Republic of Iraq Ministry of Higher Education and Scientific Research University of Diyala College of Sciences Department of Physics



## Preparation and Investigation the Structural and Electrical Properties of Bismuth Ferrite Nano powders

A Thesis

Submitted to The Council of the College of Sciences, University of Diyala in Partial Fulfillment of the Requirements for the Degree of Master of Sciences in Physics

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2014 AD

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## **DEDICATION**

I dedicate this work:

To soul of my beloved mother (May Allah have mercy on her soul and grant her the highest level of paradise).

To the one whom I hold of his own name with all pride, the first to teach me, to the big heart my dear father with all evaluation and regard for him.

To everyone who tried to guide me or teach me important life lessons.

Researcher.

300 300 300

5) 5) Prophet of Allah Muhammad (peace and blessings of Allah be upon him) say (Who does not thank people does not thank Allah).

A bove all, hidden force by almighty Allah (S.W.T) steered me in the right direction to achieve the goal, all praise of Almighty Allah, the most merciful and compassionate, the Creator of the Universe, who enable me to complete this study successfully and sincerest words of thanks to his Prophet Muhammad (peace and blessings of Allah be upon him) who is forever a torch of guidance and Knowledge for the humanity.

Special thanks are extended to the Dean of the College of Science and all the staff of Department of Physics and chemistry for their assistance

Praises and thanks belong only to ALLAH (S.W.T) for giving me this excellent opportunity to meet and work with marvelous people :Sincere Dr. Tahseen H. Mubarak and Sincere Dr. Karim H. Hassan, I am immensely grateful for them support, insight, guidance and encouragement at all times therefor special thanks from me to them, without them, I may not be able to complete this study.

Special thanks to the head of the physics department Dr. Ziad T. Khudair and all staff of teaching in Department, who gave me a light to my path.

I would like to express my appreciation to Dr. Sabah muhammed Ali for his suggestions and valuable remarks.

Special thanks to Sincere Mr.Naseer for encouragement, support, and helped me to complete my thesis.

Special thanks to Dr.Abdul kareem in University of Baghdad and Dr.Abdul Salam in University of Kirkuk .

I am also grateful to the Ministry of Sciences and Technology for their help during the electrical and X-ray tests also grateful to the physics Department at the College of Education Ibn al-Haytham for their kind help during the X -ray tests.

My thanks to my family for their unwavering support through the whole adventure; I could not have done it without them (My father, my Sisters specially Nadia for her prayer to me and my Brothers).

Finally, my gratitude is dedicated to my best colleagues :Raheem,Aram, Aws, Ahmed,watban,Rusul, Mohammad, Asra, Rudaina, Nisreen,Sara and I would also express my deep sense of gratitude to Haydar Ali ,Shahlaa ,Hala , Anfal, and Abdulwahab.

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Nor.

## Researcher.

# **Publications**

### **Published and Accepted Research Articles**

Effect of Temperature on Structural and Electrical Properties of Bismuth Ferrite Nanoparticles Prepared By Sol Gel Method, International Journal of Innovative Research in Science Engineering and Technology (IJIRSET), Vol.3, Issue10, October 2014.

Abstract

In the present study entitled bismuth ferrite nano powders (BiFeO<sub>3</sub>), were synthesized using sol-gel as a modern chemical methods. Bismuth nitrate pentahydrate Bi (NO<sub>3</sub>)<sub>3</sub>.5H<sub>2</sub>O, iron nitrate Nonahydrate Fe (NO<sub>3</sub>)<sub>3</sub>.9H<sub>2</sub>O, citric acid C<sub>6</sub>H<sub>8</sub>O<sub>7</sub> and nitric acid HNO<sub>3</sub> were used in order to get ferrite nano powders. The produced gel was dried at 150°C for two hours and then calcined at various temperatures; 350°C, 450°C, 500°C, 550°C and 700°C for two hours as well.

The structural, electrical and dielectric properties of BiFeO<sub>3</sub> Nano powders studied by using many measurements like X-ray diffraction, FTIR, SEM, AFM and LCR meter. X-ray diffraction showed that the gel dried was amorphous, but after calcined at 350°C it becomes crystalline.

After analysis all peaks appear by x-ray for all samples calcined ,it found there were many impurities phases appear with single phase BiFeO<sub>3</sub> ,where sample calcined at 450°C was the best one as far as single phase of bismuth ferrite main peak was concerned with small peak due to impure phase and impure phase appear was one only But sample calcined at 700°C was the worst one where bismuth ferrite main peak was concerned with large peaks from many impurities phases so we don't study the properties of this sample.

XRD showed that the crystallite size by using Scherrer equation were about (12.5, 12.8, 39.9 and 47.6) nm for samples calcined at 350 °C, 450°C, 500 °C and 550 °C respectively. This explained that crystallite size increased with increase in temperature.

From SEM micrographs , $BiFeO_3$  show that the size is less than 100 nm also noted that the increase in the shapes with calcination temperature

may have helped in the growth of the large particles but remained within nano scale. AFM figurers proved that particle size is very small and homogeneous and in nano scale. Because the impurity has great effects on the electrical properties of the BiFeO<sub>3</sub> so the electrical testing was done by LCR meter for only sample calcined at 450°C by using 5% PVA as a binder to it, where the values of dielectric constant are between (113.42 to 43.93) for frequency (25 KHz to 5 MHZ), indicates that the dielectric constant decrease with increase in the frequency.

The electrical resistivity values  $(1.3 \times 10^6 \text{ to } 1.1 \times 10^4 \Omega.\text{cm})$  at a frequency range of (25 KHz to 5MHz), this show that electrical resistivity decrease with increase in the applied frequency. Electrical conductivity values are  $(1.3 \times 10^{-8} \text{ to } 8.7 \times 10^{-5} (\Omega.\text{cm})^{-1})$  with range of frequency (25 KHz to 5 MHZ), this show that electrical conductivity increases with increase in frequency. Finally the tangent loss values are between (0.44 to 0.25) with the range of frequency (25 KHz to 5 MHz), this show that tangent loss decreases with increase in the applied frequency.



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Symbol	Definition	Unit
α, β, γ	lattice angles	-
T <sub>N</sub>	Neel temperature	K, °C
T <sub>C</sub>	Currie temperature	K, °C
V	Voltage	V
λ	wavelength	nm, Å
Θ	Diffraction angle	degree
ρ	Resistivity	Ω.cm
D	Crystallite size	nm
R	Electrical resistance	Ω
А	Area	$m^2$
L	Thickness	m
Е	Electron energy	eV
Т	Temperature	°C
N	Avogadro's number	mol <sup>-1</sup>
β	Full width at half maximum	rad
М	Molecular weight	g/mol
a,c	Lattice constant	Å
n	Integer	-
(hkl)	Miller indices	-
d	Interplaner spacing	Å
d <sub>x</sub>	X-Ray density.	g/cm <sup>3</sup>
δ	Loss angle	degree
I <sub>a</sub>	Active current (resistive current)	А
I <sub>r</sub>	Reactive current (capacitive current)	А
Tanð	Tangent loss angle	-
XRD	X-Ray diffraction	-

SEM	Scanning electron microscopy	-
AFM	Atomic force microscopy	-
FTIR	Fourier transform infrared	-
JCPDS	Joint committee on powder diffraction standards	-
RMS	Root mean square	-
BFO	Bismuth ferrite	-
ME	Magnetoelectric Effect	-

# **Chapter one**

# **Introduction and Applications**

### **1-1 Introduction**

Historically, the development of magnetic material for technical applications was started with the development of metallurgy and the study of metals in general.

Recently, a new application like wireless communication tools such as mobile telephones and computer local area networks have become popular and dependent on magnetism and magnetic materials [1]. Magnetic materials combined with electrical and magnetic properties are known as ferrites. Iron oxide and metal oxides are the main constituents of the ferrites. The importance of ferrite material has been known to mankind for many centuries. In the early of the twelve century the Chinese were known to use lodestones (Fe<sub>3</sub>O<sub>4</sub>) in compasses for navigation [2].

The practical use of ferrite and its study for structural, electrical and magnetic properties have started in the year 1930. Since then ferrites are extensively studied by many researchers. Ferrite materials are insulating magnetic oxides and possess high electrical resistivity, low eddy current and dielectric losses, high saturation magnetization, high permeability and moderate permittivity. No material with such wide range properties exists and therefore ferrites are unique magnetic materials which find applications in almost all fields. Ferrites are highly sensitive to preparation method, sintering condition, amount of constituent metal oxides and various additives dopants and impurities [3-5].

Ferrites are magnetic oxide materials with semiconducting nature which are of great technological importance by virtue of their interesting electrical and magnetic properties. They are used in transformer cores, antenna rods, memory chips, high-density magnetic recording media, permanent magnets, transducers, activators, microwave and computer technology etc.[6-8]. The ferrites in nanocrystalline form found applications in new fields like magnetically guided drug delivery, magnetic resonance imaging (MRI), catalyst, humidity and gas sensors, magnetic fluids etc. [9-11].

One of the ferrite kinds is Bismuth Ferrite (BiFeO<sub>3</sub> or BFO), it was discovered in 1960; recently there is a renewed interest because of it's possible novel applications in the field of radio, television, microwave and satellite communications, audio-video, digital recording and as permanent magnets. So far, BiFeO<sub>3</sub> is a well-known multiferroic at room temperature having Para- to Ferro-electric transition temperature (Tc~ 1103k) and a G-type antiferromagnetic transition at  $T_N \sim 643K$ . Also its one of the most widely studied multiferroic materials, primarily because both its electrical and magnetic ordering occurs above (room Temperature).

In particular, multiferroic BFO nanostructures exhibit interesting magnetic and optical properties because of nano scale size effects So far, BFO nanomaterial with various sizes and shapes such as nano tubes, nano wires, nano/micro cubes, nano spindles and nano rods have been reported and exhibit different properties compared to the bulk form. Therefore, the design of multiferroic BFO nanostructures with novel and well-defined morphologies is important for both fundamental research and relevant for designing new multifunctional materials combining magnetic, ferroelectric and optoelectronic properties[12].Materials which have chemical compounds with the formula RFeO<sub>3</sub> are called ortho ferrite, (where R is one or more rare-earth elements) [13]. There are some methods to prepare BiFeO<sub>3</sub> one of them is sol-gel method, it's a wet-chemical technique commonly used to synthesise a wide variety of nanomaterials.

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#### 1-2 Nano materials

Nano is derived from the Greek word for dwarf and is a prefix in the SI system of units denoting a factor of 10<sup>-9</sup>. Thus, Nano- is used in prefixing time or length units, for example, nanoseconds (ns) and nanometers (nm). In particular, one nanometer is equal to one-billionth of a meter, and ten nanometers are equal to one-thousandth the diameter of human hair. Moreover, nano- can be used as a prefix for something other than a unit of measure, as in nano science, which relates to nanotechnology or to a scale of nanometers [14].

The world is developing in all fields, and nanotechnology only marks a milestone of modern technological development, and is an the industrial field one of the most prominent beneficiaries, and we will strike with the following one example of the usefulness of this technology for the industry. It is known that the traditional method of manufacturing chemicals were mixing different materials, chemical reaction, and thus the chemical mixture to be produced, or a combination of several materials either by using nanotechnology, it is possible to guide the development of the atoms involved in the chemical reaction specific guidance. This method has several benefits, including:

1-Resulting materials will be more accurate than those made in the traditional manner.

2-Will be the degree of purity of the product more.

3-Unification of the quality of the product.

4- Reducing the cost of production.

5-Reducing the energy consumed in manufacturing.

The production of commodity preoccupy specifications of high quality and at a lower cost and large quantities are thought preoccupy industrialists smart and eager to excellence and success and deployment of their products, and this is what will help them upon nanotechnology[15]. In figure (1-1) shows innovative application of nanotechnology, where one of the ways to manufacture nanomaterials is sol-gel technique, which is the method of preparation of chemicals.



Figure (1-1): Innovative Application of Nanotechnology.

### 1-3 Sol-gel method

Sol-gel process is a wet-chemical technique widely used in the fields of materials sciences and ceramic engineering. Such methods are used primarily for the preparation of materials (typically metal oxides) starting from a colloidal solution (sol) that acts as the precursor for an integrated network (or gel) of either discrete particles or network polymers. Typical precursors are metal alkoxides and metal salts (such as chlorides, nitrates and acetates), which undergo various forms of hydrolysis and poly condensation reactions. The sol-gel technology is a typical nanotechnology because all gel products may contain nanoparticles or are nano composites. This process has the advantage of inexpensive precursors, low external energy consumption ,a simple preparation method as well as a simple equipment requirement that result into nano sized, homogeneous , highly reactive powder [16].

### **1-4 Applications of sol-gel**

### **1-4-1 Protective coatings**

The applications for sol- gel derived products are: - numerous. [17-20] For example, scientists have used it to produce the world's lightest materials and also some of its toughest ceramics. One of the largest application areas is thin films, which can be produced on a piece of substrate by spin coating or dip coating. Protective and decorative coatings and electro-optic components can be applied to glass, metal and other types of substrates with these methods. Cast into a mold, and with further drying and heat-treatment, dense ceramic or glass articles with novel properties can be formed that cannot be created by any other method. Other coating methods include spraying, electrophoresis, inkjet printing or roll coating.

### 1-4-2 Thin films and fibers

With the viscosity of a sol adjusted into a proper range, both optical and refractory ceramic fibers can be drawn which are used for fiber optic sensors and thermal insulation, respectively. Thus, many ceramic materials, both glassy and crystalline, have found use in various forms from bulk solid-state components to high surface area forms such as thin films, coatings and fibers [21, 22].

### 1-4-3 Nanoscale powders

Ultra-fine and uniform ceramic powders can be formed by precipitation. These powders of single and multiple component compositions can be produced on a nanoscale particle size for dental and biomedical applications. Composite powders have been patented for use as agrochemicals and herbicides. Powder abrasives, used in a variety of finishing operations, are made using a sol-gel type process. One of the more important applications of sol-gel processing is to carry out zeolite synthesis. Other elements (metals, metal oxides) can be easily incorporated into the final product and the silicate sol formed by this method is very stable. Another application in research is to entrap biomolecules for sensory (biosensors) or catalytic purposes, by physically or chemically preventing them from leaching out and, in the case of protein or chemically-linked small molecules, by shielding them from the external environment yet allowing small molecules to be monitored. The major disadvantages are that the change in local environment may alter the functionality of the protein or small molecule entrapped and that the synthesis step may damage the protein. To this circumvent, various strategies have been explored, such as monomers with protein friendly leaving groups (e.g. glycerol) and the inclusion of polymers which stabilize protein (e.g. PEG) [23].

Other products fabricated with this process include various ceramic membranes for microfiltration, ultrafiltration, Nanofiltration, pervaporation and reverse osmosis. If the liquid in a wet gel is removed under a supercritical condition, a highly porous and extremely low density material called aerogel is obtained. Drying the gel by means of low temperature treatments (25-100 °C), it is possible to obtain porous solid

matrices called xerogels. In addition, a sol-gel process was developed in the 1950s for the production of radioactive powders of  $UO_2$  and  $ThO_2$  for nuclear fuels, without generation of large quantities of dust.

### **1-4-4 Opto-mechanicals**

Macroscopic optical elements and active optical components as well as large area hot mirrors, cold mirrors, lenses and beam splitters all with optimal geometry can be made quickly and at low cost via the sol-gel route. In the processing of high performance ceramic nanomaterials with superior opto-mechanical properties under adverse conditions, the size of the crystalline grains is determined largely by the size of the crystalline particles present in the raw material during the synthesis or formation of the object. Thus, a reduction of the original particle size well below the wavelength of visible light (~  $0.5 \mu m$  or 500 nm) eliminates much of the light scattering, resulting in a translucent or even transparent material. Furthermore, results indicate that microscopic pores in sintered ceramic nanomaterials, mainly trapped at the junctions of microcrystalline grains, cause light to scatter and prevented true transparency. It has been observed that the total volume fraction of these nanoscale pores (both intergranular and intragranular porosity) must be less than 1% for high-quality optical transmission. The density has to be 99.99% of the theoretical crystalline density [24].

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### **1-5 Survey of Previous Studies**

In order to prepare ferrites with better qualifications, precipitation and heat treatment techniques were first performed by Forestier in 1928, Japanese also studied magnetic oxides materials between 1932 and 1935. Snoek started research on ferrites in 1936 and in the period of about ten years, he laid the foundations of physics and technology of ferrites these materials are stable, relatively inexpensive and easily manufactured. The annual production of ferrites is several tons in Europe and rest of the world. Up to now, eight international conferences on ferrites has been conducted in Japan. Beyond 1950 researchers made microwave devices [25], after that, different kinds of ferrites prepared by methods have been studied by many researchers to investigate their different properties. The following review briefly describes the history and shows the results of some previous researches.

