Dc electric conduction mechanisms and high frequency dielectric properties of different magnetoelectric composites

M A Ashmawy1, A A Sattar1, H M El-Sayed1, Mohamed M Rashad3

1 Physics Department, Faculty of Science, Ain Shams University, Abbassia, Cairo 11566, Egypt.
2 Basic Science Department, Modern Academy for Engineering and Technology, El Mokatam, Cairo, Egypt.
3 Department of Electronic and Magnetic Materials, CMRDI, Helwan, Egypt.

Abstract. Various dc conduction mechanisms and high frequency (1MHz up to 3 GHz) dielectric properties have been studied for the particulate and 0-3 core shell composites. X-ray diffraction has been used to identify the structural properties. Tetragonal and cubic structures for PZT and ferrite respectively were appeared either in the pure form or in composites form. The microstructures have been investigated by TEM and particle size distribution was calculated. The microstructure plays a significant role in the electric properties. Dc resistivity vs. temperature measurements were implemented by using ‘two probe’ method. The room temperature resistivity was large in core shell in comparison with composite due to the unique microstructure of the core shell that enhances the interfacial disability of motion of carriers and increasing the carriers hopping path. Moreover, dc electric conduction mechanisms for all investigated samples have been determined. Curie temperatures for ferrimagnetic and ferroelectric phases were the transition points between the conduction mechanisms. Curie temperature of ferrites remarkably increased in the C.S. and composite. Finally, Dielectric and ac resistivity measurements were measured at room temperature. The dielectric constant ($\varepsilon'$) was enlarged in the core shell rather composite while the tangent loss was reduced. These appreciable enhancements could be useful in the high frequency applications.

1. Introduction
Nickel, Cobalt and the mixed Ni-Co ferrites have been used extensively since few decades in the electrical and electronic industries. The structural, electrical, dielectric and magnetic properties of ferrites, in general, are sensitive to synthesizing technique. Accordingly, there may be unexpected properties that could be exploited in various applications [1-3].

On the other hand, Lead zirconate titanate PbZr0.52Ti0.48O3 (PZT), is a well known ferroelectric material. As it has an off center perovskite structure ‘tetragonal’ that displays a spontaneous polarization, it is also useful for piezoelectric, optoelectronic, pyroelectric applications as well as in non-volatile ferroelectric random access memories (FERAM) [4, 5].
Multiphase magnetoelectric multiferroics (ME) are considered as a composite between ferrimagnetic or ferromagnetic, and ferroelectric materials. They play important roles as multifunctional and smart materials and also they are the core of the magnetoelectric random access memory (MERAM). These materials’ phases could be added together by many ways to form various microstructures. The microstructure controls the magnetic, electrical and consequently the ME properties [6]. Therefore, studying of electrical and dielectric for various microstructure composites is essential for application.

Many authors discussed many properties of magnetoelectric composite (ferrite + PZT) in a certain microstructure for one type of ferrite. However, to the best of our knowledge no reports have been found to present a comparative study between two magnetoelectric with different microstructures. So in this work, we study the conduction mechanism and high frequency dielectric properties of six magnetoelectric composites with two different microstructures. Each composite contains one candidate of ferrite added to PbZr0.52Ti0.48O3 (PZT) to form both particulate composite (composite) and core shell (C.S.) composites. The ferrite candidates are (NiFe2O4 (NFT), CoFe2O4 (CFT) and Co0.1Ni0.9Fe2O4 (CNFT)). Hence, we formed three identical groups each contains one candidate of ferrite, PZT purely, ferrite+PZT composite and ferrite+PZT C.S. and each group was named according to the name of ferrite, such as CNFT group that contains CNFT, PZT, PZT+PZT composite and CNFT+PZT C.S. We found that all the three groups are similar in their structural, microstructural and electrical properties. So we will present only the electrical properties of CNFT group as an example.

2. Experimental techniques.

2.1. Synthesizing techniques

2.1.1. Co0.1Ni0.9Fe2O4 (CNFT) synthesizing.
The spinel ferrite of compositions (CoFe2O4) was prepared by sol-gel autocombustion method as previously reported [7]. Analytical grade of cobalt nitrate (Co(NO3)2.6H2O) and ferric nitrate (Fe(NO3)3.9H2O) were taken in stoichiometric proportion with citric acid and were dissolved in deionized water. This reaction yields the as prepared nanoferrite powders with relatively high hematite foreign phase. CFT powder was annealed at 600°C, for 2h with heating rate 4°C/min to get rid of the hematite phase. The obtained single phase powder was divided into three equal amounts. One part was used to study the ferrite alone and the others were used in synthesizing composite and C.S. Moreover, the part that was specified for ferrite was divided into two parts such that one part was pressed to form a tablet and the other was kept in a powder form. The powder and tablet were annealed at 600°C, for 2h with heating rate 4°C/min.

