**Structural, Magnetic, and Transport Properties of Polymer-Nano ferrite Composites**

Thesis Submitted for

Ph. D. Degree in Science,

Solis State Physics (Materials Science)

By

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Dedication

To My Great God

Then

To Every One Who Helped Me:

To

My Supervisors......................,

My Friends .........................,

And

My Family.........................
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Abstract
Abstract

In this work, a series of \( (x) \text{BaTiO}_3 / (1-x) \text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4 \) nanocomposite samples were prepared using citrate autocombustion and the samples were classified into three groups.

In first group: A series of \( (x) \text{BaTiO}_3 / (1-x) \text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4 ; 0.0 \leq x \leq 1.0 \) were prepared by double sintering technique and citrate autocombustion method in comparison study due to different characterization analysis. The comparison reveals that from X-ray diffraction; all the samples from the two methods formed in single phase in both; cubic spinel structure \( \text{NiZnFe}_2\text{O}_4 \) (NZF) ferrite and perovskite tetragonal structure \( \text{BaTiO}_3 \) (BTO). The crystallite size (L) of the two phases was obtained from ceramic method of NZF and BTO is 68nm and 119nm respectively. While from citrate autocombustion method, the crystallite size (L) is around 30 nm and 47nm. The values of lattice constant and d- spacing, and Miller indices were calculated and reported. It was found that the ratio of BTO (x=0.5) is a critical concentration. From FT- IR spectra of the samples, the spectral frequencies of the vibrational bands of different methods are reported. The IR spectral analysis of the two group's samples reveals the formation of spinel and perovskite structure. The scanning electron microscopy (SEM) and the hysteresis measurements were carried out to determine saturation magnetization (\( M_s \)), remnant magnetization (\( M_r \)) and coercivity (\( H_c \)) of the samples. The variation of the magnetic susceptibility (\( \chi_M \)) behavior with temperature as a function of field intensity was also studied, where the magnetic constants were calculated and reported. The variation of dielectric constant (\( \varepsilon' \)), dielectric loss factor (\( \varepsilon'' \)) and the \( ac \) electrical conductivity (\( \sigma_{ac} \)) of \( 0.5\text{BaTiO}_3 / 0.5\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4 \) magnetoelectric nanocomposite has been investigated as a function of both frequency and temperature. Thermal hysteresis (first-order transition) was occurred when the experimental data were collected during heating (300-830 K) and cooling (830-300 K) processes. The exact transition temperature and the amount of thermal hysteresis are dependent on the applied \( ac \) electric field. Therefore the area of the thermal hysteresis loop in between the two branches for the nanocomposite is a frequency dependent; it
Abstract

decreases as the frequency increases. The delay (lagging) time between heating and cooling processes was estimated from the hysteresis loop area versus frequency. The dielectric conduction mechanisms in the investigated nanocomposite were explained according to different models. The observed values of Seebeck coefficient indicate that the conduction is due to electron hopping mechanism which is agreement with that obtained from dielectric measurements. This study enhances the use of multiferroic system in the memory applications, this is a clear application on the so called dynamic random access memories (DRAM) which are being used in today’s computers. This result gives information about how our work is applicable in high technology.

Ultrafine BaTiO$_3$ nanorods were synthesized by improved citrate autocombustion technique using tetrabutyl titanate \{Ti (OC$_4$H$_9$)$_4$\}. With the help of X-ray diffraction (XRD), scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX), transmission electron microscopy (TEM), atomic force microscopy (AFM) and Fourier transformation infrared spectroscopy (FT-IR) have been used to characterize the prepared sample. The results indicated that, the structure is of tetragonal phase in nature with average crystallite size of 47 nm. SEM image gives a cauliflower-like morphology of the agglomerated nanorods. The stoichiometry of the chemical composition of the BaTiO$_3$ ceramic was confirmed by EDX. TEM micrograph exhibits that BaTiO$_3$ nanoparticles have rod-like shape with average length 120 nm and diameter of 43 nm. AFM was used to investigate the surface topography and its roughness. The topography image in 3D shows that the particles have almost rod shape with average particle size of 116 nm which agree well with TEM analyses.

In group two, in another compassion, multiferroic hybrid nanocomposites based on different polymers as a matrix for the prepared magnetoelectric biferroic nanocomposite system 0.5BaTiO$_3$ / 0.5Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ that has been prepared by citrate autocombustion method. Four different polymers namely polyaniline (PANI), polyvinyl acetate (PVAc), Polyvinyl pyrrolidone (PVP), and polyethylene glycol (PEG), with fixed ration (1:1) with respect to the dispersed magnetoelectric nanocomposite.
The influences of polymer type with respect to the electrical and ferromagnetic properties of NZF/BTO nanocomposites were investigated by M–H loop measurements and ac. electrical conductivity. Their structural characterization is also discussed based on Fourier transform infrared (FTIR) and scanning electron microscopy (SEM) morphology.

In group three, the nanocomposites materials with formula (1-y) [0.5BaTiO₃/0.5Ni₀.₅Zn₀.₅Fe₂O₄] / y (PEG); 0.0 ≤ y ≤ 1.0, have been prepared at room temperature by weight mixing and cold pressing. Physical properties of nanocomposite materials consisting different ratios of polyethylene glycol were investigated. With the variation of y content, typical magnetic hysteresis loops of nanocomposites have been observed in the nanocomposites at room temperature. When PEG content increase, the saturation magnetization decrease. Meanwhile, the coercive force tends to stable. Additionally, the dielectric constant ($\varepsilon'$) and dielectric loss factor ($\varepsilon''$) of nanocomposites materials shift toward higher frequency. The value of $\varepsilon'$ decreased with increasing frequency, which indicates that the major contribution to the polarization comes from orientation polarization.

Key words: Multiferroic, Nanocomposites, Ferrite, Polymer.
Chapter one
Chapter One

Literature Survey and Theoretical Background

The main focus in this work is to tailor the properties of the nanostructure multiferroic composites. Therefore, construction of composites that have ferroelectric and ferromagnetic properties should be significant for technical applications and fundamental theoretical study.

1.A. Literature Survey:

1.A.1. $\text{BaTiO}_3 / \text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ multiferroic magnetoelectric (ME) nanocomposites: Historical perspective, status, and future directions:

This review of mostly recent activities begins with a brief summary of the historical perspective of $\text{BaTiO}_3 / \text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ (BTO/NZF) multiferroic ME nanocomposites [1]. In such composites the ME effect is generated as a product property of a magnetostrictive and a piezoelectric substance. An electric polarization is induced by a weak $ac$ magnetic field oscillating in the presence of $dc$ bias field, and/or a magnetization polarization appears upon applying an electric field. The coupling interaction between nanosized ferroelectric and magnetic oxides is also responsible for the ME effect in the nanostructures as was the case in those bulk composites. The availability of high-quality nanocomposites makes it easier to tailor their properties through epitaxial strain, atomic-level engineering of chemistry, and interfacial coupling.

There are different researches dealing with $\text{BaTiO}_3 / \text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ nanocomposite due to its potential applications [2-13], among them:
M.A. Ahmed et al. (2012) [2], investigated a series of (x) BaTiO$_3$ / (1-x) Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ nanocomposites; x=0.0, 0.4, 0.5, 0.7 and 1.0 in wt.. These nanocomposites were synthesized by the classical solid state reaction between (BTO) and (NZF). The formation of the nanocrystalline composite was confirmed by X-ray diffraction and scanning electron microscopy (SEM). The values of the lattice parameters and average crystallite size were calculated from the obtained measurements. The hysteresis measurements were carried out to determine saturation magnetization ($M_s$), remanence magnetization ($M_r$) and coercivity ($H_c$) of the samples. The variation of the magnetic susceptibility ($\chi_M$) behavior with temperature as a function of field intensity was also studied and the magnetic constants were calculated and reported. The variation of the physical properties was correlated to the ratio of (x) BaTiO$_3$ / (1-x) Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$. Critical ratio was obtained at which the prepared nanocomposites become more applicable. They found that, The values of magnetization parameters, $M_s$, $M_r$, $H_c$, and $n_B$ decreases with increasing piezoelectric (PE) content in the composites, expect at $x = 0.5$, which gives the highest values for all parameters. This concentration is considered as a critical and optimum concentration in their composites. However, the optimized ratio of the composite is useful for technological applications such as magnetic probes, thermisters, transducers, etc.

M.A. Ahmed et al. (2012) [3] investigated the electrical properties of (x) BaTiO$_3$ / (1-x) Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$. The effects of frequency, composition and temperature on the ac and dc electrical conductivity were studied. The variation of dielectric constant ($\varepsilon'$) in the frequency range 100 kHz to 5 MHz at different temperatures was investigated. The conduction phenomenon was explained on the basis of electron hopping model where the value of ($\varepsilon'$) increases drastically with increasing BaTiO$_3$ content in the composite. The observed values of Seebeck coefficient indicate that the conduction is due to electron hopping mechanism which is agreement with that obtained from dielectric measurements. They concluded that, Interface effects play important roles determining the dielectric properties at low frequencies. The variation of dielectric constant is explained in terms of electron exchange between Fe$^{2+}$ and Fe$^{3+}$ suggesting that the polarization in composites is
similar to conduction process in ferrites. The dielectric behavior of composites shows normal as well as diffuse phase transition, which was explained in terms of heterogeneity of the samples and ordering of micro-regions of spontaneous polarization. The variation of Seebeck coefficient with temperature shows that both the n-type and p-type charge carriers except at $x=0$, n-type is predominant and is dependent on temperature, and composites with such composition may be useful for technological applications such as thermistor and transducers as well as electric current measurement.

M.A. Ahmed et al. (2012) [4] prepared the magnetoelectric biferroic nanocomposite with composition $0.5\text{BaTiO}_3 / 0.5\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ by ceramic technique in order to study the electrical hysteresis behavior of these nanocomposites. They characterize their nanocomposite by XRD, SEM and FTIR. The variation of dielectric constant ($\varepsilon'$), dielectric loss factor ($\varepsilon''$) and the ac conductivity ($\sigma_{ac}$) of $0.5\text{BaTiO}_3 / 0.5\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ was investigated as a function of frequency and temperature. Thermal hysteresis (first-order transition) was obtained from the heating (300 - 830 K) and cooling runs (830 - 300 K). They found that, the exact transition temperature and the amount area of the thermal hysteresis depend on applied ac electric field. They estimated the delay (lagging) time between heating and cooling processes from the hysteresis loop area versus frequency. They explained the conduction mechanism in the investigated samples according to different models. They introduced their nanocomposite system in memory applications or information storage devices.

M.A. Ahmed et al. (2012) [5] compared the synthesising of magnetoelectric biferroic composite due to the composition $0.5\text{BaTiO}_3 / 0.5\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ by dry and wet methods. The results indicated that, the biferroic crystallite size produced from wet (citrate) method was less than that obtained from the dry (double sintering) one. The difference in the crystallite size obtained from each route plays a vital role in determining the biferroic functional properties. The structural, magnetic and electrical characterizations of the investigated biferroics are reported. The formation of nanosized composite with two separate phases was confirmed by X-ray diffraction, scanning electron microscopy (SEM). The variation of dielectric constant
(\varepsilon'), dielectric loss factor (\varepsilon'') and the \textit{ac} electrical conductivity (\sigma_{ac}) of 0.5Ni_{0.5}Zn_{0.5}Fe_{2}O_{4} - 0.5BaTiO_{3} magnetoelectric nanocomposite is investigated as a function of frequency and temperature. The dielectric conduction mechanisms in the investigated composites are explained according to different models.

B. K. Bammannavar \textit{et al.} (2009) [6,7] prepared (ME) composites with the composition \((x)\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_{2}\text{O}_{4}+(1-x)\text{Ba}_{0.8}\text{Pb}_{0.2}\text{Zr}_{0.8}\text{Ti}_{0.2}\text{O}_{3}\) (BPZT-barium lead zirconate titanate), in which \(x\) varies as 0.0, 0.15, 0.30, 0.45, and 1.0 in molar ratio by the conventional double sintering ceramic technique. The presence of two phases was confirmed by X-ray diffraction analysis. The DC resistivity was measured as a function of temperature, and the \textit{ac} electrical conductivity (\sigma_{ac}) as a function of frequency (100 Hz–1 MHz). The results revealed that the conduction mechanism in these composites is due to small polarons. The relative dielectric constant with variation of frequency and temperature at four different frequencies was studied. The hysteresis behavior was studied to understand the magnetic properties such as saturation magnetization (Ms) and magnetic moment (\(\mu\) B). The static magneto electric voltage coefficient (dE/dH)H was measured as a function of applied dc magnetic field. The variation of the ME response was explained in terms of the ferrite content, the resistivity of the composites, and the intensity of the magnetic field. The maximum ME conversion factor was observed for the composite with 30% ferrite + 70% ferroelectric. They concluded that, X-ray diffraction pattern of the composites confirms the formation of a cubic spinel structure for the ferrite phase and a tetragonal perovskite structure for the ferroelectric phase, respectively. The number of ferrite peaks increases with increasing ferrite content in the composites. The temperature dependent variation of the resistivity is explained in terms of electron exchange between \(\text{Fe}^{3+}\) and \(\text{Fe}^{2+}\). The dielectric dispersion at lower frequencies is due to interfacial polarization and also heterogeneity in the samples. The variation of the dielectric constant with temperature gives the broad maximum near the Curie temperature and also the dielectric loss tangent increases with increasing temperature.
A. R. Iordan et al. (2009) [8] studied the magnetic properties related to the microstructures in the 0.5BaTiO$_3$–0.5Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ magneto-electric composites. The di-phase ceramics were prepared by two methods: (i) mixing powders of BaTiO$_3$ and Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ and (ii) by coprecipitation of Fe, Ni and Zn salts in solutions containing BaTiO$_3$ powders. Homogeneous microstructures, higher density and better mixing of the two phases were obtained by the second method, giving rise to higher magnetic moments. The magnetic properties in such composites result as determined both by the ferrite concentration and properties and by the degree of connectivity of the two phases. They found that, the microstructural differences lead to changes of the magnetic properties, which result as determined both by the ferrite concentration and properties, and by the degree of connectivity of the two phases.

R. S. Devan et al. (2009) [9] formed (Ni–Co–Cu) ferrite/BTO composites. The individual phases and their composites having the general formula (x)BaTiO$_3$ + (1-x)Ni$_{0.93}$Co$_{0.02}$Cu$_{0.05}$Fe$_2$O$_4$ were prepared by double sintering ceramic technique. The BTO was presintered at 900°C and Ni$_{0.93}$Co$_{0.02}$Cu$_{0.05}$Fe$_2$O$_4$ was presintered at 800°C for 10 h. Milling for 3-4 h after mixing 85 mol%, 70 mol% and 55 mol% ferroelectric phase with 15 mol%, 30 mol% and 45 mol% ferrite phase, respectively and pressed into pellets. Finally sintered at 1150°C for 12 h. The ferrite phase shows the cubic spinel structure and ferroelectric phase crystallizes into tetragonal perovskite structure which is evidenced from the splitting of peaks. Absence of unidentified peak confirms no chemical reaction has taken place during the final sintering. The dielectric constant increases with temperature up to Curie temperature ($T_c$) and then decreases, which is normally expected behavior in most of the ferrites and ME composites [1]. The dielectric constant reduced with increase in ferrite content.

L. Mitoseriu et al. (2007) [10] studied the magnetic properties related to the microstructures in the 0.5BaTiO$_3$–0.5Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ magneto-electric composites. The di-phase ceramics were prepared by two methods: (i) mixing powders of BaTiO$_3$ and Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ and (ii) by coprecipitation of Fe, Ni and Zn salts in solutions containing BaTiO$_3$ powders. Homogeneous microstructures, higher density and better mixing of the two phases were obtained by the second method, giving rise to
higher magnetic moments. The magnetic properties in such composites result as determined both by the ferrite concentration and properties and by the degree of connectivity of the two phases. They found that, the microstructural differences lead to changes of the magnetic properties. Important differences in the dielectric relaxation and conduction mechanisms were found as result of the microstructural difference. Moreover xtrinsic contributions play important roles in modifying the electric properties in both ceramics, causing space charge effect, Maxwell–Wagner relaxations and hopping conductivity, mainly due to the ferrite low resistivity phase. The conductivity and dielectric modulus spectra analysis allowed identifying different polaron contributions associated with the microstructural differences.

R.S. Devan et al. (2007) [11] prepared particulate composites of ferrite and ferroelectric phases with the general formula (x) BaTiO$_3$ / (1−x) Ni$_{0.92}$Co$_{0.05}$Cu$_{0.05}$Fe$_2$O$_4$ (where x = 0.85, 0.70 and 0.55) by conventional double-sintering ceramic method. The presence of constituent phases was confirmed by XRD technique. The average grain size was determined by using scanning electron micrographs. The variation of dielectric constant and tanδ with frequency in the range 20 Hz–1MHz was studied. The variation of loss tangent (tanδ) and dielectric constant with temperature at different frequencies of 1 kHz, 10 kHz, 100 kHz and 1MHz was also studied. The saturation magnetization (M$_s$) and magnetic moment (nB in Bohr magnetons) are reported for all composites. The static magnetoelectric (ME) voltage coefficient was measured as a function of intensity of applied DC magnetic field. The changes were observed in dielectric properties as well as in ME output with variation in molar fraction of constituent phases. The results indicated that, a maximum ME conversion factor was observed for the composites with 70% BTO+30% NCoCuFe$_2$O$_4$. The present ME composites may be useful in preparing devices such as magnetic sensors and cables, etc.

A. Testino (2006) [12] investigated the (x)BaTiO$_3$–(1−x)Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ composites with x = 0.5, 0.6 and 0.7 according two different procedures: (i) direct mixing powders of perovskite BaTiO$_3$ and spinel Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ which prepared by solid state and (ii) by coprecipitating Fe$_{III}$–Ni$_{II}$–Zn$_{II}$ nitric salts in a NaOH solution in which the BaTiO$_3$ powders were previously dispersed. They succeeded to have the
optimum processing parameters for good homogeneity, densification and for a reduction of the chemical reactions at the interfaces ferroelectric-ferrite. They proved that there are a temperature and composition-dependent magnetic order in all the composites, with a dilution effect of the magnetization due to the presence of the non-ferromagnetic phase. Furthermore they identify a diffuse ferroelectric–paraelectric transition due to the BaTiO$_3$ phase by the temperature-dependence of the permittivity and losses. In their composites, the interfaces play important roles in the dielectric properties, causing space charge effects and Maxwell–Wagner relaxation, particularly at low frequencies and high temperatures.

In general there are many researches deal with magnetoelectric (ME) nanocomposites; among them:

K. Uchino (2000) [13] formed 25% Co-Mn ferrite (CMFO) and 75% Ba-Zr Titnate(BZT) ferroelectric multiferroic composite. The phase of CMFO is synthesized by citrate autocombustion. AR grade BaCO$_3$, ZrO$_2$ and TiO$_2$ were milled for 2–3 h and pre-sintered at 1000°C for 10 h to synthesize BaZr$_{0.08}$Ti$_{0.92}$O$_3$ phase. The pellets were finally sintered at 1250°C for 10 h with heating rate 5°C/min. XRD shows all the peaks confirms constituent phases of the spinel cubic and tetragonal perovskite crystal structure. For spinel ferrite a (311) peak and for ferroelectric a (110) peak is more intense. The lattice constant of the ferrite phase increases with increasing Mn content, in the cobalt ferrite, from 8.38 Å to 8.42 Å. The average grain sizes for CMFO$_0$ + BZT, CMFO$_1$ + BZT, CMFO$_2$ + BZT, CMFO$_3$ + BZT and CMFO$_4$ + BZT composites are 0.62 μm, 0.83 μm, 1.10 μm, 0.71 μm and 0.65 μm respectively. Dielectric constant decreases with increasing frequency, due to dipoles resulting from changes in valence states of cations and space charge polarization. 18 small portion of it was dried at 80°C for characterization. Cobalt ferrite/water suspension was heated to 80°C with gentle stirring. Oleic acid was added to the suspension at 30 wt.% with respect to the cobalt ferrite. The temperature was raised to 90°C for 30 min and then cooled to 60°C. Adding Octane and further stirring for another 30 min. The sample was dried at 80°C from room temperature to 700°C at 5° min$^{-1}$.Core–shell-like nanostructures of CoFe$_2$O$_4$ / BaTiO$_3$ were synthesized by the sol–gel technique. Ba(C$_2$H$_3$O$_2$)$_2$ was mixed with titanium (IV) n-butoxide stearic acid
and glacial acetic acid at 90°C to form a sol. The ferrofluid was added to the sol at an adequate amount. Anhydrous 2-methoxyethanol will promote the gel formation. The obtained gels were dried overnight at 80°C and sintered at 700°C for 2 h under some conditions to prevent BTO cracking. No secondary phases were detected by this technique during XRD. The structure corresponds to a spinel type cubic crystal with an average crystallite size of 14.6 nm. The degree of tetragonality increased with the ferrite content. Taking into account that the crystallite size of the barium titanate decreased with the content of ferrite.

1. A. 2. Polymer matrix based nanocomposite material system:

In fact there are many research papers dealing with polymer matrix based nanocomposites (hybrid nanocomposites); among them:

Z. Wang et al. (2012) [14] studied the effect of high aspect ratio filler (Barium Titanate Fibers) on dielectric properties of polymer composites. They predicted that the high aspect ratio fillers increase the dielectric constant of polymer composites more efficiently than spherical fillers according to the rule of mixtures. Using high aspect ratio fillers is a promising route for creating high dielectric constant, low loss materials at a low filler volume fraction, for use as capacitor and electric field grading materials. In this work, two high aspect ratio fillers were mixed into a polymer matrix, and the dielectric properties of composites were studied. Barium titanate fibers were synthesized by electrospinning a sol-gel, followed by a heat treatment to obtain a perovskite crystal structure. The heat treatment conditions were found to be crucial for obtaining tetragonal barium titanate fibers with high dielectric constant. Graphene platelets were prepared by a thermal shock method, which was found to result in a larger dielectric constant. A combination of barium titanate and graphene platelets yielded the highest dielectric constant when used in a polydimethyl siloxane matrix. The increase in dielectric loss over the pure matrix was small when the volume fraction was below the percolation threshold of graphene platelets. Electric flux density-electric field (D-E) measurements showed a linear dielectric constant in barium titanate filled composites and higher loss when graphene was added. The ac breakdown strength was reduced compared to the neat
polymer and was affected by filler aspect ratio. The mechanisms that lead to the observed phenomena are discussed.

R. Mohan et al. (2010) [15] prepared and characterized ferroelectric polymer-ceramic nanocomposites for non-volatile memory applications. Memories based on the ferroelectric polymeric field-effect transistor (FeFET) are becoming more and more attractive because of the non-volatile data retention, re-writability, low voltage operation and low cost. This non-volatile memory works on the bistable polarization of the polymer ferroelectric, which remnantlly attenuates the charge density in the semiconductor channel. Polymer has advantage over inorganic materials that they can be easily processible. The ferroelectric properties of these materials can be considerably increased and tailored by the addition of ferroelectric inorganic nanoparticles, like Barium Titanate [BaTiO$_3$], Lead Zirconate [PbZrO$_3$] etc. Ceramics require a very large electric field in the range of kilo-volts for poling them. This can be overcome by the introduction of ceramic into a ferroelectric polymer matrix. Further, the poling field can be reduced to a few volts by preparing the composite in the form of thin films. In the present work, we have prepared thin films of Poly (vinylidene fluoride-co-hexafluoro propylene) [PVDF-HFP] - BaTiO$_3$ composite and Poly (vinylidene fluoride) [PVDF] – BaTiO$_3$ nanocomposites for non-volatile memory applications. The composite films were characterized using X-ray diffraction, Scanning Electron Microscopy, Differential Scanning Calorimetry, Thermogravimetric Analysis, etc.

Electrical properties of polymers, well known for their insulating properties, may be improved by adding various functional fillers. Polymer–ferrite composites have been a subject of recent extensive research. Electric properties of such composites depend on the size, shape and amount of added filler in general. When polymer–ferrite composites are particularly used as electromagnetic wave absorbers and EMI shielding materials, it is very important to explain the variation of permeability and permittivity in the measured frequency ranges. Acrylic–Ni ferrite composites and acrylic–NiZn ferrite composites were used [16]. The effects of the weight fraction of ferrite on the frequency dispersion characteristics of the complex permittivity were studied.
H. W. Choi et al. (2006) [17] studied the effects of ferroelectric BaTiO$_3$ particles on the dielectric behavior of BaTiO$_3$–Ni–polymethyl methacrylate composites fabricated by a two-step mixing and hot-molding method. The percolation power law in the smearing region was employed to explain the experimental results. The composites exhibit the dependence of the dielectric constant, dielectric loss, and percolation threshold on the concentration and particle size of BaTiO$_3$. The results revealed that BaTiO$_3$ particles play an important role in increasing the percolation threshold and the smearing region as well as the dielectric constant of BaTiO$_3$–Ni–polymethyl methacrylate composites.

**i) Polyaniline (PANI) Matrix Based Nanocomposites:**

Conducting polymers have emerged as an important class of electronic materials because of their potential and wide applications in energy storage systems, optoelectronic devices, organic light emitting diodes, sensors for hazardous gases and toxic fumes, corrosion inhibitors for iron and mild steel, EMI shielding in radio frequency range and microwave range, super capacitors and super conductors [18].

Among conducting polymers, polyaniline (PANI) and its analogues have been widely studied due to its ease of protonic acid doping in the emeraldine form and its environmental stability in both doped and undoped forms, also due to its high conductivity and good stability [19].

In recent years much research attention has been paid to the conducting polymer composites with one or more magnetic materials so that polymer possesses both electrical as well as magnetic properties. These conducting polymer nanocomposites can find applications as:

1. Antistatic materials for the dissipation of electrostatic charge.

2. For the shielding of electronic equipments from electromagnetic radiations in radio frequency range from 10Hz to 108Hz, microwave range and W band range.

3. For the storage of IC-chips in software and electronic packaging industries.
For the absorption of electromagnetic radiations, ferrites are incorporated in the polymers as they possess high magnetization values which make them useful at higher frequencies. Nanocomposites of polyaniline are very significant due to their wide application ranging from medical sciences to electronic applications. The composites of polyaniline with nanoparticles of different functional oxides have been studied. The prospect applicability of polyaniline–nanoferrite composite in electromagnetic shielding has allured scientific community since last decades.

Polyaniline / (NZF-BTO) hybrid nanocomposites have great applications in the field of defence. C. K. Das et al. (2012) prepared these composites. Development of RADA absorbing materials (RAMs) is the most important research area in camouflage application mainly in Defence. Aniline was polymerized in presence of dodecylbenzene sulphonic acid (DBSA) as a functionalized protonic acid in water medium to form DBSA-doped polyaniline (PANI). Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ (NZF) nanoparticles were synthesized by co-precipitation method along with Barium Titanate (BaTiO$_3$) particles to form BaTiO$_3$-Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ nanoparticles. Both DBSA-doped PANI and BaTiO$_3$-Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ nanoparticles were thoroughly mixed in different ratios and the mixtures were dispersed in Epoxy Resin (LY556) matrices to produce RAMs. The spectroscopic characterization of the composite materials were examined by using X-ray diffraction (XRD), scanning electron microscope (SEM), Energy-dispersive X-ray spectroscopy (EDX), High resolution transmission electron microscopy (HR-TEM). The microwave absorbing properties return loss (dB) and important parameters such as complex relative permittivity ($\varepsilon_r' - j\varepsilon_r''$), complex relative permeability ($\mu_r' - j\mu_r''$) were measured in different microwave frequencies in X-band (8.2-12.4 GHz) region. The results showed that a wider absorption frequency range and maximum return loss of -15.78 dB (>97% power absorption) at 10.8 GHz. The mechanism of microwave absorption occurs mainly due to the dielectric loss rather than magnetic loss. Ferrite based Polyaniline nanocomposites are also used in electromagnetic shielding applications. In other words, the absorption loss in the material is caused by the heat loss under the action between electric dipole and/or magnetic dipole in the shielding material and the electromagnetic field so that the absorption loss is the function of conductivity and the magnetic permeability of the material.