In 2005, S.Ghosh et al. [26], used low temperature synthesis of bismuth ferrite nanoparticles by a ferrioxalate precursor method, the synthesis route is simple, energy saving and cost-effective. This study showed the synthesis of bismuth ferrite by solid-state reaction of Bi<sub>2</sub>O<sub>3</sub> and  $Fe_2O_3$  results in the formation of multiphase products. Even so precipitation followed by calcination leads to the formation of impurity phases.The synthesized powders characterized were by X-ray diffractometry. Nanocrystalline powder (11–22 nm as evident from X-ray diffraction analysis) at a temperature of 600 °C was produced. Such nanosized bismuth ferrite powder may have a potential application in making lead free piezoelectric materials for actuators and magnetoelectric sensors.

In 2005,X. Y. Zhang et al. [27], studied the synthesis and ferroelectric properties of multiferroic BiFeO<sub>3</sub> nanotube arrays, this study synthesis and characterization of ordered multiferroic BiFeO<sub>3</sub> nanotube arrays. BiFeO<sub>3</sub>

nanotubes with diameters of about 250 nm and lengths of about 6 nm were fabricated by means of a sol-gel method utilizing Nano channel alumina templates. After post annealing at 700 ° C, the BiFeO<sub>3</sub> nanotubes exhibited a polycrystalline microstructure, and x-ray diffraction revealed that they are of a perovskite crystal structure.Significant ferroelectric and piezoelectric characteristics of BiFeO<sub>3</sub> nanotubes have been demonstrated by means of piezoresponse force microscopy measurement.

In 2005,Kim et al. [28], synthesized high purity BFO R- phase powders with particle size of ~ 200 nm by sol- gel process followed by leaching in diluted nitric acid. The dielectric constant of the BFO- phase was found to be ~15 in the frequency range of  $(10^4 - 10^6)$  Hz at room temperature.

In 2006, Chen et al., [29], synthesized insulating and single phase BiFeO<sub>3</sub> ceramics by rapid sintering at 800°C using sol- gel derived fine powders. The grains of (2-6)  $\mu$ m in diameter heap densely up in the ceramics. The leakage current density of the ceramics remains lower than  $3.02 \times 10^{-4}$  A/cm<sup>2</sup> under the poling field below 119kV/cm. The main conduction mechanism is space-charge-limited current generated from oxygen vacancies. The ceramics exhibit a saturated ferroelectric hysteresis loop with a large remnant polarization 2pr of 56 $\mu$ C/cm<sup>2</sup> at room temperature.

In 2006,F.Gao et al.[30],demonstrated preparation and photoabsorption characterization of BiFeO<sub>3</sub> nanowires, this study showed that: perovskite-type polycrystalline BiFeO<sub>3</sub> nanowires (~50 nm in diameter and ~5 $\mu$ m in length) were synthesized using the anodized alumina template technique. Weak ferromagnetism at room temperature and superparamagnetism at low temperature were observed for the BFO nanowires, being different from the antiferromagnetic order in bulk BFO, reflecting the significant size effects on the magnetic ordering of BFO.

In 2007, Y. Wang et al. [31], alkali metal ions-assisted controllable synthesis of bismuth ferrites by a hydrothermal method, various bismuth ferrite compouds have been controllably synthesized by a hydrothermal method assisted by alkali metal ions (K<sup>+</sup>, Na<sup>+</sup>, and Li<sup>+</sup>). The as-prepared powders were characterized by X-ray powder diffraction. It was suggested that different alkali metal ions can result in the formation of rhombohedral BiFeO<sub>3</sub>,orthorhombic Bi<sub>2</sub>Fe<sub>4</sub>O<sub>9</sub> and cubic Bi<sub>12</sub>(Bi<sub>0.5</sub>Fe<sub>0.5</sub>)O<sub>19.5</sub>, respectively.

In 2007, S. M. Selbach et al. [32], synthesis phase-pure BiFeO<sub>3</sub> by a chemical synthesis route as well as the solid-state method at 825°C. Polymeric BiFeO<sub>3</sub> precursors were obtained from aqueous solutions of nitrate salts and carboxylic acids with and without ethylene glycol added as a polymerization agent. The polymeric precursors were shown to decompose above 200°C with successive nucleation and growth of BiFeO<sub>3</sub> above 400°C. The phase purity of the product was shown to depend on the type of carboxylic acid used, tartaric, malic, and maleic acids resulted in nanocrystalline phase-pure BiFeO<sub>3</sub>. The unit cell and Neel temperature of the bulk materials obtained by the two methods were in accord with previous reports.

In 2008, Jie Wei et al. [33], used low-temperature synthesis of BiFeO<sub>3</sub> nanoparticles by ethylenediaminetetraacetic acid complexing sol-gel process, as a novel approach synthesize of pure BiFeO<sub>3</sub> nanoparticles. The pure BiFeO<sub>3</sub> nanoparticles were attained at much lower temperature as 600 °C by this process, in contrast to above 800 °C for the traditional solid-state sintering process. The SEM results showed that the prepared BiFeO<sub>3</sub> nanoparticles had a better homogeneity and fine grain morphology and a weak ferromagnetic order at room temperature, which is quite different from the linear M–H relationship in bulk BiFeO<sub>3</sub>. The origin of

the weak magnetic property in prepared samples should be attributed to the size-confinement effects of the BiFeO<sub>3</sub> nanostructures.

In 2009, M. Kisku [34], synthesized bismuth ferrite by glycine nitrate auto-combustion with addition of two different types of surfactant namely ALS (ammonium lauryl sulfate) and Triton X. surfactant. The precursor solutions were prepared from ferric and nickel nitrates. By XRD techniques investigated the effects of the surfactant on crystallite size. It has also been observed that Triton X has more suitable in preparing phase pure BiFeO<sub>3</sub> at 550°C, but the crystallite size has greater than the sample prepared with ALS.

In 2010, R. Pandu et al. [35], studied effect of sintering temperature on structural and electrical properties of BiFeO<sub>3</sub> multiferroics at low temperature by using sol - gel technique. With XRD pattern showing that crystallite size increases, the strain decreased and lattice parameter decreased with increasing temperature.SEM micrographs showed that the sample were homogeneous and analyzing the SEM micrographs it can be concluded that the particle size followed the Gaussian distribution.

In 2011, Chen et al. [36], synthesized pure perovskite bismuth ferrite (BiFeO3) microspheres and microrectangular by using the sol - gel and hydrothermal method at 180°C for 12h, using initial KOH concentration of 6M and 10M respectively. Increasing both reaction temperature and time had a positive effect on the formation of BiFeO<sub>3</sub> crystallites.

In 2011, Chandrashekhar.P.Bhole [37], reported ferroelectric and dielectric investigation of bismuth ferrite (BiFeO<sub>3</sub>) nanoceramics, by solid state reaction method. The X-ray analysis depicts that the BiFeO<sub>3</sub> sample had rhombhohedral perovskite structure. The ferroelectric measurement shows also that BiFeO<sub>3</sub> ceramic exhibits ferroelectric nature with saturation, remnant polarizations of  $p_s = 0.26\mu C/cm^2$ ,  $p_r = 0.11\mu C/cm^2$  respectively. The dielectric constant and loss tangent as a function of

temperature (30-325°C) in the frequency range 10 kHz - 1MHz shows that the dielectric constant and loss increases with increasing temperature.

In 2011, Chun Lin Fu et al. [38], prepared BiFeO<sub>3</sub> powders by sol gel process and calcined at different temperatures. After calcining at 600°C for 1h, XRD spectra had the emergence of several sharp diffraction peaks, compared with the standard XRD spectrum of the crystal BiFeO<sub>3</sub>. As the calcining temperature increased, the diffraction peak intensity of the XRD spectra of BiFeO<sub>3</sub> gradually increased and the diffraction peaks became sharply, indicating that the grain size gradually became larger. There is a clear endothermic peak near 825.1°C, which is  $\alpha$  phase to  $\beta$ phase transition from the knowledge of the phase diagram which is good agreement with the Curie temperature.

**In 2011, G.Biasotto et al. [39],** have done a novel synthesis of perovskite bismuth ferrite nanoparticles, by microwave assisted hydrothermal (MAH) method to obtain crystalline bismuth ferrite (BiFeO<sub>3</sub>) nanoparticles at temperature of 180°C. For comparison, BFO powders were also crystallized by the soft chemistry route in a conventional furnace at a temperature of 850°C. X-ray diffraction results verified the formation of perovskite BFO crystallites while infrared data showed no traces of carbonate. MAH method produced nanoparticles of 96% pure perovskite with a size of 130 nm.

In 2011, A. Johari [40], synthesized and characterized of bismuth ferrite nanoparticles by wet chemical route method using citric acid as chelating agent .By thermal treatment at 350, 450 and 550°C, it was found found that BiFeO<sub>3</sub> nanoparticles crystallized at 350 °C. The prepared samples were characterized by X-ray diffraction of powder (XRD), scanning electron microscope (SEM) for extracting their surface morphology and their crystallographic structure. The XRD analysis concludes the rhombo centered structure of synthesized nanoparticles and from XRD plot there are prominent peaks to various hkl planes of BFO, indicating formation of BFO. Besides these prominent peaks, some other peaks of low intensity are also observed, which do not belong to BFO, where powders at 350°C and 450°C are having lessees impurities phases compared with powder at 550°C. The surface morphology studies confirm the growth of bismuth ferrite nanoparticles with their diameters in the range of 200nm to 500nm.

In 2012, J. Karimi Sabet et al. [41], investigated of bismuth ferrite nanoparticles formation via a supercritical hydrothermal synthesis method. The research reported the synthesis of nanoparticles of BiFeO<sub>3</sub> (BFO) powders from bismuth nitrate and iron nitrate for first time by supercritical hydrothermal synthesis (SHS) method at 500°C and 55 MPa. The final products were characterized by X-ray powder diffraction (XRD) . The result shown that SHS method produced the nanoparticle with average particles size of about 60 nm.

In 2012, S. Layek and H. C.Verma [42], studied magnetic and dielectric properties of multiferroic BiFeO3 nanoparticles by a novel citrate combustion method .BiFeO<sub>3</sub> nanoparticles with average crystallite size of about 50 nm have been prepared by using metal nitrates and citric acid. X-ray diffraction data showed that nanoparticles were single phase in nature and crystallize in the same structure (distorted perovskite of space group R3c) as the bulk compound. The variation of both dielectric and tangent loss as a function of frequency in the range 20 Hz- 2MHz, showed these quantities decrease with increasing frequency.

In 2013, H. Y. Dai et al. [43], bismuth ferrite (BiFeO<sub>3</sub>) ceramics were synthesized by the solid-state reaction method followed by rapid liquid phase sintering. The effect of sintering atmosphere ( $N_2$ , air and  $O_2$ ) on the structure and electrical properties of BiFeO<sub>3</sub> multiferroic ceramics were investigated. XRD analysis revealed that  $N_2$  sintering was effective in reducing impurity phases and improving the crystallization behavior. The SEM investigations suggested that the grain size of the BiFeO<sub>3</sub> ceramics sintered in nitrogen were larger than those sintered in air and O<sub>2</sub>. Electrical measurements revealed that the ceramics sintered in N<sub>2</sub>, showed superior dielectric.

In 2014, Dengzhou Yan et al. [44], Structural and phase transition study of BiFeO<sub>3</sub> particles prepared by hydrothermal method and the verification of crystallization–dissolution–crystallization mechanism, they show the optimal synthesis temperature of BiFeO<sub>3</sub>. The cube BiFeO<sub>3</sub> powders have a hexagonal perovskite structure with a space group R3c, while the sphere-like BiFeO<sub>3</sub> powders have a rhombohedral structure with a space group R3m. The growth mechanism of crystallization– dissolution–crystallization has been summarized and verified. The effect of the reaction time on the particle size in hydrothermal synthetic experiment is studied. The magnetic properties of samples prepared under different alkali concentration have been measured by vibrating sample magnetometer. It was indicated that the samples with different morphologies exhibit different magnetic.

In 2014,B.Kumari et al. [45], studied magnetic, magnetocapacitance and dielectric properties of BiFeO<sub>3</sub> nanoceramics by sol gel technique. The detailed microstructural analysis has been performed through HRXRD, HRTEM and FESEM techniques. From HRXRD the Phase purity of the synthesized nanoparticles is confirmed. The nanoparticles with particle size (~ 50-100 nm) are found to crystallize with distorted rhombohedral structure having R3c space group. From both HRTEM and FESEM it is observed that the average particle size is around 80-90 nm. The variation of both dielectric and tangent loss as a function of frequency in the range 50 Hz to 1 MHz, show these quantities decrease with increasing frequency.

The previous studies proved that bismuth ferrite used for a typical applications like high tech magnetic tapes, Superconductivity, Environmental engineering and to enhance spontaneous magnetization.

### 1-6 The Aims of the Study

The aims of the present study is to synthesis bismuth ferrite that have magnetic properties which is suitable to be used in electronic application such as high electric resistibility, low eddy current losses, preserving its dielectric constant at a high frequency, in addition of high magnetic permeability and low electric conductivity by using a chemical routes, this work has been done and included:

**1-**Preparing BiFeO<sub>3</sub> nano powder by sol-gel technique, where this technique have important properties comparing with solid state reaction method to prepare powder of ferrite as (a very new technique which depends on the metal salts, method for producing solid materials from small molecules, high purity, high homogeneity, needed low temperature, to control particle size distributions in a nano-scale level and also this method is more economic because of its low cost and saving energy).

**2-** Studying the structural properties (crystallite size, lattice constant and density) of powders and the influenced of the calcination temperature to change the phases, all these by X-ray diffraction and studying other structural properties by using (FTIR, SEM and AFM).

**3-** From (XRD) test can know the best sample then studying the electrical properties (dielectric constant, the loss factor (dispersion), electrical resistivity and electrical conductivity) with the frequency from (25 KHz) to (5 MHz) by using LCR meter.


#### **2-1 Introduction**

Ferrite is a member of a whole family of magnetic ceramic materials, including spinels, garnets, magnetoplumbites, ortho ferrites, or variation of these, such as  $\gamma$  -Fe<sub>2</sub>O<sub>3</sub>. It is also a member of the class of magnetic metallic oxides, as ferrites are solid solutions of metals containing ferric Fe<sup>+3</sup> as the main element; furthermore, the name " Ferrite" deduces that iron oxide Fe<sub>2</sub>O<sub>3</sub> is generally the common oxide to all ferrites[46].

## 2-2 Structure

#### 2-2-1 Crystal Structures in General

Crystallography describes the arrangement of atoms in a material which defines its physical properties. Manipulation of atomic arrangements to enhance favourable properties in the material is the basis of materials science.

A crystal structure is composed of atoms arranged in a particular way to form a lattice, an array of points, or motif, repeated periodically in three dimensions. When these arrays are 'stripped' down to their fewest number of atoms to describe the overall structure and symmetry, a unit cell is formed. The unit cell of any structure can be categorised by one of seven lattice systems. The different shapes and sizes of these cells are described by the three cell edge lengths, or lattice vectors [47] a,b,c, and the angles between them  $\alpha,\beta,\gamma$ , (Figure 2-1) [48] as well as the presence of a body or face centred atom. The lattice systems that then describe the possible combinations of these lattice parameters are cubic, hexagonal, tetragonal, rhombohedral, orthorhombic, monoclinic and triclinic combining this with the various possible lattice centres, ones can describe any crystal structure with one of fourteen 'Bravais lattices'in (Figure 2-2)[47].



Figure (2-1) A unit cell with the Cartesian axis' (x,y,z), lattice vectors (a,b,c) and angles between them  $(\alpha,\beta,\gamma)$ .



Figure (2-2): The 14 Bravais Lattices.

## 2-2-2 Symmetry & Space Group

To further define a crystal, a definition of its inherent symmetry is required, for example its appearance after a point symmetry (mirror, rotation, inversion) or a translation operation. These are grouped into seven crystal systems. Combining the lattice parameters and the symmetry of the unit cell gives a full description of the overall structure of a material and can be categorised by one of 230 possible space groups. The space groups combine the Bravais lattice with point and translational symmetry elements, the only extra information required to describe the entire lattice is the presence of any point defects, the inclusion or exclusion of atoms within the lattice.

There are many notations for space groups but the two most commonly used are the International Union of Crystallography table number allocation, where all space groups are listed next to an allocated number 1 to 230, and the International Short Symbol (ISS) or Hermann-Mauguin notation [47], which usually consists of four symbols describing first the Bravais lattice (Table 2-1) and their symmetry.

Р	Primitive (one lattice point per cell).
С	C-Centred or Base Centred (as the faces intersect
	the c-axis)
Ι	Innenzentrierte (German for 'Body-Centred)
F	Face Centred
R	Rhombohedral Primitive

Table 2-1 The 5 space group symbols and their meanings.

## 2-2-3 Structure of Ferrites

Historically ferrites attracted the attention of the physicists and technologists since they are magnetic semiconductors. Both semiconductors and magnetic materials exhibit interesting properties that could be used in electronic devices. Hence ferrites which are ferrimagnetic semiconductors opened new vista in the physics of materials and the need for high resistivity ferrites led to the synthesis of various ferrites. The increasing demand for low loss ferrites resulted in detailed investigations on the various aspects of conductivity and on the influence of various substitutions on the electrical conductivity and magnetic properties etc., to make a comprehensive understanding of the theoretical and practical behavior of ferrites[49].Ferrites are classified according to magnetic properties and their crystal structure. As in table (2-2) represents types of ferrites with their crystal structure, general formula and replacements.