2.1.2. PbZr0.52Ti0.48O3 (PZT) synthesizing.
The tetragonal phase with composition PbZr0.52Ti0.48O3 (PZT) was synthesized by hydrothermal method to get monodisperse and low nanosize particles [8]. Zirconium (IV) oxynitrate hydrate and lead nitrate were mixed together in 20 ml distilled water and then poured in a 100 ml Teflon tube that is especially designed for autoclave reactor. Then Titanium isopropoxide was syringed in this solution without exposing to air and then stirred for 20 min. Potassium hydroxide KOH as a mineralizer solution was then added on the wall of the Teflon tube under gentle stirring to adjust the PH at 14 (extreme alkaline solution) such that the total volume in the Teflon tube was around 70 ml. Then the Teflon tube was putted in the hydrothermal autoclave reactor and firmly closed. The reactor was annealed at 200°C for 120 min. Then, the precipitates were filtered, washed with distilled water to remove the soluble nitrates and dried in air at 110°C. The obtained powder was single phase and did not need to any further heat treatment. The obtained powder was divided into two parts such that one part was pressed to form a tablet and the other was kept in a powder form. The powder and tablet were annealed at 600°C, for 2h with heating rate 4°C/min.
2.1.3 Particulate Composites (Composite) synthesizing.

Single phase of PZT and CFT powders were milled together for two hours by using Agate Mortar Grinder Mill RM100. The ratio of mixing between the ferrite and ferroelectric was kept to be 40% ferrite: 60% PZT. The obtained powder was divided into two parts such that one part was pressed to form a tablet and the other was kept in a powder form. The powder and tablet were annealed at 600°C, for 2h with heating rate 4°C/min.

2.1.4. (0-3) Core shell Composites (C.S.) synthesizing.

The preparation of C.S. will be implemented in two steps: First step is concerned with CFT ‘core’ surface modification. The single phase CFT was mixed with Oleic acid in presence of NaOH [9]. The mixture was sonicated, washed and filtered to get surface modified ferrites. Second step is about the PZT ‘shell’ formation. Glacial acetic acid was added to the mixture of citric acid + Pb Nitrate + Zr – Oxy Nitrate hydrate. The solution was heated under stirring at 80°C and then Ti-iso propoxide was syringed in the solution. The modified ferrite was added to the previous solution and then ethylene glycol was added to promote the gel formation. The solution was kept at 80°C with continuous stirring over night until the powder dried completely. The obtained powder was divided into two parts such that one part was pressed to form a tablet and the other was kept in a powder form. The tablet was formed by using an appropriate amount of water as a binder and was pressed for 15 minutes under static pressure of 250 MPa at room temperature. The powder and tablet were annealed at 600°C, for 2h with heating rate 4°C/min. [10]

2.2 Characterizations and Measurements..

XRD patterns were recorded by Malvern Panalytical device with Cu-Kα radiation. The d_{hkl}-spacing for each peak was recorded automatically and then the lattice parameter (a) was calculated by using the method of extrapolating function of Nilson-Riley. Size-Strain analysis has been done by using XRD built in program called “HIGH SCORE PLUS” program. TEM images were captured and selected area of electron diffraction (SAED) was chosen by JEOL 1200ex2 transmission electron microscope. Dc resistivity vs. temperature was performed by using ‘two probe’ method while the resistance values were recorded by Keithley electrometer 6514. High frequency (1MHz to 3GHz) dielectric and ac resistivity measurements were measured by using Agilent E4991A RF Impedance/Material Analyzer at room temperature.

3. Results and discussion.

3.1. Structural and Microstructural studies

XRD patterns for CNFT group are shown in Figure 1. CNFT and PZT show single phase patterns with cubic (Fd3m) and tetragonal (P4mm) structures respectively. Composite and C.S. show double phase of ferrite and PZT together. Insignificant foreign peaks (with total intensities less than 3%) appeared at 27° in C.S. and 33° in composite and C.S. and were assigned to Pb3O4 and α-Fe2O3 respectively.