**ii) Polyethylene glycol (PEG) Matrix Based Nanocomposites:**

Polyethylene glycol (PEG) is a condensation polymer of ethylene oxide and water with the general formula $\text{H(OCH}_2\text{CH}_2\text{O)}_n\text{OH}$, where $n$ is the average number of repeating oxyethylene groups typically from 4 to about 180. PEG is a typical non-toxic, non-immunogenic, non-antigenic and protein resistant polymer, which is widely used in the pharmaceutical field, has attracted much attention [27]. It is water soluble, inert in biological systems and does not influence cell viability. Many researchers work on the nanoferrite coated with PEG as surfactant in biomedical applications [28-32]. The coating of long-chain polymer molecules on ferrite particles serves as protective layer that prevents agglomeration of the particles and minimizes the direct exposure of the ferrite surface to the biological environment [29]. PEG remains one of the widely used polymer group of biomaterials applied for medical implants. This usage is due to its segmented block co-polymer character. This wide range of versatility is utilized in terms of tailoring their applications, such as tissue scaffolding [30], artificial cartilage [31] and biodegradable scaffolds [32].

According to literature survey there are no reports on the synthesis and characterization of hybrid three-phase nanocomposite (PEG/ME) system. However there are similar works close to some extent from our work but on two-phase nanocomposites; among them:

M.A. Ahmed et al. (2010) [33] studied PEG/nanoferrites composites prepared by cold uniaxial press. MFe$_2$O$_4$ (M=Mn$^{2+}$, Ni$^{2+}$, Co$^{2+}$ and Cu$^{2+}$) ferrite powders were prepared by flash auto-combustion reaction. The structural identification of the samples was carried out using X-ray diffraction (XRD), transmission electron microscope (TEM), selected area electron diffraction (SAED) and IR spectra. The
study established the formation of sub-nanosized particles especially for MFe$_2$O$_4$ (M= Ni, Co and Cu) ferrites. MFe$_2$O$_4$/PEG (polyethylene glycol) composites were prepared by cold uniaxial pressing. The magnetic properties were studied by carrying out the hysteresis of MFe$_2$O$_4$ and PEG/MFe$_2$O$_4$ composite at room temperature. They concluded that flash auto-combustion method was successfully used to obtain MFe$_2$O$_4$ sub-nanoparticles in one step. The results of the study promote the use of PEG/MFe$_2$O$_4$ composites in high frequency applications due to the appreciable values of the dielectric constant and the neglected losses. In addition, one suggested the use of PEG/CoFe$_2$O$_4$ in wireless endoscope capsules and as a vector in drug targeting to minimize the side effects of drugs in chemotherapy.

### iii)- Polyvinyl pyrrolidone (PVP) Matrix Based Nanocomposites:

Polyvinylpyrrolidone (PVP) is made from the monomer N-vinylpyrrolidone. PVP is soluble in water and other polar solvents. PVP was initially used as a blood plasma substitute and later in a wide variety of applications in medicine, pharmacy, cosmetics and industrial productions [34].

According to literature survey there are no reports on the synthesis and characterization of hybrid three-phase nanocomposite (PVP/ME) system. However there are similar works close to some extent from our work but on two-phase nanocomposites; among them:

H. L. Liu et al. (2007) [34] synthesized polyvinylpyrrolidone (PVP)-coated sub-5nm monosize Fe$_3$O$_4$ nanoparticles by reduction of Fe(III) acetylacetonate in the presence of PVP polymer as surfactant in one-pot polyol process. Their microstructure and magnetic properties were characterized by XRD, TEM/HRTEM and VSM. It is found that the nanoparticles have high crystallinity with distinct lattices and the magnetic measurements reveal their well-defined superparamagnetic behavior at room temperature. Such Fe$_3$O$_4$ nanoparticles with tailorable size and tunable magnetic properties are promising for biomedical applications.

G. Ghosh et al. (2006) [35] report a simple soft chemical method for the synthesis of PVP-encapsulated ZnS nanoparticles and examine the optical properties
of these ZnS nanoparticles with varying ageing time at the reaction temperature, concentrations of PVP and S\(^2\) ions. The observed photoluminescence peak of PVP capped ZnS nanoparticles at 407 nm, markedly blue shifted relative to that of the bulk ZnS, clearly indicates the strong quantum size effect.

**iv)- Polyvinyl acetate (PVAc) Matrix Based Nanocomposites:**

Polyvinyl acetate, PVAc, poly (ethenyl ethanoate), is a rubbery synthetic polymer with the formula \((\text{C}_4\text{H}_6\text{O}_2)_n\). It belongs to the polyvinyl esters family with the general formula \(-[\text{RCOOCHCH}_2]-\). It is a type of thermoplastic [36]. Polyvinyl acetate is a component of a widely-used type of glue, referred to variously as wood glue, white glue, carpenter's glue, school glue or PVA glue. As an emulsion in water, PVAc emulsions are used as adhesives for porous materials, particularly for wood, paper, and cloth, and as a consolidant for porous building stone, in particular sandstone. PVAc can also be used as coating to protect cheese from fungi and humidity.

According to literature survey there are no reports on the synthesis and characterization of hybrid three-phase nanocomposite (PVAc/ME) system; among them: However there are similar works close to some extent from our work but on two-phase nanocomposites.

S. J. Park et al. (2006) [37] used poly(vinyl acetate)/organoclay as a gate insulating material in organic thin film transistor poly(vinyl acetate) (PVAc) is currently being investigated as a potential polymeric gate insulator for organic thin film transistors (OTFTs), because it can be easily converted from poly(vinyl alcohol) through hydrolysis and can form a composite material with inorganic particles. In addition, the PVAc with a dielectric constant of 3.2–9.3 can be adopted as a good gate insulator for the OTFTs. We report characteristics of the electric transport of pentacene based OTFT using PVAc material with and without organic montmorillonite (OMMT) layer as a polymeric gate insulator. Spin coating condition of the gate insulator with PVAc was measured considering both viscosity of PVAc
dissolved in chloroform as a function of PVAc concentration and surface morphology after the spin coating process.

N. Dharmaraj et al. (2004) [38] prepared magnesium titanate/polyvinyl acetate composite nanofibres by sol–gel processing and electrospinning technique. Phase pure magnesium titanate fibres of 200–400 nm diameters were obtained by high temperature calcination of the inorganic–organic composite fibres. The magnesium titanate nanofibres thus prepared have been characterized by SEM, XRD and FT-IR, respectively. The data revealed that, the surface morphology and crystallization of magnesium titanate fibres were found to depend on the calcination temperature.

1.B. Theoretical Background:

In this part we introduce a general introduction about this work. The term "ferroic" is explained from which all our used materials are derived; ferromagnetic, ferroelectric and ferroelastic (polymers) in order to form the so called multiferroic nanocomposites. Each selected material from each category of ferroic; ferromagnetic (NiZn-ferrite), Ferroelectric (BaTiO$_3$) and polymers as ferroelastic are discussed in details to study their structure, behavior and their application separately before emerging them in the prepared multiferroic nanocomposite. Magnetic and dielectric properties also introduced.

1.B.1. Nanotechnology:

Nanoscience and nanotechnology pertain to the synthesis, characterization, exploitation and utilization of nanostructured materials which are characterized by at least one dimension in the nanometer (1 nm = $10^{-9}$ m) range. The dimensional range of 1 to 100 nm is referred as the nanoscale and materials at this scale are called nanocrystals or nanomaterials [39]. The chemical and physical properties of nanomaterials can significantly differ from those of bulk materials of same chemical composition. The uniqueness of the structural characteristics, energetics, response, dynamics and chemistry of nanostructures constitutes the experimental and
conceptual background for the field of nanoscience. Suitable control of properties and response of nanostructures can lead to new devices and technologies [40].

The deviation of properties of the nanosized materials from the bulk material properties are due to surface effects which mainly depend upon the ratio of surface area to volume and size of the particles along with the chemical composition and interaction between particles. The increase in surface to volume ratio, which is a gradual progression as the particle gets smaller, leads to an increasing dominance of the behavior of atoms on the surface of particles over that of those in the interior of particle as these atoms have lower coordination number than the interior atoms. In addition, depending on the geometry, different sites on the surface will be different in local coordination number [41].

In recent years, a lot of work has been done on nanocrystalline materials because of their unusual properties compared to the properties of bulk materials [42]. Several research groups are involved in the investigations of spinel oxide nanoparticles because of their potential applications in magnetic devices, microwave technology and high-density magnetic recording media, etc.

Various factors such as, particle size distribution, inter-particle interactions grain and grain boundary structure and meta-stable structure of the system control the properties of nanoparticles [43]. The other fields where nanostructured materials are used include electronics, medical, energy production, energy utilization, transportation and national security.

There is a relentless drive in the direction of better technology that is fuelled by investigation of new materials, to be eventually utilized as improved transducers, magnetic field sensors, and most importantly and presently, information storage technology [44]. Before beginning to apply these smart material technologies, there is great need to address fundamental properties of current materials, and to use that knowledge to improve them by way of, for example, making new materials in place of the existing structures in such a way that the resulting properties are complementary [45].
Efforts are currently under way to develop nanomaterials that have superior properties to those currently existing. This has resulted in the development of nanocomposite materials that exhibit remarkable product properties, which are created by the interaction between the constituent phases. There are many advantages to using nanocomposite materials over more traditional materials, such as the possibility of weight or volume reduction in a structure while maintaining a comparable or improved performance level [46]. The magnetoelectric coupling effect in composite materials, consisting of a piezoelectric phase and a piezomagnetic phase, has recently attracted attention due to the extensive applications for broadband magnetic field probes, electric packaging, acoustic, hydrophones, medical ultrasonic imaging, sensors, and actuators [47]. These nanocomposites are regarded as smart or intelligent materials. In the large field of nanotechnology, polymer matrix based nanocomposites have become a prominent area of current research and development [48].

1.B.2. Multifunctional Materials:

Multifunctional materials combine multiple functions including electronic, magnetic, mechanical, photonic, optical, and biological functions. They are capable of exhibiting various controllable and predictable physical responses when subjected to diverse external conditions. They are expected to bring important breakthroughs in various technological fields. In this work, we study multifunctional composite materials and concentrate on those materials which couple three physical properties: magnetic, electric and mechanical properties, also termed multiferroics [49].

1.B.3. Ferroic Nanomaterials:

A ‘primary ferroics’ is a general term that includes ferromagnetic, ferroelectric, and ferroelastic materials [50]. Generally, ferroic crystals have three characteristics: (i) a spontaneous order parameter (magnetization, electric polarization or elastic deformation); (ii) the occurrence of multiple domain states over whose length scale the order parameter is essentially uniform, and whose boundaries move under an external field; and (iii) hysteresis caused by field-induced
domain motion during order parameter reversal. A hysteresis loop of three primary ferroics and their important parameters are illustrated in Fig. (1-1). The properties of ferroic materials are often superior to conventional materials because of their spontaneous order parameters and large nonlinear coefficients. Therefore ferroic nanomaterials open the way to obtain a variety of new unique magneto-mechanical, electro-mechanical, electronic, and dielectric properties, a lot of which are useful for applications [51]. For example, their ability to store and release energy in well-regulated manners makes them very useful for sensors and actuators, telecommunications, optical and infrared detectors, pyrosensors and thermal imaging, and multidisciplinary fields such as biomedical and environment.

![Fig. (1-1): Schematic illustrate of a hysteresis loop showing the coercive field, remnant and saturation strain, polarization and magnetization.](image)

1.B.4. Ferromagnetic Material:

Ferromagnetism is a phenomenon by which a material can exhibit a spontaneous magnetization. It is responsible for most of the magnetic behavior encountered in everyday life and is the basis for all permanent magnets. Electron spin and the Pauli Exclusion Principle are the physical origin of ferromagnetism [52].

The spin of an electron combined with its orbital angular momentum, results in a magnetic dipole moment and creates a magnetic momentum. Only atoms with partially filled shells with unpaired spins can exhibit a net magnetic moment in the absence of an external field, according to the response to the external magnetic field,
the material can be classified into paramagnetism, ferromagnetism, antiferromagnetism and ferrimagnetism. Paramagnetic materials feature disordered orientations of the magnetic moments due to thermal fluctuations. Ferromagnetism is the strongest form of magnetic responses which is characterized by the parallel alignment of adjacent magnetic moments. In contrast, an antiferromagnetic behavior corresponds to an antiparallel alignment of equal moments. Finally, ferrimagnetism is characterized by antiparallel moments having different magnitudes and thus yielding a non-zero net magnetization [52].

Ferromagnetics exhibit a hysteretic response to an external magnetic field, as shown in Fig.(1-2). The saturation magnetization (M_s), coercive field (H_c) and remnant magnetization (M_r) are all shown in the Figure. Based on the value of a coercive field, magnetic materials are classified as either hard or soft magnets with large and small H_c accordingly.

1.B.5. Magnetic Interaction in Ferrites:

As mentioned above; in ferrites, the metallic ions occupy two crystallographically different sites, i.e., octahedral (B) sites and the tetrahedral (A) sites. Three kinds of magnetic interaction are possible, between the metallic ions, through the intermediate O^{2-} ions, by superexchange mechanism, namely, A-A, B-B and A-B interactions [53].

Fig.(1-2): Hysteresis loop showing magnetization switching in ferromagnetic materials.
The negative interaction or exchange force between the moments of two metal ions on different sites depends on the distances between these ions and the oxygen ion that links them and also on the angle between the three ions. The interaction is greatest for an angle of $180^\circ$ and also where the interatomic distances are the shortest. Fig. (1-3) shows the interatomic distances and the angles between the ions for the different types of interactions. In the A-A and B-B cases, the angles are too small or the distances between the metal ions and the oxygen ions are too large. The best combinations of distances and angles are found in the A-B interactions. For an undistorted spinel, the A-O-B angles are about $125^\circ$ and $154^\circ$. The B-O-B angles are $90^\circ$ and $125^\circ$ but in the latter, one of the B-O distances is large. In the A-A case the angle is about $80^\circ$. Therefore, the interaction between moments on the A and B sites is strongest. The BB interaction is much weaker and the most unfavourable situation occurs in the AA interaction [54].

The spins of the A and B site ions in ferrite will be oppositely magnetized sub lattices A and B, with a resultant magnetic moment equal to the difference between those of A and B site ions. In general, the value of saturation magnetic moment for the B lattice ($M_B$) is greater than that of the lattice ($M_A$), so that, the resultant saturation magnetization ($M_S$) may be written as [54].

Fig.(1-3): Configuration of ions pairs in spinel ferrites with favourable distances and angle for effective magnetic interaction.
\[ M_S = |M_B - M_A| \] (1.1)

With this theory Néel could satisfactorily explain the experimentally observed magnetic susceptibility and saturation data obtained for ferrites.

**1.B.6. The Bloch Wall:**

Bloch walls appear in single crystals and in polycrystalline materials; they can run right through the crystal and in certain circumstances cross the grain boundaries. A Bloch wall is the space between neighboring domains in which the magnetic vectors pass smoothly from the direction appropriate to one domain to that of another [55].

**1.B.7. The Dynamic Behavior of Domains:**

There are two general mechanisms involved in changing the magnetization in a domain and, therefore, changing the magnetization in a sample. The first mechanism acts by rotating the magnetization towards the direction of the field. Since this may involve rotating the magnetization from an axis of easy magnetization in a crystal to one of more difficult magnetization, a certain amount of anisotropy energy is required. The rotations can be small as indicated in Fig. (1-4) or they can be almost equivalent to a complete 180° reversal or flip if the crystal structure is uniaxial and if the magnetizing field is opposite to the original magnetization direction of the domain [56].

The other mechanism for changing the domain magnetization is one in which the direction of magnetization remains the same, but the volumes occupied by the different domains may change. In this process, the domains whose magnetizations are in a direction closest to the field direction grow larger while those that are more unfavorably oriented shrink in size. Fig. (1.5) shows this process which is called domain wall motion.
1.8. Magnetic Anisotropy:

In most magnetic materials, to varying degree, the magnetization tends to align itself along one of the main crystal directions. That direction is called the easy direction of magnetization. All ferromagnetic and ferrimagnetic materials possess, to a lesser or greater degree, a crystal direction or a set of directions in which the magnetization prefers to be oriented [57]. This magnetic anisotropy can have various causes. The most important in magnetic materials are the shape and magnetocrystalline anisotropies. Shape anisotropy is associated with the geometrical shape of a magnetized body, and refers to the preference that the polarization in a long body is for the direction of the major axis. The magnetocrystalline anisotropy is associated with the crystal symmetry of the material.
1. B. 9. Ferroelectric Material:

Ferroelectric materials have a spontaneous electric polarization. They have been studied since over a century ago when large piezoelectric constants were observed in Rochelle salt. For the past few decades, ferroelectric materials have received a great amount of interests because of their various uses in a range of applications, including transducers and actuators, capacitors and memory applications [58].

The polarization as a function of the applied field for a ferroelectric crystal is a hysteresis loop as shown in Fig. (1-6), which is a sign for the ferroelectric state. As the applied external field is switched off, a spontaneous polarization \( P_s \) persists. A reverse field \(-E_c\), called coercive field, has to be applied to bring the polarization of the crystal back to zero. If the reverse field is increased further the polarization of the crystal is reversed. This is one of the important features of ferroelectrics with respect to applications [58]. The ferroelectricity of a crystal disappears as it is heated up to Curie temperature \( T_c \). Above \( T_c \) the crystal is said to be paraelectric.

The value of the spontaneous polarization is dependent on temperature; thus, if the temperature of the crystal is altered a change in the polarization occurs and electric charges can be observed on those crystal faces that are perpendicular to the polar axis. This is the pyroelectric effect [59]. Ferroelectric crystals belong to the pyroelectric family, but they are a subclass in which the direction of the spontaneous polarization can be reversed by external electric field. All ferroelectric crystals are necessarily piezoelectric. The piezoelectric effect is a phenomena resulting from a coupling between the electrical and mechanical properties of a material [60]. When mechanical stress is applied to a piezoelectric material, an electric potential will be generated. Likewise, when an electric potential is applied to the material, a mechanical strain will occur.
Ferroelectric hysteresis loop, Fig. (1-6), is the characteristic of a ferroelectric material, which arises due to the presence of ferroelectric domains in the crystal [60]. Application of an external dc electric field $E > E_c$ to a polydomain ferroelectric crystal, causes the polarization, $P$, vectors having different orientations in different domains to align themselves parallel to the direction of the field via domain wall movement. The minimum dc field required to move the domain walls is a measure of the coercive field. The initial value of $P_s$ in a polydomain crystal increases with increasing dc field to a maximum that is characteristic of the material. Reversing the electric field reintroduces domain walls movement and results in the $P_s$ in different regions to be reversed. At zero applied field, the crystal will have a remnant polarization which is smaller than the spontaneous polarization. At fully reversed field, the final $P_s$ will have the same magnitude as the original $P_s$ but the opposite sign. The hysteretic loop is a function of the work required to displace the domain walls which is closely related to the defect distribution in the crystal and to the energy barrier separating the different orientational states [60].
1.B.10. **Ferroelectric phase transformations: 1st and 2nd – order phase transition:**

As stated in last section, ferroelectric phase transformations involve a change in symmetry of a crystal. Such structural phase transitions can be classified as continuous or discontinuous [61]. If the spontaneous polarization varies continuously with temperature and tends towards zero at the transition temperature it is said to be a second order transition. However, if the spontaneous polarization abruptly changes at the transition temperature, it is said to be a first order transition. In the case of continuous phase (2nd order) transformation, the symmetry group of the ferroelectric phase is a subgroup of that of the paraelectric state. However, for a 1st order transformation, there is no such simple relation between the symmetries of the two phases.

A popular and useful way to identify a ferroelectric phase transformation is the temperature dependence of the dielectric constant. Fig. (1-7) shows the dielectric constant (κ) of BaTiO₃ single crystals as a function of temperature [61]. In this figure, a phase transformation sequence can be seen with decreasing temperature. The order of each transition can be determined by Curie-Weiss plots (1/κ vs T). If 1/κ approaches zero at Tc, then the transition is 1st order; whereas if 1/κ approaches a finite value at Tc, then it is a 2nd order transition.

*Fig.(1-7): Dielectric permittivity of BaTiO₃ single crystals as a function of temperature under weak E-field. All phase transitions from high to low temperature are the first order.*
1.B.11. Polymers: Ferroelastic materials:

Ferroelastic materials display a spontaneous deformation that is stable and can be switched hysteretically by an applied stress [50]. Ferroelasticity occurs when a material has two or more orientation states which are identical in crystal structure in the absence of mechanical stress; a mechanical stress will then favor one or the other and cause shifting between them.

Some polymers represent ferroelastic materials, where polymer is an example of a substance composed of molecules with large molecular mass composed of repeating structural units, or monomers, connected by covalent chemical bonds [62].

Polymers affect every day of our lives. These materials have so many varied characteristics and applications that their usefulness can only be measured by our imagination. Polymers are the materials of past, present, and future generations.

Polymers may be classified according to their constituents of monomers. If all the structural units are identical the polymer is called homopolymer. If there are two or more types of structural units in the chain the polymer is termed copolymer [63]. Technologically polymers may be classified into thermoplastic and thermosets. Thermoplastics are substances that soften upon heating and can be remolded and recycled. They can be semi-crystalline or amorphous. Thermoplastics are generally carbon containing polymers synthesized by addition or condensation polymerization. This process forms strong covalent bonds within the chains and weaker secondary Van der Waals bonds between the chains. Usually, these secondary forces can be easily overcome by thermal energy, making thermoplastics moldable at high temperatures. Thermoplastics will also retain their newly reformed shape after cooling. A few common applications of thermoplastics include: parts for common household appliances, bottles, cable insulators, tape, blender and mixer bowls, medical syringes, mugs, textiles, packaging, and insulation [64]. Thermosets are substances that do not soften under heat and pressure and cannot be remolded or recycled. They must be remachined, used as fillers, or incinerated to remove them.
from the environment [65]. Thermosets have the same Van der Waals bonds that thermoplastics do. They also have a stronger linkage to other chains. Strong covalent bonds chemically hold different chains together in a thermoset material. The chains may be directly bonded to each other or be bonded through other molecules. This "cross-linking" between the chains allows the material to resist softening upon heating. Thus, thermosets must be machined into a new shape if they are to be reused or they can serve as powdered fillers [66]. In this work we have used some polymeric materials such as polyethylene glycol (PEG), polyaniline (PANI), polyvinyl pyrrolidone (PVP), and polyvinyl acetate (PVAc). They will be discussed in details in the next sections.

1.B.12. Electrical properties overview:

Herein we concern the conduction mechanisms in different ferroic phases; ferromagnetic (ferrites), ferroelectric (piezoelectric), and ferroelastic (polymers). In the next chapter we will correlate between all these conduction mechanisms in the three ferroic phases side by side to the interface effects in order to deal the conduction mechanism in multiferroic composites.

1)- Conduction Mechanism in ferrites:

The conduction mechanism in ferrites is quite different from that in semiconductors [67]. In ferrites, the temperature dependence of mobility affects the conductivity and the charge carrier concentration is almost unaffected by the temperature variation. Unlike in semiconductors, wherein the charge carriers occupy states in wide energy bands, the charge carriers in ferrites are localized at the magnetic atoms. In ferrites, the cations are surrounded by close-packed oxygen anions and as a first approximation can well be treated as isolated from each other, hence a localized electron model is more appropriate in the case of ferrites rather than the collective electron (Band) model. These factors that differentiate the electrical behaviour of ferrites from that of semiconductors, led to hopping electron model. There are different model dealing with the conduction mechanisms in ferrite [67].
i)- **Hopping Model:**

If there is phonon scattering in the narrow band it must be a multiple-phonon process and then the electron motion will be random and incoherent. For this reason a hopping model may be preferable to the band model [68]. The major characteristic of hopping conduction is the strong temperature dependence of the associated mobility. This arises because at low temperatures, the lattice vibrates sluggishly, and the chances of obtaining two nearest-neighbour equivalent sites are very small. However, at high temperatures the lattice vibrations are vigorous and the hopping probability is exponentially larger. Thus hopping conduction is in principle distinguishable from band conduction by of mobility measurements. Band model showed some difficulties for electrical transport in materials in which the carrier mobility is very low. It can be imagined that for narrow bands the absorption or emission of single phonons becomes impossible in view of energy and wave vector conservation. If there are phonons scattering in the narrow band it must be a multiple-phonon process and then the electron motion will be random and incoherent. For this reason, a hopping model may be preferable than the band model. A carrier can move from one molecule together by jumping over the barrier via an excited state as in Fig. (1-8).

The criterion to determine whether the charge transport in molecular crystals takes place coherently according to the band model or by random jumps according to the hopping model depends on the electron-lattice interactions which is, depends on whether the strongest coupling is with intermolecular (lattice) or intermolecular (nuclear) vibrations, whether it is linear or quadratic in the phonon coordinates, and whether it is strong compared with the intermolecular electron-exchange interactions. The vibration periods are typically $10^{-12}$ sec for intermolecular modes and $10^{-14}$ sec for intermolecular modes. By denoting the electron relaxation time, intermolecular vibration period and intermolecular vibration period by $\tau$, $\tau_{v1}$, and, $\tau_{vn}$ respectively.
ii)- **Verway Conduction Mechanism:**

Consider a very high resistivity oxide (ferrite) is doped with small quantities of foreign ions up to 1% of different valences, then the already exist ions are forced to change its valence state. The electrical conductivity in such systems is due to simultaneous presence of Fe^{2+} and Fe^{3+} in equivalent lattice site, and electrons will travel with very low activation energy along the lattice points. The conduction electrons are that of 3d electrons localized in metal ions from Fe^{3+} to Fe^{2+} [69].

iii)- **Koops Model:**

Koops gave a phenomenological theory of dispersion based on the Maxwell-Wagner interfacial polarization model for in-homogeneous dielectric structure. It was assumed that the solid consists of well conducting grains separated by poorly conducting layers [70]. The parallel resistance $R_p$ and the parallel capacitance $C_p$ are determined:

$$X^{-1} = R_p^{-1} + j\omega C_p$$  \ (1.2)
From $R_p$ and $C_p$ the apparent resistivity $\rho_p$ and the apparent relative dielectric constant $\varepsilon_p$ of the material are given with the help of:

$$R_p = \frac{\rho_p d}{\Omega} \quad (1.3)$$

$$C_p = \frac{\varepsilon_p \varepsilon_0}{\Omega/d} \quad (1.4)$$

It is clear that neither dimensional effect as found by Brockman nor skin effect play a part in the dispersion of both $\rho_p$ and $\varepsilon_p$. The material being an electronic semiconductor, it is also very unlikely that an intrinsic dispersion of the conduction mechanism itself would exist at such very low frequencies, as is the case here.

A good phenomenological theory of the dispersion can be based, however, upon the assumption that $R_p$ and $C_p$. From a purely circuit-theoretical point of view, it can be proved that two capacitors and two resistors are needed in order to build up a two-pole having a finite value of dc resistance. Self-inductance has been omitted, in any real model obviously only resistors with parallel capacitors may be assumed.

The model indicated might be justified by taking into account the barrier layers which may be present between the material and the electrodes (caused by impurities). The electrodes proved to have no influence upon the measurements of $\rho_p$ and $\varepsilon_p$ since $\rho_p$ and $\varepsilon_p$ were quite the same with a thick disk and a thin one. It is very probable, therefore, that layers of lower conductivity must be assumed to be present in the solid itself. It must be noted here that, an inhomogeneity model has already been proposed as a means of explaining certain characteristics of the $\tan\delta \text{ vs } \omega$ curves of dielectrics. The solid is imagined to consist of well-conducting grains separated by poorly conducting layers, while current is assumed to flow along parallel alignments grains, as has been drawn.
2)- Polarization and dielectric properties of ferroelectric phase:

The dielectric properties as a function of temperature of BaTiO$_3$ (ferroelectric phase) are described in Fig. (1-7). In BaTiO$_3$, Ti$^{4+}$ is displaced from its site to create a dipole as in Fig. (1-9). In the paraelectric BaTiO$_3$ there is a random dipole orientations, and in the ferroelectric form there is an aligned dipole orientations. Under an applied electric field dipole orientations can be reserved, i.e. the structure is polarisable. Dipoles tend to be “frozen in” at room temperature, as increase temperature, thermal vibrations increase the polarisability [71].