No.	Types	Crystal	General	Replacements
		Structure	Formula	
1	Spinel	Cubic	A <sup>II</sup> Fe <sub>2</sub> O <sub>4</sub>	A <sup>II</sup> _Mn, Zn, Ni, Mg, and
				Co.
2	Garnet	Cubic	Ln <sup>III</sup> <sub>3</sub> Fe <sub>5</sub> O <sub>12</sub>	$Ln^{III}$ -Y, Sm, Eu, Gd, Tb,
				Dy, Ho, Er, Tm and Lu
3	Ortho ferrite	Perovskite	Ln <sup>III</sup> FeO <sub>3</sub>	Ln <sup>III</sup> -Y, Sm, Eu, Gd, Tb,
				Dy, Ho, Er, Tm and Lu
4	Magnetoplumbite	Hexagonal	A <sup>II</sup> Fe <sub>12</sub> O <sub>19</sub>	$A^{II}$ -Ba, Sr and Pb

Table (2-2): Represents types of ferrites.

It has been focused on ortho ferrite, the ortho ferrite (RFeO<sub>3</sub>) is a subclass of the large perovskite crystal class (ABO<sub>3</sub>), so, in order to understand its structure ones must first understand that of the larger category .The perovskite structure is shown schematically in figure (2-3). Where large divalent or trivalent ions (A) occupy the corners of a cube, its represents yttrium or a rare earth and small trivalent or tetravalent metal ions (B) occupy the centre of the cube. The oxygen ions are situated centrally on the faces of the cube. Perovskite in the bulk typically take on one of four crystal: cubic (e.g. SrTiO<sub>3</sub>), tetragonal (e.g. BaTiO<sub>3</sub> at room temperature), orthorhombic (e.g. GdFeO<sub>3</sub>) or rhombohedral (e.g. BiFeO<sub>3</sub>) [50].



Figure (2-3): Perovskite structure of an ortho ferrite.

Ortho ferrites are magnetic because of exchange interaction between the  $Fe^{+3}$  atoms on the B-site. The magnetic structure inside of a sub lattice is usually collinear ferromagnetic, but the different sub lattices are coupled antiferromagnetically. Due to the different number of magnetic ions in different sub lattices, there is a net resulting magnetic moment, giving rise to ferrimagnetism. The nature of the super exchange interaction depends not

only on the type of the magnetic ion, but rather strongly on the bond length and bonding angle. This makes it possible to change the strength and type of the super exchange interaction.

The combination of high magnetic resonance frequencies with very large magneto optical effects makes the ortho ferrites interesting objects for study of laser-induced dynamics. Ortho ferrites are transparent, and can modify the polarization of a beam of light under the control of a magnetic field (Faraday rotation). This makes them potentially useful as optical sensors and actuators for use in optical communications [51].

#### 2-3 Magnetization of Ferrite

Due to the persistence of their magnetization, the ferrites are of two types i.e. hard and soft. This classification is based on their ability to be magnetized or demagnetized. Soft ferrites are easily magnetized or demagnetized whereas hard ferrites are difficult to magnetize or demagnetize [52].

#### **2-3-1 Soft Ferrites**

Soft Ferrites are those that can be easily magnetized or demagnetized. This shows that soft magnetic materials have low coercive field and high magnetization that is required in many applications.

The hysteresis loop for a soft ferrite should be thin and long, as shown in figure (2-4-a), therefore the energy loss is very low in soft magnetic material. Examples are nickel, iron, cobalt, manganese etc. Which are used in transformer cores, inductors, recording heads and microwave devices [53]. Soft ferrites have certain advantages over other electromagnetic materials including high resistivity and low eddy current losses over wide frequency ranges. Also have high permeability and are stable over a wide temperature range. These advantages make soft ferrites paramount over all other magnetic materials.

## 2-3-2 Hard Ferrites

Hard ferrites are difficult to magnetize or demagnetize. They are used permanent magnets. A hard magnetic material has high coercive force and a wide hysteresis loop, as shown in figure (2-4-b). Examples are alnico, rare earth metal alloys etc. [54] .The development of permanent magnets began in 1950s with the introduction of hard ferrites. These materials are ferrimagnetic and have quite a low remanence (~400 MT). The coercivity of these magnets (~250 kAm<sup>-1</sup>), however, is far in excess of other materials. The maximum energy product is only ~ 40 kJm<sup>-3</sup>. The magnets can also be used to moderate demagnetizing fields and hence can be used for applications such as permanent magnet motors. The hexagonal ferrite structure is found in both BaO.6Fe<sub>2</sub>O<sub>3</sub> and SrO6Fe<sub>2</sub>O<sub>3</sub>, but Sr ferrites have superior magnetic properties.



Figure (2-4): Represented hysteresis loop of: (a) soft ferrites and (b) hard ferrites.

#### 2-4 Perovskite Structure

The term perovskite was first used by Gustav Rose in the 1830's to describe  $CaTiO_3$  and in fact all ferroelectric perovskite materials exhibit the ABO<sub>3</sub> nomenclature, where A and B are cations, and O is the oxygen anion. Below the temperature termed its Curie point,Tc, the perovskite material exhibits a dipole polarization, due to the smaller B cation within the oxygen octahedron assuming a non-centrosymmetric position in relation to the A ion, allowing it to attain a stable bonding pattern. Many multiferroics have a crystal structure similar to the mineral perovskite, in which a transition metal is the central atom of a cubic or nearly cubic unit cell [55,56] a large number of fluoride based materials are magnetic ferroelectrics, but as of yet none have magnetic and ferroelectric ordering at room temperature.

Perovskites that are magnetic ferroelectrics in particular are quite rare because the partially filled d orbitals of the transition metal, which lead to magnetic ordering, tend to eliminate the cation displacement that causes ferroelectricity [57].Bismuth-based multiferroics avoid this problem, since the ferroelectricity arises from the bismuth 6s<sup>2</sup> orbitals [58]. The perovskite structure is robust and will expand contract, and rotate bond angles in order to accommodate a wide range of action sizes. The family of oxides with perovskite-derived structures has a variety of fascinating properties. Ferroelectricity, large dielectric constants, superconductivity, ferromagnetism, and antiferromagnetism have all been observed in materials with the perovskite structure [59].

The versatility of the perovskite structure makes it sensitive to forces which may be too weak to have significant effects in other structures. Thus, small displacements and distortions from the ideal structure are an important factor in understanding and manipulating the wide variety of properties in these materials. In the ideal perovskite structure, the cubic unit cell has A site atoms in the corners of the cube, B site atom in the center, and oxygen atoms centered on the faces of the cube this is called the aristo type structure .Most materials that are described as having a perovskite structure deviate from the aristo type slightly. The modified structure is called a hetto type [60].

Hetto types can differ from the aristo type in many ways; changes to the lattice constants, non-cubic symmetry, and displacements of the A or B atoms.

Two parameters are commonly used to describe how well a material fits in the perovskite structure. The tolerance factor, t, quantifies the degree to which a particular  $ABO_3$  compound fits in this structure as explain in equation (2-1).

$$t = r_A + r_O / \sqrt{2} (r_B + r_O)$$
 ..... (2-1)

Where  $r_A, r_B$  and  $r_O$  are the A site, B site, and oxygen ionic radii, respectively [61,62].Most materials that are stable in the perovskite structure have tolerance factors between 0.75 and 1.05. BiFeO<sub>3</sub> has a tolerance factor of 0.95. The ratios between A and B ionic radii and  $r_B/r_O$ are also important in stabilizing the perovskite structure [63]. If the B radius is too small, then the oxygen octahedra are unstable due to oxygen -oxygen ionic repulsion. A site atoms that have radii less than  $r_A < \sqrt{2}(r_B+r_O)/r_O$  can be accommodated to some extent by rotations of oxygen octahedral [60].

Compressive strain can also be accommodated by increasing the rotation angle.One of the more common modifications to the aristo type is the distortion or rotation of the oxygen octahedra. Rotations can be caused by A or B site atoms which do not fit, polar displacements of the A or B site atom, highly directional bonds (for example  $Bi^{+3}$  on the A site), and Jahn-Teller distortions of the  $BO_6$  octahedra. Tilt systems are described in terms of rotations of the octahedra about the (a, b, and c) lattice vectors in the notation used by Glazer [64].

A tilt system with rotations about each axis is written a+,b+,c+. The first, second and third letter represent a rotation about the (a, b, and c) axis respectively. Rotations of the same magnitude about different axes are indicated by using the same letter, such as a+a+c+. The superscript is (+) when octahedra along the same axis have identical rotations about that axis. A superscript of (-) indicates an equal but opposite rotation in adjacent octahedra, and a 0 superscript means no rotation about that axis. Glazer described 23 tilt systems found in a  $2\times2\times2$  pseudo cubic unit cell structure, although Woodward later found there are only 15 systems in which it is possible to keep octahedra of neighboring cells connected [65, 66].

# **2-5 Multiferroic Materials**

# 2-5-1 Definition of Multiferroics

As the name suggests multiferroic are materials those posses more than one of the so called ferroic (ferroeletricity/ferromagnetism / ferroeleasticity) properties. In recent years this term is loosely used for the materials in which magnetism and ferroelectricity coexist. In 1894, P.Cuire [67] predicted that crystals could be simultaneously ferromagnetic and ferroelectric and magnetization in the crystal can be induced by the application of electric field and vice versa. This effect is known as "magneto electric effect" and the coupling between ferroelectric and magnetic interactions is known as "magneto electric coupling".

It is clear from the definition of magneto electric coupling that the coexistence of ferroelectric and ferromagnetic orders is a necessary condition for the material to be classified as a magneto electric material; however, magneto electric coupling is an independent phenomenon that need not arise in all materials that are both magnetically and electrically

polarizable. In practice, it is likely to arise in all materials that are both magnetically and electrically polarizable, either directly or via strain.

This concept is pictorially depicted by several authors [68,69] through a schematic diagram shown in (Fig.2-5), in this diagram, ferromagnets (ferroelectrics) form a subset of magnetically (electrically) polarizable materials, such as paramagnets and antiferromagnets (paraelectrics and antiferroelectrics) shown. The intersection of ferroelectric and ferromagnetic materials represents materials that are multiferroic and the smallest circle in the middle represents the materials that would show magneto electric coupling.



Figure (2-5): Relationship between multiferroic and magnetoelectric materials.

# 2-5-2 Requirements for Magnetoelectric Multiferroics

Although the experimental evidences of multiferroics and magnetoelectric phenomenon were started in the first half of 20<sup>th</sup> century, the numbers of the materials that exhibit magnetoelectric coupling were found to be rare. The coexistence of ferroelectric and magnetic orders itself is a challenging problem. Hill [70] discussed in her review, the conditions required for ferroelectricity and ferromagnetism to be compatible in oxides; however, she also declared that these conditions are contradictory to each other and area difficult to be met in a material. The limiting factors which restrict the simultaneous existence of ferroelectricity and ferromagnetism are given below.

# 2-5-2-1 Symmetry

The magnetoelectric effect was predicted by Curie [67] on the basis of symmetry considerations. The primary conditions for ferroelectricity are the non-centrosymmetric structure, which allows the dipole formation and spontaneous polarization. There are 31 (out of 122) Shubnikov Heesch point groups that allow spontaneous electric polarization and 31 that allow spontaneous magnetization [71]. There is only 13 Shubnikovn points, which allow both spontaneous magnetization and spontaneous electric polarization in same phase. The symmetry considerations itself restrict the number of multiferroics.

## 2-5-2-2 Electrons occupancy in d-orbital

In most of the perovskite multiferroics (ABO<sub>3</sub>), the B-site is occupied by transition metals. According to electronic configuration, transition elements have empty, fully filled or partially filled d-orbitals that contribute to the electrical, magnetic and other physical properties of the material.

## 2-5-3 Types of Multiferroics

The microscopic origin of magnetism is basically the same in all magnets; it is the presence of localized electrons, mostly in the partially filled d or f shells of transition metal or rare earth ions, which have corresponding localized spin, or magnetic moment. Exchange interactions between localized moments lead to magnetic order. However the situation is different in case of ferroelectrics. There are several different microscopic origins of ferroelectricity and accordingly one can have different types of multiferroics.

Generally, the multiferroics are categorized in two groups: (1) type I multiferroics and (2) type II multiferroics, on the basis of the origin of ferroelectricity in them [72].

# 2-5-3-1 Type I Multiferroics

This group of Multiferroics contains those perovskite in which ferroelectricity and ferromagnetism have different sources (cations at A-site and B-site respectively). Ferroelectricity typically appears at higher temperatures than magnetism and they exhibit large spontaneous polarization. Examples are BiFeO<sub>3</sub> (Tc~ 1110K, T<sub>N</sub>~ 643K, P~90 $\mu$ C/cm<sup>2</sup>), YMnO<sub>3</sub> (Tc<sup>FE</sup> ~914K, T<sub>N</sub>~ 76 K, P ~ 6  $\mu$ C/cm<sup>2</sup>). These materials have been extensively studied since 1960s. However, major challenge in these materials is to enhance the values of magnetoelectric coupling coefficient. Type I Multiferroics are further classified in many subclasses on the basis of origin of ferroelectricity.

## i-Ferroelectricity due to shifting of B-cation

In the literature, there are a number of perovskites materials reported that show ferroelectricity due to non-Centro symmetry of B- site cation [73]. However, as discussed above the B-site cation in perovskites usually is the cause of magnetic ordering (if any) in these perovskite [74].Clearly,"d<sup>0</sup>

vs.d<sup>n</sup> problem" as discussed in the above section creates difficulty in such situations. Shown in figure (2-6) [72]. Where this figure show in "mixed" perovskites with ferroelectricity active  $d^0$  ions (green circles) and magnetic  $d^n$  ions (red circles), shifts of  $d^0$  ions from oxygen octahedral (yellow plaquettes) lead to polarization (green arrows), coexisting with magnetic order (red arrows).



Fig. (2-6): Explain Mixed Perovskites.

## ii- Ferroelectricity due to lone pairs

These multiferroic materials exhibit ferroelectricity due to lone pair at Asite cation. Most of bismuth and lead based perovskites show ferroelectricity due to lone pair, for example BiFeO<sub>3</sub>, BiMnO<sub>3</sub> and PbVO<sub>3</sub>. In these materials Bi<sup>+3</sup> and Pb<sup>+2</sup> have two outer 6s electrons that do not participate in chemical bonds. These electrons are called "lone pairs" or sometimes dangling bonds. Microscopically, one can explain the origin of ferroelectricity in these compounds by the ordering of these lone pairs (with certain admixture of p-orbitals) in the direction of electric field. The magnetism in these materials is originated from B-cation. All these are shown in figure (2-7) [72].this figure show in materials like BiFeO3 and PbVO3, the ordering of lone pairs (yellow "lobes") of Bi+3 and Pb+2 ions (orange), contributes to the polarization (green arrow).



Fig. (2-7): Ferroelectricity due to lone pairs.

## iii- Ferroelectricity due to charge ordering

This is another group of ferroelectrics, in which the electric polarization is induced due to the non-Centro symmetry of charges.

The non-Centro symmetry of charges is normally observed in transition metal compounds (especially transition metal ions with different metal states) e.g. Pr<sub>0.5</sub>Ca<sub>0.5</sub>MnO<sub>3</sub> or in Nickelates RNiO<sub>3</sub> [75,76].

# iv- "Geometric" ferroelectricity

In this category of Multiferroics, some geometric disorder in the lattice causes ferroelectricity. For example in case of YMnO<sub>3</sub>, ferroelectricity has nothing to do with individual cations, but is caused by the tilting of practically rigid MnO<sub>5</sub> block with respect to Y-ions [77]. This tilting occurs just to provide closer packing, and as a result the oxygen ions moves closer to the rather small Y ions. Figure (2-8) the "geometric" mechanism of generation of polarization in YMnO<sub>3</sub>[77] describes the tilting of a rigid MnO<sub>5</sub> block with a magnetic Mn remaining at the center. Because of the tilting, the Y-O bonds form dipoles (green arrows), and there appears two"up" dipoles per one "down" dipole so that the system becomes

ferroelectric (and multiferroic when Mn spins order at lower temperatures) [72].



Fig. (2-8): Explain geometric ferroelectricity.

## 2-5-3-2 Type II Multiferroics (Magnetic Multiferroics)

The materials in which the ferroelectricity is originated from magnetism and implies strong magnetoelectric coupling. However, the polarization in these materials is usually much smaller  $(10^{-2} \,\mu\text{C/cm}^2)$ . These Multiferroics are recently discovered. TbMnO<sub>3</sub> and TbMn<sub>2</sub>O<sub>5</sub> are typical examples of these materials [78, 79]. Kimura et al., [78] demonstrate strong influence of magnetic field on electric polarization. In TbMnO<sub>3</sub> ,the polarization rotates (or "flops") by 90 degrees when a critical field is applied in a certain direction [78]. Influence of magnetic field is even stronger in case of TbMn<sub>2</sub>O<sub>5</sub> [79]. The polarization changes sign with magnetic field. Since the discovery of these materials, a number of other type-II Multiferroics with strong magnetoelectric coupling have been discovered and studied. On the basis of mechanism of multiferroic behavior, one can divide type-II

Multiferroics in two categories.