The lattice parameter of the CNFT in pure ‘single’ form, composite and C.S. didn’t show any remarkable change. On one hand, the crystallite size of CNFT in composite was the largest one because the formed shell of PZT prevents the crystal growth of the ferrite. On the other hand, the microstrain of CNFT in C.S. had the largest value among other candidates because of the distinct microstructure of the C.S. that expressed on good interface interaction. Knowing, the microstrain will play a significant role in the dielectric properties.
Figure 1. XRD patterns for CNFT group candidates.

Figure 2 (a-d) show TEM images for each candidate in the CNFT group. Histograms that express the particle size distribution for these candidates were performed and mean particle sizes were calculated.

Figure 2. TEM images for (a) CNFT, (b) PZT, (c) CNFT Core shell (C.S.) and (d) CNFT Composite

The particle size of CNFT, PZT, CNFT in C.S., PZT in C.S., CNFT in composite and PZT in composite were 25nm, 6nm, 33nm, 11nm, 50nm, 15nm respectively. Also, the crystallite sizes calculated from XRD were typical to the average particle size deduced from TEM. As shown in Figure 2 (c) and (d), the microstructures of C.S. and composite are completely different which affect on the structural and electrical properties.
3.2. Dc conduction mechanisms.

Figure 3 shows the relation between ln\(\rho_{dc}\) and 1000/T. It is obvious that the curve of CNFT could be divided into three regions while PZT, composite and C.S. could be divided into four regions. This means that there are different conduction mechanisms. Generally, the conduction mechanisms are governed by two main factors, either the mobilities (\(\mu_e, \mu_h\)) or the charge carrier concentrations (\(n_e, n_h\)). The conductivity \(\sigma\) is calculated according to the relation

\[
\sigma = n_e e \mu_e + n_h h \mu_h
\]  

where e and h refer to electrons and holes.

![Figure 3. \(\rho_{dc}\) vs. T for CNFT group. I, II, III, IV refer to different regions of conduction mechanisms.](image_url)

In ferrites, the change in conductivity is mostly due to change in mobility with temperature and rarely due to change in charge carrier concentration. This is the characteristic of the hopping mechanism. However, in lead zirconate titanate PZT the conduction mechanism is mainly due to change in carrier concentrations with temperature which is called the band conduction mechanism. Table 1 contains ferrimagnetic \(T_{c,FMag.}\) and ferroelectric \(T_{c,F.Elec.}\) Curie temperatures determined through this experiment compared with the results of ferrimagnetic Curie temperature measured through permeability experiment. Also it presents room temperature resistivity \(\rho_{dc,R.T.}\) and all the values of activation energies at different regions for CNFT group.

**Table 1.** Ferrimagnetic and ferroelectric Curie temperatures, room temperature resistivity \(\rho_{dc,R.T.}\), and activation energies for CNFT groups.

| \(T_{c,FMag.}\) (°C) | \(T_{c,F.Elec.}\) (°C) | \(\rho_{dc,R.T.}\) (Ω.cm) | \(E_I\) (eV) | \(E_{II}\) (eV) | \(E_{III}\) (eV) | \(E_{IV}\) (eV) |
|-----------------|-------------------|------------------|---------|---------|---------|---------|
|                  |                   |                  |         |         |         |         |
For CNFT, the conduction in the first (I) region is due to extrinsic impurity conduction mechanism. It is evolved due to the probability of presence of small percentage of Fe$^{2+}$ which is formed on account of Fe$^{3+}$ to compensate the oxygen loss during the thermal treatment. The ions of Fe$^{2+}$ act as donor centers. The activation energy of this mechanism lies in the range between (0.01-0.25 eV) which is compatible with value in table 1[11]. The activation energy increased at region (II) which ends at Curie temperature of CNFT. According to the values of the activation energy in this region (0.57 eV) the mechanism in this region could be attributed to the intrinsic conduction mechanism. In this mechanism the mobility of the carriers increases with temperature, leading to a decrease of the resistivity [11]. Curie temperature is the temperature at which the material changes from ferrimagnetic to paramagnetic state. This corresponds to transition temperature from region (II) to region (III) according to the results obtained from magnetic measurement, as shown in table1. Additionally, the presence of short range order of the paramagnetic phase after $T_c$ F.Mag. may be the reason for decreasing the activation energy at region (III) [12].