3)- Dielectric properties of ferroelastic (polymer) phase:

Polymers are, in general, good electrical insulators, with volume resistivities up to $10^{22}$ ohm.cm. Various polymers are commonly used in the electronics industry as housings or assemblies. Many applications require that the polymer be made conductive in order to shield electronic components from electromagnetic interference. Conductive reinforcement may be added to the polymer in order to achieve conductivity as well as to improve mechanical properties [72].

![BaTiO$_3$ unit cell in an isometric projection and viewed looking along one face, which shows the displacement of Ti$^{4+}$ and O$^{2-}$ ions from the center of the face.](image)

The permittivity describes the material polarizability under external electric field and the net polarization in dielectric material consists of several frequency...
dependent mechanisms illustrated in Fig. (1-10); where a typical polarizability for a dielectric is plotted as a function of frequency \[72\].

Dielectric polarization is the polarized condition of a dielectric resulting from an applied \textit{ac} or \textit{dc} electric field. There are two types of charging currents and condenser charges, which may be described as rapidly forming or instantaneous polarizations, and slowly forming or absorptive polarizations. The total polarizability of the dielectric is the sum of contributions due to several types of displacement of charge produced in the material by the applied field. The relaxation time is the time required to form or disappear polarization. Generally, the dielectric constant of polymer arises due to polarization of molecules and the dielectric constant increases with increase in polarizability \[73\].

The different types of polarizations possible in polymer material are the polarization arising from, electronic polarization, atomic polarization and orientation polarization due to the orientation of dipoles parallel to the applied field \[74\].

4)- Dielectric Mechanisms:

A dielectric is an electrical insulator that may be polarized by the action of an applied electric field. When a dielectric is placed in an electric field, electric charges do not flow through the material, as in a conductor, but only slightly shift from their average equilibrium positions causing dielectric polarization. Because of dielectric polarization, positive charges are displaced along the field and negative charges shift in the opposite direction. This creates an internal electric field which partly compensates the external field inside the dielectric \[75\] if a dielectric is composed of weakly bonded molecules, those molecules not only become polarized, but also reorient so that their symmetry axis aligns to the field \[76\].
There are a number of different dielectric mechanisms, Fig. (1-10), connected to the way a studied medium reacts to the applied field. Each dielectric mechanism is centered around its characteristic frequency, which is the reciprocal of the characteristic time of the process. In general, dielectric mechanisms can be divided into relaxation and resonance processes. The most common, starting from high frequencies, are:

**i)- Electronic polarization:**

This resonant process occurs in a neutral atom when the electric field displaces the electron density relative to the nucleus it surrounds. This displacement occurs due to the equilibrium between restoration and electric forces. Electronic polarization may be understood by assuming an atom as a point nucleus surrounded by spherical electron cloud of uniform charge density.

**ii)- Atomic polarization:**

Atomic polarization is observed when the electronic cloud is deformed under the force of the applied field, so that the negative and positive charge is formed. This is a resonant process.
iii)- **Dipole relaxation:**

This originates from permanent and induced dipoles aligning to an electric field. Their orientation polarisation is disturbed by thermal noise (which mis-aligns the dipole vectors from the direction of the field), and the time needed for dipoles to relax is determined by the local viscosity. These two facts make dipole relaxation heavily dependent on temperature and chemical surrounding.

iv)- **Ionic relaxation:**

Ionic relaxation comprises ionic conductivity and interfacial and space charge relaxation. Ionic conductivity predominates at low frequencies and introduces only losses to the system. Interfacial relaxation occurs when charge carriers are trapped at interfaces of heterogeneous systems. A related effect is Maxwell-Wagner-Sillars polarization, where charge carriers blocked at inner dielectric boundary layers (on the macroscopic scale) or external electrodes (on a macroscopic scale) lead to a separation of charges. The charges may be separated by a considerable distance and therefore make contributions to the dielectric loss that are orders of magnitude larger than the response due to molecular fluctuations [75].

v)- **Dielectric relaxation:**

Dielectric relaxation as a whole is the result of the movement of dipoles (dipole relaxation) and electric charges (ionic relaxation) due to an applied alternating field, and is usually observed in the frequency range $10^2$-$10^{10}$ Hz. Relaxation mechanisms are relatively slow compared to resonant electronic transitions or molecular vibrations, which usually have frequencies above $10^{12}$ Hz.

5)- **Electrical conductivity and carrier transport of ferroelastic (polymer) phase:**

A great deal of work had been done for the characterization and understanding of electrical transport in conducting polymers [74]. The factor limiting the conductivity is the carrier mobility, along with the carrier concentration. The doping process produces a generous supply of potential carriers, but to
contribute to conductivity they must be mobile. There are at least three factors contributing to the carrier mobility: single chain or intramolecular transport, interchain transport, and interparticle contact. These three factors comprise a complicated resistive network which determines the effective mobility of the carriers. Thus, the mobility and therefore the conductivity are determined on both a microscopic (intra- and interchain) and a macroscopic (interparticle) level.

In conjugated polymers, ionisation results in substantial distortion of the lattice around the ionised states, similar to all organic materials. So, as a charge carrier moves through the polymer, due to this distortion of the lattices, mobility is reduced. Since disorder plays such a dominant role in conducting polymer systems, the mechanism of carrier transport is more akin to that in amorphous semiconductors (hopping transport) [74].

The theoretical work on conducting polymers has been mainly concerned with radical and ionic sites [75], referred to as neutral and charged defects, respectively. The movement of the defect can be described mathematically as a solitary wave, or "soliton" in the language of field theory [76]. The radical defect is referred to as a neutral soliton; the anion and cation defects are charged solitons. Charged solitons (anions or cations) can explain the spinless transport, since they carry charge but no spin. The initial species formed on the ionisation of a conjugated polymer is a radical ion, which possess both spin and charge. In the language of solid-state physics, the radical ion is referred to as a polaron. A polaron is either a positively charged hole site (radical cation) or a negatively charged electron site (radical anion), plus a lattice relaxation (distortion) around the charge. Theoretical models” demonstrate that two radical ions (polarons) on the same chain react exothermically to produce a dication or dianion (bipolaron) ,which are responsible for spin less conductivity in these polymers.

1.B.13. Multiferroic Materials:

A brief view on the concept of multiferroic materials is present with a simple review on the recent research discoveries related to this topic. In this presentation, we
will first explain what is so called multiferroic materials and then set some popular ones as examples. What’s more, we are going to explore the concept and applications of multiferroic nanocomposite system.

“Multiferroics” are characterized by the co-existence of more than one spontaneous order parameter [77]. Accordingly, these materials have at least (i) two types of hysteresis loops; (ii) two types of domain structures and (iii) exchange between primary order parameters. The relation between multiferroic and primary ferroics are shown in Fig. (1-11), where A represents the coexistence of magnetization and electric polarization; B the coexistence of electric polarization and ferroelastic strain; C the coexistence of magnetization and ferroelastic strain; and D the coexistence of all these spontaneous order parameters. For primary ferroic materials, an order parameter only appears below a certain critical symmetry transformation temperature and domain states can only be switched by a field that is conjoint to the order parameter. In the contrast, the Curie temperature of a multiferroic material is dependent on multiple ordering fields (magnetic field, electric field or stress). Accordingly, their domain states can be switched by more than one field type. For example, magnetoelectric (ME) materials are characterized by the switching of an electric polarization upon applying a magnetic or electric field, and vice versa [31]. In recent years, much attention has been paid to multiferroics—materials because they offer a wide opportunity for potential applications in information storage, spintronic devices and sensors [78]. Clearly, multiferroic materials can offer the potential for revolutionary device designs, as they are at the heart of multifunctionality.

**1. B. 14. Biferroic Materials:**

As mentioned in chapter one, Ferroic materials are those that display a spontaneous magnetization (ferromagnetic), polarization (ferroelectric) and strain (ferroelastic, shape memory alloy) [79].

Materials that possess two “ferro” properties simultaneously are called “biferroics”. There are three kinds of biferroic materials, Electroelastic material, Magnetoelectric material and Magnetoelectric material.
Electroelastic materials are essentially piezoelectric materials, which have been widely studied and used in many applications. Magnetoelastic materials are magnetic shape memory alloys, which has also been widely studied. The magnetoelectric materials simultaneously possess ferromagnetic and ferroelectric. Possible applications of magnetoelectric materials include magnetic-electric energy converting components, solid state nonvolatile memory, multi-state memory which can find application in quantum computing area and electric/optical polarization components which can find applications in communication, light computing and solid state memories based on spintronics [80].

The magnetoelectric effect was firstly predicted by P. Curie in 1894 as mentioned in [81]. The first magnetoelectric material discovered was nickel iodine boracite, Ni$_3$B$_7$O$_{13}$I, in 1960’s. However, due to the complexity of the boracite structure, little applications and understanding behind the phenomena was found. The other attempt to the magnetoelectric material was to replace certain cations in the ferroelectric perovskite oxide by magnetic cations. However, due to the dilution of the magnetic ions, these materials have Curie temperatures far below room temperature. Recently, YbMn$_2$O$_7$ with a modified perovskite structure has been reported having magnetoelectric properties, but the Curie temperature is still far
below room temperature. These two kinds of structures are the only possible structures for the magnetoelectric crystals. A lot of work has been done around these two structures and many modifications with different compositions have been reported, but no real application has been developed based on these crystals. There are two inherent problems with these crystals, one is low coupling efficient, and the other is low Curie temperature. Therefore, composites become the natural choice.

If materials with magnetostriction and electrostriction were coupled together mechanically, the mechanical interaction between the magnetostriction phase and the electrostriction phase can lead to a functional magnetoelectric material. If a magnetic field is applied to such a composite, due to the magnetostriction effect, the ferromagnetic phase deforms. Because the electrostrictive phase is mechanically coupled with the magnetostriction phase, the electrostriction phase also deforms to adapt to the strain. As the electrostriction materials have piezoelectric effect, the spontaneous polarization of the electrostriction phase changes. If an electric field is applied to the composite, reverse effect will happen and the spontaneous magnetization changes [82].

The major advantage of the composite approach over the single crystal approach in the engineering side is that the Curie temperatures of the material are expected to stay close to their bulk values. From the reported experimental data, the coupling coefficient is much higher than that of single phase crystals [83].

1.B.15. Nanocomposites:

Many materials used in our daily life are composites. Composite is an engineered material consisting of two or more different materials to form a new material of new properties depends on the different physicals and chemicals properties of the constituent materials which remain separate and distinct on a macrospace level within the finished structure [84]. Nanocomposites are a subset of composites that take advantage of unique materials properties on the small scale (at which at least one of its constituents is in nanoscale) [85]. Composites usually have three parts; namely, a matrix (background), structural constituents and an interface. The matrix is a homogeneous material which surrounds the other phases and the
interface is the boundary or surface between the phases. Composites are of interest for the engineering of materials either with desired properties, or new characteristics that are absent in single-phase materials. However the main advantage of composites is the ability to tailor materials for special purposes. In composite, hosting material or the matrix which carries or mobiles the guest materials to form composites. In our case the matrix is polymer. Different types of polymers will be used as matrices to select the optimum one which gives the optimum conditions suitable for applications. The material that will be added to polymers to obtain new and different properties is biferroic magnetoelectric (ME) material system. This means that, three-phase multiferroic nanocomposites (hybrid system) here means that polymer-matrices materials containing two-phase magnetoelectric biferroic nanocomposite.

With the development of electronic technology, composite materials have been widely used for electronic devices where higher densities, limited space and multifunction are required [86]. Recently the ferroelectric–ferromagnetic composite materials were intensively researched for two uses: the magnetic–electric sensors in radio-electronics, optoelectronics, microwave electronics and transducers and the compact electrical filters for suppressing electromagnetic interference (EMI).

As for the magnetic–electric sensors, high ferroelectric content was necessary for the composite materials with sufficient resistivity to generate magnetoelectric effect.

Magnetoelectric (ME) coupling describes the influence of a magnetic field (or an electric field) on the polarization (or magnetization) of a material.

In the past few years, extensive research has been conducted on magnetoelectric effect in single phase and composite materials. Direct polarization of a material under a magnetic field or an in induced magnetization under an electric field requires the simultaneous presence of long range ordering of magnetic moments and electric dipoles. Magneto Electric materials are of two types:

- Single Phase
- Composites
In a magnetoelectric (ME) composite the magnetostrictive strain in the magnetic phase creates an electric polarization in the adjacent piezoelectric phase and hence is capable of converting magnetic field into electric field and vice versa. Such product property can be utilized in smart materials used in sensors, processors and feedback systems.

The first magneto electric effect was predicted in Cr_2O_3, but magneto electric materials with a single phase show a weak magneto electric effect, hence the need of composites.

Magneto electric composites on other hand have large magneto electric coefficients of magnitude of magneto electric voltage coefficients. The composites are made exploiting the product property of materials.

Composite materials can be divided into two categories as proposed by Van Suchtelen [87]: (a) sum properties and (b) product properties as shown in Fig. (1-12).

A sum property of a composite is the weighted sum of the contributions from the constituent phases that is proportional to the volume or weight fractions of these phases. Physical quantities such as density and resistivity are examples of sum properties.

For product properties, consider a composite material with two component phases. The first phase has a property $A \rightarrow B$ with a proportionality tensor $dB/dA = X$; and the second phase has a property $B \rightarrow C$ with a proportionality tensor $dC/dB = Y$. Then the composite will have the property $A \rightarrow C$ with a proportionality tensor $dC/dA = Z$, where $Z = Y \cdot Z$; hence, the name “product property.” The product property is achieved in a composite but not seen in the individual phases.

In a biphasic composite material, if one phase exhibits a property $A \rightarrow B$ (application of an independent variable $A$ resulting in an effect $B$) with a proportionality tensor $dB/dA = X$ (maybe a constant or dependent on $A$ or $B$) and the second phase exhibits a property $B \rightarrow C$ with a proportionality tensor $dC/dB = Y$, then the composite will exhibit a property $A \rightarrow C$ which is absent in either of the initial
phases. The property $A \rightarrow C$ is called a product property of the composite. A typical example is the magnetoelectric effect in a composite material with one magnetostrictive and one piezoelectric phase such as $\text{BaTiO}_3 - \text{NiZnFe}_2 \text{O}_4$ composite.

Since the 1970s when the first magnetoelectric (ME) composite consisting of a piezoelectric phase and a ferromagnetic phase was reported [88], a variety of ME composites have been fabricated. ME composites have drawn much attention since they show new classes of physical properties. These new classes of physical properties are characterized by a secondary coupling of individual physical properties of each component of a composite system. The concept of such “product property” is explained in the following section.

To prepare ME nanocomposites, improved strategies are needed to provide very large interfacial areas and controlled connectivity between piezoelectric and magnetostrictive components. Solution-based approaches for the thin film deposition are particularly desirable and flexible. Therefore, the solution-based bottom up paradigm is a promising route toward nanoscale multifunctional materials’ synthesis, a method that combines sol-gel chemistry with self-assembly and phase separation to produce ME thin film nanostructures or bi-crystals with a tailored morphology. The bottom up nanotechnology builds upon synthesis of nanoscale objects and their assembly into functional architectures. This has already been successfully used in the preparation of photonic crystals [89], three-dimensional superlattices of magnetic nanocrystals, 3 magnetic nanocomposites [90], and ferroelectric nanostructures [91].
1.B.1. Composites in modern technology:

Composite materials with regard to the tremendous ability to modify their properties have found wide application in many various branches of modern engineering. Generally they are used in automobiles, boats, airplanes, sports equipment, appliances and many other products. Constantly they are a challenge for modern and future science [92].

Fig. (1-12): Composite properties; (a) sum properties, (b) product properties, and (c) combination properties.
Composites consisting of one or two magnetic phases have been receiving significant research interests in recent years. For example, alternating Fe-Cr multilayered system has been found to have a magnetoresistance ratio of 50%, a magnitude larger than other known magnetoresistive materials at the time of discovery [93]. These giant magnetoresistive devices based on magnetic metal/nonmagnetic metal (or insulator) nanoscale composites are now the base of the high density memory industry. Another hot spot of recent research is multiferroics which will be the next generation memory. Materials with simultaneous ferromagnetic and ferroelectric ordering have potential applications in multiple state memory and direct control of polarization by magnetic field or vice versa. Due to chemical incompatibility, multiferroic materials are scarce in nature. Composites consisting of a ferromagnetic phase and a ferroelectric phase such as a composite of CoFe$_2$O$_4$ and BaTiO$_3$ are found to have magnetoelectricity due to the elastic coupling between the two phases [94].

1.B.17. Multiferroic Magnetoelectric Nanocomposites:

Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ – BaTiO$_3$ (NZF–BTO) nanocomposite is an applicable example on ME nanocomposites which possess piezoelectric and magnetostrictive at the same time [108]. These materials become magnetized when placed in an electric field, and electrically polarized when placed in a magnetic field [95].

Ferrite-based nanocomposites are the most widely used as magnetic materials with excellent chemical stability and the coast of their production are relatively cheap. Barium titanate has very important applications such as accumulating and processing of information [96].

The strengths of ME nanocomposites rather than single phase compounds which show ME behavior such as Cr$_2$O$_3$ are: first single phase compounds exhibits ME behavior at low temperature and sometimes even at high external field. Second, ME nanocomposites which are materials with good magnetic properties can be combined with materials with piezoelectric properties leading to magnetoelectric nanocomposites even at room temperature [51].
1.B.18. Polymer Matrix Based Nanocomposites:

As mentioned above, nanocomposite is defined as a material with more than one solid phase, metal ceramic, or polymer, compositionally or structurally where at least one dimension falls in the nanometers range. Many nanocomposite materials are composed of just two phases; one is termed the matrix, which is continuous and surrounds the other phase, often called the dispersed phase. The properties of nanocomposites are a function of the properties of the constituent phases, their relative amounts, and the geometry of the dispersed phase. There have been great effort to fabricate nanocomposite to obtain unique physical properties since these properties become increasingly size dependent at low dimension. The combination of the nanomaterial with polymer is very attractive not only to reinforce polymer but also to introduce new electronic properties based on the morphological modification or electronic interaction between the two components. The properties of a nanocomposite are greatly influenced by the size scale of its component phases and the degree of mixing between the two phases. Depending on the nature of the components used and the method of preparation, significant differences in nanocomposite properties may be obtained.

Polymer-based nanocomposites [97-101] represent a new concept in the development of systems exhibiting functional properties resulting from the synergistic interaction between the disperse phase and the matrix.

Polymer/ceramic nanocomposites (polymer matrices filled with ceramic nanopowders) are a promising material for embedded capacitors. They combine the high dielectric constant of ceramic powders and the processability and flexibility of polymers.

In this thesis, using polymers as matrices for the prepared magnetoelectric nanocomposite for the following reasons:

Unfortunately, piezoelectric and piezomagnetic materials are usually brittle ceramics, therefore the nanocomposite consisting of those two phases would be susceptible to brittle fracture. Thus, the third phase, the elastic phase (polymer), is
introduced to increase the ductility. A three-phase electro-magneto-elastic nanocomposite consisting of piezoelectric and piezomagnetic phases separated by a polymer matrix would have greater ductility and formability [100]. Recently, R. Talreja et al. (2001) [101] presented a method for using arrays of MEMS (Micro-Electro-Mechanical Systems) electrodes and electromagnets to achieve microscale positioning of piezoelectric and piezomagnetic particles in liquid polymers, which would then be solidified to make a polymer matrix magnetoelectric nanocomposite. The ability to pattern the particles into microscale unit cells would reduce concentrations of stress, electric field, and magnetic field, thereby increasing effective threshold properties such as strength, electric breakdown field, and magnetic saturation field. Furthermore, one can hope that someday arrays of MEMS can be used to control the microscale distribution of the poling direction of piezoelectric and piezomagnetic particles.

In other words, Coupling between the electric field, magnetic field, and strain of nanocomposite materials is achieved when electro-elastic (piezoelectric) and magneto-elastic (piezomagnetic) particles are joined by an elastic matrix (polymer) [102]. Although the matrix is neither piezoelectric nor piezomagnetic, the strain field in the matrix couples the E field of the piezoelectric phase to the B field of the piezomagnetic phase. This three-phase electromagneto-elastic nanocomposite should have greater ductility and formability than a two-phase nanocomposite in which E and B are coupled by directly bonding two ceramic materials with no compliant matrix. In addition, the addition of inorganic spherical nanoparticles to polymers allows the modification of the polymers physical properties as well as the implementation of new features in the polymer matrix. Hence in the light of medical applications as an example ceramic/polymer nanocomposite possesses significant advantages of high mechanical reliability and excellent biocompatibility for applications in load bearing areas and has gained momentum in the field of orthopedics [103].
1.B.19. Dielectric and magnetic properties of nanocomposites:

Generally, as depicted previously that, the resultant property of the nanocomposite is either sum or product property. Therefore the performance of the resultant nanocomposite depends to large extent on the degree of connectivity between the different phases, the dispersion quality (degree of homogeneity), viscosity, microstructure (morphology), particle size and particle size distribution, the volume fraction of each phase (shape and amount of constituent phases) and the interface effects in addition to the own properties of each individual phase [104].

The different types of polarizations possible in nanocomposite material are the polarization arising from electronic polarization, atomic polarization and orientation polarization due to the orientation of dipoles parallel to the applied field [73].

For heterogeneous materials like nanocomposites, there is also possibility for interfacial polarization, which arises due to the differences in conductivities of the two phases [105]. The time required for each type of polarization to reach the equilibrium level vary with the nature of polarization. The orientation polarization requires more time compared to electronic and atomic polarization to reach static field value. Therefore, the orientation polarization decreases with increase in frequency. The interfacial polarization generally occurs at much lower frequencies.

i) Dielectric nature of the polymer composites:

It is well known that composites can be produced exhibiting enhanced properties that the constituent materials may not exhibit [106] For instance, from the combination of different fibers or fillers with polymer matrices one can produce polymer-matrix composites, a material important to the electronic industry for its dielectric properties in the use of capacitors. The effective utilization of filled polymers depends strongly on the ability to disperse the fillers homogeneously throughout the matrix. The interface properties also strongly affect the characteristics and performance of these composites. One of the most attractive features of these filled composites is that their dielectric properties can be widely changed by choice
of shape, size, and the conductivity of filled constituents in the polymeric matrix. Most of the interesting properties of polymers are attributable to the complex motions within their molecular matrix. In the polymeric system, molecular relaxations exhibit various transitions [107]. As very little work has been reported on double-layer systems, the intention in the present work is to study dielectric properties of such a system. The polymeric interfaces act as charge-carrier trapping sites. Therefore, it has become essential to study the effect of interfaces on the charge-carrier generation, transport and storage in polymeric systems. The study of dielectric constant and dielectric loss, as a function of temperature and frequency is one of the most convenient and sensitive methods of studying polymeric structure. For polymer composites in the solid or viscoelastic state, the physical structure is of great importance in determining the dielectric behavior [108]. The dielectric properties of polymer composite materials have been studied with a view to modifying the properties of polymer systems for practical applications. The conventional inorganic insulators and dielectrics have to a large extent been replaced by polymers on account of their unique ability to be tailor made for specific needs. Epoxies and polyesters have been used in electronics as insulators, dielectrics, substrates, potting compounds, embedding materials and conformal coatings [108].

**ii) Percolation phenomena in composite:**

Consider a composite material made of homogeneously distributed insulator and conductor phases. When the composite is of purely insulator or purely conductor, i.e. the volume fraction of conductor is 0 or 1, the effective conductivity of the material is as low as the insulator or as high as the conductor phase, respectively. For composites of conductor volume fraction between 0 and 1, the effective conductivity changes from that of insulator to that of conductor. However, the change is not linear, when the volume fraction of conductor increases to a certain value, at which the macroscopic sample of the composite material can be traversed from one side to the other on a path covered entirely by the conductor particles [109]. This phenomenon is called percolation and the critical value is called percolation threshold, below this value, the conductor particles are scattered or at best forming only clusters, the effective conductivity of the composite is low, above this value; the
conductor particles form a path for current, the effective conductivity rise abruptly up to a very high value.

1.B.20. **Magnetic properties of polymer matrix based nanocomposites:**

Magnetic properties of the polymer magnetic composite materials depend on the shape and type of filler and on chosen manufacturing technology. Remanence of bonded magnets depends on e.g. quantity of non-magnetic binder, polymer matrix isolate the magnetic grains of powder reducing the influence of interchangeable between them [109]. Composite materials filled with ferrite particles based on polymer matrix materials – called bonded magnets – are of current research interest due to possible applications.

Composites with magnetic fillers dispersed in a polymer matrix represent a system with physical and chemical properties that are influenced by the ferrite powder fillers and polymer matrix characteristics as well as by the interaction at the ferrite-polymer interface [110]. The magneto-polymer composites due to their specific mechanical properties, good formability and toughness (typical for the polymers) allow preparing the products for magnetic circuits of complicated shapes. At the same time the interesting mechanical, magnetic and chemical properties of these new materials allow to use them in many special applications, eg implementation of low profile coils for identification systems, sensors and/or contact-less smart cards.

The presence of the non-magnetic phases and the interface effects were expected to influence the magnetic properties in composites by changing the distribution of the magnetic ions and their spin orientation particularly at interfaces and consequently affect the magnetic interactions.
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2.1: Investigated Samples:

The investigated samples in this work are divided into three groups of magnetoelectric nanocomposites with different compositions as follow:

1. **First Group**: A series of \((x) \text{BaTiO}_3 / (1-x) \text{Ni}_{0.5} \text{Zn}_{0.5} \text{Fe}_2 \text{O}_4; x=0.0, 0.4, 0.5, 0.7 	ext{ and } 1.0\) were prepared by double sintering technique and citrate autocombustion method in comparison study.

2. **Second group**: A series of magnetoelectric nanocomposite with different polymers with fixed ratio \((1:1); (0.5) [0.5 \text{BaTiO}_3 / 0.5 \text{Ni}_{0.5} \text{Zn}_{0.5} \text{Fe}_2 \text{O}_4 ] / 0.5\) Polymer. The polymers used were polyaniline (PANI), polyvinyl acetate (PVAc), Polyvinyl pyrrolidone (PVP) and polyethylene glycol (PEG). The polymer in this work is considered as a matrix for the magnetoelectric nanocomposite (dispersed phase).

3. **Third group**: A series of \((1-y) (0.5 \text{BTO} / 0.5 \text{NZF}) / (y) \text{PEG}; y= 0.0, 0.1, 0.3, 0.5, 0.7, 0.9, \text{and } 1.0\).
2.2. Preparation methods:

2.2a. Solid-state reaction route:

The solid-state reaction route [111] is the most widely used method for the preparation of polycrystalline solids from a mixture of solid starting oxides. These oxides do not react together at room temperature over normal time scales and it is necessary to heat them to much higher temperatures, often to 1000 to 1500°C in order for the reaction to occur at an appreciable rate depending on the type of oxides used [112]. The factors on which the feasibility and rate of a solid state reaction include, reaction conditions, structural properties of the reactants, surface area of the solids, their reactivity and the thermodynamic free energy change associated with the reaction [113]. This method results in powders with coarse-grained, agglomerated structures with very low surface. High temperatures needed for solid state compound formation.

The investigated nanocomposites containing the two individual phases; ferrite (Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$) and ferroelectric (BaTiO$_3$) materials were prepared by standard double sintering technique [114]. The ferromagnetic phase was prepared by mixing the anlar grade 99.999 % (Aldrich) raw materials NiO, ZnO, and Fe$_2$O$_3$ in appropriate molar proportions. The component oxides were mixed and grounded in agate mortar for three hours and presintered at 950°C for 5h with heating rate of 4°C/min. The ferroelectric phase was also prepared following the same route by mixing BaCO$_3$ and TiO$_2$ in appropriate molar proportions and presintered at 950°C for 5h. The ME nanocomposites were prepared by mixing 40, 50, 60, and 70 wt. % of BaTiO$_3$ phase and 60, 50, 40, and 30 wt. % of Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$, respectively. The nanocomposite mixture was finally sintered at 1150°C for 5h with a heating rate of 4°C/min to yield the final products.