## i- Spiral Type-II Multiferroics

In this type of Multiferroics, the ferroelectricity appears in conjunction with a spiraling magnetic phase, mostly cycloid type. TbMnO<sub>3</sub>, Ni<sub>3</sub>V<sub>2</sub>O<sub>6</sub> and MnWO<sub>4</sub> are typical examples of this type of multiferroics. Therefore, these type-II multiferroics are usually found in frustrated magnetic systems. Figure (2-9) Different types of spin structures relevant for type-II Multiferroics (a) Sinusoidal spin density wave, in which spins point along one direction but vary in magnitude. This structure is centrosymmetic and consequently not ferroelectric. (b) The cycloidal spiral with the wave vector Q = Qx and spins rotating in the (x, z)-plane. It is in this case where one finds nonzero polarization,  $Pz \neq 0$ . (c) In a so-called "proper screw" the spins rotate in a plane perpendicular to Q. Here the inversion symmetry is broken, but most often it does not produce polarization, although in certain cases it might [80].



Figure (2-9) Different types of spin structures.

#### ii- Type-II Multiferroics with Collinear Magnetic Structures

In this group of Type-II, multiferroics ferroelectricity appears in collinear magnetic structures; i.e., all magnetic moments are aligned along a particular axis without the necessary involvement of spin-orbit interaction. Polarization can appear in these materials as a consequence of exchange striction because the magnetic coupling varies with atomic positions. The simplest example of this type of multiferroics is Ca<sub>3</sub>CoMnO<sub>6</sub> [81].

#### 2-5-4 Status of Multiferroicity in Bi-Based Compounds

Bi-based compounds are of main interest due to their multiferroic behavior. There are many Bi- based perovskite compounds in which B-site is accommodated by transition metals e.g. BiFeO<sub>3</sub> [82], BiMnO<sub>3</sub> [83] and BiCrO<sub>3</sub>[84] etc. However BiFeO<sub>3</sub> and BiMnO<sub>3</sub> [81-85] are most extensively studied compounds due to the evidence of coexistence of ferroelectricity and magnetic ordering in them. These compounds fall into the category of "type-I multiferroics". Ferroelectricity originates from the alignment of lone pair of Bi<sup>+3</sup> ion and magnetism comes from B-site atom (Mn or Fe).

## 2-6 Synthesis and Phase Diagram of BiFeO<sub>3</sub>

BFO is usually prepared from equal parts of  $Bi_2O_3$  and  $Fe_2O_3$ . But BFO is very prone to show parasitic phases that tend to nucleate at grain boundaries and impurities. There were reports in literature in which the difficulties of single phase formation of BFO were discussed. So it is a challenge to prepare single phase  $BiFeO_3$ . The phase diagram of  $Bi_2O_3$  and  $Fe_2O_3$  is shown in the Figure (2-10) [86]. It is clear from the phase diagram that the stochiometry is an important parameter to get a single phase for BFO. It is also noted that the calcination temperature and melting point of BFO is very close to each other due to which the BFO can decompose to these starting materials as shown in equation (2-2) [86].Table (2-4) explains some important properties of (Bismuth oxide and Iron oxide) [87].



Figure (2-10) Phase diagram of Bi<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> system[86].

Molecular formula	Bi <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>		
Molar mass	465.96 g/mol	159.69 g/mol		
Appearance	Yellowish, solid	red-brown, solid		
Density	8.90 g/cm <sup>3</sup> , solid	5.242 g/cm <sup>3</sup> , solid		
Melting point	817 °C	1,566 °C		
Solubility in water	Insoluble	Insoluble		

Table (2-3) explain some imp	oortant properties of	(Bi <sub>2</sub> O <sub>3</sub> and	<b>Fe</b> <sub>2</sub> <b>O</b> <sub>3</sub> )
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# 2-7 Crystal structure of BiFeO<sub>3</sub>

BFO exhibits rhombohedrally distorted structure with space group symmetry R3c at room temperature as in figure (2-11). The corner positions are occupied by Bi ions, at the center of the cube lies the transition Fe ion and the face centers are occupied by the oxygen ions. The lattice parameters of the rhombohedral unit cell are a = 5.59 Å<sup>o</sup> and  $\alpha$  = 60.68°. In such a distorted structure, the R3c symmetry permits the development of spontaneous polarization (P<sub>s</sub>).The Fe-O-Fe angle controls the magnetic exchange and orbital overlap between Fe and O, and as such it determines the magnetic ordering temperature and the conductivity.



Figure (2-11): Crystal structure of BiFeO<sub>3</sub>

Each  $Fe^{+3}$  spin is surrounded by six antiparallel spins on the nearest Fe neighbours, that is, a G-type antiferromagnetic. This means that the Fe magnetic moments are coupled ferromagnetically within the pseudo cubic (111) planes and antiferromagnetically between adjacent planes [86].

# **2-8 Electrical Properties**

# 2-8-1 Electrical Conductivity Mechanisms

This section deals with response of ceramics to the application of a constant electric field and the nature and magnitude of steady- state current that is proportional to a material property known as conductivity. In metal, free electrons are solely responsible for conduction. In semiconductors, the conducting species are electrons and/ or electron holes. In ceramics, however, because of presence of ions, the application of electric field can induce these ions to migrate. Therefore, when dealing with conduction in ceramics, one must consider both the ionic and the electronic contributions to the overall conductivity. The proportionality constant  $\sigma$  is the conductivity of material, which is the conductance of a cube of material of

unit cross section. The unit of conductivity is siemens per meter or S m-1, where  $S = \Omega^{-1}$ .

Ferrites can be classified as somewhere between semiconductors and insulators.Ferrites materials have low electrical conductivities when compared to other magnetic materials and hence they find wide use at microwave frequencies [88].

## 2-8-2 Electrical Resistivity at Very Low Frequencies

The range of published values of resistivity of ferrite materials is wide, from about  $(10^{-4} \text{ to } 10^9 \Omega.\text{m})$  at room temperature. In ferrite, the low conductivity is associated with the simultaneous presence of ferrous and ferric ions on equivalent lattice sites.

A mechanism of conduction is known, the extra electron on a ferrous ion requires little energy to move a similarly- situated adjacent ferric ion [89]. The valence states of the two ions are interchanged under the influence of an electric field, these extra electrons can be considered to constitute the conduction current, jumping or hopping from one iron ion to next. Since the materials are semiconductors, their resistivity  $\rho$  should decrease with increase in temperature according to a relation of the form:

$$\rho = \rho_{\circ} \exp\left(\frac{\Delta E}{KT}\right) \qquad (2-3)$$

where E activation energy, T temperature, k is the Boltzmann constant  $(k = 8.62 * 10^{-5} \text{ ev } . \text{k}^{-1})$  and ( $\rho_o$  is a constant).

This relation is indeed often observed and the activation energy  $\Delta E$  can then be interpreted as the energy required to cause the electron jump referred to above [90,91].

 $\sigma = 1/\rho \qquad \qquad (2-4)$ 

Where  $\sigma$ , is the electrical conductivity.

#### **2-8-3 A Perfect Dielectric**

It can be shown that the capacitance C farads, of a parallel plate capacitor, neglecting edge effects, is given by:-

Where A m<sup>2</sup> is the area of electrodes, d m the thickness. This device will obey ohms law under d.c.fields but under a.c. it will impede the flow of current by an amount that varies with frequency f Hz (one Hz is one cycle per second).One therefore defines the a.c. equivalent of resistance R  $\Omega$  as the ' impedance' Z  $\Omega$ .In the simplest case of a perfect dielectric R= $\infty$  and

$$Z = \frac{1}{\mathrm{w}\,\mathrm{C}} \dots \dots (2\text{-}6)$$

Where w= $2\pi f$ .

## 2-8-4 A Real Dielectric

Any real dielectric conducts electricity to some small extent when a d.c. voltage is placed across it .To describe this situation we define our terms by considering a parallel combination of resistance R and capacitance C as in figure (2-12) where the capacitance C has the same nature as the perfect capacitor considered above and the conductance G represent an ideal resistor, i.e. one having no Capacitive or inductive parts. Clearly then, the d.c. conductance G ohms<sup>-1</sup>, of our perfect dielectric is given by:-

For the parallel plate configuration , neglecting edge effects ,where  $\sigma$  is conductivity (ohm<sup>-1</sup> meter<sup>-1</sup>) ,A m<sup>2</sup> the area of electrodes ,d m electrode separation and R  $\Omega$  the resistance .As above ,the capacitance C F is related

to the geometry by:





Figure (2-12): The defined equivalent circuit (a) of a dielectric (b) sandwiched between two metal plates for measurement purposes ,this arrangement being known as a capacitor.

This is very simple when we consider a real dielectric subjected to a d.c. potential , but when an a.c. voltage waveform is applied to such a material the current induced does not reach maxima and minima at the same time as the applied voltage does-it 'lead in phase 'the potential applied .It is convenient to use a vector diagram to describe this,with real and imaginary parts as in figure(2-13). The angle  $\Theta$  (the phase angle) then represents the angle by which current waveform leads the voltage waveform .Thus if G is zero as with an ideal capacitor,  $\Theta=90^{\circ}$ , and if C=0 as for perfect resistor ,then  $\Theta=0$  ,using complex notation ,where  $j=\sqrt{-1}$ , the impedance z of the

real dielectric is given by :

$$\frac{1}{z} = \frac{1}{R} + jwc$$
 .....( 2-9)

To describe this it is convenient to define a generalized permittivity that has a real and imaginary part and will include resistive as well



Figure (2-13 ): Vector diagram of the electrical response of a dielectric.

As capacitive contributions. We are simply defining terms in a way that be convenient later. Now write:

$$\epsilon^* = \epsilon j \epsilon'' \dots (2-10)$$

Where  $\dot{\varepsilon}$  is the relative permittivity as used before and  $\varepsilon''$  is associated with the resistive vector. Using a little algebra, expressions are obtained for  $\varepsilon''$  and a very useful quantity, the loss tangent (tan  $\delta$ ).By analogy with an ideal capacitor, one can express the complex capacitance (C\*) of a real slab of dielectric as

$$C^* = \varepsilon^* C_0 \dots (2-11)$$

Where  $C_0 = \varepsilon_0$  A/d for a parallel plate capacitor, i.e. it is merely a geometrical constant , and the impedance Z is given by:

$$Z = \frac{1}{jwC*} = \frac{1}{jwC0(\ell - j\varepsilon'')} \dots (2-12)$$

Describing both the resistive and the capacitive parts in a consistent fashion .Now ,from equation (2-9)

$$Z = \frac{R}{1 + jwCR} \dots \dots (2-13)$$

Hence, combining equation (2-12,2-13) and equating real and imaginary parts,  $\epsilon = C/C_0$ , the relative permittivity as expected, and

$$\varepsilon'' = \frac{1}{w \text{COR}} = \frac{\sigma}{w \varepsilon 0} \dots \dots \dots \dots \dots (2-14)$$

It is important to note that

$$\frac{1}{\text{wRC}} = \varepsilon'' / \acute{\epsilon} \dots \dots (2-15)$$

 $\varepsilon''/\varepsilon$  is defined as being equal to quantity tan  $\delta$ .(Note this is for any material of any geometry ).By reference to figure (2-13), this definition is consistent with  $\delta=90^{\circ}-\Theta$  as drawn .Thus

$$\tan \delta = \varepsilon'' / \dot{\varepsilon} = \frac{1}{wRC} = \frac{\sigma}{w\dot{\varepsilon}\varepsilon_0} \dots (2-16)$$

Let us now consider some general features of a real dielectric. Conduction through a resistor, unlike a perfect capacitor, must always cause joule heating and the equivalent circuit defined above is no exception .From consideration of figure (2-13), sin  $\delta$  is a measure of the resistive impedance and hence the heat dissipated or electrical power absorbed. Since we concerned with materials with very little conduction, e.g. tan  $\delta < 0.5$ , one can usually write sin  $\delta * \tan \delta$  and therefore the energy absorbed is proportional to tan  $\delta$ .

Accordingly, if one has a device for measuring the tan  $\delta$  of a material as a function of the frequency of the field applied, one is carrying out a form of spectroscopy. It is simply measuring the energy absorbed as a function of frequency of electromagnetic radiation for frequencies typically between 1 Hz (1Hz =1cycle per second ) and 10<sup>9</sup> Hz .Spectroscopy in the visible range refers to measurement of the absorption of electromagnetic radiation as a function of frequency at frequencies a round 10<sup>15</sup> Hz [ 92 ].

#### 2-9 Polarization

Electrical insulators have very few free electrons to take-part in normal electrical conductivity. Such a material has interesting electrical properties because of the ability of an electric field to polarize the material to create electrical dipole, thus insulating material moleculars are called (Non polar

molecules)[93,94]. As well as appearing dipole in a material in the presence of a field, dipoles may be present as a permanent feature of the molecular structure.

Such dipoles are called (Permanent dipoles) in which the center of the positive charge does not coincide with the center of the negative charges such insulating material molecular are called (polar molecules). Induction of the dipoles is called electric polarization [95].

Phenomenon of polarization (P) down to the change in the arrangement of electrically charged particles of a dielectric in space, or is the surface charge density in a dielectric, equal to the dipole moment per unit volume of material being defined as follow:

P=Nm.....(2-17)

#### Where:

N: is the number of dipoles per unit volume.

M: is the average dipole moment.

The electric dipole moment corresponds to two electric charges of opposite polarity  $\pm q$  separated by the distance (d) [96]:

m=qd ..... (2-18)

We can represent the electrical displacement (D) as the sum of the electric field (E) at a given point of dielectric and the polarization at the same point:

 $D = \varepsilon_0 E + P \dots (2-19)$ 

#### Where:

 $\varepsilon_{o}$ : is the permittivity of vacuum (8.85x10<sup>-12</sup> F/m)

The relationship between the electrical displacement and the electric field through a dielectric medium is:

$$D = \varepsilon_o \varepsilon_r E \dots (2-20)$$

 $\varepsilon_r$ : is called the relative permittivity or dielectric constant of the medium, for vacuum  $\varepsilon_r$ =1, so

$$D = \varepsilon_0 E \dots (2-21)$$

By substitute equation (2-21) in (2-19) we get [97, 98]:

 $P = \varepsilon_o \varepsilon_r E - \varepsilon_o E$ 

P=  $ε_o(ε_r-1)$  E .....(2-22)

# **2-10 Types of Polarization**

## 2.10.1 Electronic Polarization

Electronic polarization may be induced to one degree or another in all atoms. It results from a displacement of the center of the negatively charged electron cloud relative to the positive nucleus of an atom by the electric field. This polarization type is found in all dielectric materials and, of course, exists only while an electric field is present.

## 2.10.2 Ionic Polarization

Ionic polarization occurs only in materials that are ionic. An applied field acts to displace actions in one direction and anions in the opposite direction, which gives rise to a net dipole moment.

## 2.10.3 Orientation Polarization

The third type, orientation polarization, is found only in substances that possess permanent dipole moments. Polarization results from a rotation of the permanent moments into the direction of the applied field. This alignment tendency is counteracted by the thermal vibrations of the atoms, such that polarization decreases with increasing temperature. [99].

## 2.10.4 Interfacial Polarization

The final type of polarization is space-charge polarization, sometimes called interfacial polarization, and results from the accumulation of charge at structural interfaces in heterogeneous materials. Such polarization occurs when one of the phases has a much higher resistivity than the other, and it is found in a variety of ceramic materials, especially at elevated temperatures [100,101].

Other polarizations that based on the composition chemical of the material and its components and it's called (Interfacial or space charge polarization), that occurs at frequencies of low little and very under audio waves, depending on the type of defects and heterogeneity that causes the polarization [102].

### **2-11 Temperature Dependence of Dielectric Constant**

Dielectric constant increases with temperature at all frequencies. At lower frequencies (~1 kHz), the increase in dielectric constant is very large with the increase in temperature while at higher frequencies (~1MHz) this increase is very small. In fact, the dielectric constant of a material depends upon four kinds of polarizations; i.e. dipolar, interfacial, electronic and ionic. Dipolar and interfacial polarizations are important at lower frequencies ; both polarization depend upon the variation in temperature. The interfacial polarization increases with increasing in temperature; this increasing in polarization is due to the creation of crystal defects. The dipolar polarization decreases with the rise in temperature at lower frequencies shows that the effect of temperature is more pronounced on the interfacial than on the dipolar polarization. At higher frequencies, electronic and ionic polarizations are the main partners and their temperature dependence is important [103].