Despite PZT is a highly insulating material, the first region of the conduction profile is metallic. Such a behavior was previously observed [13]. It may be due to the appearance of a new source of conductivity among the nano particles that is called ‘tunneling current’. It is a consequence of the large surface area of nano size particles [15]. Also, the presence of small amount of impurity, Pb$_3$O$_4$, leads to the extrinsic conduction mechanism. In this case localized states between the valence band (V.B.) and conduction band (C.B.) of PZT are incorporated. These localized states participate in decreasing the resistivity of the material as well as the activation energy, as reported in table 1 [14]. The transition to region (II) may be attributed to the competition between the factors in region (I) and the main mechanism of PZT in region (III). The main mechanism of the PZT which is the changing of the hole concentration (or p-conduction). The p-conduction arises from the A-site vacancy in the structure ABO$_3$ that produced due to the volatility of Pb during thermal treatment. Consequently, the A-site vacancy will act as acceptor centers [4]. Thus, it is expected to get high activation energy (0.84 eV) in region (III). After the Curie temperature $T_c$ F.Elec. of ferroelectric is reached which is close to the value reported before in [4], region (IV) begins. Thereafter, the activation energy increased apparently due to the presence of high resistive blocking layer at the domain boundaries, inside the particles.

The conduction mechanism of C.S. and composite samples will be controlled by either competition or reinforcement among the aforementioned mechanisms in CNFT and PZT. The competitions between the mechanisms arose in activation energies regions (I) and (IV). On the other hand, the reinforcements between the mechanisms revealed in activation energies in regions (II) and (III), such that the small percentage of α-Fe$_2$O$_3$ appeared in CNFT in C.S. and composite increases the resistivity and make the activation energy larger than the pure CNFT and PZT in regions (II) and (III).

Room temperature resistivity of PZT was the largest among other candidates then C.S, then composite and the lowest was CNFT. The high value of PZT is a natural behavior [4]. While, the C.S. resistivity was the largest among the other candidates due to the unique microstructure of the C.S., as shown in figure 2.

| Material     | from μ Exp. | from dc Exp. | $E_a$ (eV) | $\rho_0$ ($\Omega\cdot m$) |
|--------------|-------------|--------------|-----------|--------------------------|
| PZT          | ----        | 390          | 2.88 x 10^9 | -0.35 0.17 0.84 1.46     |
| CNFT         | 568         | 567          | 1.59 x 10^9 | 0.05 0.57 0.32 ----      |
| CNFT C.S.    | 605         | 600 400      | 2.66 x 10^9 | -0.07 0.74 1.61 0.29     |
| CNFT Composite| 600 597    | 398          | 1.91 x 10^9 | -0.07 0.67 1.69 0.32     |
(c). The microstructure promotes not only the interfacial disability of motion of carriers among the PZT particles but also increasing the hopping path of carriers in CNFT particles.

3.3. High frequency dielectric and ac resistivity properties

The variation of dielectric constants and ac resistivity at high frequency (1MHz up to 3GHz) of CNFT group is shown in figure 4 (a) and (b). The figure 4 (a) reveals that there are two relaxations and losses for PZT and CNFT, while there are two relaxations and losses for C.S. and composite. The intensity of the main relaxation of C.S. is larger than composite than CNFT than PZT. The main (large) relaxation of $\varepsilon'$ in any candidate belongs to dipolar relaxation [16]. The second relaxation that appeared in PZT and CNFT may be attributed to the homogeneous interfacial polarization while in C.S. and composite they cancel each other and vanished [17].

![Figure 4](image)

Figure 4. (a) $\varepsilon'$ and $\varepsilon''$ (b) $\varepsilon''$ and $\rho_{ac}$ for CNFT group. Red color for C.S., blue for composite and black for CFT. Hint in (b), Offsets of zero have been done to CNFT and composite by 100, 50 in $\varepsilon''$ and by 1000, 500 in $\rho_{ac}$ respectively.

It was expected that the relaxation frequencies of C.S. and composite should be in between PZT and CNFT relaxation frequencies. However, the relaxation frequency of C.S. is close to the PZT, while the composite it is close to CNFT. This may be due to the effect of microstructure such that in C.S. the shell material is PZT, as shown in Figure 2 (c) that make the PZT is the first and final acting material with ac electric field. Contrary with the microstructure of composite, as shown in Figure 2 (d), at which the first and final acting material with ac electric field may be PZT or CNFT, so it is noticeably away from relaxation frequency of PZT and more close to the relaxation of CNFT. The intensity of the C.S. first relaxation is larger than any candidate because the large mutual microstrain and strong heterogeneous interfacial interaction between PZT and CNFT permit to increase the amount of dipoles. So, because the large value of dipolar polarization than any candidate, the relaxation is larger than any candidate as well.