Solid state setup and reaction procedure is illustrated in Fig.(2.1) and Fig.(2.2) respectively.
Fig. (2.1): The standard ceramic technique setup.
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**Fig.(2.2): Flow chart of standard ceramic procedure of synthesizing**

\[ (x)BaTiO_3/(1-x)Ni_{0.5}Zn_{0.5}Fe_2O_4 \text{ nanocomposite.} \]
2.2b. *Citrate–autocombustion method:*

Combustion synthesis is an easy and convenient route for the synthesizing of a variety of advanced ceramics, catalysts and nanomaterials [115]. In this technique, a thermally induced redox reaction takes place between an oxidant and a fuel [116]. Many types of combustion synthesis exist which differ mainly in the physical state of the reactants or in the combustion modality [117]. By combustion-based methods it is possible to produce monophasic nanopowders with relatively homogeneous microstructure, at lower temperatures or shorter reaction times when compared with other conventional methods like solid-state synthesis [118] or nitrate method [119].

Citrate autocombustion synthesis (CAS) is a popular method [120], where the fuel (citric acid) and metal nitrates are used as metal and oxidant source. CAS method shows high similarities with the very well known Pechini process [121], and it can be more properly described as a “sol–gel combustion method” [122]. Nevertheless the CAS method differs from Pechini process in that the nitrates are not previously eliminated as NO$_2$, but remain in the mixture with metal citrates causing the auto-combustion.

The main target is to clarify the correlation between the structure, microstructure, and properties of the nanocomposites due to different preparation methods, different types of polymers, and different concentration of selected polymer to optimize the best physical properties of our nanocomposites where the challenge in preparing such materials is to find equilibrium ferroelectric and magnetic structures preserving both properties close to the room temperature.

2.2b.1. *Nano - BaTiO$_3$ powder preparation by citrate autocombustion method:*

Improved citrate autocombustion technique used to prepare fine powder of BaTiO$_3$ using butyl titanate. The modified and details of new citrate process is shown schematically in flow chart; Fig.(2.3). Reagent grade Ba (NO$_3$)$_2$, tetrabutyl
titanate \([\text{Ti} (\text{OC}_4\text{H}_9)_4], 97\%\) and citric acid were the starting materials. Stoichiometric amount of \(\text{Ba(NO}_3)_2\) (0.1 mole) was dissolved into 500 ml deionized water in a beaker then 0.2 mole of citric acid was mixed well with 0.1 mole tetrabutyl titanate under mechanical stirring. The two solutions were mixed well under stirring and heating at 70\,^\circ\text{C} till evaporating all volatile components and water from the beaker and then a very dense gel was formed after which a black powder was observed at Fig.(2.4a). The black powder was grinded mechanically well in agate mortar and added to alumina crucible which is inserted in a furnace for sintering at 700\,^\circ\text{C} for 5 hrs, with a heating rate 5^\circ\text{C}/\text{min} (Fig.(2.4b)). A white fine powder was formed and observed after annealing predicting that the formation of \(\text{BaTiO}_3\).
Preparation of BaTiO$_3$ by modified citrate method using Butyle Titanate

0.2 M Citric Acid solution (pH 6)

0.1 M Butyl Titanate Ti(OC$_4$H$_9$)$_4$(>99 %)

500 ml. deionized water

0.1M Ba(NO$_3$)$_2$(>99%)

Mixed solution with stirring at 70°C for 1 h

Mixed solution with stirring at 70°C adjust pH at 7-9

Combustion on hot plate at 120°C

Formation of a fluffy black mass

Grinding of the powder for fine and homogeneous powder

Sintering at 700°C for 5 hours with heating rate of 5°C/min

XRD

EDX

SEM

AFM

TEM

Fig (2.3): Flow chart of synthesizing BaTiO$_3$ perovskite.
2.2b.2. Preparation of Nickel–Zinc Ferrite (Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$) by citrate method:

The following flowchart; Fig.(2.5) indicates the reaction procedure of citrate autocombustion technique for Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ preparation. Reagent grade Fe(NO$_3$)$_3$ •9H$_2$O, Ni(NO$_3$)$_3$ •3H$_2$O, Zn(NO$_3$)$_2$ •6H$_2$O, deionized water, and citric acid were used as starting materials. Nitrates are first dissolved in citric acid solution and followed by stirring to yield a transparent aqueous solution. The mole ratio of citric
acid to the total metal cation content was 1:1. The pH value of the solution was adjusted to have a neutral value (pH=7) by adding droplets of ammonia solution. The precursor solution was heated to form a sol and subsequently a gel. The gel was calcined at 700°C for 5 h in air.

**Fig.(2.5): Flow chart of synthesizing Nickel–zinc ferrite nanoparticles by citrate method.**
2.3. Magnetolectric nanocomposite in comparison between

Ceramic route and Citrate technique:

The powders with the nominal composition of $0.5\text{BaTiO}_3 / 0.5\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ were synthesized by two different methods; the ceramic method ($\text{C}_1$) [122] and citrate method ($\text{C}_2$) [123]. The details of the two synthesis process have been described in the flowchart Fig.(2.6). In the two methods, the nanocomposite constitutes that have been already prepared by either methods were good mixed together in agate mortar for a time of 3 hrs and then loaded to the programmable Lenton Furnace UAF 16/5 furnace in material science lab. (1). The formation temperature for the two methods is different where, the sintering temperature of ceramic method is around 1150°C with 4°C/min as a heating/cooling rate, while the calcination temperature in case of citrate method is around 700°C.
**Comparison; C₁ & C₂**

**Citrate (C₂)**

**Raw materials**
- Fe(NO₃)₃, Ni(NO₃)₃, Zn(NO₃)₂, Ba(NO₃)₂, butyl titanate, deionized water, and citric acid

- 0.2 M Citric Acid solution
- 0.1M Ti(OC₄H₉)₄

**Mixed solution with stirring at 70°C**

**Ceramic (C₁)**

**Raw materials**
- NiO, ZnO, Fe₂O₃

**Mixing, grounded, pressed to pellet**

**Presintering at 950°C for 5h**

**Final sintering at 1150°C for 5h**

Mixed solution with stirring at 70°C adjusts pH at 7-9 and drying to fluffy powder, calcinations to 800°C with 5°C/min.

**Fig. (2.6): Flow chart of comparison of 0.5BaTiO₃ / 0.5Ni₀.₅Zn₀.₅Fe₂O₄ nanocomposite prepared by two different methods.**
2.4. Synthesis of hybrid nanocomposites/ Polymer Matrix based nanocomposites:

Different polymers; polyaniline (PANI), polyvinyl acetate (PVAc), Polyvinyl pyrrolidone (PVP) and polyethylene glycol (PEG) are used as a matrix for the prepared magnetoelectric nanocomposite with a nominal composition of (0.5BaTiO$_3$ / 0.5Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$) that has been prepared by citrate autocombustion method. 1:1 ratio of polymer – magnetoelectric nanocomposite is selected to investigate the optimum polymer that shows optimum magnetoelectric properties with the hosted magnetoelectric nanocomposite. The selected optimum polymer which is PEG as will be depicted latter from the results is used with different selected ratios; by mixing 0.0, 0.1, 0.3, 0.5, 0.7, 0.9 and 1.0 wt. % of PEG phase respectively and well mixed by grounding. The polymer-based nanocomposites were prepared via ball-milling.

2.5. Characterization techniques:

2.5.1. X-ray Diffraction:

X-ray Diffraction (XRD) is a powerful technique used to uniquely identify the crystalline phases present in materials and to measure the structural properties (strain state, crystallite size, epitaxy, phase composition, preferred orientation, and defect structure) of these phases [124-127].

In order to determine the lattice parameter and the average crystallite size in the investigated samples we have performed standard 0-20 scans.

The X’pert Phillips X-Ray Diffractometer, Fig.(2.7) at Ain Shams University operating with 40 kV and 20 mA, with a resolution of 0.03° and CuK$_\alpha$ of 1.54056Å was used.

2.5.1.1. Crystallite size estimation by XRD:

In this work; Scherer's equation is used to estimate the crystallite size (L) of the resultant nanophases. The Scherer's equation is as follow [128]:

\[
L = \frac{K\lambda}{\beta\cos\theta}
\]
\[ B(2\theta) = \frac{K\lambda}{L \cos \theta} \]  

(2.1)

Where \( B \) is the full width at half maximum (FWHM), \( \lambda \) is the wavelength of the radiation, and \( K \) is the shape factor. The most common values for \( K \) are:

* 0.94 for FWHM of spherical crystals with cubic symmetry
* 0.89 for integral breadth of spherical crystals with cubic symmetry

From X-ray diffraction results, the lattice parameter (\( a \)) was calculated using the relations [129, 130]:

\[
\frac{1}{d_{hkl}^2} = \frac{(h^2 + k^2)}{a^2} + \frac{l^2}{c^2} \quad \& \quad V = a^2 c \]

(2.2)

Where \( d_{hkl} \) is the interplaner distance for a given plan with Miller indices (hkl). The theoretical density [131] was determined using formula:

\[
D_x = \frac{ZM}{NV} \]

(2.3)

Where \( M \) is the molecular weight, \( N \) is Avogadro's number, \( Z \) is the number of molecules per unit cell and \( V \) is the unit cell volume.

\[ \theta \]

\[ \lambda \cos^2 \theta \]

\[ K B \]

\[ \text{Fig.}(2.7): \text{Phillips X-Ray Diffractometer.} \]
2.5.2. Scanning Electron Microscopy (SEM):

The shape and size of the grain samples was determined from the micrographs taken using the scanning electron microscope (SEM) (JEOL JSM-5600LV (Central Lab. Atomic Energy Authority) as in Fig.(2.8).

![JEOL JSM-5600LV SEM instrument and its EDX.](image)

2.5.3. Energy dispersive X-ray spectroscopy (EDX):

EDX is a standard procedure for identifying and quantifying elemental composition of sample areas as small as a few cubic micrometers [132]. Characteristic X-rays are produced when a material is bombarded with electrons in an electron beam instrument, such as a scanning electron microscope (SEM). The model of the EDX which was used in this thesis is JEOL JSM-5600LV samples.

2.5.4. Transmission Electron Microscopy (TEM):

Transmission electron microscopy is a valuable method in the research of materials [133, 134]. TEM is a type of microscope, using electron beams for imaging
solid samples at atomic resolution. Sample preparation was made by suspending composites powder in distilled water or pure acetone or ethylene glycol before fixing the suspension on a mesh copper grid. TEM images were obtained by JEOL 4010 instrument (Central Lab. Atomic Energy Authority), with objective lens of 30 μm, used at 80 kV as in Fig.(2.9).

Fig. (2.9): JEOL 4010 400kV TEM instrument.

2.5.5. Atomic Force Microscopy (AFM):

The atomic force microscope (AFM) is ideally suited for characterizing nanoparticles [135]. It offers the capability of 3D visualization and both qualitative and quantitative information on many physical properties including size, morphology, surface texture and roughness. Statistical information, including size, surface area, and volume distributions, can be determined as well. A wide range of particle sizes can be characterized in the same scan, from 1 nanometer to 8 micrometers. In addition, the AFM can characterize nanoparticles in multiple mediums including ambient air, controlled environments, and even liquid dispersions [136]. For individual particles, size information (length, width, and height) and other physical properties (such as morphology and surface texture) can be measured.
Whenever data from single-particle techniques is processed to provide statistical information, the concern over statistical significance exists. It is easy to attain greater statistical significance in AFM by combining data from multiple scans to obtain information on the larger population [137].

In our work we used Agilent 5500 AFM (Central Lab. Atomic Energy Authority) equipment indicated in Fig.(2.10) for studying nano-BaTiO₃ separately and the prepared magnetoelectric nanocomposite.

![Fig.(2.10): Agilent 5500 AFM equipment.](image)

**2.5.6. Fourier Transform Infrared (FTIR) Spectroscopy:**

Infrared absorption spectroscopy [138] is an important and non-destructive characterizing tool, which provides qualitative information regarding structural details of crystalline materials. A Fourier transformation is a mathematical operation, whence a infrared spectrum can be calculated. Identified materials of the FTIR library are necessary to analyze the FTIR spectral pattern. The presence of characteristic peaks of di-phase and tri-phase nanocomposites are investigated into a 400-4000 cm⁻¹ range by spectrophotometer, Nicolet iS10 FT-IR spectrometer (Central Lab. Atomic Energy Authority) as in Fig.(2.11).
The analyses were run using the KBr pellet technique. The KBr pellets of samples were prepared by mixing (1.5–2.00) mg of samples, finely grounded, with 200 mg KBr (Spec. Pure KBr, FT-IR grade) in a vibratory ball mixer for 20 s. Careful grinding is of great importance for eliminations of error caused by scattering. A fundamental advantage of this method is that, there is no absorption band in the IR spectral region for the KBr.

2.5.7. Thermal characterization:

Thermal analysis will be used to characterize materials by measuring physical and reactive properties as a function of temperature [139]. Temperature range becomes one of the most important criteria when considering such applications as the transportation industry.

The instrument in the thermal analysis allow us to measure many temperature-dependent phenomenon, such as decomposition, chemical reaction, melting point, glass transition and other phase transition. A variety of thermal analysis techniques are in use: thermogravimetric analysis (TGA), dynamic...
mechanical analysis (DMA), differential scanning calorimetry (DSC) and thermomechanical analysis (TMA).

Thermal analysis was studied in our work by Differential thermal analysis (DTA) and Thermogravimetry analysis (TGA).

2.5.7a. Differential Thermal Analysis (DTA):

DTA is a “fingerprinting” technique that provides information on the chemical reaction, phase transformations, and structural changes that occur in a sample during a heat-up or a cool-down cycle. In this experiment, DTA-50 was used to monitor the decomposition process of the precursor.

2.5.7b. Thermogravimetry Analysis (TGA):

TGA uses heat to force reactions and physical changes in materials. TGA provides quantitative measurement of mass change in materials associated with transition, thermal degradation and chemical reaction. The TGA records change in mass from dehydration, decomposition, and oxidation of a sample with time and temperature.

Fig.(2.12): Thermal analyzer DTA-50-Japan with TGA in the same setup
2.6. Electrical transport measurements:

2.6a. ac conductivity measurements:

The electrodes required for the electrical measurements were applied on both faces of the samples by applying conducting silver paint (Du Pont). Dielectric measurements as a function of temperature on different samples were performed employing the pellets from room temperature (R.T) up to 800°C using a computer controlled LCR meter (Model 3532-50, HIOKI-Japan). Capacitance and dielectric loss were measured over the frequency range of 50 Hz–5 MHz. The ac electrical conductivity was evaluated from the dielectric data [140]. The bridge has the following measuring ranges:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Capacitance</td>
<td>0.001 PF- mF</td>
</tr>
<tr>
<td>Resistance</td>
<td>0.01 ohm up to 10 Gega Ohm</td>
</tr>
<tr>
<td>Dielectric loss (D)</td>
<td>0.0001 to 9.9999</td>
</tr>
</tbody>
</table>

The measurements were carried out using a home built LabVIEW program that is suitable for dielectric measurements. The bridge is good earthed and all connected cables are good shielded and connected to the earth. The measurement accuracy was better than ±1%. The sample was then inserted in a suitable sample holder, and a calibrated non-inductive furnace was used for heating the sample with a constant rate. The temperature of the sample was measured using a K-type thermocouple connected to a Digi-sense meter “USA” with junction just in contact with the sample. The accuracy of measuring temperature is ±1°C.
2.6b. Dielectric constant measurements:

There are two basic methods for measuring the dielectric properties namely. Lumbed and distributed-circuit methods [141]. The lumbed circuit method is always used at low frequency and depends on the determination of the equivalent electrical circuit of the specimen is in which a capacitance $C_p$ is connected in parallel with a resistor $R_p$. The total impedance $Z$ will be
The alternating voltage represented by the real part of $V$ will produce an out of phase or capacitive Current $I_c$.

$$V = V_0 e^{i\omega t} \quad (2.5)$$

$$I_c = \text{ImaginaryPart}(\frac{V}{Z}) \quad (2.6)$$

and an in phase or resistive current $I_R$

$$I_R = \text{Real Part}(\frac{V}{Z}) = \frac{V}{R_p} \quad (2.7)$$

since

$$I_c = i\omega C_0 \varepsilon' V; \quad I_R = \omega C_0 \varepsilon'' V; \quad \text{so} \quad \varepsilon' = \frac{C_p}{C_0}; \quad \varepsilon'' = \frac{1}{\omega R_p C_0} \quad (2.8)$$

$$\tan(\delta) = \frac{\varepsilon''}{\varepsilon'} = \frac{1}{\omega R_p C_p} \quad (2.9)$$

Alternatively the specimen may be regarded in terms of a series circuit. If the equivalent series component of capacitance and resistance are $C_s$ and $R_s$ respectively then the total impedance will be

$$Z = R_s + \frac{1}{i\omega C_s} \quad (2.10)$$

Comparing the out of-phase and in-phase currents after application of an alternating voltage, we obtain

$$\begin{align*}
\varepsilon' &= \frac{C_p}{C_0} (1 + \tan^2 \delta) \\
\varepsilon'' &= \frac{R_s}{\omega} \frac{C_p}{C_0} (1 + \tan^2 \delta) \\
\tan(\delta) &= \frac{\varepsilon''}{\varepsilon'} = \frac{\omega R_s C_s}{C_0} 
\end{align*} \quad (2.11)$$

Therefore, the real part of the dielectric constant ($\varepsilon'$) and dielectric loss ($\varepsilon''$) of a material can be calculated from the measured values of either equivalent series or
parallel circuit component specimen. At high frequencies the electromagnetic wavelength becomes comparable with sample dimension and lumbed circuit method is favorable than the disturbed one. In the lumbed circuit the sample becomes the medium for the propagation of electromagnetic wave and the dielectric properties must then be obtained from the attenuation characteristics of the sample.

2.7. Thermoelectric Power:

In the measurement of the thermoelectric power (Seebeck effect) [142] the point of contact with one of the voltage detecting electrodes is kept at a temperature higher than that of sample other ends, as shown in Fig.(2.14).

![Fig.(2.14): The principle of thermoelectric power voltage measurements A is the sample, B and B are the electrodes for detecting the voltage V, T1, T2 are the temperature of the sample two surfaces, measured by two thermocouples.](image)

The polarity of the voltage that was appeared between the two electrodes depends on the current carrier type. Thus the measurement of the thermoelectric power permits the determination of the sign of the charge carriers. It can be made either by integral method (the temperature of sample’s end is held constant while the other is varied) or the differential method (the temperature of the two ends are varied while the temperature between them is maintained small and constant).

Figure (2.15), shows a simple cell used to carry out the Seebeck coefficient measurements. These measurements was performed under zero current conditions in order to avoid temperature variations caused by the current passing through the sample at the electrodes contact Points. A positive Seebeck voltage coefficient can
arise for several reasons, first in an intrinsic semiconductor in which the mobility of the positive charge carriers is greater than that of the negative carriers. Second: for a dielectric material in which, the polarons share in the conduction process. The concentrations of electrons and/or holes (n) are calculated from the relation.

\[ n = 2(2\pi m^* k / h^2)^{3/2} \exp(-E/kT) \]  

(2.12)

where \( m^* \) is the effective mass of charge carrier (assumed to be equal to the rest mass of electron or hole), \( E \) is the exponential energy term obtained from temperature dependence of resistivity, \( k \) is the Boltzmann constant, \( h \) is the Planck's constant and \( T \) is the absolute temperature. The conductivity is given by

\[ \delta = e(n\mu_h + \mu_e)n\mu_h(1+c) \]  

(2.13)

Fig.(2.15): A typical sample holder for Seebeck coefficient measurement. The points A, D: represents non-inductive furnace. B, C: represents two silver electrodes, E: is the position where the sample to be inserted. F: is the position where two Cu-Constantan thermocouples to be located, And G: is Ceramic plate for isolation purpose.
where \( |e| \) is the electronic charge, \( \mu_h, \mu_e \) are the mobilities of holes and electrons respectively and \( c_e \) equals \( \mu_c/\mu_e \). The equation for Seebeck coefficient is given by:

\[
S = -k / |e| (c - 1/c + 1)[E/kT+2]
\]

(2.14)

2.8. Magnetic properties:

**Magnetic field measurements and calibration using search coil method:**

In the present work, T2B-type fluxmeter (HEME) made in England, with a resolution of 0.01 mT is used. The calibration of the magnetic field is shown in Fig. (2.15 a-c). In Fig. (2.15 a) the magnetic field varies linearly with the current (I) and decreases with increasing the gap width. Saturation of the magnetic field takes place at high currents (larger than the range of measurements). Figure (2.15b) shows the variation of the magnetic field as a function of the distance from the center of the air gap width at different currents. From the figure, the magnetic field gradient (dH/dz) versus the distance from the center of the pole pieces is shown in Fig. (2.15c). The figure shows the point of maximum force at each separate field. Under this condition the magnetic susceptibility of the investigated samples is measured by using Faraday’s method [143, 144].

2.8a. Magnetic susceptibility measurements:

Two main classes of magnetic susceptibility measurements are known. The first involves a measurement or a comparison of mutual or self inductance using an ac. bridge method. This method has been widely used for the measurements of magnetic susceptibility of paramagnetic salts at low temperature but not for absolute or at high temperature measurements. The second class depends on the force exerted on a sample placed in homogenous magnetic field. Within these two general classes, there are versions in the experimental techniques.
Fig. (2.16: a, b): Calibration of the magnetic field as a function of the air gap width.
If a substance is placed in a magnetic field of intensity $H$, which may be either smaller or larger than the surrounding field, depending whether the substance is “diamagnetic” or “paramagnetic” respectively. In case of “ferromagnetism” the intensity of the field within the substance may be increased. All substances, even though paramagnetic, have at least an underlying diamagnetism that must be corrected for in precise determination of the permanent magnetic moment. A substance may be both diamagnetic and paramagnetic, but generally whenever paramagnetism is present it is so much large that it hides the diamagnetism. Generally, the induction of the field within the substance is given by $B$, where:

$$B = H + 4\pi M$$ (2.15)

Where $M$ is the magnetization intensity and $(k = M / H)$ is the volume magnetic susceptibility while the susceptibility per unit mass $\chi$ obtained by dividing $k$ by the density, and the molar magnetic susceptibility $\chi_M$ which is the magnetic susceptibility per gram-molecular weight is given as $\chi_M = \chi \times$ molecular weight.
In general, the magnetic susceptibility of diamagnetic substances is independent of temperature and field strength, and the paramagnetic is often inversely proportional to the sample temperature, and is independent of field strength and the susceptibility of ferromagnetic substances is dependent on both temperature and field strength. The choice of a method for the measurement of magnetic susceptibility depends on the nature of the material, the available amount of the material, the accuracy required and the temperature range beside the available equipment. Faraday and Gouy are the most suitable methods for measuring the magnetic susceptibility.

2.8b. Faraday’s Method:
(The non-homogeneous field method):

The Faraday balance is designed as in Fig.(2.17) for solid sample measurements which may be of almost any form, single crystal, polycrystalline solid, alloys, etc.

A very small quantity of the sample is held in a suitable tube attached to the balance. This tube must be heavy to resist a lateral motion of the magnetic sample which may be attracted to one of the magnet pole pieces trying to hand it vertically. If the poles of a magnet are inclined toward each other, there exists a non-homogeneous field with an axis of symmetry. If a substance is now placed in a region of maximum inhomogeneous magnetic field where the strength of the field (H) changes rapidly with displacement along the axis of symmetry (x), then the substance will be subjected to a force along this axis

\[ F = M\chi H_0 \frac{dH}{dyz} \]  \hspace{1cm} (2.16)

where, \( H_0 \) is the field at the center between pole pieces.

from which
\[ \chi = \frac{F}{MH_0 \left( \frac{dH_x}{dz} \right)} \]  

(2.17)

Where \( M \) is the mass of the sample, \( \chi \) the mass susceptibility, \( H_x \) is the magnetic field intensity, \( F = mg \), \( m \) is the net pull on the sample and \( dH_x /dZ \) is the field gradient along the \( Z \) axis. This method is the most convenient one. Small amounts of material are required, and no separate determination of density is necessary. The method is used extensively by Pierre Curie; these classical measurements have been used by many investigators since then. When moving the sample to a small distance up or down, \( \frac{dH_x}{dz} \) will vary and also the force will be changed. Precautions should be taken that the value of \( H_0 \frac{dH_x}{dz} \) remains constant in the region in which measurements should be taken as shown in Fig. (2.18).

Fig. (2.17): Schematic diagram of Faraday's method for measuring magnetic susceptibility.
2.9. **Hysteresis measurements:**

**Vibrating Sample Magnetometer (VSM):**

The hysteresis and magnetization measurements were performed using vibrating sample magnetometer (VSM; 9600-1 LDJ, USA) with a maximum applied field of 6000 Oe at room temperature.

VSM is a basic research tool for determining the magnetic properties of a material. When a sample material is placed in a uniform magnetic field and made to undergo sinusoidal motion, a dipole moment will be induced in the material [145].

---

*Fig.(2.18): Specimen in non-homogeneous field.*

*Fig.(2.19): Vibrating sample magnetometer setup.*
Chapter Three
Chapter Three

Results and Discussions

In this thesis 6-papers were published, they are:


The sample under investigation are divided into mainly three groups:

*First Group:

(A):

3.1. A series of (x) BaTiO$_3$ / (1-x) Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$; x=0.0, 0.4, 0.5, 0.7 and 1.0 prepared by ceramic method:

In this section, we aimed to characterize the nanocomposites of the formula (x) BaTiO$_3$ / (1-x) Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ with x= 0.0, 0.4, 0.5, 0.6, and 0.7 in wt. to improve their properties where the present BTO/NZF ceramic is a possible candidates for ME applications. In this work we use the abbreviations; BTO and NZF for referring to BaTiO$_3$ and Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ respectively.

3.1.1. Thermal studies:

To investigate the formation of the nanocomposite phase, thermal analysis for the typical sample x = 0.6 was carried out Fig. (3.1: a, b). From the data, it is clear that, the minor weight loss before 100°C in thermal gravimetric analysis (TGA) curve is attributed to evaporation of residual water molecules. As the temperature increases from room temperature up to 500°C, the dried precipitate lost about 0.2 % of its weight. The differential thermal analysis (DTA) curve shows broad exothermic peak centered at 267.7°C, which is probably due to the formation of oxide from its hydroxides meaning thereby a formation of crystalline phase of the ferrite/BTO nanocomposite sample. It is indicating that the formation of nanocomposite phase takes place at a temperature around 267.7°C while thermal analysis is a dynamic processes. Thus, the temperature recorded by TGA–DTA for nanocomposite formation is expected to be higher.
Chapter Three

Results and Discussions

3.1.2. X-Ray Diffraction (XRD):

The XRD patterns of (x) BaTiO$_3$ / (1-x) Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ ; x=0.0, 0.4, 0.5, 0.6, and 0.7 ME nanocomposites are shown in Fig. (3.2). It is clear that there are two phases; cubic spinel structure (NZF) ferrite (piezomagnetic PM) and perovskite tetragonal crystal structure BaTiO$_3$ (BTO) (piezoelectric PE). No significant extra peaks were observed in the XRD, which means that no significant chemical reaction takes place during sintering of the mixed powders. The pattern revealed also that the highest peak value corresponding to perovskite phase of PE phase that appeared at $2\theta = 31.53^\circ$. However, this peak height gradually increases due to an increasing percentage (x) of the BTO in the nanocomposites with a simultaneous decrease in intensities of ferrite peaks. X-ray diffraction peaks were used to determine the crystallite size (L) of the two phases using Debye-Scherer's equation [146]; $L = \frac{0.89 \lambda}{\beta \cos\theta}$, where $\beta$ is the corrected full width at half maximum (FWHM), $\lambda$ is
the wavelength of the radiation and $2\theta$ is the diffraction angle. The calculated values of the crystallite size (L) of the two phases were obtained from the most intensive peaks of NZF and BTO, (311) and (110), respectively. It reveals that, the crystallite size of NZF $\approx 68$ nm, whereas that of BTO $\approx 119$ nm. The data obtained from XRD (d-spacing); equation (3.2); were used to determine the values of lattice constants (a) for cubic phase (NZF) and (a & c) for the tetragonal phase (BTO), as reported in Table (3.1). The volume of the unit cell was also calculated for PM and PE phases, respectively.