# **Chapter three**

**Experimental Work** 

# **3-1 Introduction**

This Chapter describes the way in which BiFeO<sub>3</sub> nanopowder is prepared. We knew that availability of some specific techniques is essential. Furthermore, each technique gives different information. A brief introduction of these systems is given in this chapter. The materials presented in current study are characterized by powder X-Ray diffraction, SEM, AFM, FTIR, electrical studies like dielectric constant, electrical resistivity, electrical conductivity and tangent loss also determined.

# **3-2** Synthesis of nanoparticles and nanomaterials

Two basic strategies are used to produce nanoparticles: "top-down" and "bottom -up". The term "top-down" refers here to the mechanical crushing of source material using a milling process. In the "bottom-up" strategy, structures are built up by chemical processes [104]. The selection of the respective process depends on the chemical composition and the desired features specified for the nanoparticles, this is shown in Figure (3-1) [105].



Figure (3-1): Methods of nanoparticle production.

Bottom-up methods: This method based on physicochemical principles of molecular or atomic self-organization. This approach produces selected, more complex structures from atoms or molecules, better controlling of shapes and size ranges [104]. The methods of bottom-up is [15]:

1-Sol-gel method: It starts from liquid phase (sol) then the material evaporates for change to phase (gel) therefore, it's called (sol-gel).

2- Aerosol method: It likes sol- gel method but it starts from gas phase and ends by liquid phase.

3- (CVD) method: Shortly to chemical vapour deposition.

# **3-3** Synthetic Methods of Bismuth Ferrite Nanoparticles

Bismuth Ferrite (BiFeO<sub>3</sub> ,also called Bismuth Iron oxide) is an inorganic chemical compound with perovskite structure and one of the most promising multiferroic materials. The room temperature phase of BiFeO<sub>3</sub> is classed as rhombohedral belonging to the space group  $R^3c$  [106]. It is synthesized in bulk and thin film form and both its antiferromagnetic (G type ordering) Neel temperature and ferroelectric Curie temperature are well above room temperature (approximately 653 K and 1100 K,respectively)[107,108]. Ferroelectric polarization occurs along the pseudocubic 111 direction with a magnitude of 90-95  $\mu$ C/cm<sup>2</sup> [109,110].

Bismuth ferrite is not a naturally occurring mineral and several synthesis routes to obtain the compound have been developed such as:

- 1- Solid state synthesis
- 2- Single crystal growth.
- **3-** Chemical routes.

## 4-Thin films.

From all methods above, the focus will be put on chemical routes because sol-gel method is one of them, where wet chemical synthesis routes based on sol-gel chemistry, modified pechini routes [111] or hydrothermal [112] synthesis have been used to prepare pure phase  $BiFeO_3$ . The advantage of the chemical route is the compositional homogeneity of the precursors and the reduced loss of bismuth due to the much lower temperature needed. In sol-gel route, an amorphous precursor is calcined at 300-600°C to remove organic residuals and to promote crystallization of the bismuth ferrite perovskite phase, while the disadvantage is that the resulting powder must be sintered at high temperature to make a dense polycrystal. Sol-gel have some properties compared with other methods table (3-1) explain it [16].

Synthetic Method.	Sol-gel.		
Synthesis	Simple ambient conditions.		
Reaction Temp[°C]	100-300.		
Reaction period	Hours.		
Solvent	Water- ethanol.		
Surface- capping agents	Needed, added during or after		
	reaction.		
Size distribution	Relatively narrow.		
Shape control	Very good.		

# **3-4 Raw Materials**

Ferrite powders were prepared by sol gel method, by using bismuth nitrate pentahydrate  $Bi(NO_3)_3.5H_2O$ , ferric nitrate nonahydrate  $Fe(NO_3)_3.9H_2O$ , Citric Acid  $C_6H_8O_7$  and Nitric Acid HNO<sub>3</sub>. Table (3.2) represents the characteristics of these materials.

Name	Chemical	Molecular	Origin	Color	Purity%
	formula	weight			
		g/mol			
Bismuth nitrate	Bi (NO <sub>3</sub> ) <sub>3</sub> .5H <sub>2</sub> O	485.07	Hlmedla	White	99%
Ferric nitrate	Fe(NO <sub>3</sub> ) <sub>3</sub> . 9H <sub>2</sub> O	404.0	India	Red	98%
Nitric acid	HNO <sub>3</sub>	63.01	Fluka	Liquid	98%
Citric acid	C <sub>6</sub> H <sub>8</sub> O <sub>7</sub>	192	India	White	99%

<b>Table (3-2):</b>	The	characteristics	of t	the	materials
	I IIC	chur acter istics	UI I		materials

# 3-5 Tools and equipment

Volumetric flasks, filter paper, a sensitive balance, pH meter, beakers, hot plate magnetic stirrer, funnel, deionized water, oven and furnace.

# 3-6 Preparation of Bismuth ferrite Nano powder

Bismuth ferrite powder was prepared by sol-gel method. The preparation procedure process is as follows: The molar ratio of Bi to Fe was 1:1 to make a solution of 0.2M for each of Bismuth and Iron nitrates .Then 20 ml of nitric acid was diluted in deionized water and then 10gm of citric acid was dissolve in this acid solution using magnetic stirrer (VELP SCIENTIFICA, EUROPE) at room temperature. Solution one was prepared by dissolving 9.70 gm of bismuth nitrate in the above acid solution as shown in Figure( 3-2-a) and solution two was prepared by dissolving 8.07 gm of iron nitrate also in a similar acid solution as shown in Figure ( 3-2 -b). Then solution one is added to solution two as shown in Figure ( 3-2 -c) with continuous stirring at temperature of (65-70°C) for 15hour and 18 minute as shown in Figure ( 3-2 -d,e,f,g,h and i).

At the end of the reaction a fluffy mass (gel) was produced at the base of beaker as shown in Figure (3-2-j).

The gel was dried in an oven (BINDER, Germany) for two hour at a temperature of 150°C as shown in Figure (3-2-k,l and m) to give brownblack powder as shown in Figure (3-2 -n) .Finally the powder calcined in a furnace at different temperature, to obtain the crystallized bismuth ferrite nanoparticles with different particle size. Figure (3-3) show the sol gel synthesis flow diagram that was used for the synthesis of the bismuth ferrite nano powders.



Figure(3-2):Schematic representation of preparation by Photographs (a) Bismuth nitrate acid solution, (b) Iron nitrate acid solution, (c) mixing (a) and (b), (d,e,f,g,h,i) are the changes occur during heating, (j) gel form , (k,l,m) are dry gel in the oven and (n) is dry gel after grinding.


Figure (3-3): Show the sol gel synthesis flow diagram that was used for the synthesis of the bismuth ferrite nano powders.

#### **3-7 Calcinations process**

The preparation bismuth ferrite (BiFeO<sub>3</sub>) nanopowders were calcined in programmed electrical furnace (LABTECH DAIHAN, KOREA) figure (3-4) shows it. The thermal regime of the furnace was controlled through "Eurotherm" programmer-cum-controller. Bismuth ferrite nanopowders were calcinated at temperatures (350,450,500,550 and 700°C) for two hours as a soaking time, then the powders was cooled to room temperature.



Figure (3-4): The furnace.

#### **3-8 Pelleting of Powder**

There are many types of equipments used in powder compacting which called molds. A mold is designed for the manufacture of samples in the form of pellet in diameter 12 mm and thickness of to 1-3 mm under a uniaxial pressure of 500 psi using hydraulic press. Plating the inner surface and its borders with a thin layer from naphthalene oil to prevent adhesion between the powder material and mold. After one installs the

template and the cleaning is placed on a flat surface to be ready for casting the composite materials.Figures (3-5) and (3-6) shows the molding used and the transformation of powder to compact sample respectively.



Figure (3-5): The molding



Figure (3-6): Transformation of powder to compact sample.

#### **3-9** Sintering

Sintering may be defined as the heating of loose or compacted aggregate of metal powder below the melting point of the base metal with or without the application of external pressure in order to transform it to a more dense material by interparticle bonding. Sintering process is concerned with the diffusion of particle to particle, the formation of grain boundary and the closing of voids present in the green briquettes. Sintering is a rather very complex process in which physical, chemical and metallurgical effect interact because of the numerous changes occurring simultaneously within the material. It is very difficult to define and analyse sintering under heat; bonding takes place between the porous aggregate particles and once cooled powder has also bonded to form a solid piece .Sintering can be considered to proceed in three stages:

1-Neck growth proceeds rapidly but powder particles remain discrete.

2-Most densification occurs, the structure recrystallizes and particles diffuse into each other.

3-Isolated pores tend to become spheroidal and densification continues at a much lower rate. Figure (3-7) show three stages of sintering process [113].



Fig (3-7): Three stages of sintering process.

#### 3-10 Structural and electrical properties

Devices for characterization of structural and electrical properties of material prepared in this research were:

#### **3-10-1** Structural properties

#### **3-10-1-1 X-Ray Diffraction Tests**

To investigate the crystal structure of the prepared samples after calcining and for phase analysis, X-ray diffraction (XRD) with Cu-K<sub> $\alpha$ </sub> radiation, and wavelength  $\lambda = 1.54060$  Å was used the range of the Braggs angles taken (2 $\theta$ =20°- 60°) for the samples. The type of this device is (XRD -6000) with an accelerating voltage of (220/50) HZ and made in Japan by SHIMADZU.Figure (3-8) explain the picture of it.



Figure (3-8):X-ray diffraction instrument used.

The conditions for scattered radiation peaks are: 1- the X-rays should be specularly reflected in any one atom plane and 2- the reflected rays of consecutive atom planes should constructively interfere. These two conditions lead to the Bragg condition:

$$n \lambda = 2 d \sin\theta.....(3-1)$$

Where, n: is an integer and is the order of the reflection, d: is spacing between neighboring planes at the Bragg angle 2 between primary beam and scattered radiation,  $\lambda$ : is the wavelength of Cu-K<sub> $\alpha$ </sub> radiation.

Figure (3-9) shows a representation of incident rays interacting with the different crystal planes where d is the distance between atomic planes,  $\theta$  is the angle of incidence from the sample surface and n is an integer giving the diffraction order. Since the details of the diffraction pattern are due to the specific nature of the crystal, diffraction can be used to determine the crystal structure.



Figure (3-9): Representation of Reflected X-rays in a Crystal.

X-ray diffraction is one of the most important characterization tools used in solid state chemistry and materials science. XRD is an easy tool to determine the size and the shape of the unit cell for any compound. Diffraction pattern gives information on translational symmetry – size and shape of the unit cell from peak positions and information on electron density inside the unit cell, namely where the atoms are located at peak intensities .It also gives information on deviations from a perfect particle, if size is less than roughly (100 nm), extended defects and micro strain from peak shapes and widths.

From X-ray diffraction the average particle size of ferrites samples was determined from high intensity (3 1 1) x-ray line broadening using Debye-Scherrer equation [114] as follows:-

$$D=0.9 \lambda /\beta \cos\theta....(3-2)$$

Where, D is the crystallite size,  $\lambda$  is the wavelength of the radiation,  $\theta$  is the Bragg's angle and  $\beta$  is the full width at half maximum (FWHM) [115,116].Where figure (3-10) show the geometry for Debye-Scherrer scattering.



Figure (3-10): Geometry for Debye-Scherrer scattering.

#### **3-10-1-2 Scanning electron microscope (SEM)**

The scanning electron microscope (SEM) uses to study the surface morphology, can too calculate the grain size of samples, where its uses a focused beam of high- energy electrons to generate a variety of signals at the surface of solid specimens. The signals that derive from electron sample interactions reveal information about the sample including external morphology (texture), chemical composition, and crystalline structure and orientation of materials making up the sample. In most applications, data are collected over a selected area of the surface of the sample, and a 2-dimensional image is generated that displays spatial variations in these properties. Areas ranging from approximately (1 cm) to (5 microns) in width can be imaged in a scanning mode using conventional SEM techniques (magnification ranging from 20X to approximately 30,000X, spatial resolution of 50 to 100 nm) . The SEM is also capable of performing analyses of selected point locations on the sample; this approach is especially useful in qualitatively or semi-quantitatively determining chemical compositions [113]. The scanning electron microscope used in imaging the nanoparticles is a VEGA//Easy Probe which is a favorable combination of a scanning electron microscope and a fully integrated energy dispersive X-ray microanalyser produced by TESCAN, s.r.o.,Libusina trida 21 SEM. vega 3 from Belgium .Figure (3-11) explain the picture of SEM.



Figure (3-11): SEM instrument.

#### 3-10-1-3 Atomic Force Microscopes (AFM)

Atomic force microscopy, or AFM, is a high resolution type of scanning probe that gathers topographical information by scanning a special tip across the surface of a sample. The advantage to this system over, called the SEM, is that while the SEM can provide a detailed 2-d image of the surface, the AFM provides a 3 dimensional profile of the surface. AFM allows ones to see and measure surface features with unprecedented resolution and accuracy and almost any sample type can be imaged [117].

The Digital Instruments, Veeco Metrology Group SPM \_AA 3000, AFM contact Mode, Angstrom, Advanced, Inc., 2008, USA. Was used for further investigation of BFO surface structures.Figure (3-12) explain the picture of it.



Figure (3-12): AFM instrument used.

There are several working modes of the AFM for different needs. Tapping mode was used to study the BFO sample and is usually the most common and least damaging method. Tapping mode AFM operates by scanning a special tip attached to the end of an oscillating cantilever across the sample surface. This intermittent contact method reduces surface damage. This special precision tip is designed with radius of curvature on the order of nanometers and attached on the end of the cantilever. The cantilever has a mirrored surface on the opposite side of the tip. The cantilever and tip are then mounted to the scanner and a laser is aligned onto the end of the mirrored side of the cantilever. The cantilever is oscillated at or slightly below its resonance frequency with a set amplitude. A sample is then placed on the AFM sample stage and held in place by a vacuum chuck. The sample stage is then rotated till the sample is under the scanner and cantilever tip. The tip is then brought into working distance from the surface. The tip is then scanned along the surface in a raster pattern in a desired size and area. The systems feedback loop maintains constant oscillation amplitude by maintaining a constant RMS of the oscillation signal interpreted by the reflected laser from the oscillating cantilever the vertical adjustments from the feedback loop are stored and interpreted as topographical information of the sample [118].

#### **3-10-1-4 Fourier Transform Infrared (FTIR)**

FT-IR stands for Fourier Transform Infrared, the preferred method of infrared spectroscopy. In infrared spectroscopy, IR radiation is passed through a sample. Some of the infrared radiation is absorbed by the sample and some of it is passed through (transmitted). The resulting spectrum represents the molecular absorption and transmission, creating a molecular fingerprint of the sample. Like a fingerprint no two unique molecular structures produce the same infrared spectrum. This makes infrared spectroscopy useful for several types of analysis. So, FTIR can

provide some information such as:

1- It can identify unknown materials.

2-It can determine the quality or consistency of a sample.

3-It can determine the amount of components in a mixture [119].

FTIR spectra of prepared samples were recorded using FTIR-8400S, japan, by SHIMADZU.Figure (3-13) explain the picture of it.



Figure (3-13) :FTIR instrument used.

#### **3-10-2 Electrical properties**

Electrical properties, inductance (L), capacitance (C) and resistance (R) of samples were measured using LCR meter (IA: impedance analyzer device, (4294A), Agilent) which is shown in figure (3-14).Its range of frequency (25 KHz - 5 MHz). LCR meter is based on the principle of automatic balancing bridge method. It can obtain the electrical capacitance as a function of frequency and obtain tan $\delta$  and it can used equations in chapter two to obtain: dielectric constant (real and imaginary) and alternating conductivity  $\sigma_{ac}$ . The samples were tableted with a hydraulic press (model PI type 10B, Italy) for dielectric properties measurement.



Figure (3-14): LCR meter.

#### **3-10-2-1** Dielectric constant

The dielectric constant was measured by computerized LCR meter, the sample was placed between the poles to make sure that the poles touch sample surface. Dielectric constant data have been recorded on computer screen after being calculated via mathematic formulas described previously from equations up.

## **3-10-2-2** Electrical resistivity, Electrical conductivity and Dispersion Factor (Tangent Loss)

These are measured by LCR meter by the same way above. Formula used to find electrical resistivity is  $\rho = R.A/L$ , where A represents the surface area:  $A=\pi r^2$ , L= thickness of sample and R is electrical resistance.

Electrical conductivity, Dispersion Factor (Tangent Loss) studied in equation (2-4) and (2-16).

# **Chapter four**

### **Results and Discussion**

#### **4-1 Introduction**

This chapter explains the results and discussions of the preparation of bismuth ferrite nanoparticles and the structural properties (XRD analysis, crystallite size calculation, lattice constant, material density, SEM, AFM, and FTIR) in addition to the electrical properties such as (dielectric constant, tangent loss, electrical resistivity and electrical conductivity) supported by diagrammatic planning and illustration of the samples.

#### 4-2 Preparation Bismuth Ferrite (BiFeO<sub>3</sub>)

The gel obtained was dried in an oven at temperature of  $150^{\circ}$ C for two hours and then calcined at 350,450,500,550 and  $700^{\circ}$ C for two hours. The images of the produced BiFeO<sub>3</sub> nano powders are shown in figure (4-1).