Figure 4 (b) shows ac resistivity and imaginary part of permittivity as a function of frequency. The reverse behavior of $\varepsilon''$ with $\rho_{ac}$ is expected that shows abrupt increase in the resistivity due to small decrease in $\varepsilon''$ that follow the relation [18]. This property is promising in high frequency applications.
Dielectric constants and ac resistivity at 1MHz are presented in Figure 5 for CNFT group. On one hand as is shown in figure 5, the $\varepsilon'$ and $\varepsilon''$ for C.S. and composite are larger than CNFT and PZT. This is attributed to the increased amount of dipoles after coating PZT shell on the surface of CNFT. It is known that Co$^{2+}$, Ni$^{2+}$ and Fe$^{3+}$ cations at their respective positions form the electric dipoles with the surrounding O$^{2-}$ ions, contributing to complex permittivity of CNFT [19], so the coating of PZT means that more electric dipoles arise. Therefore the orientation polarization process of electric dipoles gets enhanced and subsequently $\varepsilon'$ and $\varepsilon''$ values get increased. In C.S. the $\varepsilon'$ is larger than composite due to the previous reason particularly which is related to the microstructure. In addition to the aforementioned reason, the electric dipole moment could be enhanced also due to the probability of presence of Fe$^{2+}$. Compared with Ni$^{2+}$ and Co$^{3+}$ ions; Fe$^{2+}$ ions are more prone to polarization [20]. Furthermore, Fe$^{2+}$ ions enhance the electronic hopping between Fe$^{2+}$ and Fe$^{3+}$ in B-site of CNFT and intensify the assembling of electrons at the interface, leading to an enhanced interfacial polarization [21]. Therefore, the $\varepsilon'$ and $\varepsilon''$ values should be larger in C.S. than composite and than any other candidate.

On the other hand, the tangent loss ($\tan \delta$) and resistivity of C.S is smaller than composite and both of them are relatively small. This property makes C.S. is promising material for application at high frequency such that ($\varepsilon'$=181 and $\tan \delta$= 0.0431, $\rho_{ac}$=2.3k$\Omega$) at 1MHz and all these results are due to the unique microstructure of the C.S. over the other candidates.

![Figure 5. Dielectric constants and ac resistivity at 1MHz.](image)

4. Conclusion

0-3 Core shell composites (C.S.) and particulate composites (composite) were successfully synthesized by sol-gel and standard mixing methods respectively. The composites generally contained 60% PZT and 40% CNFT, CFT and NFT. The results were only presented for CNFT, PZT, CNFT+PZT C.S. and CNFT+PZT composite as an example and called CNFT group. CNFT was successfully synthesized by sol-gel technique to be used in composite and acted as seeds in C.S. PZT was synthesized by hydrothermal technique to be used in particulate composite only and was synthesized fresh in C.S. over the CNFT seeds. XRD was used to identify the crystal structure and to calculate the values of microstrain and crystallite size of the samples. The microstrain of PZT and ferrite in C.S. was larger than its correspondence in composite. The size of ferrite lowered in C.S. due to the effect of shielding of PZT. TEM identified the microstructure directly and revealed the unique microstructure of the C.S. sample among other samples. The dc conduction mechanisms were investigated for all samples. The metallic behavior of PZT was noted at the first region due to the effect of nanosize while p-conduction band
mechanism was noted for the other regions. On the other hand, large polaron mechanism was the main mechanism of the ferrite. The conduction mechanisms of composite and core shell samples showed a reinforcements and competition between the mechanisms of PZT and CNFT. There were not a noticeable variation of the values of activation energies of composites and C.S. Core shell sample had the highest room temperature resistivity after PZT sample because of its unique microstructure. The high frequency dielectric measurements were conducted for all samples. Two relaxations appeared for CNFT and PZT, while only one relaxation arose for composite and C.S. The main relaxation in all samples was assigned for dipolar relaxation and the other small relaxation for CNFT and PZT was for homogeneous interfacial polarization. Core shell sample got the highest value of the relaxation because its unique microstructure that enhances further dipoles at the interfaces. High dielectric electric constant, small tangent loss and small resistivity at 1MHz were reported for C.S. that made this material promising for high frequency applications.

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