![XRD pattern of the composites](image)

**Fig. (3.2): XRD pattern of the composites (1-x) $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4 + (x) \text{BaTiO}_3$; x=0.0, 0.4, 0.5, 0.6, and 0.7 ME nanocomposite.**
Table (3.1): Lattice constants of NZF and BTO phases for (x) BaTiO$_3$ / (1-x)Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$; x=0.0, 0.4, 0.5, 0.6, and 0.7 nanocomposites.

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<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
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<td>PM</td>
<td>PE</td>
<td>PM</td>
<td>PE</td>
<td>PM</td>
</tr>
<tr>
<td>BTO (x)</td>
<td>a (Å)</td>
<td>a (Å)</td>
<td>c (Å)</td>
<td>V(Å$^3$)</td>
<td>L(nm)</td>
</tr>
<tr>
<td>0.0</td>
<td>8.3632</td>
<td>..........</td>
<td>..........</td>
<td>..........</td>
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<td>4.0062</td>
<td>64.33</td>
<td>103.8</td>
</tr>
</tbody>
</table>

3.1.3. Scanning electron microscopy analysis (SEM):

Very thin layer from the sample was inserted on the microscope sample holder to be investigated by the SEM to assure the uniform dispersion of the samples and for the prepared nanocomposites to assure their formation in the proper nanosized scale.

The typical SEM micrograph of x=0.0, x=0.4, x=0.5, x=0.6 and x=0.7 wt. % are shown in Fig. (3.3:a-f) for the prepared nanocomposites. It is observed that there are two dissimilar particle shapes corresponding to the two different phases forming the nanocomposite. The energy dispersive X-ray spectroscopy (EDX) was used to distinguish between the two different constituent phases. It was found that; large bright particles are BaTiO$_3$ (PE), whereas the small grey ones indicate NZF. It was also appeared that ferromagnetic particles are dispersed at piezoelectric matrix grain boundary. At the same time, the increase observed in pores is due to the difference in thermal expansion between PE matrix and PM particles. SEM was used to determine the particle size of the two particle phases with different shapes by using counting method [147]. It is revealed that the particle size determined by SEM is larger than that obtained from XRD measurements, this may be due to XRD determines crystallite size while SEM counting method determines the grain size.
Also XRD sees the secondary small particles than SEM; moreover there may be some agglomeration in micrograph due to humidity [148]. Fig. (3.4:a,b) shows the particle size distribution determined using imaging program.

Fig. (3.3:a,b): SEM photographs of nanoocomposite \((x)BTO/(1-x)NZF; x=0.0 \text{ and } 0.4\).

\[ \text{Bright Bigger particle} = \text{BTO} \]

\[ \text{Grey smaller particle} = \text{NZF} \]

Fig. (3.3c): SEM photograph with EDX for distinguishing between the two phases.
Fig. (3.3d): SEM photographs of nanaocomposite (0.5BTO/0.5NZF) with different magnifications.

Fig. (3.3e,f): SEM micrograph for the investigated composite at $x = 0.6$ and $0.7$ respectively.
3.1.4. Fourier Transform Infrared (FTIR) Analysis:

FTIR is usually used to investigate the chemical bonding or the chemical composition of materials. The absorption FTIR spectra of (x) BaTiO$_3$ / 0.5Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ nanocomposite and its constituents were carried out and recorded in the range 400-4000 cm$^{-1}$.

Figure (3.5), shows that, in Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ systems Ni$^{2+}$ is stabilized in the octahedral crystal site whereas Zn$^{2+}$ prefers tetrahedral sites because of its facility to form covalent bonds involving sp$^3$ hybrid orbitals. The $v_1$ band observed at ~ 420
cm$^{-1}$, involves the stretching vibration of ($\text{Fe}^{3+} + \text{O}^{2-}$) on the octahedral site and the $\nu_2$ band observed at $\sim 579$ cm$^{-1}$ can be assigned to the stretching vibration of ($\text{Fe}^{3+} + \text{O}^{2-}$) on tetrahedral site. These results are in agreement with that published earlier [149]. One of the fingerprint stretches for BaTiO$_3$ was also observed at $\sim 480$ cm$^{-1}$; while it appears at $\sim 420$ cm$^{-1}$ due to the exchange interaction between Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ and BaTiO$_3$ within the nanocomposite. The band at 2360 cm$^{-1}$ indicates the presence of OH group [150,151].

*Fig. (3.5): FTIR spectra of (x)BTO/(1-x)NZF nanocomposite, x = 0.0, 0.4, 0.5, 0.6, and 0.7.*
3.1.5. Magnetic measurements:

Figure (3.6a) illustrates the relation between the molar magnetic susceptibility \( \chi_M \) and absolute temperature ranging from 300- 700K as a function of the magnetic field intensity \( H \) (1340, 1660, and 1990 Oe.). The results show that, the values of \( \chi_M \) decreases with increasing temperature up to Curie temperature (\( T_C \)) as in Table (3.2). This reduction in \( \chi_M \) is attributed to the thermal agitation which disturbs the oriented dipoles in random and different directions. This reduction will continue till it reaches \( T_C \) at which the sample is completely changed from ferromagnetic to paramagnetic behavior. This reduction is due to the presence of nonmagnetic compound (BaTiO\(_3\)) which leads to reducing in the magnetization.

The values of Curie temperature were determined from the 1st derivative of magnetization [152] as illustrated in Fig.(3.6b). The data reveal that, the decrease of \( T_C \) with increasing PE content \( x \) is clearly evident due to increasing of nonmagnetic (BTO) on the expense of the magnetic (NZF). Exceptional case was obtained for \( x = 0.5 \) BTO which exhibit the highest value of \( T_C \). This means that, this content is a critical concentration according to the geometry of the lattice, the range of interaction strength, and the anisotropy in the system. According to the Percolation theory [153] where, below this critical concentration we expect that the system is made up of infinite magnetic clusters with finite nonmagnetic clusters of BTO ions. Increasing the BTO concentration up to \( x = 0.5 \), the system is expected to be made up exclusively of isolated clusters of both magnetic and nonmagnetic ions and in this case no infinite clusters exist. Above the critical concentration the number of small magnetic clusters increases and the mean number of sites per clusters is expected to increase. Besides, from Table (3.2), it is clear that, the values of the effective magnetic moment \( \mu_{\text{eff}} \) increases with increasing the magnetic field intensity \( H \) and the largest value was obtained at \( x = 0.5 \) which agree well with other properties of the investigated nanocomposites.

The dependence of magnetization on the applied magnetic field \( H \) for BTO / NZF nanocomposites is shown in Fig. (3.7a) and Table (3.3). The graph exhibits typical ferromagnetic behavior with small area of the hysteresis loop. It is also clear
that, all the magnetization parameters such as saturation magnetization ($M_s$), remanence magnetization ($M_r$), coercive field ($H_c$), decrease notably with the increase in BTO content ($x$) except the critical concentration ($x = 0.5$) which gives the highest value of these parameters due to the effect between grain and grain boundaries interface. Moreover, presence of the order magnetic structure due to the unbalanced antiparallel spins ($x=0$), causes strong nonlinear and almost non-hysteretic character. The decrease in saturation magnetization except at $x = 0.5$ ($M_s = 38.21 \text{emu/g}$) with diamagnetic BTO content is caused by the gradual weakening of ferrimagnetic order. In other words, the increase in magnetization at $x = 0.5$ could be explained as due to the change in magnetic ion distribution in the spinel network of NZF where Fe$^{3+}$ ions (with $5\mu B$ – Bohr magneton) are equally distributed in tetrahedral (A) and octahedral (B) positions, while Ni$^{2+}$ ions (with $2\mu B$) take octahedral positions exclusively: Zn$^{2+}$Fe$^{3+}$[Ni$^{2+}$Fe$^{3+}$]O$_4^2^-$. The dominant interaction is the one of superexchange AB between the ions in position (A) and (B). Since Fe$^{3+}$ ions in (A) and (B) positions have equal and opposite magnetic moments, they compensate each other and the complete magnetic moment is exclusively determined by Ni$^{2+}$ ion. While Zn$^{2+}$ ions are introduced in the network they are disposed only in tetrahedral positions, dislocating Fe$^{3+}$ ions, which migrate to the octahedral positions as Zn$^{2+}$Fe$^{3+}$[Ni$^{2+}$Fe$^{3+}$]O$_4^2^-$. In this case, the magnetic moments of Fe$^{3+}$ ions in the two sub-lattices (A) and (B) compensate each other. After reaching the critical concentration, a weakening of the AB superexchange interaction takes place and the parallel orientation of the magnetic moments in the (B) network is altered; two distinct orientations of the magnetic moments appear in the (B) network, that compensate each other only partially [154]. This leads to a progressive decrease of the saturation magnetization reaching the value of 12.02 emu/g of ferrite with $x = 0.7$.

Relatively no contribution of BTO ions in the magnetic moment ($\eta_B$) takes place as in Fig.(3.7b) and Table (3.3). It is clear that, the AB exchange interaction is weakened and thereby the saturation magnetization decreases. The remanent magnetization ($M_r$) also decreases in the same manner as that of $M_s$, because each individual grains act as a magnetic materials having circuit to produce resultant magnetization. Whatever a deviation exists and may be due to porosity effects
which were introduced at the sintering time, different conditions, atmosphere of firing, and different attendant cation distribution.

Moreover, as mentioned earlier [155-157], the porosity increases with BTO content, the presence of pores breaks the magnetic circuit present among the grains and results in a net reduction of magnetic properties. The magnetic moment \( n_B \) in Bohr-magnetron (the saturation magnetization per formula in Bohr magneton) at 300K is obtained from the magnetization data for all samples as calculated from the relation: \( n_B = \frac{M M_s}{5585} \) [158] where \( M \) is the molecular weight and \( M_s \) is the saturation magnetization of the sample. The reported data in Fig. (3.7b) and Table (3.3), indicates that, the values of \( n_B \) decreases with increasing \( x \) expect at \( x = 0.5 \) because the magnetic properties are affected by interface between grain and grain boundaries as mentioned before.

Table (3.2): Values of Curie temperature \((T_C)\) and the effective magnetic moment at different magnetic field intensity \((\mu_{eff})\) of \((x)\text{BTO/(1-x)NZF} \) nanocomposites; \( x = 0.0, 0.4, 0.5, 0.6, \) and 0.7.

<table>
<thead>
<tr>
<th>BTO ((x))</th>
<th>(T_C) ((K))</th>
<th>(\mu_{eff}(\mu_B))</th>
<th>(\mu_{eff}(\mu_B))</th>
<th>(\mu_{eff}(\mu_B))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
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<td>1340 Oe</td>
<td>1660 Oe</td>
<td>1990 Oe</td>
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<td>6.93</td>
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<td>513</td>
<td>4.85</td>
<td>3.56</td>
<td>4.16</td>
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</table>

Table (3.3): Values of magnetic parameters of \((x)\text{BTO/(1-x)NZF} \) nanocomposites; \( x = 0.0, 0.4, 0.5, 0.6, \) and 0.7.

<table>
<thead>
<tr>
<th>BTO ((x))</th>
<th>(M_r) ((\text{emu/g}))</th>
<th>(M_s) ((\text{emu/g}))</th>
<th>(H_C) ((\text{Oe}))</th>
<th>(n_B) ((\mu_B))</th>
<th>(M_r/ M_s)</th>
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</tr>
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<td>1.02</td>
<td>23.05</td>
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<td>0.08</td>
</tr>
</tbody>
</table>

* \(M_r/M_s\) is the squarness ratio
Fig. (3.6a): Variation of magnetic susceptibility ($\chi_M$) of the investigated composite with temperature at different magnetic field intensity.
Chapter Three

Results and Discussions

Fig. (3.6b): The calculated values of Curie temperature ($T_c$) for the composites $(x) \text{BaTiO}_3/(1-x) \text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$, from the first derivative of magnetization.
Fig. (3.7: a, b): a. Magnetic hysteresis loop of ferroelectric content in the composites. 
b. Variation of saturation magnetization ($M_s$) and magnetic moment with wt.% of ferroelectric content in the composites.
3.1.6. Transport properties and Dielectric parameters:

The variation of dielectric constant ($\varepsilon'$) in the frequency range 100 kHz to 5 MHz at different temperatures was carried out for the composition ($x$) BaTiO$_3$ / (1-$x$) Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$; $0.0 \leq x \leq 0.7$. The conduction phenomenon was explained on the basis of electron hopping model where the value of ($\varepsilon'$) increases drastically with increasing BTO ($x$) content in the nanocomposite.

Figure (3.8: a- c) is a typical curve correlates the real part of dielectric constant ($\varepsilon'$) and absolute temperature (TK) at different frequencies (100 kHz – 5 MHz) as a function of compositions for $x=0, 0.4, 0.5$. The general trend of all samples is the increase in $\varepsilon'$ with increasing temperature up to the transition temperature at which $\varepsilon'$ gives maximum values. Table (3.4) reports the transition temperature for different compositions. The appearance of more than one transition temperature at $x=0.4$ and $x=0.5$ is due to the presence of the two phases in the prepared nanocomposites. From the data, it also clear that, the first transition took place at $\approx 430$ K can be ascribed to the structural phase transition temperature of BaTiO$_3$ from tetragonal to cubic which agrees well with that reported in the literatures [159]. The second transition temperature appeared at $\approx 720$ K which is considered the dielectric transition point of Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$, and matches with that reported earlier for similar Ni and Zn substituted ferrites [160].

The effect of frequency on the dielectric constant ($\varepsilon'$) at different BaTiO$_3$ content is shown in Fig. (3.9). The data reveal that, dielectric constant $\varepsilon'$ decreases steeply at lower frequencies and remains constant at higher frequencies showing dispersion of $\varepsilon'$ related to the charge transport relaxation time. This dispersion in $\varepsilon'$ is attributed to Maxwell and Wagner interfacial polarization [161, 162]. The large values of ($\varepsilon'$) in the nanocomposites investigated are ascribed to the fact that ferroelectric grains are surrounded by ferrimagnetic grains which agrees well with Koop’s theory [163]. The large value of $\varepsilon'$ is associated with space charge polarization and inhomogeneous dielectric structure which assume that impurities are grain structure and pores [164]. In other words, since an assembly of space
charge carriers in the inhomogeneous dielectric structure described requires finite time to line up their axes parallel to an alternating electric field, the dielectric constant naturally decreases, if the frequency of the reversal field increases [165, 166]. This behavior is also observed by earlier researches [167, 168].

The influence of temperature on the electrical conductivity (ln$\sigma_{ac}$) is shown in typical Fig. (3.10: a-c). The data show that, the $ac$ conductivity increases with increasing of frequency and shows a small dip at higher frequencies. The same variation was obtained for samples with different BTO content (x). Besides, from these plots it was observed that, all samples show three distinct regions with different slopes indicating different conduction mechanism. The variation of conductivity was explained on the basis of actual location of cation in the nanocomposite structure where in ferrite it is due to electron transfer between divalent and trivalent ions. The conduction at low temperature region ($< 550$ K) is due to impurities, whereas at higher temperature region ($> 550$ K), it is due to electron hopping. Besides, the values of activation energy ($\Delta E$) were calculated and found to be less than 0.4 eV which is clearly assume that the conduction is due to electron hopping [169] and the nanocomposites behave like semiconductor but without significant change in the charge carriers concentration, indicated that the temperature dependence of electrical conductivity in such case involves less temperature dependent concentration of carriers and mostly associated with temperature dependent mobility.

The variation of $dc$ conductivity for the investigated nanocomposites is shown in Fig. (3.11: a, b). The plots show also semiconducting behavior of the samples like that observed in ac conductivity. The conduction mechanism in our investigated nanocomposites results from the hopping process of charge carriers. The activation energy for conduction was calculated using the relation $\sigma = \sigma_0 \exp\left(-\frac{\Delta E}{kT}\right)$ where; $\sigma$ is the conductivity at temperature $T$, $\sigma_0$ is the temperature independent constant, $k$ is Boltzmann constant and $\Delta E$ is the activation energy for conduction process. Two regions of conductivity with two different slopes were obtained. The activation energy for conduction was calculated using the above relation where the conduction at high and low temperature is due to electron
hopping. Fig. (3.11b) clarifies the decrease of the conductivity with increasing BTO content ($x$), also the nanocomposite with $x=0.5$ reveals highest value of conductivity which agree well with $ac$ conductivity data.

The variation of Seebeck coefficient ($\alpha$) for the nanocomposites with temperature is shown in Fig. (3.12). The plots show the type of charges responsible for conduction mechanism. A $p$–$n$ transition is observed in all the compositions except $x=0$ gives n-type like behavior with increasing temperature. The occurrence of $p$–$n$ transition is independent on transition temperature [170, 171]. At lower temperature all samples shows p-type like behavior. The variation of $\alpha$ at low temperature region (<400 K) may be attributed to impurity conduction. The observed p-type conduction in BaTiO$_3$ is attributed to Ti$^{4+} \leftrightarrow$ Ti$^{3+}$ transition [172,173] and p-type to n-type conduction in ferrite is attributed to Ni$^{2+} \leftrightarrow$ Ni$^{3+}$, releasing a hole and Fe$^{3+} \leftrightarrow$ Fe$^{2+}$ releasing an electron [174, 175]. This behavior is in agreement with that obtained in dielectric measurements.
Fig. (3.8: a- c): Typical variation of dielectric constant $\varepsilon'$ with temperature as a function of frequency for (x) BTO / (1-x) NZF nanocomposite.
Table (3.4): The values of the activation energies $E_1, E_{11}, E_{111}$ and the different transition temperatures $T_1$ and $T_2$ for $(x)BTO/(1-x)NZF$ nanocomposites for different BTO contents.

<table>
<thead>
<tr>
<th>BTO (x)</th>
<th>$E_1$ (eV)</th>
<th>$E_{11}$ (eV)</th>
<th>$E_{111}$ (eV)</th>
<th>$T_1$ (K)</th>
<th>$T_2$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.53</td>
<td>0.29</td>
<td>0.07</td>
<td>720</td>
<td>720</td>
</tr>
<tr>
<td>0.4</td>
<td>0.27</td>
<td>0.17</td>
<td>0.09</td>
<td>450</td>
<td>720</td>
</tr>
<tr>
<td>0.5</td>
<td>0.32</td>
<td>0.15</td>
<td>0.12</td>
<td>470</td>
<td>610</td>
</tr>
<tr>
<td>0.6</td>
<td>0.73</td>
<td>0.43</td>
<td>0.05</td>
<td>550</td>
<td>690</td>
</tr>
<tr>
<td>0.7</td>
<td>0.50</td>
<td>0.014</td>
<td>0.16</td>
<td>400</td>
<td>490</td>
</tr>
</tbody>
</table>

Fig. (3.9): Frequency- dependent of dielectric constant for $(x)BTO/(1-x)NZF$ nanocomposites at 400 K.
Fig. (3.10: a- c): Typical variation of $\ln \sigma_{ac}$ with $1000/T$ as a function of frequency for $(x)$ BTO / $(1-x)$ NZF nanocomposite.
Fig. (3.11:a, b): a- The variation of dc. electrical conductivity ($\ln \sigma$) with temperature $1000/T_K$ at different BTO content ($x$).

b- The variation of dc electrical conductivity ($\ln \sigma$) with BTO content ($x$) at selected temperature (443K).
Fig. (3.12): The variation of Seebeck coefficient ($\alpha$) as a function of temperature at different compositions.
3.1.7. First – Order Studies of Nanometric 0.5Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ / 0.5BaTiO$_3$ Biferroic Material System:

The results of (1-x)Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ / (x)BaTiO$_3$ biferroic nanocomposites revealed that the equal ratio (1:1) is considered as a critical concentration that verifies the aspect ratio and percolation theory. Therefore this nanocomposite with composition 0.5Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ / 0.5BaTiO$_3$ was examined in some detail.

3.1.7.1. Structural Characterization

The XRD patterns of 0.5 Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ - 0.5 BaTiO$_3$ ME nanocomposites is shown in Fig. (3.13). It is clear that, there are two phases; cubic structure NZF (piezomagnetic PM) and perovskite tetragonal crystal structure BaTiO$_3$ (piezoelectric PE). No third phase coexists in the prepared nanocomposites. This means that, no significant chemical reaction takes place during sintering of the mixed powders. The pattern revealed that, the highest peak value of XRD intensity corresponding to perovskite phase of PE which occurred at 2\(\theta\) = 31.53°. The values of lattice constant (a) for the PM phase is 8.3885 Å, while those of (a, c) for tetragonal PE phase are 4.0049 Å and 4.0048 Å respectively. The calculated crystallite sizes (L) of the PM and PE phases using Debye- Sherrer’s equation are 69 nm and 100 nm respectively.

The typical SEM micrograph is shown in Fig. (3.14) for the prepared nanocomposite system. It is observed that there are two dissimilar particle shapes corresponding to the two different phases forming the nanocomposite. Energy dispersive X-ray (EDX) was used to distinguish between the two phases. It is found that; white contrast is corresponding to BaTiO$_3$ phase whereas the dark contrast is the Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ one. It was observed also that; ferromagnetic particles are dispersed at the piezoelectric matrix grain boundaries.

Fourier Transform Infrared Spectroscopy (FT-IR) spectra, Fig.(3.15), shows that, at Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ systems Ni$^{2+}$ is stabilized in the octahedral crystal site whereas Zn$^{2+}$ prefers tetrahedral sites because of its facility to form covalent bonds involving sp$^3$ hybrid orbitals. The \(\nu_1\) band observed at \(\sim\) 420 cm$^{-1}$, involves the
stretching vibration of (Fe$^{3+}$– O$^{2-}$) on the octahedral site and the $\nu_2$ band observed at ~579 cm$^{-1}$ can be assigned to the stretching vibration of (Fe$^{3+}$– O$^{2-}$) on tetrahedral site. These results are in agreement with that published earlier [176]. One of the fingerprint stretches for BaTiO$_3$ was also observed at ~ 480 cm$^{-1}$; while it appears at ~ 420 due the exchange interaction between Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ and BaTiO$_3$ within the nanocomposite. The band at 2360 cm$^{-1}$ indicates the presence of OH group [177].
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Fig. (3.13): XRD pattern of 0.5BaTiO$_3$ / 0.5Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ Biferroic System.

Grey smaller particles = Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$  
Bright bigger particles = BaTiO$_3$

Fig. (3.14): SEM of 0.5BaTiO$_3$ / 0.5Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ Biferroic system
3.1.7.2. Dielectric Properties:

a) Dielectric constant:

Figure (3.16) correlates, the real part of dielectric constant ($\varepsilon'$) and absolute temperature as a function of frequencies for the nanocomposite $0.5\text{Ni}_0.5\text{Zn}_0.5\text{Fe}_2\text{O}_4$ - $0.5\text{BaTiO}_3$. The data clarify that the dielectric constant increases with increasing temperature and decreases with increasing frequency. It is clear that, there are two small humps around the temperatures 420 K, 520 K and one maximum at 600 K for each frequency. These transitions represent the resonance of the nanocomposite system takes place at the transition points [178]. These relaxation points can be observed when hopping frequency of electrons or holes between different valence cations becomes approximately equal to the frequency of the applied field frequency [179].

The variation of the dielectric constant with frequency reveals dispersion due to Maxwell-Wagner type interfacial polarization which is in good agreement with Koop's phenomenological theory [180]. According to this model the nanocomposite structure is supposed to be composed of the fairly well conducting grains, separated
by ultra-thin insulating layer of grain boundaries. These grain boundaries could be formed either in each phase separately, due to the superficial reduction or oxidation of crystallites in the porous materials as a result of their direct contact with the firing atmosphere during the sintering process [181].

Fig. (3.16): Variation of the real part of dielectric constant $\varepsilon'$ versus absolute temperature at different frequencies.

Fig. (3.17): Variation of dielectric constant as a function of frequency at 400 K.
Figure (3.18) correlates the real part of dielectric constant ($\varepsilon'$) and absolute temperature during heating and cooling runs; in the temperature ranging from R.T up and down 830 K at different frequencies for the nanocomposite $0.5\text{BaTiO}_3 / 0.5\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$. The curves indicated that, $0.5\text{BaTiO}_3 / 0.5\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ nanocomposite possess a thermal hysteresis loop behavior which could be attributed to a first-order transition temperature [182]. At this transition the physical properties such as dielectric constant, polarization, etc. change discontinuously with temperature [183], where the two runs gives hysteresis curve with different areas depending on the applied frequency. This hysteresis behavior confirms that, $\text{BaTiO}_3$ has dual effects namely piezoelectric and pyroelectric properties.

When heating the prepared nanocomposite, $\text{BaTiO}_3$ undergoes a structural phase transition behavior from tetragonal to cubic phase. With gradual cooling from 830 K down to the 300 K, the cooling curve did not overlap on the heating one due to the relaxation process. The interesting features of the dielectric constant versus temperature diagram are the following: the cooling curve lies above the heating one and they do not merge to each other. This indicates that the cooling process could cause a substantial increase in the dielectric constant due to the increase in the density of the dipole moments towards the transition from paraelectric to ferroelectric nature. In other words, this transition can be attributed to the generation of phonons is due to lattice vibrations or lattice scattering from the thermal energy. These phonons interact with the aligned dipoles to decrease their alignment and then reduce the polarization which decreases the dielectric constant as a result. While during cooling, the dipoles will be reorient again and hence the polarization will increase as well as the dielectric constant.

The dielectric constant of ferroelectric materials is extremely high near the transition temperature, the polarization induced in the paraelectric (non-polar) region at $T > T_c$ by an applied electric field along the ferroelectric axis goes gradually over into the spontaneous polarization region upon cooling below $T_c$. The effect of this field tends to shift $T_c$ to a higher temperature [184]. At $T_c$, the
ferroelectric phase is favored by an applied field; therefore, the Curie temperature is raised.

On drawing the calculated values of the area of the loop versus frequency Fig.(3.19), the obtained graph shows exponential decay behavior of the second order which can be fitted to the following equation:

\[ y = y_0 + A_1 \exp\left\{ -\frac{x}{x_1} \right\} + A_2 \exp\left\{ -\frac{x}{x_2} \right\} \] (3.1)

where \( y \) represents the hysteresis loop area, \( y_0 \) is the area at zero frequency, \( A_1 \) and \( A_2 \) are constants, \( x \) represents the applied frequency and \( 1/x_1 = t_1 \), \( 1/x_2 = t_2 \) are the relaxation (life, delay or lagging) times required for dipoles to rearrange again during cooling process. The calculated values of \( t_1 \) and \( t_2 \) are \( 7 \times 10^{-6} \) and \( 8 \times 10^{-7} \) sec. respectively. Time dependent dielectric constant measurements reveal memory effects of the investigated nanocomposite [185]. The area between the two curves can be attributed to the heat dissipation due to the friction between the dipoles. The behavior of the area between the two curves versus frequency has the same trend as that of the real part of the dielectric constant versus frequency in the same temperature range.
Fig. (3.18): Variation of $\varepsilon$ versus absolute temperature ($T_K$) at different frequency during heating from R.T up to 830 K and cooling from 830 K down to R.T.
b) Dielectric loss factor:

All dielectric materials have two types of losses. One is a conduction loss, representing the flow of actual charges through the dielectric material. The other loss is due to the movement or rotation of atoms in an alternating field [186].

Figure (3.20) shows the variation of the dielectric loss factor \( \varepsilon'' \) with absolute temperature at different frequencies of the nanocomposites 0.5BaTiO\(_3 \) / 0.5Ni\(_{0.5}Zn_{0.5}Fe_2O_4 \). The data in the figure show that the high losses corresponding to high \( \varepsilon'' \) at low frequency and high temperature due to interfacial intergranular space charge polarization at the heterointerface between the two different PE and ME phases or at phase boundary.