Figure (4-1) Pictures of: (a) Dry gel, (b) sample calcined at 350°C, (c) 450°C, (d) 500°C, (e) 550°C and (f) 700°C.

#### **4-3 Structural Studies**

#### 4-3-1 XRD analysis

X-ray diffraction of BiFeO<sub>3</sub> has been investigated in the 2 $\Theta$  range of  $(20^{\circ}-60^{\circ})$ . The x-ray pattern of dry gel is shown in figure (4-2) and samples calcined at different temperatures (350,450,500,550 and 700°C) are shown in figures(4.3-4.7). Where the dry gel sample before calcination is amorphous and become crystallized after calcination .Also strongest three peaks for these samples are shown in tables (4.1-4.5):



Figure (4-2): XRD pattern of dry gel.



Figure (4-3): XRD pattern of BiFeO<sub>3</sub> sample calcined at 350°C.

No.	Peak No.	2 Theta (deg)	d(Å)	FWHM (deg)	Intensity (counts)
1	4	32.0541	2.79002	0.65830	682
2	1	22.5712	3.93613	0.39690	376
3	17	57.1552	1.61033	0.51590	249

Table (4-1): Strongest three peaks of BiFeO<sub>3</sub> sample calcined at 350°C



Figure (4-4): XRD pattern of BiFeO<sub>3</sub> sample calcined at 450°C.

Table (4-2): Strongest three peaks of BiFeO<sub>3</sub> sample calcined at 450°C

No.	Peak No.	2 Theta (deg)	d(Å)	FWHM (deg)	Intensity (counts)
1	5	32.0231	2.79265	0.64370	479
2	1	22.5362	3.94217	0.39470	256
3	16	57.1376	1.61078	0.48700	192



Figure (4-5): XRD pattern of BiFeO<sub>3</sub> sample calcined at 500°C.

No.	Peak No.	2 Theta (deg)	d(Å)	FWHM (deg)	Intensity (counts)
1	8	32.1973	2.77794	0.20710	918
2	7	31.8843	2.80449	0.22520	859
3	2	22.5559	3.93877	0.21470	554



Figure (4-6): XRD pattern of BiFeO<sub>3</sub> sample calcined at 550°C.

No.	Peak No.	2 Theta (deg)	d(Å)	FWHM (deg)	Intensity (counts)
1	7	32.1778	2.77958	0.17370	1024
2	6	31.8561	2.80691	0.19400	944
3	1	22.5266	3.94383	0.20070	595

Table (4-4): Strongest three peaks of BiFeO<sub>3</sub> sample calcined at 550°C



Figure (4-7): XRD pattern of BiFeO<sub>3</sub> sample calcined at 700°C.

Table (4-5): Strongest three peaks of  $BiFeO_3$  sample calcined at  $700^{\circ}C$ 

No.	Peak No.	2 Theta (deg)	d(Å)	FWHM (deg)	Intensity (counts)
1	6	32.0213	2.79280	0.16590	491
2	5	31.7052	2.81992	0.18540	488
3	2	22.3739	3.97040	0.17520	306

Tables (4.1-4.5) demonstrate the detailed analysis of the XRD data together with the assignment of the various reflections .By comparing the peaks appear in the XRD spectra the peaks in figures (4.3-4.7) with those of (JCPDS) files of BiFeO<sub>3</sub> NO.(20-0169) one can conclude that there are some impurities phases with the main single BiFeO3 phase and this is observed in sample calcined at 350°C which shows (Bi<sub>25</sub>FeO<sub>40</sub> No.of JCPDS 46-0416) , Bi<sub>3.43</sub>Fe<sub>0.57</sub>O<sub>6</sub> (No.of JCPDS 43-0184) and  $\alpha$  -Bi<sub>2</sub>O<sub>3</sub> (No. of JCPDS 27-0053 )) and sample calcined at a temperature of 450°C which shows only (Bi<sub>25</sub>FeO<sub>40</sub>) and sample calcined at a temperature of 500°C which shows (Bi<sub>25</sub>FeO<sub>40</sub>, Bi<sub>3.43</sub>Fe<sub>0.57</sub>O<sub>6</sub>) and sample calcined at a temperature of 550°C which shows (Bi<sub>25</sub>FeO<sub>40</sub>, Bi<sub>3.43</sub>Fe<sub>0.57</sub>O<sub>6</sub>) finally sample calcined at a temperature of 700°C which shows (Bi<sub>25</sub>FeO<sub>40</sub>, Bi<sub>24</sub>Fe<sub>2</sub>O<sub>39</sub> (No. of JCPDS 42-0201), Bi<sub>2</sub>O<sub>3</sub> (No.of JCPDS 41-1449) ,  $\beta$ -Bi<sub>2</sub>O<sub>3</sub> (No.of JCPDS 40-1139) , Fe<sub>2</sub>O<sub>3</sub> (No. of JCPDS 39-1346) and Fe<sub>3</sub>O<sub>4</sub> (No. of JCPDS 26-1136)).

For the above -mentioned reasons, one can conclude that the sample calcined at 450°C is the best one as far as purity of bismuth ferrite main peak is concerned with small peak due to impure phase and impure phase appear is one only. But sample calcined at 700°C is the worst one where bismuth ferrite main peak is concerned with big peaks from many impurities phases so can cancel it. The integrated XRD pattern of all samples is shown in figure (4-8).



Figure (4-8): Integrated XRD patterns of sample calcined at different temperatures.

Now one can fit results to know deviation between theoretical and experimental and standard deviation for crystal planes and Brage angle for every peaks of  $BiFeO_3$ . These are shown in table (4-6).

#### Where:

1-(\*):- is high deviation between theoretical and experimental.

2- d (obs):- is distance between crystal planes from X-Ray diffraction (experimental).

3-d(calc):-is distance between crystal planes from X-Ray diffraction(theoretical).

4- res (d):- is standard deviation for distance between crystal planes (d).

5-(2 $\Theta$ ).obs:- is brage angle (experimental).

 $6-(2\Theta)$ .calc:-is brage angle (theoretical).

7- res  $(2\Theta)$ :- is Standard deviation for brage angle.

Theoretical values are taken from (JCPDS) cards.

	Sample calcined at 350°C							
No	h k l	d(obs)	d(cal)	res(d)	20.obs	20.calc	$res(2\Theta)$	
$ \begin{array}{c} 1 \\ 1 \\ 2 \\ 3 \\ 4 \\ 5 \\ 6 \\ \end{array} $	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	2.79002 2.30283 2.27270 1.77378 1.76105 1.62677 2.79265	2.78273 2.30329 2.27549 1.77434 1.76153 1.62618 Sample 2.78634	0.00729* -0.00046 -0.00279 -0.00056 -0.00048 0.00059 e calcined at	32.054 39.084 39.624 51.477 51.877 56.525 <b>450°C</b> 32.023	32.140 39.076 39.573 51.460 51.862 56.548	-0.086 0.008 0.051 0.017 0.015 -0.022	
2 3 4 5 6 7 8	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$2.30354 \\ 2.27459 \\ 1.97714 \\ 1.77539 \\ 1.76105 \\ 1.62677 \\ 1.61078$	2.76034 $2.30328$ $2.27812$ $1.97829$ $1.77526$ $1.76367$ $1.62641$ $1.60869$	0.00026 -0.00353* -0.00115 0.00013 -0.00262 0.00036 0.00209	39.072 39.590 45.859 51.427 51.877 56.525 57.138	39.076 39.526 45.831 51.431 51.794 56.539 57.219	-0.075 -0.005 0.064 0.028 -0.004 0.083 -0.014 -0.081	
			Sample	e calcined at	500∘C			
1 2 3 4 5 6 7 8	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	3.93877 2.80449 2.77794 2.30379 2.27369 2.26394 1.77508 1.76159	3.94899 2.80706 2.77789 2.30415 2.27205 2.27205 1.77347 1.75871	-0.01022* -0.00257 0.00005 -0.00036 0.00164 0.00811* 0.00161 0.00288	22.556 31.884 32.197 39.067 39.606 39.784 51.437 51.860	22.497 31.854 32.198 39.061 39.636 39.636 51.487 51.951	$\begin{array}{c} 0.059\\ 0.030\\ -0.001\\ 0.006\\ -0.030\\ 0.148\\ -0.050\\ -0.091 \end{array}$	
			Sample	calcined at	550°C			
1 2 3 4 5 6 7 8	$\begin{array}{c} 0 & 1 & 2 \\ 1 & 1 & 0 \\ 0 & 0 & 3 \\ 0 & 2 & 1 \\ 1 & 1 & 3 \\ 2 & 1 & 1 \\ 1 & 0 & 4 \\ 6 & 2 & 0 \end{array}$	2.80691 2.77958 2.30519 2.27480 1.77636 1.76218 1.62888 1.60724	2.84946 3.24740 2.20330 2.58783 1.82325 2.02382 1.58547 0.78000	-0.04255 -0.46782* 0.10189 -0.31303 -0.04689 -0.26164 0.04341 0.82724*	31.856 32.178 39.043 39.586 51.397 51.841 56.445 57.275	$31.368 \\ 27.443 \\ 40.927 \\ 34.634 \\ 49.983 \\ 44.744 \\ 58.136 \\ 161.906$	0.488 4.734 -1.884 4.952 1.414 7.098 -1.691 -104.631	

## Table (4-6): deviation between theoretical and experimental results and standard deviation.

#### 4-3-2 Crystallite Size and Lattice Parameter

The crystallite size calculated from Deby- Scherrer formula in equation (3-2) for bismuth ferrite calcined at different temperatures  $350^{\circ}C,450^{\circ}C,500^{\circ}C$  and  $550^{\circ}C$  are shown in table (4-7). It is obvious that the crystallite size increase with temperature increased and this is agree with the results of previous studies [26, 33, 35 and 45] and other researchers. Figure (4-9) explain this relation graphically.

BiFeO <sub>3</sub> samples	Crystallite Size (nm)
350°C	12.5
450°C	12.8
500°C	39.9
550°C	47.7

Table (4-7): Crystallite size for BiFeO<sub>3</sub> samples.



Figure (4-9): Explain relation between crystallite size and calcination temperature.

BiFeO <sub>3</sub> samples	a(Å)	c(Å)	c/a	V (Å <sup>3</sup> )	a*	С*
350°C	5.56546	6.90988	1.241565	185.3543	0.2074764	0.1447203
450°C	5.57267	6.90984	1.239951	185.8342	0.2072078	0.1447211
500°C	5.55577	6.91244	1.244191	184.7783	0.2078379	0.1446668
550°C	6.49480	6.60989	1.017720	241.4663	0.1777885	0.1512884

Table (4-8): shows lattice parameter, volume of unit cell and lattice Reciprocal parameters for BiFeO<sub>3</sub>.

Table (4-8) shows lattice parameter, volume of unit cell and lattice reciprocal parameters for BiFeO<sub>3</sub> samples except that prepared at temperature 700°C was neglected, by using computer program special of XRD may define atom dimension for crystalline composition, where crystal structure is rhombohedral distorted perovskite structure belonging to a space group R3c ,this is agree with the results of previous studies [37,42 and 45]. The peaks of BiFeO<sub>3</sub> is separating for each sample and neglect the rest of the eccentric impurity then our table includes values of d spacing and intensity , which it has obtained for each sample and the values of (h k l) from JCPDS Card number (20-169). Where a= 5.573 and c=6.915 for BiFeO3 from JCPDS card.

It has been noticed from table (4-8) above (c) increased once and decreased once and too (a), this is because of incidence convolution in the structure of rhombohedral or reversed or change it shape but retained same structure all that because the thermal stresses. (c/a)Indicator for deformity that happen in lattice, where  $\Delta$  (c/a) represents quantity of deformity that happen in lattice.

Where (a\* and c\*) are lattice Reciprocal parameters and its values: a\*= $2\pi b x c/a$ . b x c and c\*=  $2\pi a x b / a$ . b x c. Also it can be calculated the lattice parameter (a and c) manually without the use of the program and the results are shown in table (4-9).where the perpendicular distance separating each lattice plane in a stack is denoted by the letter d, d spacing and the relationship to the particular lattice plane is  $d_{hkl}$  (i.e.,  $d_{101}$  or  $d_{104}$  and  $d_{110}$ ) with the Miller indices for the particular plane shown in the subscript, this is the common notation used in crystallography and X-ray diffraction. The values of d spacing in terms of Hexagonal systems are shown in the relationship (4-1) .Where BiFeO<sub>3</sub> is a rohombohedrally distorted perovskite belonging to the space group R3c with rhombohedral lattice parameter (a) or alternatively, hexagonal parameters (a and c).

$$d = \left[\frac{4}{3a^2}(h^2 + hk + k^2) + \frac{l^2}{c^2}\right].....(4-1)$$

BiFeO <sub>3</sub>	a(Å)	c(Å)	c/a	$V(Å^3)$
samples				
350°C	5.580	6.8877	1.234355	185.7208
450°C	5.5839	6.8162	1.220688	184.0499
500°C	5.5558	6.8577	1.234332	183.3114
550°C	5.558	6.8763	1.23719	183.9542

Table (4-9): shows lattice parameter and cell volume of BiFeO<sub>3</sub>.

#### 4-3-3 X-ray density

X-ray density of the samples has been computed from the values of lattice parameters using the formula [120]:

$$d = \frac{nM}{Na V} \qquad (4-2)$$

Where n represents the number of molecules in a unit cell of a perovskite lattice which is (5 atoms) [121], M the molecular weight of BiFeO<sub>3</sub> (312.83 g/mol), Na the Avogadro's number ( $6.022*10^{23}$  atom/mol) and (V) represents the volume of unit cell. Table (4-10) explains the X-ray density for samples. Theoretical density of BiFeO<sub>3</sub> at room temperature is 8.31 g/cm<sup>3</sup>.

Table (4-10):X-ray density of samples calcined at different temperatures.

Samples	X-ray density (DX) g/cm <sup>3</sup>
350°C	12.135705
450°C	12.10439269
500°C	12.17356437
550°C	9.315621868

From table (4-10) ones see increase the density with the increase of temperature as a result of the diffusion or growth of crystals and closed the vacancies or crystalline defects, after that, the density decreased as a result of the emergence of crystalline defects or dislocation as a result of high temperature or increase energy particles, which led to the appearance of defects in the structure.

#### 4-3-4 Scanning Electron Microscope (SEM) test

The micro structure and the morphological studies of the nano ferrite powder were carried out using a scanning electron microscope (SEM) type VEGA//Easy Probe which is a favorable combination of a scanning electron microscope. The SEM images of the BiFeO<sub>3</sub> samples prepared by sol gel method and calcined at temperatures 350 °C, 450°C, 500 °C and 550 °C are shown in figures (4.10-4.13) respectively.



Figure (4-10): SEM for sample calcined at 350°C.



Figure (4-11): SEM for sample calcined at 450°C.



Figure (4-12): SEM for sample calcined at 500°C.



Figure (4-13): SEM for sample calcined at 550°C.

From figures (4.10-4.13) its noticed that there are many of agglomerations, probably due to lack of good crushing after drying the gel, which made it difficult to measure the particle size, however resides a few particles non- agglomeration and noted clearly in the pictures (SEM) that the size of less than 100 nano, especially when the shapes in which the magnification high and the ruler of one micron. In the low temperatures probably the agglomeration reason is presence of some residual organic materials that help on agglomeration and shown in figures above. It has been noticed that the increase of the shapes with calcination temperature may helped in the growth of the large particles

and may have come in some cases, to the beginning of the melting, which is also helped on agglomerations. Finally SEM results explain probability the appear of some impurities phases with single phase bismuth ferrite (BiFeO<sub>3</sub>),all these are agree with the results of previous studies [33 and 35].

#### **4-3-5 Atomic Force Microscopy (AFM) 4-3-5-1 AFM for Sample calcined at 350°C**

The surface morphology of BiFeO<sub>3</sub> calcined at temperature 350°C was examined by AFM with images shown in Figure (4-14), where AFM giving statistics minute about improved particle size and its distribution, values of coarseness of surface (Surface Roughness) depended on root mean square of coarseness(Root Mean Square) (RMS) as well as providing many important information and its accuracy is more than XRD analysis . AFM model used is The Digital Instruments, Veeco Metrology Group (CSPM \_AA 3000), AFM contact Mode, Angstrom, Advanced, Inc.,2008, USA.



Figure (4-14): AFM for sample calcined at 350°C.

The figure (4- 14) which explains images of AFM for sample of 350°C with area(size=2000nmX2000nm)and ability analytical (pixels=512,512). Where figure (4-14-a) is AFM picture in three dimensions (3D) ,it explains structural shape for grains , figure (4-14 -b) is AFM picture in two dimensions (2D) ,it found Average Roughness is 0.209nm and RMS(Root mean square) is 0.248nm and figure (4-14 -c) represents particles distribution , where grains number is 234, it found to have grain size of 45.31 nm.



