compared with the dielectric constant of ferroelectric phase. Hence decrease in dielectric constant of composites with ferrite content is attributed to the incorporation of non – ferroelectric (ferrite) phase in pure ferroelectric phase. As the content of ferrite increases, a decrease in value of dielectric constant is seen [Fig. 4 - 6]. Similar behavior by ferrites has been reported earlier [17, 18, and 19]. The increase in ferrite content results in a decrease in polarization efficiency that results in increased conductivity. This is because the ferrite material has small dielectric dipoles than the ferroelectric material [20]. Hence the magnetic ordering is responsible for dielectric changes with temperature [21].

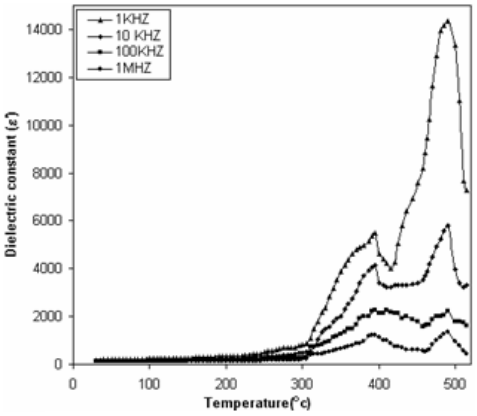

Figure 4: Variation of dielectric constant with temperature for 15% $Ni_{0.6}Zn_{0.4}Fe_2O_4$ + 85% $PbZr_{0.52}Ti_{0.48}O_3$ ME composites.

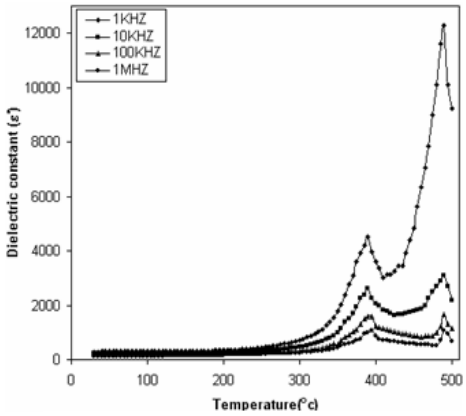

Figure 5: Variation of dielectric constant with temperature for 30% $Ni_{0.6}Zn_{0.4}Fe_2O_4$ + 70% $PbZr_{0.52}Ti_{0.48}O_3$ ME composites.

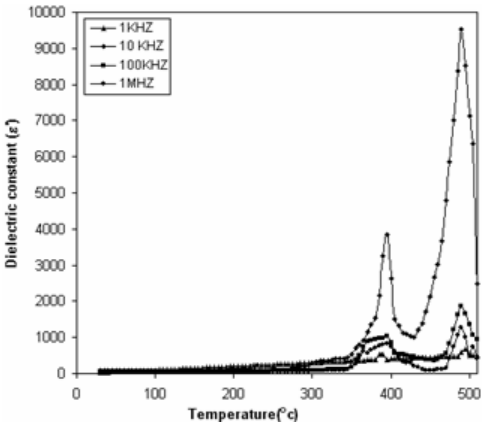

Figure 6: Variation of dielectric constant with temperature for 45% $Ni_{0.6}Zn_{0.4}Fe_2O_4$ + 55% $PbZr_{0.52}Ti_{0.48}O_3$ ME composites.

The transition temperatures of composites vary with variation of constituent phases [Table -1]. This is because; the electric field induced magnetic phase transition depends on the electric and magnetic interactions in the composites, which in turn depends on the mole ratio of the component phases. [17].

Ac Conductivity

The ac conductivity was determined at room temperature in the frequency range20 Hz to 1 MHz, to study the mechanism of conduction [Figer7].

The ac conductivity of the sample was calculated using the relation [22]-

$$\sigma_{ac} - \sigma_{dc} = \acute{\varepsilon}\, \varepsilon_o \omega \tan \delta \qquad (2)$$

Where ω is the angular frequency.

The conductivity is observed to increase with increase in frequency for all the composites under study. Linear variation of ac conductivity indicates that the conduction is due to small polarons in the composite [23].

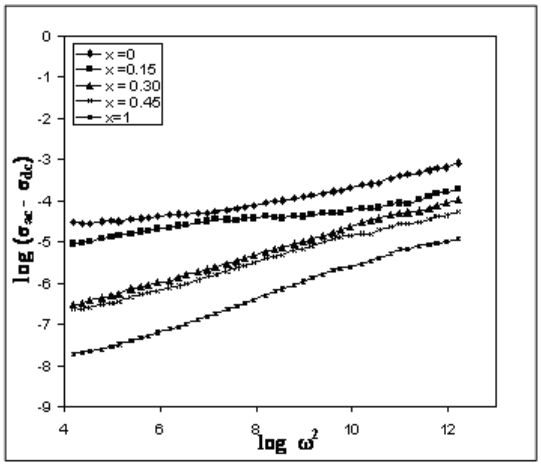

Figure 7: Variation of ac conductivity with frequency for (x) $Ni_{0.6}Zn_{0.4}Fe_2O_4$ +(1- x) $PbZr_{0.52}Ti_{0.48}O_3$ ME composites.

Conclusions

The ME composites with general formula (x) $Ni_{0.6}Zn_{0.4}Fe_2O_4$ + (1-x) $PbZr_{0.52}Ti_{0.48}O_3$ were prepared by the conventional double sintering ceramic method. The x-ray diffraction patterns of composite confirm the formation of cubic spinel structure for a ferrite phase and tetragonal perovskite structure for a ferroelectric phase respectively. The dielectric dispersion observed at lower frequencies is attributed to interfacial polarization and also heterogeneity in the samples. The variation of dielectric constant with temperature gives the broad maximum near the Curie temperature. The variation of AC conductivity with frequency has a linear nature suggesting that the conduction is due to small polaron hopping.

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