Also \( \varepsilon'' \) reveals a hysteresis behavior with temperature as shown in Fig. (3.21). An exponential decay of the hysteresis area versus frequency (Fig. (3.22)) is

![Graph showing the calculated loop area between the heating and cooling curves of \( \varepsilon' \) versus absolute temperature (TK) at different frequencies.](image-url)
fitted with the same equation of the dielectric constant. The resultant values of \( t_1 \) and \( t_2 \) are in the same order of magnitude and are very close to those obtained from \((T–\varepsilon')\) measurements. The lagging of \((\varepsilon'')\) versus temperature on cooling rather than on heating may be due to an asymmetric and irreversible arrangement of dipoles as mentioned above. In other words, there is a relation between the relaxation time and what happened in the structure of the material. There will be disordering due to the temperature increasing which makes randomizing for the dipoles during heating. While during cooling process the structure takes a time to restore its original case or it is expected that there will be permanent dipole moment change due to the transition of ions from their position to other positions. On cooling, the dielectric loss factor is higher than its value on heating due to the adding value from the reorientation of individual dipoles to the permanent dipole moment.

*Fig. (3.20): Variation of the dielectric loss factor \((\varepsilon'')\) with temperature at different frequencies.*
Dielectric loss factor \( \varepsilon' \times 10^3 \)

Imaginary part of dielectric constant \( \varepsilon'' \times 10^{-3} \)

Fig. (3.21): Variation of \( \varepsilon'' \) with absolute temperature (TK) at different frequency during heating and cooling runs from R.T up to 830 K and cooling from 830 K down to R.T.
c) \textit{ac Conductivity (}\(\sigma_{ac}\)\textit{)}

In order to explain the conduction mechanisms of the investigated nanocomposite consisting of two separate phases, we have to explain not only the contribution of each phase but also the effect of heterointerface between the two different phases (phase boundary) rather than the homointerface or the intergrainular space charge interfacial region between grains of the same material (grain boundary) [187].

It is known that, the conduction mechanisms in ferrite and piezoelectric phases are separately attributed to the Verwey-de Boer model [188] of electron and/or hole hopping which involves exchange of electrons (Fe\(^{2+}/\)Fe\(^{3+}\), Ti\(^{3+}/\)Ti\(^{4+}\)) or holes (Ni\(^{3+}/\)Ni\(^{2+}\), Ba\(^{3+}/\)Ba\(^{2+}\)) between ions of the same element present in different valence state, and distributed randomly over crystallographic equivalent lattice.

\begin{center}
\includegraphics[width=\textwidth]{fig322.png}
\end{center}

\textit{Fig. (3.22): The estimated loop area between the heating and cooling curves of (}\(\varepsilon''\)\textit{) versus absolute temperature (}\(T_K\)\textit{) at different frequencies.}
sites. The small polaron hopping or tunneling as well as the intergrainular space charge interfacial region between ferrite and piezoelectric grains plays an important role in explaining the electrical current transport mechanisms in nanocomposite. The contribution of the heterointerface in conduction mechanisms appears as a space charge interfacial polarization at the dissimilar grain boundaries. This mechanism is dominated at low frequencies and high temperatures; it depends on the distribution of the two phases with respect to each other and the volume fraction of each phase [189].

To determine the most dominant ac conduction mechanisms of the present nanocomposite, the dependence of $\sigma_{ac}$ on frequency at different temperatures is considered. The relation between the ac conductivity ($\sigma_{ac}$) and the applied angular frequency ($\omega$) is described from the equation [190]:

$$\sigma_{ac} (\omega) = A \omega^s$$

(3.2)

where A is constant, while the exponent s is very important factor which determining the dominant type of conduction mechanisms. According to the quantum mechanical tunneling (QMT) model [191], the exponent s is either temperature independent or an increasing function with temperature. On the other hand, the correlated barrier hopping model (CBH) [192] predicts that the power s is a decreasing function with temperature. The conduction mechanism also depends on the value of the exponent s, either greater than or less than or equals unity [193].

Figure (3.23) represents $\ln(\sigma_{ac})$ versus $\ln(\omega)$ graphs at different temperatures in both heating and cooling processes. It is clear that, at the same temperature; $\ln(\sigma)$ versus $\ln(\omega)$ plot gives two different graphs in a hysteresis behavior for heating and cooling processes. It is also observed that; $\ln(\sigma)$ versus $\ln(\omega)$ plots change their trend at temperature around 500 K. Therefore, two temperature regions are considered indicating that, there are two types of conduction mechanisms differs from one temperature region to another according to the variation of the slopes of the two lines.
According to the literatures [194], the trend of $\ln (\sigma)$ versus $\ln (\omega)$ graph predicts the type of conduction predominant current mechanism that is predominant at a certain temperature range. It is illustrated from Fig. (3.23) that the conductivity increases monotonically with increasing frequency and becomes weakly dependent at both high frequency and temperature. Therefore, the small polaron quantum mechanical tunneling is predicted to be the dominated current transport mechanism in the temperature range from 300 K up to 500 K in both cooling and heating processes. The linearity of the plots confirms the small polaron type of conduction. However, the slightly decreases in conductivity is attributed to conduction by mixed polarons. It has been shown that for ionic solids, the concept of small polarons is valid [195]. At temperatures higher than 500 K, the conduction mechanism can be explained with hopping of electrons between $\text{Fe}^{2+}/\text{Fe}^{3+}$ and $\text{Ti}^{3+}/\text{Ti}^{4+}$, whereas, hopping mechanism needs high thermal energy to occur. There is also contribution from p type charge carriers by hole hopping between $\text{Ni}^{2+}/\text{Ni}^{3+}$, but this contribution is lower as compared with the electronic contribution [196]. The dependence of the $ac$ conductivity on the angular frequency confirming that, migration of ions has a contribution on the electrical conduction [197].

The calculated values of the exponent $(s)$ of equation (3.2) were derived from $\ln \sigma_{ac}$ versus $\ln (\omega)$ plots; Fig. (3.23); and then plotted versus temperature in case of heating and cooling processes as depicted in Fig. (3.24). It is observed that, the exponent $s$ increases with increasing temperature at the relatively lower temperature region (300-500 K). So that, the behavior in this region is due to polaron quantum tunneling, while above 500 K the conduction is limited by hopping mechanism where $s$ decreases with increasing temperature. This result is in agreement with that observed above from Fig. (3.23). It is noted that the value of $s$ is less than unity, i.e., $0 \leq s < 1$ at the whole temperature range.

The variation of $ac$ conductivity with temperature at different frequencies from 100 kHz up to 5 MHz is illustrated in Fig. (3.25). It is clear that the investigated nanocomposite shows a semiconductor nature behavior. As the temperature increases the conductivity increases. The increase in conductivity with rise of temperature is due to the increase in the thermally activated drift mobility of
charge carriers according to the hopping conduction mechanism [198]. Besides, the figures give that, a hysteresis behavior with area depends on the frequency as shown in Fig. (3.26). The two curves; heating and cooling process have almost very close slopes and hence very closes activation energies in the different temperature regions.

Figure (3.23) shows that there are three straight lines in each plot corresponding to three temperature regions with different slopes obeying Arrhenius equation [199]:

$$\sigma_{ac} = \sigma_0 \exp\left(-\frac{E_a}{kT}\right)$$  \hspace{1cm} (3.3)

where $\sigma_0$ is constant and $E_a$ is activation energy.

The estimated values of the activation energy are 0.12 eV, 0.15 eV and 0.32 eV for $E_{aI}$, $E_{aII}$ and $E_{aIII}$ respectively. It is noted that the activation energy increases with temperature resulting in a decrease in energy barrier for carrier hopping.

At the first region observed at lower temperatures (< 350 K) the thermally activated tunneling mechanism of polaron is considered with activation energy of 0.12 eV. At the second region (350 K-500 K), corresponding to the ordered state or the ferroelectric state of the nanocomposite, the conduction mechanism can be explained with hopping of electrons between Fe$^{2+}$/Fe$^{3+}$ and Ti$^{3+}$/Ti$^{4+}$, and by hole hopping between Ni$^{2+}$/Ni$^{3+}$ and Ba$^{3+}$/Ba$^{2+}$. Also polaron tunneling mechanism may take a part in this temperature region.

At the third temperature region, above 500 K, the explanation of conduction mechanisms depends mainly on the ferrite phase because there is no structure phase transition for ferrite with temperature rather than the piezoelectric phase that transferred into paraelectric phase after transition temperature called Curie temperature. After 500 K the hopping mechanism is mainly from the transition of electrons and holes between Fe$^{2+}$/Fe$^{3+}$ and Ni$^{3+}$/Ni$^{2+}$ respectively in the ferrite phase with activation energy equals 0.32 eV. Also at higher temperatures the (homo- and
hetero-) interfacial space charge polarization mechanism will be dominated according to the Koop’s theory [200].

The variation of Seebeck coefficient ($\alpha$) versus temperature (T) is shown in Fig. (3.27). The positive and negative values of Seebeck coefficient ($\alpha$) indicate that, the majority net charge carriers are holes and electrons respectively [201]. It is observed that, the positive Seebeck coefficient corresponding to p-type conduction is due to $\text{Ni}^{2+} \leftrightarrow \text{Ni}^{3+}$ and $\text{Ba}^{3+} \leftrightarrow \text{Ba}^{2+}$ hole transition. While n-type conductivity related to negative Seebeck coefficient is mainly due to $\text{Fe}^{2+} \leftrightarrow \text{Fe}^{3+}$ and $\text{Ti}^{3+} \leftrightarrow \text{Ti}^{4+}$ electron transition. The transition from p-type to n-type conductivity and vice versa is a temperature dependent according to which current mechanism is predominated at this temperature region.
Fig. (3.23): $\ln(\sigma_{ac})$ versus $\ln(\omega)$ at different temperatures in both heating and cooling processes.

Fig. (3.24): Variation of $s$ with temperature in case of heating and cooling processes.
Fig. (3.25): ln (\(\sigma_{ac}\)) versus 1000/T at different (f) during heating and cooling processes.
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Fig. (3.26): The estimated area between the heating and cooling curves of \( \ln(\sigma) \) versus the reciprocal of absolute temperature \( (1000/T) \) at different frequencies.

Fig. (3.27): Seebeck coefficient of 0.5BaTiO\(_3\) / 0.5Ni\(_{0.5}\)Zn\(_{0.5}\)Fe\(_2\)O\(_4\) Biferroic material.
3.2. Biferroic nanocomposite $0.5\text{BaTiO}_3 / 0.5\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ prepared by Citrate – autocombustion method:

In this part we will discuss the results of structural, magnetic and dielectric characterizations of $0.5\text{BaTiO}_3 / 0.5\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ nanocomposite prepared by citrate–autocombustion method. Advanced imaging techniques are used to structural characterization of $0.5\text{BaTiO}_3 / 0.5\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ multiferroic nanocomposite. Atomic force microscope (AFM) is one of the most important tools for imaging, measuring, and manipulating matter at the nanoscale. AFM is used at different sample areas to confirm the data obtained from scanning electron microscope (SEM) and transmission electron microscope (TEM). Moreover AFM gives 3D visualization for the surface texture and roughness showing the morphology of the two distinguish phases. The traditional characterizations techniques have been used such as X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR) to identify the formation of the two individual phases separately and to study the chemical composition of the prepared nanocomposite respectively.

Before displaying the results of $0.5\text{BaTiO}_3/0.5\text{NZF}$ nanocomposite consisting of ferroelectric and ferromagnetic phases, we will discuss the results of ferroelectric phase separately due to special studies on $\text{BaTiO}_3$ that has been prepared by advanced citrate–autocombustion route using Butyl Titanate $\text{Ti(OC}_4\text{H}_9)_4$ and characterized by advanced characterization techniques.

(B1):

3.2.1. Results and Discussion of nano-$\text{BaTiO}_3$:

3.2.1.1. XRD Analysis:

Figure (3.28) shows the X-ray diffraction pattern for the obtained white powder to examine its crystallization. The obtained chart indicated that, the formation of perovskite $\text{BaTiO}_3$ in single phase with tetragonal crystal structure was formed as compared with ICDD card (067519). Moreover, the results of XRD revealed the nanocrystalline nature of $\text{BaTiO}_3$ with the average crystallite size ~ 47
nm. The combination of (002) and (200) peaks was sufficiently broad to suggest the nanometric tetragonal structure. These results agree also with those obtained for BaTiO$_3$ [105]. The observation of the peaks (001) and (100) confirms also the tetragonal structure of BaTiO$_3$ and the lattice parameters are $a=0.39949$ nm, $c=0.401308$ nm and $V=0.064045$ nm$^3$.

Figure (3.29) reveals the calculated crystallite size distribution at different diffraction angle ($2\theta$). The crystallite size ($L$) was calculated from X-ray broadening of the main peak (110) using Debye-Scherer's equation [146]:

$$L = \frac{0.89 \lambda}{\beta \cos\theta}$$

$\beta$ is the FWHF and $\lambda$ is the wavelength of the radiation.

![Image of XRD pattern](image1.png)

**Fig. (3.28):** XRD pattern of nanopowder BaTiO$_3$

![Image of crystallite size distribution](image2.png)

**Fig. (3.29):** Crystallite size distribution at different diffraction angle ($2\theta$).
3.2.1. b. FT-IR Analysis:

In order to investigate the chemical bonding or the chemical composition of BaTiO$_3$ nanoparticles, FTIR spectrum of BaTiO$_3$ nanopowder was carried out using thermo scientific Nicolet iS10 FT-IR Spectrometer. The FTIR spectrum and the appeared absorption bands around 1600 and 3600 cm$^{-1}$ of BaTiO$_3$ coincide with that published in the literatures [2]. The band around 3600 cm$^{-1}$ is due to O$\equiv$H stretching vibrations of hydroxyls present in this system because O$\equiv$H bonds form chelation organic complex in the solution. The band at 1600 cm$^{-1}$ is due to the symmetric and asymmetric stretching vibrations of the carboxylate functional group (-COO-). One of the fingerprint stretches for BaTiO$_3$ was also observed at $\sim$ 420 cm$^{-1}$ which is mainly due to the formation of metal oxides (M$\equiv$O: Ba$\equiv$O, Ti$\equiv$O).

![FTIR spectrum of BaTiO$_3$ nanoparticles.](image)

3.2.1. c. SEM-EDX Analysis:

Figure (3.31) shows the scanning electron micrograph (SEM) image of synthesized barium titanate sample. It confirms the porous nature with some agglomerations indicating the cauliflower- like morphology. This morphology is similar to that obtained by other authors [193]. Point analysis of the chemical
composition in the micro-area for BaTiO$_3$ was studied by energy dispersive-X-ray analysis (EDX). Stoichiometric ratios of the main metallic components of BaTiO$_3$ were recalculated in mass %: Ba – 58.88 %, O – 20.6 %, Ti – 20.53 %. Results of the EDX depicted in Fig. (3.32), reveals the following chemical composition: Ba – 52.17 %, O – 25.92 %, Ti – 21.87 % which is nearly similar to the nominal composition.

![SEM micrograph of BaTiO$_3$ with different magnification.](image)

**Fig. (3.31): SEM micrograph of BaTiO$_3$ with different magnification.**

![EDX analysis of BaTiO$_3$ perovskite sample](image)

**Fig. (3.32): EDX analysis of BaTiO$_3$ perovskite sample**
Table (3.5): EDX analysis of BaTiO₃ perovskite sample.

<table>
<thead>
<tr>
<th>element</th>
<th>Percentage%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba</td>
<td>52.17</td>
</tr>
<tr>
<td>Ti</td>
<td>25.92</td>
</tr>
<tr>
<td>O</td>
<td>21.87</td>
</tr>
<tr>
<td>Total %</td>
<td>99.96</td>
</tr>
</tbody>
</table>

3.2.1. d. TEM Analysis:

Figure (3.33) presents the TEM image of the prepared BaTiO₃ sample. It is evident that, the image exhibits rod-like morphology for BaTiO₃ with length of 120 nm and width of 43 nm. TEM images prove that the modified citrate autocombustion method was a successful and easy method for obtaining nanorods bundle filaments in this perovskite.

![TEM micrograph of nano-BaTiO₃](image)

**Fig.(3.33): TEM micrograph of nano-BaTiO₃.**
3.2.1. e. AFM Analysis:

AFM offers the capability of 3D rather than 2D visualization and both qualitative and quantitative information on many physical properties including size, morphology, surface texture and roughness as in Fig. (3.34a). Statistical information, including size, surface area, and volume distributions, can be determined for BaTiO$_3$ [149, 167]. It is clear from the photograph that the surface, in general, is relatively smooth. The grains are densely and regularly packed without cracks or voids. Besides, the particles have almost rod shape with average particle size 116 nm. It is important to note that the average particle size estimated by AFM images is larger than the size calculated by the Debye–Scherrer formula [146], pointing out a possible polycrystalline nature of BaTiO$_3$ grains. The surface roughness determined from Fig. (3.34b) has the value of 653 nm for this selected area. Fig. (3.34. c, d) depicts the AFM image for one island, with mean volume of 139 nm$^3$, mean height of 6.68 μm and mean height to surface ratio equals to 0.162 V/ μm$^2$ indicated that the crystal structure of BaTiO$_3$ is tetragonal phase. Figure (3.34e) illustrates the statistical information, including size, surface area, and volume distributions of the investigated sample.

Fig. (3.35a, b) provide the analysis of ATM and give qualitative information about the surface topography and grains shape of BaTiO$_3$ which has grains of rod-like shape with average particle size 59.1 nm.

Figure (3.35c,d) provide quantitative or statistical information about roughness, spatial parameters and grains size.

Deep look to these images, we can say that, the surface, in general, is relatively smooth due to almost small values of roughness parameters such as average roughness Ra=29.3 nm, maximum profile peak height (Rp=84.3 nm), maximum profile valley depth (Rv=89.1.5 nm), and total roughness (Rt =Rp+Rv = 173 nm) as shown in Fig.(10d).
Fig. (3.34): AFM topography image (6×6 μm² area and 1.32 μm in height); (a): AFM topography image in 3D, (b): The surface roughness, (c, d): AFM image for one island showing the surface roughness, (e): number of grains per μm².
Fig. (3.35a): AFM images for BTO for a surface area = 6×6 µm² showing the surface topography and grain shape and size.
Fig. (3.35b): AFM images for BTO nanopowder for a surface area = 6.4×6.4μm² showing the surface morphology in 3D and grain size.
Fig. (3.35c): AFM analysis for BTO nanopowder showing the roughness profile and its parameters.
(B2):

3.2.2. 0.5BTO / 0.5NZF nanocomposite synthesized by citrate-autocombustion route:

3.2.2. a. XRD Analysis:

Figure (3.36) illustrates the X-ray diffraction spectrum for Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$. The obtained chart confirms the cubic single phase spinel structure for Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ with $a = 0.83883$ nm, as compared and indexed with ICDD card no. 08-0234. It was found that the crystallite size of NiZn ferrite $\cong 20$ nm.

Figure (3.37) shows X-ray diffraction pattern of the nanocomposite 0.5 BaTiO$_3$ / 0.5 Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$. It reveals the presence of both the tetragonal perovskite and spinel structure phases, corresponding to NiZnFe$_2$O$_4$ and BaTiO$_3$ respectively without any extra peaks. This indicates that, no significant chemical interaction has been occurred between BaTiO$_3$ and NiZnFe$_2$O$_4$. Besides, the estimated particle size (L) is around 30 nm for ferrite phase which confirms that, the calcination temperature is suitable, where 700 °C just increases the particle size from 20 nm to 30 nm.

![XRD pattern of nanopowder NZF.](image)
3.2.2. b. FT-IR Analysis:

FTIR spectra of BaTiO$_3$ / 0.5Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ nanocomposite and its constituents were carried out at Fig. (3.38). It is revealed that, for (BTO) the absorption bands appeared around 1600, 3600, 3600 and 420 cm$^{-1}$, while they appear at ~ 420 and 579 cm$^{-1}$ for (NZF). The spectrum of 0.5BTO+0.5NZF nanocomposite represents the sum of the two constituent's spectra taking into consideration the factor of connectivity, interface effects and exchange interaction between the two phases within the composite (steric hindrance). It is observed that the net absorption band at 420 cm$^{-1}$ is due to the overlapping between the two bands of the two phases which was appeared at almost the same wave number. These bands are considered as finger print and they are mainly due to the formation of metal oxides (M–O: Ba–O, Ti–O, Fe–O, Ni-O, Zn-O). It involves the stretching vibration of (Fe$^{3+}$ + O$^{2-}$) on the octahedral site for NZF phase. The absorption band observed at ~579 cm$^{-1}$ assigned to the stretching vibration of (Fe$^{3+}$ + O$^{2-}$) on tetrahedral site. These results are in agreement with that published earlier [202]. The band at 2360 cm$^{-1}$ indicates the presence of OH group [8]. The band around 3600 cm$^{-1}$ is due to O–H stretching vibrations of hydroxyls present in this system.
band at 1600 cm\(^{-1}\) is due to the symmetric and asymmetric stretching vibrations of the carboxylate functional group (-COO-) due to some residual of butyl titanate.

*Fig. (3.38). FTIR spectrum of BTO, NZF, and 0.5BTO / 0.5NZF nanocomposite.*
3.2.2. c. SEM-EDX Analysis:

Figure (3.39) shows the scanning electron micrograph (SEM) for the investigated nanocomposite. It is observed that there are two dissimilar particle shapes corresponding to the two different phases forming the nanocomposite. The two phases were distinguished by using EDX. The SEM micrograph confirms the porous nature with some agglomerations indicating the cauliflower-like morphology for images at magnification 4000 x and 7000 x, while at lower magnification (270 x and 1500 x) the two phases are distributed like core-shell shape. Moreover there may be some agglomeration in micrograph due to humidity [124, 42].

*Fig. (3.39) : SEM micrograph for 0.5BTO/0.5NZF nanocomposite at different magnifications.*
3.2.2. d. TEM Analysis:

Figure (3.40: a, b) represents the TEM images for 0.5BTO / 0.5NZF nanocomposite. It is shown that, the two phases have a homogeneous distribution confirming that there is a good mixing of the two phases. It has a core shell-like shape, where BaTiO$_3$ represents the core and ferrite is the shell. It is evident from the photos that the ferrite has a spherical shape with a size of 40 nm, while the BTO has nanorod shape with average length 120 nm and width of 43 nm.

Fig. (3.40 a, b): TEM morphology of 0.5BTO/0.5NZF nanocomposite.
3.2.2. **e. AFM measurements and data analysis:**

Figures (3.41: a-d) show typical atomic force microscopy (AFM) images and their analysis for 0.5BTO/0.5NZF nanocomposite taken at different cantilever positions (areas) on the sample surface. The measurements show the surface topography and the histogram which gives information about the surface roughness, particle or grain size distribution.

Figure (3.41a, b) show also that, AFM topography micrograph illustrating the presence of grains with two stable states: bright plateaus indicated to arise from the tetragonal phase, and areas of dark contrast indicated to arise from the spinel phase. Thus, AFM micrographs indicate the existence of some nanodomains with tetragonal phase (white contrast) involved in a matrix formed globally by spinel structure. Moreover, the same figure provides qualitative information about the surface topography and grains shape when the shape of the two particles are agree well that appeared in TEM studies as shown in Fig.(3.40). In TEM and AFM micrographs, the particles has almost rod-like shape with average particle size 38.2 nm for NZF, 96.4 nm for BTO. Besides, there exists a high degree of homogeneity and better mixing of the two phases because of the grains are densely and regularly packed without cracks or voids, similar to that obtained from SEM and TEM micrographs. It is also observed that, there exist two particles shape with different contrast, one is bright white (BTO) and the other is brown (ferrite).

Figure (3.41c,d) provide statistical information about roughness, spatial parameters and grains size. It is clear that, the surface, in general, is relatively smooth due to very small values of roughness parameters such as average roughness $R_a=7$ nm, maximum profile peak height ($R_p=15.7$ nm), maximum profile valley depth ($R_v=30.5$ nm ), and total roughness ($R_t=R_p+R_v=46.3$ nm) as shown in Fig.(3.41d).

Figures (3.42: a-d) show different trails of AFM imaging at different cantilever positions. These measurements show the surface topography and the histogram which gives the data about the surface roughness, particle or grain size.
distribution. It is revealed that, there exists almost homogeneous distribution similar that obtained from SEM micrograph. It is also observed that, there exist two particles shape with different contrast, one is bright white (BTO) and the other is brown (ferrite). The two phases are distributed in circular manner such that they wound on each other like core-shell shape. It can be seen from the images in general that, the surface is almost smooth. The grains are densely and regularly packed without cracks or voids. Besides, the particles have almost rod shape with average particle size 116 nm. It is important to note that the average particle size estimated by AFM images is larger than the size calculated by the Debye–Scherrer formula [104], pointing out a possible polycrystalline nature of BaTiO$_3$ grains. The surface roughness determined from Fig. (3.42b) has the value of 653 nm. Figure (3.42, c, d) depicts the AFM image for one island, with mean volume of 139 nm$^3$, mean height of 6.68 µm and mean height to surface ratio equals to 0.162 V/ µm$^2$ indicated that, the crystal structure of BaTiO$_3$ is tetragonal phase. Figure (3.42e) illustrates the statistical information, including size, surface area, and volume distributions of the investigated sample.
Fig. (3.41a): AFM images for 0.5BTO/0.5NZF nanocomposite for a surface area = 1×1 μm² showing the surface topography and grain shape and size.
Fig. (3.41b): AFM images for 0.5BTO/0.5NZF nanocomposite for a surface area = 1×1 µm² showing the surface morphology in 3D and grain size.
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Results and Discussions

Fig. (3.41c: i, ii): AFM analysis for 0.5BTO / 0.5NZF nanocomposite representing the spacing profile, parameters, and average particle size.
Fig. (3.41d): AFM analysis for 0.5BTO/0.5NZF nanocomposite showing the roughness profile and parameters.
Fig. (3.42.a): AFM images and their analysis for 0.5BTO/0.5NZF nanocomposite for a surface area = 0.46×0.46 μm².
Fig. (3.42b): AFM images and their analysis for 0.5BTO/0.5NZF nanocomposite for a surface area = 50×50 μm².
Fig. (3.42c): AFM images and their analysis for 0.5BTO/0.5NZF nanocomposite for a surface area = 11.7×11.7 μm².
Fig. (3.42d): AFM images and their analysis for 0.5BTO/0.5NZF nanocomposite for a surface area = 1.5×1.5 μm².
3.2.2. f. Magnetic measurements and data analysis of $0.5\text{BaTiO}_3/0.5\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ nanocomposite:

The magnetic properties of $0.5\text{BTO} / 0.5\text{NZF}$ nanocomposite prepared by citrate autocombustion technique result as determined both by the own magnetic properties of ferrite phase and by the degree of connectivity of the two phases [111]. Therefore, the presence of non-magnetic perovskite phase and the interface effects influence the magnetic properties of nanocomposite by changing the distribution of magnetic ions and their spin distribution particularly at the heterointerface and consequently to affect the magnetic interaction [111]. It was found from the prepared series of nanocomposites by ceramic method that; the concentration $x = 0.5$ is the aspect ratio or the critical concentration at which the so called percolation theory is verified. This means that, $x = 0.5$ the system is expected to be made up of exclusively of isolated clusters of both magnetic and non-magnetic ions and in this case no infinite clusters exist [4].

Figure (3.43a) represents the variation of molar magnetic susceptibility ($\chi_M$) with absolute temperature ranging from 300 - 800 K as a function of the magnetic field intensity $H$ (1340, 1660, and 1990 Oe). It is shown that, the values of ($\chi_M$) decreases with increasing temperature up to Curie temperature ($T_C$). This reduction in ($\chi_M$) is due to the thermal agitation which disturbs the oriented spins in random and different directions leading to the sample is completely changed from ferromagnetic to paramagnetic behavior. The accurate method to determine the Curie temperature is as mentioned before from the the $1^{\text{st}}$ derivative of magnetization ($dM/dT$) versus $T$ [86] as illustrated in Fig.(3.43b). The estimated values of $T_C$ at different magnetic field strength are tabulated in Table (3.6), also other magnetic parameters such as effective magnetic moment $\mu_{\text{eff}}$ ($\mu_B$), Curie point $\theta$ (K), exchange interaction constant $J$ (eV). One can observe that the magnetic parameters slightly increase with increasing in magnetic field strength.