#### 4-3-5-2 AFM for Sample calcined at 450°C

Figure (4-15): AFM for sample calcined at 450°C

The figure (4-15) above explains images of AFM for sample at 450°C with area (size=2000nmX2000nm) and ability analytical (pixels=512,512). figure (4-15-a) is AFM picture in three dimensions (3D) ,it explain structural shape for grains , figure (4-15 -b) is AFM picture in two dimensions (2D) ,it found Average Roughness is 0.303nm and RMS(Root mean square) is 0.349nm and figure (4-15-c) represent particles distribution , where grains number is 200, it found to have grain size of 83.08 nm .



#### 4-3-5-3 AFM for Sample calcined at 500°C

Figure (4-16): AFM for sample calcined at 500°C.

The figure (4-16) above explains images of AFM for sample calcined at 500°C with area (size=2000nmX2000nm) and ability analytical (pixels=512,512).Figure (4-16-a) is AFM picture in three dimensions (3D) ,it explain structural shape for grains , figure (4-16-b) is AFM picture in two dimensions (2D) ,it found Average Roughness is 0.646nm and RMS(Root mean square) is 0.766nm and figure (4-16-c) represent particles distribution ,where grains number is 186, it found to have grain size of 89.81 nm .



#### 4-3-5-4 AFM for Sample calcined at 550°C

Figure (4-17): AFM for sample calcined at 550°C

The figure (4-17) above explains images of AFM for sample calcined at 550°C with area (size=2000nmX2000nm) and ability analytical (pixels=512,512). Where figure ( 4-17-a) is AFM picture in three dimensions (3D) ,it explain structural shape for grains , figure (4-17-b) is AFM picture in two dimensions (2D) ,it found Average Roughness is 0.662nm and RMS(Root mean square) is 0.779 nm and figure (4-17-c) represent particles distribution ,where grains number is 149, it found to have grain size of 93.78 nm .

Also AFM figurers proved that particle size is very small and homogeneous and in nano scale, naturally; the degree of calcination has helped in the growth of the particles with the increase in temperature but remained within nano particles. Also low surface coarseness meaning that, particles change to spherical shape and when temperature increase the distance between the particles as shown from the tops of the curve as in the diagram are increasing its values are (0.93,1.21,3.07 and 3.1nm) at (350°C,450°C,500°C and 550°C) respectively, which prove the agreement between grain growth and temperature increase. Table (4-11) explains (RMS), Surface Roughness and grain size increase with increase temperature. Figure (4-18) explains the relation between (RMS) and Surface Roughness and calcination temperature and figure (4-19) explains the relation between grain size and calcination temperature.

Sample	RMS (nm)	Surface Roughness (nm)	Grain size (nm)
350°C	0.248	0.209	45.31
450°C	0.349	0.303	83.08
500°C	0.766	0.646	89.81
550°C	0.779	0.662	93.78

Table (4-11): (RMS) and surface roughness and Grain size of samples calcined at different temperature.



**Fig (4-18): explain relation between Surface Roughness and RMS and calcination temperature.** 



Figure (4-19) Relation between grain size and temperature.
# **4-3-6 Fourier Transform Infrared (FTIR) analysis 4-3-6-1 FTIR for dry gel**

The figure (4-20) shows the FT-IR spectrum obtained for Dry-Gel .The absorption features at 400-600 cm<sup>-1</sup>, attributed to the Fe–O stretching and bending vibrations, being characteristics of the octahedral FeO<sub>6</sub> groups in the perovskite compounds. The broad absorption band in the range of 420.4, 599.8, 792.6 and 902.6 cm<sup>-1</sup> are assigned to citric acid corresponding to the vibrations bands of Bi–O or Fe–O, respectively. The bands located at around 1342.3, 1076.2 and 848.6 cm<sup>-1</sup> indicated the existence of nitrate ions. The band 1600.81 cm<sup>-1</sup> was assigned to the H<sub>2</sub>O and 1718.46 cm<sup>-1</sup> assigned to the C=O. The bond 1076.21 cm<sup>-1</sup> was assigned to the C-O while the absorption bands in the range of 2989.4, 3051.1, 3288.4, 3357.8, 3434.9 and 3938.37 were assigned to the C-H and O-H respectively [122].



Figure (4-20): Fourier transforms infrared spectrum of Dry Gel.

#### 4-3-6-2 FTIR for sample calcined at 350°C

Figure (4-21) shows the FT-IR spectrum obtained BiFeO<sub>3</sub> at 350°C. The absorption features at 400-600 cm<sup>-1</sup>, attributed to the Fe–O stretching and bending vibrations, being characteristics of the octahedral FeO<sub>6</sub> groups in the perovskite compounds, the bands located at around 1394.4, 1022.2, and 846.6 cm<sup>-1</sup> indicated the existence of nitrate ions, The broad absorption bands 439.7 and 549.67cm<sup>-1</sup> are assigned to citric acid were corresponding to the vibrations bands of Bi–O or Fe–O, respectively. The absorption band in the range of 2362 cm<sup>-1</sup> is assigned to nitrile, while the bond 3336.62 cm<sup>-1</sup> is attributed to the C-H and also may be attributed to the O-H in addition to the bands 3444.63 and 3975.0 cm<sup>-1</sup>. We observed that the some peaks in this sample was disappear because that some impurity was burnt [122].



Figure (4-21) Fourier transforms infrared spectrum for BiFeO<sub>3</sub> calcined at 350°C.

# 4-3-6-3 FTIR for sample calcined at 450°C

Figure (4-22) shows the FT-IR spectra obtained for BiFeO<sub>3</sub> calcined at 450°C. The absorption features at 400-600 cm<sup>-1</sup>, attributed to the Fe–O stretching and bending vibrations, being characteristics of the octahedral FeO<sub>6</sub> groups in the perovskite compounds. The peaks at 443.6, 680.8 and 819.6 can be assigned to the bands of Fe-O and Bi-O respectively. The bands located at 2480.2 and 1546.8 cm<sup>-1</sup> indicated the existence of ferric nitrate and NO<sub>2</sub> respectively. The band located at 1074.2 cm<sup>-1</sup> is assigned to C-O .While the bands at 2908.4 and 3012.6 cm<sup>-1</sup> are assigned to C–H stretching. Finally the broad absorption band in the range of 3593.1 to 3976.9 cm<sup>-1</sup> is assigned to O–H stretching [122].



Figure (4-22) Fourier transforms infrared spectrum for BiFeO<sub>3</sub> calcined at 450°C.

## 4-3-6-4 FTIR for sample for sample calcined at 500°C

Figure (4-23) shows the FT-IR spectrum obtained for BiFeO<sub>3</sub> calcined at 500°C. The absorption features at 400-600 cm<sup>-1</sup>, attributed to the Fe–O stretching and bending vibrations, being characteristics of the octahedral FeO<sub>6</sub> groups in the perovskite compounds. The broad absorption band in the range of 447.4 and 547.7 cm<sup>-1</sup> are assigned to citric acid were corresponding to the vibrations bands of Bi–O or Fe–O, respectively also 547.7 cm<sup>-1</sup>. The band in the range of 1514.0 to 1550.6 cm<sup>-1</sup> is assigned to NO<sub>2</sub>.While the band in the range of 3107.1 to 3975.0 cm<sup>-1</sup> is assigned to O-H [122].



Figure (4-23) Fourier transforms infrared spectrum for BiFeO<sub>3</sub> calcined at 500°C.

### 4-3-6-5 FTIR for sample calcined at 550°C

Figure (4-24) shows the FT-IR spectrum obtained for BiFeO<sub>3</sub> calcined at 550°C. The absorption features at 400-600 cm<sup>-1</sup>, attributed to the Fe–O stretching and bending vibrations, being characteristics of the octahedral FeO<sub>6</sub> groups in the perovskite compounds. The band 441.6 and 549.6cm<sup>-1</sup> are assigned to citric acid were corresponding to the vibrations bonds of Bi–O or Fe–O, respectively also 549.6 cm<sup>-1</sup>. The broad absorption band in the range of 2993.3 and 3039.6 cm<sup>-1</sup> are assigned to C-H and the broad absorption band in the range of 3039.6 to 3975.0 cm<sup>-1</sup> are assigned to O-H [122]. From all figures one can see that increase of temperature indicates that some peaks appear and some disappear such as nitrate and H<sub>2</sub>O and other peaks as a result of heating and dissociation of samples. All results are agree with the results of previous studies such as [39].



Figure (4-24) Fourier transforms infrared spectrum for BiFeO3 calcined at 550°C.

### **4-4 Electrical Properties**

Due to the impurity that has great effects on the electrical properties of BiFeO<sub>3</sub> ,it is important that the studied BFO do not contain any impurity or parasitical phase or contain with very small intensity. So from the prepared samples only we choose the sample calcined at temperature 450°C for studying its electrical properties because of its low impurity phase with very small intensity compared with the other samples. The test was done by using LCR meter (IA: impedance analyzer device, (4294A), Agilent).

### 4-4-1 Dielectric constant

Dielectric constant have been computed at frequencies in the range of (25 KHz to 5MHz), figure (4-25) shows high magnitude of Dielectric constant at low frequencies then it decreased rapidly with increasing of frequency till to MHZ for BiFeO<sub>3</sub> calcined at  $450^{\circ}$ C.



Figure (4-25): Relation between dielectric constant and frequency for BiFeO<sub>3</sub> calcined at 450°C.

A high value of dielectric constant is observed at lower frequencies which later falls down rapidly with frequency increase. The dielectric constant values are between (60.3 to 23.1) with range of frequency (25 KHz to 5 MHZ). This behavior can be explained on the basis that at lower frequencies there exist four different types of polarization (i.e. electronic, ionic, dipolar and space charge) contributions take a part in the dielectric constant, but at higher frequencies only electronic polarization is responsible for the dielectric constant result in the lowering of dielectric constant [123].

#### **4-4-2 Electrical resistivity**

The electrical resistivity at a frequency range of (25 KHz to 5MHz) posse's very high magnitude at low frequencies and decrease gradually with increasing of frequency as shown in figure (4-26).Where The electrical resistivity values are between  $(1.47 \times 10^6 \text{ to } 2.6 \times 10^4 \Omega.\text{cm})$  with range of frequency (25 KHz to 5MHz)



Figure(4-26): Relation between electrical resistivity and frequency for  $BiFeO_3$  at 450°C.

It shows that when frequency increase electrical resistivity decrease, because the increasing in frequency lead to increasing of particles mobility in addition to temperature increasing which lead to crystal growth both caused to decrease in the resistivity.

The resistivity of ferrites depends on the purity of the starting materials and the preparation details such as sintering temperature [25]. ones must noted from Limitations of BiFeO<sub>3</sub> is Electrical Resistivity where BFO exhibits semiconducting behavior at and above room temperature, which does not allow electric poling and causes high dielectric losses in the sample at room temperature due to this, it is difficult to measure the ferroelectric properties of BFO at and above room temperatures[86]

#### **4-4-3 Electrical conductivity**

The electrical conductivity ( $\sigma$ ) of the sample was determined for different frequencies using LCR meter with range of frequency (25 KHz to 5 MHZ), it was observed that the electrical conductivity increases with increase in frequency and this is due to the increasing of mobility agreement with decreasing of grain boundaries [124]. The figure (4-27) shows that. Where the values of electrical conductivity are (6.8x10<sup>-7</sup> to  $3.7x10^{-5}$  ( $\Omega$ .cm)<sup>-1</sup>) with range of frequency (25 KHz to 5 MHZ)



Figure (4-27): Relation between electrical conductivity and frequency for BiFeO<sub>3</sub> calcined at 450°C.

# 4-4-4 Dielectric losses (tan $\delta$ )



Fig (4-28): Variation of frequency with tangent loss for BiFeO<sub>3</sub> calcined at 450°C.

Figure (4-28) shows the relation between frequency and tangent Loss for sample, it explains that increase frequency give rise to increase in tangent loss.where values of tangent loss are between (0.223 to 0.329) with range of frequency (25 KHz to 5 MHZ).

It seems clear that, this is causing by porosity which makes high loss so the solution is to make a pellet under pressure and using polyvinyl alcohol (PVA) as a binder to it. After adding binder to sample calcined at  $450^{\circ}$ C and increase pressure to 5 tan/cm<sup>2</sup> to make a pellet, then ones can study electrical properties (Dielectric constant, Electrical resistivity, Electrical conductivity and Tangent loss) for it, all these are shown in figures (4.29-4.32).



Fig (4-29): Relation between dielectric constant and frequency for BiFeO<sub>3</sub> calcined at 450°C after adding binder.

The dielectric constant values are between (113.42 to 43.93) with range of frequency (25 KHz to 5 MHZ) are shown in figure (4-29), it shows that the dielectric constant decrease with increasing of frequency. This is agreeing with results of previous studies [42 and 45].



Figure (4-30): Relation between electrical resistivity and frequency for BiFeO<sub>3</sub> calcined at  $450^{\circ}$ C after adding binder.

The electrical resistivity values are between  $(1.3 \times 10^6 \text{ to } 1.1 \times 10^4 \Omega.\text{cm})$  with range of frequency (25 KHz to 5MHz) are shown in figure (4-30) ,where the electrical resistivity values decrease with increase of frequency applied.



Fig (4-31): Relation between electrical conductivity and frequency for BiFeO3 at 450°C after adding binder.

Electrical conductivity values are  $(1.3 \times 10^{-8} \text{ to } 8.7 \times 10^{-5} (\Omega.\text{cm})^{-1})$  with range of frequency (25 KHz to 5 MHZ) are shown in figure (4-31), it shows that electrical conductivity increases with increasing of frequency.

Figure (4-32) down explains the relation between tangent loss and frequency ,where values of tangent loss are between (0.44 to 0.25) with range of frequency (25 KHz to 5 MHZ). It shows tangent loss decrease with increasing of frequency, this is agreeing with results of previous studies [42 and 45]. The values of tangent loss (tan  $\delta$ ) are high at low frequencies and low at high frequencies. At higher frequencies, where the resistivity is small and the grains are more effective in electrical conductivity therefor small amount of energy is required for the electrons to be exchanged between ions located in the grains and thus the energy losses (tan  $\delta$  or  $\mathcal{E}$ ") are also low [125].



Fig (4-32): Relation between frequency and tangent loss for BiFeO<sub>3</sub> calcined at 450°C after adding binder.



#### **5-1 Conclusions**

The following conclusions are drawn in the current study:

1- Comparison with ceramic traditional methods, the sol-gel method is very good to preparation of bismuth ferrite because of its saving the energy where the best result obtained with a temperature 450°C and its grain size is 12.8 nm, so this method is more economic as well as that producing material be in the nano scale.

**2-** The powder calcined at  $450^{\circ}$ C is the best sample, but sample calcined at  $700^{\circ}$ C is the worst sample .

**3-** The crystallite size has been estimated by using Debye-Scherrer formula; it increases with the increase in temperature.

**4-**The alternation in values of lattice parameter (a and c) due to the absence of possibility to get high-purity raw materials and also because of the thermal stresses.

**5-** The FTIR analysis establishes this analytical method as an impressive way for specific bond and structure confirmation.

**6-** SEM images for samples calcined at (350,450,500 and 550°C) show the BFO powder. Its evident from figures that the grains are uniform in shape and size and in nano scale.

**7-**AFM test for samples calcined at (350,450,500 and 550°C) proved that the particle size is in nano scale and the grain size of bismuth ferrite increases with the increase in temperature.

**8-** In low frequencies the dielectric constant of  $BiFeO_3$  increase, so it can be used in insulator application.

**9-**The decrease in electrical resistivity of  $BiFeO_3$  and electrical conductivity increase with frequency increase.

**10-** The tangent loss of  $BiFeO_3$  decrease with the increase of frequency, so that it can be used as dielectrics, where the decrease with the increase

of frequency and not get to zero makes this ferrite users within a wide range of frequencies.

11- Macroscopic test to attract prepared samples to natural magnet prove that the material is magnetic, where the attraction for the dry gel is weak, sample calcined at  $(350,450,500 \text{ and } 550^{\circ}\text{C})$  are very good but after sintering at  $(350,450,450 \text{ with binder}, 500,550 ^{\circ}\text{C})$  are good except sample at  $550^{\circ}\text{C}$  is weak.

**12-** Difficulty in the formation of single phase bismuth ferrite, because of few impurities phases which appear.

### **5-2 Future Works**

Researchers consistently complete their research and attempting to cover the largest possible number of measurements to enable them to get a greater knowledge and clearer picture about the study until they are employed in the way of scientific and technical way to be better and more accurate, so suggest the following researches:

**1-**Preparing the same ferrite (bismuth ferrite) by hydrothermal method and comparing the results with the results of the present work.

**2**- Characterizing the prepared bismuth ferrite by transmission electron microscope (TEM) to calculate the average size of powders.

**3-** Using other carboxylic acids instead of citric acid as chelating agent.

**4-** Studying the dielectric constant and tangent loss as a function of temperature at different frequencies.

**5-** Studying of the UV-Vis absorption spectra to calculate the bandgap of  $BiFeO_3$  in different temperatures.

**6**-Characterizing the magnetic properties for prepared bismuth ferrite by using vibrating sample magnetometer (VSM).

7- Preparing bismuth ferrite nano powder by the same method and same temperatures but change of calcinations time to three or four hours and study the changes in phases.