The magnetization ($M$) due to the hysteresis loop at R.T (Fig.(3.43c )) shows the presence of the ordered magnetic structure causing a non-linear hysteric
character. Since the investigated composite is considered a nanosystem, so the surface to volume ratio (S/V) is large, this in turn leads to superficial spin canting, spin pinning or broken exchange bonds [86]. Our results is explained by considering the sample's microstructure in which NZF areas are percolated by a large number of small BTO particles, causing an increasing number of disordered regions at the interface, similar as in nanosystems. Consequently, the magnetic properties of in 0.5BTO/0.5NZF nanocomposite are determined not only by the NZF concentration and properties as a sum property [13], but also by the degree of connectivity of the two-phase component grains. It is noted that, our nanocomposite exhibits low values of magnetization and hence saturation magnetization. This can be attributed to (a) a better isolation (dilution) of the magnetic phase by the non-magnetic one which causes a diminishing of the effective magnetostatic interactions and (b) by demagnetization field contribution in the magnetic subsystem, the magnetic properties affected by the particle size and homogeneity of the composite material system [194].
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Fig. (3.43a): Variation of magnetic susceptibility of the investigated composite with temperature at different magnetic field.

Fig. (3.43b): The calculated values of Curie temperature($T_c$) for 0.5 BTO / 0.5 NZF nanocomposite prepared by citrate auto combustion method.
Table (3.6): Values of Curie temperature ($T_C$) and other magnetic parameters ($\mu_{eff}$, $\theta$, $J$) of 0.5BTO / 0.5NZF nanocomposite.

<table>
<thead>
<tr>
<th></th>
<th>H(1340 Oe)</th>
<th>H (1660 Oe)</th>
<th>H (1990 Oe)</th>
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<tbody>
<tr>
<td>$T_C$ (K)</td>
<td>613.5</td>
<td>621.4</td>
<td>594</td>
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<tr>
<td>$\mu_{eff}$ ($\mu_B$)</td>
<td>0.4900</td>
<td>0.5700</td>
<td>0.7100</td>
</tr>
<tr>
<td>$\theta$ (K)</td>
<td>690</td>
<td>720.6</td>
<td>728</td>
</tr>
<tr>
<td>$J$ (Exchange interaction $ct.$) eV)</td>
<td>0.0132</td>
<td>0.0134</td>
<td>0.0128</td>
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</table>

Fig. (3.43c): Hysteresis loop of 0.5 BTO / 0.5 NZF nanocomposite prepared by citrate autocombustion method.
3.2.2. g. Transport and Dielectric properties of 0.5BaTiO$_3$/0.5Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ nanocomposite:

The temperature dependences of relative permittivity ($\varepsilon'$) and loss factor ($\varepsilon''$) at different frequencies (100 kHz – 5 MHz) are plotted in Fig. (3.44a,b). The general trend of the 0.5BTO/NZF nanocomposite is the increase in $\varepsilon'$ and $\varepsilon''$ with increasing temperature up to the transition temperature at which $\varepsilon'$ gives maximum values. It is worth to note that, there exist two transition temperatures $T_1$ and $T_2$ corresponding to the presence of the two phases in the prepared nanocomposites. From the data, it also clear that, the first transition took place at $\approx$ 588 K and can be ascribed to the structural phase transition of BaTiO$_3$ from tetragonal to cubic which agrees well with that reported in the literatures [169]. The second transition appeared at $\approx$ 853 K is the dielectric transition point of Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ and matches with that reported with earlier for similar Ni and Zn substituted ferrites [159]. One could argue that the electrons which are involved in hopping process are responsible for electronic polarization in ferrites, since the later has the same origin as the former. It is worth to note also that, the transition temperatures of the 0.5BTO/0.5NZF nanocomposite prepared by citrate autocombustion method are greater than those of that prepared by ceramic method. This can be attributed to different factors such as grain size, degree of connectivity, degree of homogeneity, nanocomposite fine grained microstructure, and hence the interface effects which are different in case of citrate method than ceramic method.

The effect of frequency on the dielectric constant ($\varepsilon'$) and ($\varepsilon''$) at different temperatures is shown in Fig.(3.45a,b). The data reveal that, dielectric constant $\varepsilon'$ and dielectric loss factor $\varepsilon''$ decreases steeply at lower frequencies and remains almost constant at higher frequencies showing dispersion of $\varepsilon'$ related to the charge transport relaxation time. This dispersion in $\varepsilon'$ is attributed to Maxwell and Wagner interfacial polarization [159, 169]. The weak frequency dependence of relative permittivity can be attributed to the fine-grained microstructures of 0.5BTO/0.5NZF nanocomposite prepared by citrate autocombustion method.
Fig. (3.44a): Real part of dielectric constant versus temperature at different frequencies for ME nanocomposite: 0.5BTO / 0.5NZF prepared by citrate autocombustion method.

Fig. (3.44b): Variation of the dielectric loss factor ($\varepsilon''$) with temperature at different frequencies of the nanocomposite: 0.5BTO / 0.5NZF prepared by citrate autocombustion method.
Fig. (3.45a): Real part of dielectric constant versus frequency at different selected temperature for ME nanocomposite 0.5BTO / 0.5NZF prepared by citrate autocombustion method.

Fig. (3.45b): Variation of the dielectric loss factor \((\varepsilon'')\) with frequency at different temperatures of the nanocomposite: 0.5BTO / 0.5NZF prepared by citrate autocombustion method.
The influence of temperature on the electrical conductivity ($\ln \sigma_{ac}$) is shown in typical Fig. (3.46: a, b). The data show that, the $ac$ conductivity increases with increasing temperature and shows a small dip at higher temperatures. Besides, from Fig.(3.46b) it was observed that, there are three distinct regions with different slopes indicating different conduction mechanism. The variation of conductivity was explained on the basis of actual location of cation in the composite structure where in ferrite it is due to electron transfer between divalent and trivalent ions. The conduction at low temperature region (i.e. < 550 K) is due to impurities, whereas at higher temperature region (i.e. > 550 K), it is due to electron hopping. Besides, the values of the activation energy ($\Delta E$) were calculated and found to be 0.17, 0.75, and 3.8 eV for $\Delta E_1$, $\Delta E_2$, and $\Delta E_3$ respectively which is clearly suggest that the conduction is due to electron hopping in the first and second regions because $\Delta E < I$ [167] While at the third region where $\Delta E > I$, the interfacial space charge polarization mechanism will be dominated according to the Koop’s theory [190].
**Fig. (3.46a):** $\ln(\sigma_{ac})$ versus $\ln T_K$ at different frequencies for $0.5\text{BaTiO}_3/0.5\text{Ni}_0.5\text{Zn}_0.5\text{Fe}_2\text{O}_4$ nanocomposite prepared by autocombustion citrate method.

**Fig. (3.46b):** Variation of $\ln (\sigma_{ac})$ versus $(1000/T_K)$ at different frequencies for $0.5\text{BaTiO}_3/0.5\text{Ni}_0.5\text{Zn}_0.5\text{Fe}_2\text{O}_4$ nanocomposite prepared by citrate autocombustion method.
Figure (3.46c) represents $\ln(\sigma_{ac})$ versus $\ln f$ (Hz) graph at different temperatures. It is clear that, the conductivity increases monotonically with increasing frequency and becomes weakly dependent at both high frequency and temperature. The linearity of the plots confirms the small polaron type of conduction. However, the slightly decreases in conductivity is attributed to conduction by mixed polarons. It has been shown that for ionic solids, the concept of small polarons is valid [54]. At temperatures higher than 500 K, the conduction mechanism can be explained with hopping of electrons between Fe$^{2+}$/Fe$^{3+}$ and Ti$^{3+}$/Ti$^{4+}$, whereas, hopping mechanism needs high thermal energy to occur. There is also contribution from p type charge carriers by hole hopping between Ni$^{2+}$/Ni$^{3+}$, but this contribution is lower as compared with the electronic contribution [186].

Recalling equation (3.2), the calculated values of the exponent (s) plotted versus temperature in Fig. (3.46d). It is observed that, the exponent s increases with increasing temperature at the relatively lower temperature region (300-650 K). So that the behavior in this region is due to polaron quantum tunneling, while above 650 K the conduction is limited by hopping mechanism where s decreases with increasing temperature. This result is in agreement with that observed above from Fig. (3.46b). It is noted that the value of s is less than unity, i.e., $0 \leq s \leq 1$ at the whole temperature range.
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Fig. (3.46c): $\ln(\sigma_{ac})$ versus $\ln(f)$ at different temperature for 0.5BTO / 0.5NZF nanocomposite prepared by citrate autocombustion method.

Fig. (3.46d): Variation of $s$ with temperature at different frequencies for 0.5BaTiO$_3$ / 0.5Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ nanocomposite prepared by citrate autocombustion method.
The variation of Seebeck coefficient ($\alpha$) for the nanocomposite with temperature is shown in Fig. (3.47). The plot shows the type of charges responsible for conduction. An n –p transition is observed. The occurrence of n –p transition is independent on transition temperature [53]. At lower temperature the nanocomposite shows n-type like behavior. The variation of $\alpha$ at low temperature region (<400 K) may be attributed to impurity conduction. The observed p-type conduction in BaTiO$_3$ is attributed to Ti$^{4+} \leftrightarrow$ Ti$^{3+}$ transition [28,29] and p-type to n-type conduction in ferrite is attributed to Ni$^{2+} \leftrightarrow$ Ni$^{3+}$, releasing a hole and Fe$^{3+} \leftrightarrow$ Fe$^{2+}$ releasing an electron [54, 59].

Fig. (3.47) : Seebeck coefficient of of 0.5BaTiO$_3$ / 0.5Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ Biferroic material prepared by citrate autocombustion method.
3.3: **0.5 BaTiO$_3$ / 0.5 Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ multiferroic nanocomposite in comparison between Ceramic route and Citrate technique:**

In the present study, nanocomposite 0.5 (BaTiO$_3$) / 0.5(Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$) powder has been synthesized by two different techniques including conventional ceramic technique and citrate autocombustion technique to compare and throw light on the influence of the preparation method on the structural and physical properties of the nanocomposites. In order to tailor the optimum method of the nanostructured composites where the challenge in preparing such materials is to find equilibrium ferroelectric and magnetic structures preserving both properties close to the room temperature.

3.3.1. **Microstructure and phase characterization of 0.5BaTiO$_3$/0.5Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ nanocomposite:**

X-ray diffraction patterns of the nanocomposite 0.5BTO / 0.5NZF prepared via different methods {Citrate (C$_1$), Ceramic (C$_2$)} are shown in Fig. (3.48: a, b). It is revealed that, the presence of both the spinel and tetragonal perovskite structure phases corresponding to NiZnFe$_2$O$_4$ and BaTiO$_3$ respectively. The obtained phases confirm the cubic spinel structure for the ferrite phase and tetragonal perovskite structure for the ferroelectric phase as compared and indexed with ICDD card no. 08-0234 and 79-2264 respectively. No other phases were detected. This indicates that no significant chemical interaction has occurred between the BTO and NZF. Besides, from Table (3.7) it is clear in comparison between the two methods that, the lattice constant (a) is 8.3883Å in C$_1$ while it is 8.8335Å in C$_2$ method and the crystallite size (L) in citrate method (C$_1$) is about 30 nm which is smaller than that in ceramic method (C$_2$) which is about 119.7 nm. Moreover, the values of the lattice constants; a, c, c/a, and the volume of the unit cell (V) were listed in Table (3.8) indicating that the particle growth rate for different methods is different and the citrate method is the lowest.
Figures (3.49: a,b), (3.50:a, b) show the typical SEM and TEM photographs respectively for the composite prepared using C₁ and C₂ methods. In the present study SEM and TEM were used to calculate the particle size. It is observed that there are two dissimilar particle shapes corresponding to the two different phases forming the composite. Besides, dense, homogeneous, and fine-grained ceramics are obtained from method C₁ as a result of strong bonds between Ni₀.₅Zn₀.₅Fe₂O₄ and BaTiO₃ nanosized powders as well as the strong adhesion between the Ni₀.₅Zn₀.₅Fe₂O₄ and the BaTiO₃ powders while poor homogeneity and densification, with big non-percolated aggregates of NZF octahedral crystals and large pores from method C₂. Thus, the preparation method influences the degree of connectivity of the two phases and this can yield to different properties. Fig.(3.50:a, b) represents the TEM images for 0.5BTO / 0.5NZF nanocomposite. It is shown that, the two phases have a homogeneous distribution confirming that, there is a good mixing of the two phases. It has a core shell-like shape; where BaTiO₃ represents the core while the ferrite the shell. It is evident from the photos that the ferrite has a spherical shape with a size of 40 nm, while the BTO has nanorods shape with average length 120 nm and width of 43 nm. Besides, it is revealed that the particle size determined by TEM is larger than that obtained from XRD measurements; this is because XRD determines crystallite size while TEM measures the particle size. The agglomeration appeared in micrograph was reported previously [101, 171].
Fig (3.48:a, b): XRD patterns of 0.5BaTiO$_3$ / 0.5NiZnFe$_2$O$_4$ nanocomposite prepared by: a)-citrate autocombustion and b)-ceramic methods.
### Table (3.7): Comparison between the structure and physical properties data to citrate ($C_1$) and ceramic ($C_2$) methods for $0.5\text{BaTiO}_3/0.5\text{NiZnFe}_2\text{O}_4$ nanocomposite.

<table>
<thead>
<tr>
<th></th>
<th>Citrate method ($C_1$)</th>
<th>Ceramic method ($C_2$)</th>
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<tbody>
<tr>
<td>$M_s$ (emu/g)</td>
<td>25.92</td>
<td>38.31</td>
</tr>
<tr>
<td>$M_r$ (emu/g)</td>
<td>2.26</td>
<td>4.47</td>
</tr>
<tr>
<td>$M_s/M_r$</td>
<td>0.087</td>
<td>0.12</td>
</tr>
<tr>
<td>$H_c$ (Oe)</td>
<td>100</td>
<td>28.36</td>
</tr>
<tr>
<td>$n_B$ ($\mu_B$)</td>
<td>1.092</td>
<td>1.6</td>
</tr>
<tr>
<td>$T_c$ (K)</td>
<td>541</td>
<td>508</td>
</tr>
<tr>
<td>$\mu_{\text{eff}}$ ($\mu_B$)</td>
<td>0.49</td>
<td>5.99</td>
</tr>
<tr>
<td>$L$ (nm)</td>
<td>30</td>
<td>119.7</td>
</tr>
<tr>
<td>$a$ (nm)</td>
<td>0.83883</td>
<td>0.88325</td>
</tr>
</tbody>
</table>

### Table (3.8): The values of lattice constants ($a, c$), $c/a$, and the volume of the unit cell of ($\text{BTO}$) prepared by citrate ($C_1$) and ceramic ($C_2$) methods.

<table>
<thead>
<tr>
<th></th>
<th>$a$ (nm)</th>
<th>$c$ (nm)</th>
<th>$c/a$</th>
<th>$V$ (nm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_1$ (BTO)</td>
<td>0.39949</td>
<td>0.40131</td>
<td>1.00455</td>
<td>0.06405</td>
</tr>
<tr>
<td>$C_2$ (BTO)</td>
<td>0.40049</td>
<td>0.40084</td>
<td>1.00087</td>
<td>0.06422</td>
</tr>
</tbody>
</table>

Fig (3.49a, b): SEM micrographs of $0.5\text{BaTiO}_3/0.5\text{NiZnFe}_2\text{O}_4$ nanocomposite prepared by a)-citrate, and b)-ceramic methods.
3.3.2. Magnetic properties of $0.5\text{BaTiO}_3/0.5\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ nanocomposite:

The presence of the non-magnetic perovskite phase and the interface effects was expected to influence the magnetic properties in composites by changing the distribution of the magnetic ions and their spin orientation particularly at interfaces and consequently, to affect the magnetic interactions. The susceptibility-
temperature dependences are shown in Fig. (3.51: a, b) and Table (3.7). The behavior of magnetic susceptibility ($\chi_M$) with different preparation methods reported that, the value of magnetization ($\chi_M$) is larger in C_2 (9.79) than in C_1 (4.58) due to the increase of the surface/ volume ratio in C_1 which in turn leads to superficial spin canting, spin pinning or broken exchange bonds [194-196]. The Curie temperature $T_C$ (Fig. 3.51c) was defined as the temperature corresponding to a minimum in the temperature dependence of the first order derivative of the magnetization ($dM / dT$). It can be clearly seen that with increasing temperature, the magnetization drops abruptly at Curie temperature $T_C$ of 541 K (C_1) and 508 K(C_2). This variation is related to the preparation method. The magnetic phase transition temperatures are roughly in agreement with the previous work [197]. This means that, the magnetic properties in the BTO / NZF composites are determined not only by the NZF concentration and properties as a sum property [148], but also by the degree of connectivity of the two-phase component grains.

![Fig. (3.51:a-c): The variation of magnetic susceptibility ($\chi_M$) with different temperatures for (a): Citrate method (C_1), (b): Ceramic method (C_2), and (c): Curie temperature $T_C$ from the first order derivative of magnetization $dM/dT$ for 0.5BaTiO_3 / 0.5NiZnFe_2O_4 nanocomposite.](image)

The magnetic hysteresis loops $M(H)$ obtained at room temperature for both methods; C_1 and C_2 are presented in Fig. (3.52). It is clear that, composites materials exhibit typical ferromagnetic hysteresis of the magnetic materials at C_2 method with tightly hysteresis loops and saturation magnetization ($M_s = 38.31 \text{ emu/g}$), indicating that the composites are magnetically ordered while at C_1 method, the saturation magnetization is lower ($M_s=25.92 \text{ emu/g}$). This suggests that the
spontaneous magnetizations of the ceramics originate from unbalanced antiparallel spins, leading to net spins other than those introduced by the structural distortion [198]. In other words, the lower magnetization is due to: (i) a better isolation of the magnetic phase by the nonmagnetic one (BaTiO₃) in the composite, which causes a diminishing of the effective magnetostatic interactions and (ii) by the demagnetizing field contributions in the magnetic subsystem. Thus, the observed different values for the magnetization at a given field and at saturation are expected to result from the microstructural differences of the two types of composites. Other more subtle differences might also result from particular nanoscale characteristics (interfaces, interconnectivity), as previously found in other BTO / NZF nanocomposites by a detailed thermomagnetic investigation [199]. Table (3.7) indicated the variation of magnetic parameters at different preparation methods.

![Magnetic hysteresis loops](image)

**Fig. (3.52):** Magnetic hysteresis loops of 0.5BaTiO₃ / 0.5NiZnFe₂O₄ nanocomposite prepared by ceramic and citrate methods.
3.3.3. Electrical properties of 0.5BaTiO$_3$/0.5Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ nanocomposite:

Figure (3.53: a, b) show the variation of $\varepsilon'$ with temperature at different frequencies for samples C$_1$ and C$_2$ respectively. $\varepsilon'$ at both methods gives the same trend where $\varepsilon'$ increases with temperature at fixed frequency while different. This is true for the two samples at all frequencies. At lower frequencies this effect is more prominent. The increase in $\varepsilon'$ with temperature is due to greater release of movement dipoles at high temperature. At lower temperature, as the dipoles are rigidly fixed in the dielectric, the field cannot change the condition of dipoles. As the temperature increases, the dipoles comparatively become free and they respond to the applied electric field. Thus polarization increased and hence dielectric constant is also increased with the increase of temperature [200].

The variation of the electrical conductivity with temperature for both samples (C$_1$ and C$_2$) is shown in Fig. (3.54: a, b). The influence of temperature on conductivity can be explained due to the mobility of charge carriers responsible for hopping. As temperature increases the mobility of hopping ions also increases thereby increasing conductivity. The electrons which are involved in hopping are
responsible for electronic polarization in this composite. Also hole hopping between Ni\(^{2+}\) and Ni\(^{3+}\) on B site will also contribute to electric conduction in composites. The data show that the conductivity between Fe\(^{2+}\) and Fe\(^{3+}\) ions on the octahedral sites increases up to a temperature of 668 K for C\(_1\) while 430K for C\(_2\). Further increase of temperature reduces the conductivity.

Figure (3.55: a, b) shows the linear variation of \(\ln\sigma_{ac}\) with ln(f) at certain temperature (590K) for both the samples C\(_1\) and C\(_2\). It is known that [201], interfacial polarization is exhibited by the composites due to structural inhomogeneity and existence of free charges. The hopping electrons at low frequencies may be trapped by the inhomogenites. At a particular frequency, the increase in \(\varepsilon'\) with temperature is due to the drop in the resistance of the composite with increasing temperature. Electron hopping is promoted by the low resistance and hence resulting a larger polarizability or larger \(\varepsilon'\). The variation of real part of dielectric constant \(\varepsilon'\) with frequency for different preparation methods is shown in Fig. (3.55b) at \(T = 400\) K. The dielectric constant increases sharply with decreasing frequency for the two methods and such behavior can be attributed to the presence of large degree of dispersion due to charge transfer within the interfacial diffusion layer present between the electrodes. The magnitude of dielectric dispersion
depends on the temperature. At lower temperature the relaxation process becomes easier due to the freezing of the electric dipoles and thus there is decay in polarization with respect to the applied electric field. So a sharp increase in $\varepsilon'$ is observed at lower frequency region. Therefore the inhomogeneous nature of the samples containing different permittivities and conducting regions, governs the frequency behavior of $\varepsilon'$ where the charge carriers are blocked by the poorly conducting regions. The frequency dependence can be explained with the help of Maxwell–Wagner two-layer model or the heterogeneous model of the polycrystalline structure of ferrites [1] where two layers formed dielectric structure. The first layer consists of ferrite grains of fairly well conducting (ferrous ions), which is separated by a thin layer of poorly conducting substances, which forms the grain boundary. These grain boundaries are more active at lower frequencies; hence the hopping frequency of electron between Fe$^{3+}$ and Fe$^{2+}$ ion is less at lower frequencies. As the frequency of the applied field increases, the conductive grains become more active by promoting the hopping of electron between Fe$^{2+}$ and Fe$^{3+}$ ions, thereby increasing the hopping frequency. Thus we observe a gradual increase in conductivity with frequency. But at higher frequencies the frequency of hopping between the ions could not follow the applied field frequency and it lags behind it. This causes a dip in the electric conductivity at higher frequencies.

![Fig.3.55:a,b): a. Variation of conductivity with frequency at selected temperature (T=590K) of (C$_1$) and (C$_2$) methods for BTO/NZF nano composite. b. Effect of frequency on dielectric constant ($\varepsilon'$) of (C$_1$) and (C$_2$) methods.]
* Second group:

3.4. Innovative physical properties of BTO / NZF doped different polymers

"Hybrid nanocomposites"

The present investigation study deals with the direct room temperature synthesis of BTO / NZF composites using citrate auto mixed with different polymers such as polyethylene glycol (PEG), polyaniline (PANN), polyvinyl acetate (PVA), and polyvinyl pyrrolidone (PVP). The influences of polymer type.

The properties of the composites are studied by comparing the structure, morphology, electrical, and magnetic to select the optimum applicable composite. The main goal in this research is that how a reduction in the magnetic powder particle size to a lower scale can lead to production of permanent polymeric composite magnets with superior properties as well as prepare magneto-polymer composites to optimal the applicable combination in our technological life.

3.4. 1. Structure and morphology study:

FT-IR spectra of the as prepared samples are show in Fig. (3.56). It is clear that, the absorption peaks due to polymer part of the samples are observed in the frequency range 3000–800 cm⁻¹. While the absorption peak at 570 cm⁻¹ can be attributed to Ni-Zn spinel ferrite. From the figure it is revealed that, all the samples shows very broad peak at 560 cm⁻¹ thereby indicating that both α-Fe₂O₃ and Ni-Zn spinel ferrites coexists in the sample. It is known that [203, 204], the absorption bands $v_1$ and $v_2$ around 600 and 400 cm⁻¹ are attributed to the stretching vibration of tetrahedral and octahedral group complexes of ferrites, respectively. The metal ions in ferrites are situated in two different sub-lattices designated tetrahedral and octahedral according to the geometrical configuration of the oxygen nearest neighbors. The $v_1$ (400–450 cm⁻¹) band is attributed to the intrinsic vibrations of the tetrahedral groups, the $v_2$ (520–580 cm⁻¹) band to the octahedral groups and the $v_3$ (800 cm⁻¹) band to octahedral or tetrahedral environments of ferrites. Thus, IR
studies also suggest the peak at 1754.45 cm$^{-1}$ originates from the stretching vibration of C=O of ester bond, peak centered at 1089.54 cm$^{-1}$ originates from the stretching vibration of -C-O-. Compared with the IR spectrum of pure ME, one new peak (1681.71 cm$^{-1}$ is presented in Fig. (3.56). This peak centered at 1681.71 cm$^{-1}$ originates from the stretching vibration of C=O.

The SEM images at different composites doped different polymers were used to estimate the grain size of each powder. It can be seen from Fig. (3.57) that, ME powder has the smallest grain size, approximately 120 nm, followed by PANN powder. Finally PVA powder has the highest grain size. It can be seen that the change in the grain size related to change in the polymer type which is attributed to the addition of polymers fill the voids present in the BTO / NZF composite.
Fig. (3.56): FT-IR spectra for different polymers doped BTO / NZF nanocomposites.

The arrow refers to the IR absorption peak not band
Fig. (3.57): SEM photographs of 0.5(0.5BTO / 0.5NZF) / 0.5 polymers; PVAc, PVP, PANI, PEG, and ME nanocomposite.
3.4.2. Magnetic measurements of (BTO/NZF) / different polymers nanocomposites:

The dependence of magnetization on the applied magnetic field (H) for BTO/NZF doped different polymers composites are shown in Fig. (3.58). The graph exhibits typical ferromagnetic behavior with tightly hysteresis loop except the sample ME. The absence of hysteresis, remanence, and coercivity at room temperature suggests the superparamagnetic nature of the nanocomposite. The lack of saturation magnetization at high field occurs in association with high field irreversibility and open loop for only ME sample. This is attributed to the spin-glass like surface layer on the nanocrystalline nickel zinc ferrites with a ferromagnetically aligned core [205] of the ferrite nanoparticles.

The variation of the magnetization parameters; \( M_s \), \( M_r \), and \( H_c \) in our composites doped polymers are shown in Fig. (3.59: a, b). It is clear that, the presence of polymers in the composite cause an almost immeasurable coercivity \( (H_c) \) and remanence \( (M_r) \) are observed. Also there is non-attainment. The highest value of \( H_c \) (140 Oe) for PEG, PVP, and PVA samples higher than ME sample (100 Oe). Moreover, variation of saturation magnetization of our samples depends on the type of the doping polymer, which implies the magnetization of all other samples as in Table (3.9). These values are significantly lower than that reported for the multidomain bulk nickel ferrite (55 emu/g) [206], but comparable to that obtained for the nanocrystalline nickel ferrite (25.4 emu/g) [207]. This reduction on the magnetization parameters can be explained according to the core shell morphology of the nanoparticles consisting of ferromagnetically aligned core spins and a spin-glass like surface layer (polymer). If this surface layer was absent, the magnetization of the particles would have saturated with increase in applied field. Up to a particular magnetic field, the core magnetic moments align with the applied magnetic field. At some stage the resource of the ‘core mode’ of the magnetization response is exhausted and the ‘core magnetization’ of the system is saturated in a usual Langevin's way. Beyond this stage any increase in the magnetic field on the particles has an effect only on the surface layer of the particles and thus the increase in the magnetization of the particles slows down. This specific state of the surface
entails a virtual absence of magnetic saturation that keeps the hysteresis loops unclosed even in very strong fields. Nanoparticles with large surface/volume ratio show enhanced spin disorder relative to large particles when measured with the same values of applied field and temperature [208]. The surface layer magnetic moment anomalies may be due to broken exchange bonds, high anisotropy layer on the surface, or a loss of the long-range order in the surface layer. These effects are more intense in case of ferrites because of the super-exchange interactions through the oxygen ions. The presence of another atom (ion) in the form of impurity or an absence of the oxygen ions at the surface leads to the breakage of the super-exchange bonds between the magnetic cations inducing a large surface spin disorder [209].

![Graph showing the effect of different polymers on the magnetization of (BTO / NZF) nanocomposite.](image-url)

*Fig. (3.58): The effect of different polymers on the magnetization of (BTO / NZF) nanocomposite.*
Fig. (3.59: a, b): 

a. Variation of coercive field ($H_c$) and $M_r/M_s$ with different Polymers types.

b. Effect of different polymers on the Magnetic parameters; $M_s$ and $M_r$ of 0.5 (BTO / NZF) nanocomposite.

Table (3.9): Magnetic parameters for BTO / NZF composite doping with different polymers; PANI, PEG, PVAc, and PVP.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$M_s$ (emu/g)</th>
<th>$M_r$ (emu/g)</th>
<th>$H_c$ (Oe)</th>
<th>$M_r/M_s$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ME</td>
<td>25.92</td>
<td>5.40</td>
<td>100</td>
<td>0.21</td>
</tr>
<tr>
<td>PANI</td>
<td>21.60</td>
<td>2.16</td>
<td>120</td>
<td>0.10</td>
</tr>
<tr>
<td>PEG</td>
<td>15.18</td>
<td>2.07</td>
<td>140</td>
<td>0.14</td>
</tr>
<tr>
<td>PVAc</td>
<td>13.80</td>
<td>2.07</td>
<td>140</td>
<td>0.15</td>
</tr>
<tr>
<td>PVP</td>
<td>8.63</td>
<td>1.38</td>
<td>140</td>
<td>0.16</td>
</tr>
</tbody>
</table>
3.4.3. Electrical properties:

Electrical properties of polymers doping ferrites, well known for their insulating properties, may be improved by adding various functional fillers; Fig. (3.60). Polymer–ferrite composites have been a subject of recent extensive research. Electrical properties of such composites depend on the size, shape and amount of added filler in general as in Figures (3. 61, 62). The results reveal a significant change of conductivity value of composite particles by varying the type of the polymer at room temperature where the highest value of $\varepsilon'$ and $\varepsilon''$ for PANN sample indicated that, the dielectric properties of polycrystalline ferrite–polymer composites arise mainly due to the contribution of orientation polarization [210], which is mainly a result of the process of electron transfer between ferrous (Fe$^{2+}$) and ferric ions (Fe$^{3+}$) [211]. Electronic and atomic polarizations are also responsible for the polarization at microwave frequencies [212], occur at a period shorter than the period of a microwave [213].

The imaginary part of the complex permittivity, $\varepsilon''$; or the dielectric loss is a result of the lag in polarization with the applied electric field. The dielectric constant and the dielectric losses in the composites doping PANN are very high found to from about 5720 and 3056 respectively while other polymers in the range 12-21 and 0.003-4.2 respectively as seen in Fig. (3.63: a, b), these results may possibly be explained in the following manner. The composite may be considered to be a homogeneous phase of composite particles. Each composite particle consists of a ferrite particle surrounded by a layer of polymer, although there can be distributions in the layer thickness which different from polymer to other. In addition, in the composite particles, some ferrite particles which are not covered by the polymer layer (due to a different in the polymer type), thus leading to a heterogeneous mixture. With change in the polymer type, therefore, this heterogeneity change which results in a change in loss. Fig. (3.63b) reveal the high electrical conductivity (ln$\sigma$) for composite doping PANN indicated that, this composite can be used in electronic and microwave applications.
Fig. (3.60): Variation of $\ln \sigma$ with different polymers types for 0.5 (BTO / NZF) nanocomposites.
Fig. (3.61): Real part of dielectric constant ($\varepsilon'$) of 0.5 (BTO/NZF) nanocomposite dispersed in different polymer matrices.
Fig. (3.62): Imaginary part of dielectric constant ($\varepsilon''$) of 0.5 (BTO/NZF) nanocomposite doped different polymers.
Fig. (3.63: a, b): a). Variation of dielectric constant ($\varepsilon'$) and dielectric loss factor ($\varepsilon''$) as a function of different polymers type at selected frequency. b). Effect of polymer type on the electrical conductivity ($\ln \sigma$) of 0.5 (BTO / NZF) nanocomposites.
Third group:

3.5. A series of (1-y) (0.5BTO / 0.5NZF) / (y) PEG; 0.0, 0.1, 0.3, 0.5, 0.7, 0.9, and 1.0:

"Polyethylene glycol (PEG) based nanocomposites"

Hybrid nanocomposites (1-y) $[\text{BaTiO}_3 / \text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4 ] / (y) \text{PEG}$, $0 \leq y \leq 1$, have been prepared via citrate auto-combustion method as mentioned in chapter 3. In the present section, the main goal is to achieve bi-modal improvement of the physical characteristics of 0.5BTO / 0.5NZF nanocomposite due to influence of different concentrations of PEG powder and gain more insight in the morphology and chemical structure of these materials. This is performed through room temperature mixing and cold pressing of the PEG ratio of $0 \leq y \leq 1$.

3.5.1. Structure characterization:

3.5.1. a. Scanning electron microscopic analysis:

Figures (3.64:a-f) illustrate SEM of hybrid nanocomposites based Polyethylene glycol (PEG) with different selected ratios; 0.0, 0.1, 0.3, 0.5, 0.7, 0.9 and 1.0 wt. % respectively and at different magnifications as matrices for BTO / NZF nanocomposite.

It is clear that all micrographs show three phases in almost good dispersion and high degree of homogeneity. The magnetic phase arranged or distributed in a circular manner and forced the other two phases to respect and follow the same trend. Therefore the PM (NZF) forms the center of two successive shells; BTO and PEG respectively and. The large bright contrast is PEG particles while the small bright one is BTO particles and the grey contrast is NZF particles. It is also observed that, as the ratio wt. % increases instead of ME phase, the density of PEG increases and hence the arrangements or the distribution of PEG becomes better and clear. In addition, it is clearly seen in the micrographs that, the average grain size of PEG increase with increases its ratio.
Fig (3.64a): SEM photographs of 0.9(0.5BTO/0.5NZF) / 0.1PEG nanaocomposite with different magnifications.
Chapter Three

Results and Discussions

Fig (3.64b). SEM photographs of 0.7(0.5BTO/0.5NZF)/0.3PEG nanocomposite with magnifications.
Fig. (3.64c): SEM photographs of 0.5(0.5BTO/0.5NZF)/0.5PEG nanocomposite with magnifications.
Fig.(3.64d): SEM photographs of 0.3(0.5BTO /0.5NZF) / 0.7PEG nanocomposite with magnifications.
Fig. (3.64e): SEM photographs of 0.1(0.5BTO / 0.5NZF ) / 0.9PEG nanaocomposite with magnifications.

Fig. (3.64f): SEM photograph of pure PEG at 25X magnification.
3.5.1. b. FT-IR analysis:

Figure (3.65) show FTIR spectra of (1-y) (0.5BTO / 0.5NZF) / (y) PEG nanocomposites; y = 0, 0.1, 0.3, 0.5, 0.7, 0.9, and 1 respectively in the range 4000–400 cm\(^{-1}\). It is revealing that, the broad peak observed at 2860 and 1420-1450 cm\(^{-1}\) respectively attributed the adsorbed water which are assigned to the vibration of O-H and H-O-H groups [212, 213]. These bands are observed in the all concentrations of PEG and as well as in blank PEG with different intensities. The band around 550 cm\(^{-1}\) corresponding to the stretching vibration of the interactions produced between the oxygen and the cation occupying the octahedral and the tetrahedral sites [214]. While, for pure PEG, clear bands are observed at around 3200-3250 cm\(^{-1}\) (v\(_{O-H}\)) and 1000-1030 cm\(^{-1}\) (v\(_{C-O}\)) which indicates the presence of –OH and C-O group vibration modes. Bands between 1200 – 600 cm\(^{-1}\) and 2880 – 1600 cm\(^{-1}\) are corresponding to the plane deformation of C-H group bending and stretching vibrations respectively. The band at 1470 cm\(^{-1}\) is due to the stretching vibration of C-C of PEG [215]. The above bands show a change in intensity and positions with the different concentrations of PEG. Besides, when the PEG content is greater than 50%, FTIR spectra of the (BTO/NZF) / PEG composites are almost the same as that of normal PEG sample [216]. As shown in the figure, with the increase of PEG content, the intensity of the band at 570 cm\(^{-1}\) corresponding to (BTO/NZF) composite [217] increased distinctively, and those bands corresponding to PEG characteristics, such as 2900 cm\(^{-1}\), shift to higher wave numbers. This indicates that there is some interaction between PEG and (BTO/NZF) nanoparticles. Moreover, the adsorbed water is featured by bands at 3420 and 1620–1630 cm\(^{-1}\), which are assigned to O–H stretching and H–O–H bending modes of vibration [211, 212]. These bands are observed in all the PEG coated and as well as in blank PEG but the intensity of these bands is different. Table (3.10) represents the main absorption bands of PEG that appeared in all PEG contents except.
Table (3.10): Main function groups of PEG within PEG/ME nanocomposites.

<table>
<thead>
<tr>
<th>Characteristic Group</th>
<th>Peaks Band (cm(^{-1}))</th>
<th>Molecular Vibrations</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-O-C</td>
<td>Ether</td>
<td>1100</td>
</tr>
<tr>
<td>C-O</td>
<td>Alcohols</td>
<td>850, 1000</td>
</tr>
<tr>
<td>C-H</td>
<td>Alkanes</td>
<td>2850 - 2960</td>
</tr>
<tr>
<td>C-H</td>
<td>Alkanes</td>
<td>1350 - 1460</td>
</tr>
<tr>
<td>O-H</td>
<td>Hydroxyl</td>
<td>3480</td>
</tr>
</tbody>
</table>
3.5.2. Magnetization measurements:

In order to study the effect of PEG on the magnetic behavior of the investigated composite, magnetization measurements were performed. Figure (3.66) illustrates the variation of hysteresis magnetic loops of composite (1-y) [BTO / NZF] / (y) (PEG); 0 ≤ y ≤ 1. It is clear that, composites materials exhibit typical magnetic hysteresis of the magnetic materials, indicating that the composites are magnetically ordered. Moreover, it could be observed that there is no hysteresis and a complete reversibility at 300 K was found: it is more clearly denoted in the inset of Fig. (3.66), where neither coercivity nor magnetic remanence in the composite is observed corroborating with a typical superparamagnetic behavior [218].

The variation of the magnetization parameters such as saturation magnetization (M_s), remanence magnetization (M_r), and M_r/M_s of the composites with different PEG content (y) is plotted in Fig. (3.67a) and Table (3.11). It is clearly indicated that, M_s of the composites decreases linearly with the increasing PEG content. These reductions are mainly due to the finite size effect of the nanoparticles (NZF) besides to the contribution of the volume of the nonmagnetic (PEG) coating layer to the total sample volume. While the saturation magnetization of BaTiO_3 is unity due to its inherent nonmagnetic nature and magnetic nature of PEG. Therefore, the magnetization parameters (M_s and M_r) of composites decreases linearly with the increasing PEG content while the ratio M_r/M_s is still constant. In other words, the nonmagnetic coating layer can be considered as a magnetically dead layer at the surface, thus affecting the uniformity or magnitude of magnetization due to quenching of surface moments [219].
Table (3.11): The effect of PEG content (y) on the magnetic parameters of (1-y)(0.5BTO / 0.5NZF)/ (y)PEG nanocomposites; y = 0.1, 0.3, 0.5, 0.7, 0.9 and 1.

<table>
<thead>
<tr>
<th>y</th>
<th>$M_s$ (emu/g)</th>
<th>$M_r$ (emu/g)</th>
<th>$H_C$ (Oe)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>25.92</td>
<td>2.26</td>
<td>100</td>
</tr>
<tr>
<td>0.1</td>
<td>20.52</td>
<td>2.00</td>
<td>120</td>
</tr>
<tr>
<td>0.3</td>
<td>18.36</td>
<td>1.60</td>
<td>120</td>
</tr>
<tr>
<td>0.5</td>
<td>15.18</td>
<td>2.07</td>
<td>140</td>
</tr>
<tr>
<td>0.7</td>
<td>14.40</td>
<td>1.50</td>
<td>120</td>
</tr>
<tr>
<td>0.9</td>
<td>17.28</td>
<td>1.55</td>
<td>120</td>
</tr>
</tbody>
</table>
3.5.3. Electrical conductivity measurements of hybrid nanocomposite based PEG:

Figure (3.67: a, b) shows the variation of dielectric constant ($\varepsilon'$) and dielectric loss factor ($\varepsilon''$) with frequency as a function of PEG content ($y$). It is evident that the dielectric constant and loss factor decrease with increasing both frequency and PEG content ($y$) giving rise the same trend but with different values. In the starting low frequency range both ($\varepsilon'$) and ($\varepsilon''$) have higher values. As the frequency increased both $\varepsilon'$ and ($\varepsilon''$) are decreased and become almost constant up to 1 MHz for all compositions. The observation may be explained on the basis of dipole relaxation [220] indicating the inability of the electric dipoles to follow up the field variations. The low frequency dielectric dispersion was increased with the increase in PEG concentration. This due to the fact that, the ferroelectric regions are surrounded by nonferroelectric ones as the case of relaxer ferroelectric materials [221], resulting in interfacial polarization because the two media have different permittivities and conductivities, the applied electric field will produce space charges provided by the NZF phase which accumulated at the interface of the two phases. In other words, the dielectric loss factor is considered to be the most important part of the total core loss in composites [222]. The dielectric loss factor is seen to be similar to that of dielectric constant as in Fig. (3.68b). The low dielectric loss values make these composites to be used in the higher frequency applications. The low dielectric parameters obtained for the present samples and the small abnormal behavior was observed at lower frequencies is due to the collective contribution of both positive and negative (p, n) charge carrier [223] where the electronic exchange between Fe$^{2+}$ Fe$^{3+}$ are responsible for such behavior. Furthermore, the jumping frequencies of localized charge carrier are almost equal to that of the applied a. c. electric field.

Variation in electrical conductivity of the composite materials at different PEG content ($y$) is shown in Fig. (3.68: a, b). It is clear that, the value of conductivity decrease with increase ($y$) up to 0.5 then increases. It is clear that, the doping increasing ratio of PEG decreases the conductivity up to $y =0.5$ then increases. This may be attributed to the difference in the conductivity of ferrite and ferroelectric phases as well as the conductivity of composite is an effective of its
constituent phases. The maximum conductivity is observed at \( y = 0.5 \) perhaps due to the addition of conductivity of the constituent phases. Moreover, the increase in conductivity of the composites as compared to constituent phase may be ascribed to the serial arrangement of ferrite and ferroelectric grains with adding PEG content. \[222\].

Besides, the plots are straight lines indicating the dependence of conductivity with frequency of the investigated samples. It is clear that, the hopping of electron between \( \text{Fe}^{2+} \) and \( \text{Fe}^{3+} \) ions on the octahedral sites is responsible for conduction in ferrites. Also hole hopping between \( \text{Ni}^{2+} \) and \( \text{Ni}^{3+} \) on B site will also contribute to electric conduction in ferrites. The frequency dependence can be explained with the help of Maxwell–Wagner two-layer model or the heterogeneous model of the polycrystalline structure of ferrites \[223\] According to this theory, two layers formed dielectric structure. The first layer consists of ferrite grains of fairly well conducting (ferrous ions), which is separated by a thin layer of poorly conducting substances, which forms the grain boundary. These grain boundaries are more active at lower frequencies; hence the hopping frequency of electron between \( \text{Fe}^{2+} \) and \( \text{Fe}^{2+} \) ion is less at lower frequencies. As the frequency of the applied field increases, the conductive grains become more active by promoting the hopping of electron between \( \text{Fe}^{2+} \) and \( \text{Fe}^{3+} \) ions, thereby increasing the hopping frequency. It was also noticed that this remains the same for samples with different volume fractions of the magnetic filler.
Fig. (3.67: a, b): a. Effect of applied frequency on dielectric constant ($\varepsilon'$) at different PEG concentration for 0.5BTO / 0.5 NZF nanocomposite. 
b. Effect of applied frequency on dielectric loss factor ($\varepsilon''$) at different PEG content ($y$) for 0.5BTO / 0.5 NZF nanocomposites.
Fig. (3.68: a, b): a). Variation of electrical conductivity (ln σ) at different PEG content (y) for 0.5 (BTO /NZF) nanocomposites.
b). Effect of different PEG concentration on the electrical conductivity at a selected frequency.
Conclusion
Chapter Four

Conclusion

Three groups of multiferroic nanocomposites, namely:

1- **First group**: A series of \((x) \text{BaTiO}_3 / (1-x) \text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4\) were successfully prepared by double sintering technique and citrate autocombustion method, where \(x=0.0, 0.4, 0.5, 0.7\) and \(1.0\) in comparison study, were allowed to formulate the following statements:

- All the samples from the two methods formed in single phase in both; cubic spinel structure \(\text{NiZnFe}_2\text{O}_4\) ferrite and perovskite tetragonal structure \(\text{BaTiO}_3\).

- The calculated values of the crystallite size \((L)\) of the two phases were obtained from ceramic method of NZF and BTO; \((311)\) and \((110)\), is \(68\) nm, and \(119\) nm respectively. While from citrate autocombustion method, the crystallite size \((L)\) is around \(30\) nm and \(47\) nm respectively indicated that, the crystallite size decreased by \(0.44\%\) for ferrite and \(0.39\%\) for perovskite.

- TEM images of citrate method, it is shown that the two phases have a homogeneous distribution with core shell-like shape, where ferrite represents the core and BTO the shell. It is evident from the photos that the ferrite has a spherical shape with a size of \(40\) nm, while the BTO has nanorod shape with average length \(120\) nm and diameter of \(43\) nm.
- In both methods, the critical concentration is at $x = 0.5$ and $T_C$ value for citrate method is higher than (610K) that the ceramic method (528K).

- The values of magnetization parameters, $M_s$, $M_r$, $H_c$, and $\mu_B$ decreases with increasing BTO content in the composites expect at $x = 0.5$ which gives the highest values for all parameters.

- In both methods, the variation of dielectric constant is explained in terms of electron exchange between $\text{Fe}^{2+}$ and $\text{Fe}^{3+}$ suggesting that the polarization in composites is similar to conduction process in ferrites depending on heterogeneity of the samples and ordering of micro regions of spontaneous polarization.

- In both methods, the variation of Seebeck coefficient ($S$) is due to the majority net charge carriers of holes and electrons.

- SEM produced by citrate synthesis has large number of pores, but ceramic powder is nearly free from porosity.

- In citrate method, Atomic Force Microscopy (AFM) topography micrograph illustrated the presence of grains with two stable states: bright plateaus that raised from the tetragonal phase, and areas of dark contrast that are interpret to arise from the spinel phase. This was indicated by the existence of some nanodomains with tetragonal phase (white contrast) involved in a matrix formed globally by spinel structure.

2- **Second group**: Innovative physical properties of BTO / NZF doped different polymers (Hybrid nanocomposites):

- Magnetic measurements for nanocomposites of BTO / NZF with different polymers matrices; PEG, PANI, PVAc, and PVP were carried out at room temperature characteristics of superparamagnetizm with absence of hysteresis and lack of saturation magnetization.
- The reduction in saturation magnetization is due to two-component nanoparticle system consisting of a spin-glass like surface layer and ferromagnetically aligned core spins.
- Sample doped PANI has the highest magnetization and electrical conductivity reveal used in electronic applications.

3- **Third group**: (1-\(y\)) (0.5BTO / 0.5NZF) / (\(y\)) PEG; 0.0, 0.1, 0.3, 0.5, 0.7, 0.9, and 1.0, prepared using the citrate auto-combustion method for ME biferroic and by weight mixing for hybrid nanocomposite:

- X-ray diffraction enabled the identification of both ferrite and ferroelectric phases before adding PEG content.

- SEM images reveal that the shape of PEG particles is irregular while the size increase with increases PEG ratio.

- The conductivity of the composite increases with increase PEG content.

- Composites with \(y = 0.5\) composition shows maximum conductivity at room temperature.

- The frequency dependent ac conductivity measurements suggest that conduction is due to small polaron hopping.

- The decrease in \(\varepsilon'\) with increase of frequency is due to the orientation polarization indicates that the dielectric constant of BT / NZF can be improved by introducing PEG.

- The increase in conductivity of the composites as compared to constituent phase may be ascribed to the serial arrangement of ferrite and ferroelectric grains with adding PEG content.

- Saturation magnetization of the composites decreases linearly with the increasing PEG content due to the finite size effect of the nanoparticles (NZF).
- Coercivity ($H_c$) has high value for all the concentrations of PEG.

**Finally, concluded the important points as:**

- Citrate method has been applied successfully for preparing specific multicomponent nanocrystalline ceramics and show coexistence of ferromagnetic and ferroelectric phases.

- This chemical method offer possibly a preparation at lower temperatures, a homogenous primary structure and limited higher order aggregation and a small distribution of particle sizes which is a prospect for improving existing method into less cumbersome, more versatile and cost effective methods for large scale productions.

- The optimized ratio of the composite at $x = 0.5$ may be useful for technological applications such as magnetic probes, thermistors, transducers as well as electric current measurement.

- The composites with doping PEG polymer may be useful for technological applications such as thermistors, transducers, magnetic probes, etc.
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Arabic Abstract

الملخص
المجموعة الأولى:

(أ): تم فيها تحضير عينات من الفيبرات (نيكل-زنك-فيبرات ) من أكسيد الحديد ومغنيسيز النحاس والنيكل وذلك بواسطة طريقة السيراميك (الفرق المزدوج) . تم تحضير تيتانات الباريوم بنفس الطريقة باستخدام كربونات الباريوم وأكسيد النيكل في الثاني وارتفاع النقالة و بخلط نسب مختلفة: ( 0.7, 0.6, 0.5, 0.4) من المادتين والدهان الجيد للحصول على مسحوق متجانس وناعم . تم عمل أفراد من المترابط ذات النسب المختلفة . تم التأكد من تكوين المترابط بنجاح وعدم تكون أي أطوار (phases) أخرية وذلك معرفة الحجم البولوري أو الجيوفي بواسطة تقنيات توصيفية مختلفة منها تقنية حبوب الأشعة السينية ، وباستخدام الميكروسكوب الإلكتروني الماسح والنافذ وكذلك تم عمل دراسة الأشعة تحت الحمراء وذلك للتتأكد من الترتيب الكيميائي للمترابط المحضرة . حيث دلت النتائج على نجاح المترابط دون ظهور أيّة أطوار أخرى للمادة المتكونه أو أي تداخل ناتج من تفاعل المادتين
مع بعضهما . كما أعطت النتائج الحجم البولاري في حدود 68, 119 نانومتر لكلا من النيكل-زئك. فبرايت وتيتانيت البالوروم على الترتيب . كما تم توصيف المتراكبات حرارية لاختبار مدى الثبات الحراري للمتراكبات المحضرهة . تم دراسة الخواص المغناطيسية للمتراكبات المحضرهة . كما تم توصيف المتراكبات كهربيا عن طريق قياس التوصيلية الكهربائية (ac و dc) وقياس ثابت العزل الكهربائي .

وبمقارنة جميع النتائج : التركيبية ، المغناطيسية والكهربائية منها تم ملاحظة أنه عند التركيز 0.5 يحدث تغير مفاجئ لسلوك المتراكبات ومن ثم تم استنتاج أن هذه النسبة هي النسبة الحرجة (Critical concentration) والتي لها خواص مميزة ويحقق عنها نظرية (Percolation theory)

تم دراسة التوصيلية الكهربائية وثابت العزل والفقد الكهربائي ومن ثم تم استنتاج أليات التوصيل الكهربائي للمتراكبات ذو النسبة الحرجة وذلك كدالة في درجة الحرارة أثناء التسخين (ارتفاع درجة الحرارة ) وايضاً أثناء التبريد ( نقصان درجة الحرارة ) . حيث تم الحصول على منحنى أو عروة التخفيف الكهربية والتي تميز تيتانيت البالوروم كمادة بيوزوالكترية أو فيروالكترية . ومن النتائج لوحظ أن مساحة منحني التخفيف يختلف مع تغير التردد حيث يقل مع زيادة التردد . بحيث تعر مساحة المنحنى عن السعة التخزينية "capacity" للمادة إذا ما أستخدمت كذاكرة ، أيضاً يمكن ان تمثل طاقة فقد الناتجة من الاحتكاك ما بين ثنائيات القطب

وتمثل الاسترخاء الذي حدث نتيجة التبريد.

(ب): تم اختيار التركيز الحرج ( Critical concentration ) كيميائية وذلك باستخدام مواد كيميائية عالية القدرة من النترات. وتشمل المجموعة الثانية تحضير كلا من البالوروم تيتانيت والنيكل زئك فبرايت كلا منهما على حدة كما يلي: تم تحضير تيتانيت البالوروم بطريقة السيربرت المعهدة باستخدام نترات البالوروم والأيزويتويت تيتانيت بمشاركة حمض الستريك كعامل مساعد على الحرق وتكون العينة . باستخدام تقنيات جيود الأشعة السينية وبالدماك الميكروسكوب الإلكتروني الماسح والناذف وكذلك دراسة الأشعة تحت الحمراء تم التأكد من تكون البالوروم تيتانيت في حجم النانو وعدم تكون أية أطوار أخرى . تم دراسة الشكل الخارجي للسطح واعطاء صورة ثلاثية الابعاد وكذا تحديد درجة التجانس من حيث حجم وشكل الحبيبات للكرب المحرض بالاستخدام.
ميكروسكوب الفيزيائي الذري AFM. وتم دراسة منحنى التجاوز الثابت العزل الكهربائي والتوصيلية مع التردد المختلفة.
(ج) : تم تحضير النيكل – أتيوم و الفرايت بطريقة السيبريت ثم تم خلط كل من تيتانات الباريوم و الفرايت بنسبة 1:1 لعمل متراكب نانومتربي. تم اجراء جميع التقنيات التوصيفيه والتحليلية للمتراكب لدراسة سلوك المتراكب المحضر بطرقتين مختلفتين ومن ثم اختلاف النتائج التي تم الحصول عليها.

(د) : تم عمل دراسة مقارنة بين الطرقتين والنتائج المتباينة بينهما.

وباستخدام "AFM"، تم التفرقة ما بين الطرقين المكونين للمتراكب وأعطي صورة للسطح ثنائي وأحدي الثلاثية الابعاد في مساحات اختيارية مختلفة وتم تعيين الحجم الحبيبي وتوزيع الاحجام وتحديد درجة تجانس وتوزيع المادة داخل المتراكب بالنسبة لبعضهما البعض.

المجموعة الثانية: وباستخدام مجموعة من البوليميرات المختلفة مثل البولي ايثيلين، البولي فينيل استيتيت، البولي ايثيلين جليكول، البولي بيرولينيد كلا منهم على حدة مع المتراكب الكهرومغناطيسي بنسبة ثابتة 1:1. تم الحصول على متراكب ثلاثي الاتوار من المتراكب الكهرومغناطيسي والذي يتكون من طورين مختلفين مع البوليمر والذي يلعب دور كبير في التأثير على خواص المتراكب النانومتربي. حيث تم عمل مقارنة بين الخواص التركيبية، المغناطيسية والكهربائية للمتراكبات المحضرة لاختبار أفضل بوليمر يعطي خواص مثلى للتطبيقات البحثية والتقنية.

المجموعة الثالثة: تم اختبار البولي ايثيلين جليكول وذلك بتغير نسبة مع المتراكب النانومتربي بنسبة (0.0, 0.1, 0.3, 0.5, 0.7, 0.9, 1) ، وتم عمل دراسة مقارنة ما بين التركيزات المختلفة. وقد دلت النتائج أن نسبة 0.5 هي النسبة المثلى والتي أظهرت نتائج تمكنها من الاستخدام في التطبيقات المختلفة.
الخواص التركيبية والمغناطيسية والانتقالية للمتراكبات البوليمر مع الفيرآيات النانومترية

رسالة دكتوراه

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كما أشكر قسم الطبيعة النووية التجريبية بهيئة الطاقة الذرية وأشكر قسم الطبيعة بكلية البنات جامعة عين شمس وأشكر أصدقائي وأهلي جميعاً.