**8-** Studying the effect of Laser on the porosity of  $BiFeO_3$ , or treatment by laser.

**9-** Studying the electrical properties of  $BiFeO_3$  calcined at 450°C for two hours after sintering at 450°C for five hours with and without binder.





[1]S.Sugimoto, K.Okayama, S.Kondo, H. Ota, M. Kimura, Y. Yoshida, H. Nakamura, D. Book, T. Kagotani and M. Homma," barium m-type ferrite as an electromagnetic microwave absorber in the GHz range", Mater. Trans., JIM, Vol.39, No.10, P.1080, 1998.

[2]J. Smit and H. P. J. Wijn, "Ferrites", Philips Technical Library, Eindhoven, 1959.

[3]A.B. Gadkari, T.J. Shinde, P.N. Vasambekar, "structural analysis of  $Y^{+3}$  –doped Mg-cd ferrites prepared by oxalate co-precipitation method", materials chemistry and physics - mater chemphys, Vol. 114, No. 2, P. 505, 2009.

[4]L. Gama, A.P. Diniz, A.C.F.M. Costa, S.M. Bezende, A. Azevedo,

D.R. Cornejo, "magnetic materials and their application", Physica B: Conden. Matter, Vol. 384, No.1-2, pp.97, 2006.

[5] S.E. Jcoba, S. Dukalde, H.R. bertorella, "rare earth influence on the structural and magnetic properties of NiZn ferrites", J. Magn. Magn.Mater, Vol. 2253, P.272,2004.

[6]A. Verma, T.C. Goel, R.G. Mendirattaand R.G. Gupta, "magnetic properties of nickel –zinc ferrites prepared by citrate precursor method", J. Magn. Magn.Mater, Vol. 192, P.271,1999.

[7]T. Nakamura, T. Miyamoto and Y. Yamada, "magnetic properties of  $Cu_{1-x} Zn_xFe_2O_4$  ferrites with the variation of zinc concen-tration", J. Magn. Magn. Mater, Vol. 256, P. 340, 2003.

**[8]**H.Waqus and A.H.Quresghi,J. ThermAnaly.Calori. ,V.98, p.355,2009. **[9]**N. Rezlescu, E. Rezlescu, F. Tudorach and P.D. Popa, "MgCunano crystalline ceramic with  $La^{+3}$  and  $Y^{+3}$  ionic substitutions used as humidity sensor",J. Opt. Adv. Mater,Vol. 6, P.695,2004. [10]X. Chu, B. Cheng, J. Hu, H. Qin and M. Jiang, "semiconducting gas sensor for ethanol based on  $LaMg_xFe_{1-x}O_3nanocrystals$ ", Sensors and ActuatorsB:chemical, Vol.129, P.53, 2008.

[11]K. Raj, R. Moskowitz and R.Casciari, "advances in ferrofluid technology", J.Magn.Magn.Mater, Vol. 149, P.174, 1995.

[**12**]J.B. Neaton, C. Ederer, U.V. Waghmare, N.A. Spaldin and K.M. Rabe, "First-principles study of spontaneous polarization in multiferroic BiFeO<sub>3</sub>", Phys. Rev, Vol.B 71,2005.

[**13**]S. Li,R. Nechache,I. A. Velasco Davalos,G. Goupil,L. Nikolova,M. Nicklaus,J. Laverdiere,A. Ruediger and F. Rosei, "Ultrafast Microwave Hydrothermal Synthesis of BiFeO3Nanoplates",J.Am. Ceram.Soc., Vol.96, No. 10, P.3155–3162, 2013.

[14]J.B. Neaton, C. Ederer, U.V. Waghmare, N.A. Spaldin and K.M. Rabe, "First-principles study of spontaneous polarization in multiferroic BiFeO3", Phys. Rev. Vol. B 71, 2005.

[16]A. Safa'aAlddin," Effect of Copper Ions on the Structural and Electrical Properties of Ni-Zn Ferrite Nanoparticles", M.Sc. thesis, University of Technology, p.13, 2012.

[17]Jean Phalippou, "sol -gel: a low temperature process for the materials of the new millennium",(2000).

[18]Brinker, C.J. and Scherer, G.W., "Sol Gel Science: the physics and chemistry of sol-gel processing", (Academic Press, 1990).

**[19]** German Patent 736411 (Granted 1943) Anti-Reflective Coating (W. Geffcken and E. Berger, JenaerGlasswerk Schott).

[20]Klein L.C, "sol-gel optics: processing and applications", springer - verlag, (1994).

[21]Sakka S. *et al.*, "the sol-gel transition: formation of glass fibers & thin films", J. non-crystalline solids, Vol. 48, p.31,1982.

[22]Patel P.J., *et al.*, "Transparent ceramics for armor and EM window applications", Proc. SPIE, Vol. 4102, p. 1, Inorganic Optical Materials II, Marker, A.J. and Arthurs, E.G., Eds, 2000.

[23] Gupta. R, Chaudhury.N.K., "Entrapment of biomolecules in sol-gel matrix for applications in biosensors: problems and future prospects", BiosensBioelectron, Vol.22, P. 2387-2399, 2007.

[24]Yoldas, B. E, "Monolithicglass formation by chemical polymerization", Springer, Journal of materials science, Vol.14, P.1843-1849, 1979.

[25]E. C. Snelling, "Soft Ferrites: Properties and Applications", 1 st Edition, Iliffe Books Ltd., London, 1969.

[26] S. Ghosh, S. Dasgupta, A. Sen and H. S. Maiti, "Low temperature synthesis of bismuth ferrite nanoparticles by a ferrioxalate precursor method", Materials Research Bulletin, Vol. 40, no.12, p. 2073–2079, 2005.

[27] X. Y. Zhang, C. W. Lai, X. Zhao, D. Y. Wang, and J. Y. Da, "synthesis and ferroelectric properties of multiferroic BiFeO<sub>3</sub> nanotube arrays", American Institute of Physics, applied physics letters, Vol. 87, 143102, 2005.

[28] Jong Kuk Kim Sang Su Kim and Won-Jeong Kim, "sol-gel synthesis and properties of multiferroic BiFeO<sub>3</sub>", materials letters Vol.59, P.4006 – 4009, 2005.

[29] F. Chen, Q. F. Zhang, J. H. Li, Y. J. Qi, C. J. Lu, X.B.Chen, X.M.Renand and Y.Zhao, "sol-gel derived multiferroic BiFeO<sub>3</sub> ceramic with large polarization and weak ferromagnetism", Appl. Phys. Lett. Vol.

89, 092910, 2006.

[**30**]F. Gao, Y. Yuan, K. F. Wang, X. Y. Chen, F. Chen, and J.-M. Liu, "preparation and photoabsorption characterization of  $BiFeO_3$  nanowires", applied physics letters, Vol. 89,102506, 2006.

[**31**]Yonggang Wang, Gang Xu, Linlin Yang, ZhaohuiRen, Xiao Wei, WenjianWengPiyi Du, GeShen and Gaorong Han, J. Am .Ceram. Soc, Vol. 90,No.11, p. 3673–3675, 2007.

[**32**]S.M.Selbach, M\_Ann.Einarsrud, T.Tybell and T.Grande, "synthesis of BiFeO<sub>3</sub> by wet chemical methods," J.Am.Ceram.Soc., Vol.90, No. 11 , P.3430-3434, 2007.

[**33**]J. Wei and D.Xue, "Low-temperature synthesis of BiFeO3 nanoparticles by ethylenediaminetetraacetic acid complexing sol–gel process", Materials Research Bulletin, Vol.43,No.12,p.3368–3373,2008.

[**34**]MomataKisku ,"surfactant assisted autocombustion synthesis of bismuth ferrite", B.Sc. thesis, national institute of technology,Rourkela,2009.

[**35**]RatnakarPandu, K. L Yadav, Amit Kumar, Ravinder Reddy and AVSSKS Gupta, "Effect of sintering temperature on structural and electrical properties of BiFeO<sub>3</sub>multiferroic",Indian J. of Engineering and Materials Sciences Vol.17, p.481-485,2010.

[**36**]Zhiwu Chen, Guanghui Zhan, Xinhua He, Hu Yang, and Hao Wu,"synthesis pure perovskite bismuth ferrite (BiFeO3) microspheres and microrectangular",Cryst. Res. Technol,vol. 46, no. 3, p.309 – 314, 2011.

[**37**]Chandrashekhar P. Bhole, "ferroelectric and dielectric investigation of bismuth ferrite (BiFeO<sub>3</sub>) nanoceramics", archives of appl. science research, Vol. 3, No, 5, P.384-389 2011.

[38] Chun Lin Fu, MengHuo, Wei Cai and Xiao Ling Deng, "Bismuth Ferrite Nanopowders Prepared by Sol-Gel", advanced materials research, Vol.412, P.142-145, 2011.

[**39**] Glenda Biasotto, , Alexandre Z. Simoes, , Cesar R. Foschini,Selma G. Antonio, Maria A.Zaghete and Jose A. Varela ,"A novel synthesis of

perovskite bismuth ferrite nanoparticles", Processing and Application of Ceramics, Vol. 5 ,P.171–179. 2011.

[**40**]AnoopshiJohari, "Synthesis and Characterization of Bismuth Ferrite Nanoparticles", akgec international journal of technology, Vol. 2, No. 2, 2011.

**[41]** J. KarimiSabet, A. Golzary and C.Gotbi,"Bismuth ferrite nanoparticles formation via a supercritical hydrothermal synthesis method",proceedings of the 4<sup>th</sup> international conference on nanostructures (ICNS4), Kish Island, I.R. Iran, 2012.

[42] Samar Layek and H. C. Verma," magnetic and dielectric properties of multiferroic BiFeO3 nanoparticles synthesized by a novel citrate

combustion method", Adv. Mat. Lett, Vol.3, No.6, P.533-538, 2012.

[43] H. Y. Dai, Z. P. Chen, T. Li, R. Z. Xue and J. Chen," Structural and Electrical Properties of Bismuth Ferrite Ceramics Sintered in Different Atmospheres", Journal of Superconductivity and Novel Magnetism, Vol.26, No. 10, P. 3125-3132, 2013.

**[44]** Dengzhou Yan, Changlong Sun, JikangJian, Yanfei Sun, Rong Wu and Jin Li, Journal of materials science: materials in electronics, Vol. 25, No. 2, p. 928-935, 2014.

[45] B. Kumari, P. R. Mandaland T. K. Nath, "magnetic, magnetocapacitance and dielectric properties of BiFeO3 nanoceramics", Adv. Mat. Lett., Vol.5, No. 2, P.84-88, India, 2014.

[46] Abbas. F. Hadi, "Samples Preparation of Cu, Ni, Mg Ferrite for Absorbing Spectrum of X-Band Waves", M.Sc. thesis, al-mustansiriyah University, 2012.

[47] C. Hammond, "Introduction to crystallography", (revised edition), Oxford University Press, Oxford, UK, 1992.

[48] Callister, W , "Materials Science and Engineering An Introduction" , Fifth Edition. John Wiley & Sons, 2000  $\,$  .

[**49**] Editors B. Viswanathan and V.R.K.Murphy, "Ferrites Materials science and technology", Springer–Verlag, Norosa publishing house, p.(26, 2, 7–8, 8,9,12, 14, 14–15), 1990.

[**50**]Alexander.R.Taussing, "growth and characterization of bismuth perovskite thin films for integrated magneto-optical isolater application", M.Sc. thesis, Harvard University, p.(43, 44), 2007.

[51]Didosyan, Hauser, Reider, Nicolics, Sensors and Actuators on Orthoferrites, IEEE 2004.

[52] M. D. Nersesyan, A. G. Peresada, A. G. Merzhanov, Int. J. SHS , Vol.7, P.60,1998.

[**53**]Z. Yue, L. Li, J. Zhou, H. Zhang, Z. Gui, Mat. Sci. Engg., V.B64, No. 1, p. 68, 1999.

[54]B.H. Sohn, R.E. Cohen, Chem. Mater., Vol.9, P. 264–269, 1997.

[55] S. W. Cheong and M. Mostovoy, "Multiferroics: a magnetic twist for ferroelectricity", Nature Mater., Vol. 6, P.13, 2007.

[56]J F Scott and R Blinc, "Multiferroicmagnetoelectric fluorides: Why are there so many magnetic ferroelectrics", J. Phys.: Condens. Matter, Vol.23, No. 11,113202, 2011.

[**57**] N. A. Hill, "Why are there so few magnetic ferroelectrics", J. Phys. Chem. Vol.B 104, P.6694 ,2000.

**[58]**J. B. Neaton, C. Ederer, U. V. Waghmare, N. A. Spaldin, and K. M. Rabe, "First-principles study of spontaneous polarization in multiferroic BiFeO3", Phys. Rev. ,Vol.B 71, 014113 ,2005.

**[59]** Y. Tokura (ed.), Colossal Magnetorestive Oxides, (Gordon and Breach Science Publishers, Amsterdam, Netherlands, 2000.

[60] H. D. Megaw and C. Darlington, "Geometrical and Structural Relations in the RhombohedralPerovskites", ActaCryst., Vol. A 31, P.161, 1975.

[61]M. Johnsson and P. Lemmens, "Crystallography and Chemistry of Perovskites", in Handbook of Magnetism and Advanced Magnetic Media, (ed. H. Kronmuller), John Wiley & Sons, New York, 2006.

[62]V.M. Goldschmidt, Skrifer Norske Videnskaps-Akad. Oslo, I.Mat.-Nat. Kl. 8 1926.

[63] C. Li, K. C. K. Soh, P. Wu, "Formability of ABO3 Perovskites", Journal of Alloys and Compounds, Vol.372, P.40, 2004.

[64] A. M. Glazer, "The Classification of Tilted Octahedra in Perovskites", Acta Cryst., Vol.B28, PP.3384, 1972.

[65]P.M. Woodward, "Octahedral Tilting in Perovskites. I. Geometrical Considerations" ActaCryst., Vol. B 53, P. 32, 1997.

[66]P.M. Woodward, "Octahedral Tilting in Perovskites 2. Structure Stabilizing Forces", ActaCryst., Vol. B 53, P.44 (1997).

[67]P.Curie, "Introduction to ferroic materials", J. Physique., Vol. 3, p.393, 2000.

**[68]**W. Eerenstein, N. D. Mathur and J. F. Scott, "Multiferroic and Magnetoelectric Materials", Nature 442, 759, 2006.

[69]H.Bea,M.Gajek, M.Bibes and A.Barthelemy, "Spintronics with multiferroics", J. Phys.: Condens. Matter., Vol. 20, 434221, 2008.

[70] N.A. Hill, "Why are there so few Magnetic ferroelectrics", J. Phys. Chem., Vol. B 104, p. 6694, 2000.

[71]H. Schmid, "Introduction to the proceedings of the 2nd international conference onmagnetoelectric interaction phenomena in crystals", MEIPIC-2, Ferroelectrics, Vol.161, No.[1-4], p.1-28, 1994.

[72] D. Khomskii," classifying multiferroics: mechanisms and effects", Physics, V. 2, p.20, 2009.

[73]J.B.Goodenough and J.M.Longo, Landolt-Bornstein, Numerical Data and Functional Relationships in Science and Technology, New Series Vol.III.4, 126, Springer, Berlin, 1970.

[74] T. Mitsui, Landolt-Bornstein, Numerical data and Functional Relations in Science and Technology, New Series Vol. 16,No. 1,Springer, Berlin, 1981.

**[75]**S.W.Cheong , Maxim Mostovoy, "Multiferroics : a Magnetic twist for ferroelectricity", Nature Materials ,Vol.6,p.13 ,2007.

[76] Special issue," Special Sections Containing Papers on Multiferroics and On Multiferroics and Manganites", J. Phys. Condens. Matter .20, 434201–434220 ,2008.

[77] B. B.vanAken et al., Nature Mater., Vol. 3, p. 164, 2004.

[**78**]T. Kimura, T. Goto, H. Shintani, K. Ishizaka, T. Arima and Y. Tokura, "Magnetic control of ferroelectric polarization", Nature ,Vol.426, p.55,2003.

[79] N. Hur et al., "Electric polarization reversal and memory in a multiferroic material induced by magnetic fields", Nature. ,Vol.429, p.392, 2004.

[80] T .Arima," Ferroelectricity induced by proper-screw type magnetic order", J. Phys. Soc. Jpn 76, 073702 ,2007.

[**81**]Y.J.Choi, H.T.YI, S.Lee, Q.Huang, V.Kiryukhin and S.W.cheong, "Ferroelectricity in an Ising chain magnet", Phys. Rev. Lett. ,100, 047601 ,2008.

[82]G.Catalan and J.F.Scott, "physics and applications of bismuth ferrite", Adv. Mater. 21, 2463 ,2009.

**[83]** A. Moreira dos Santos, S. Parashar, A. R. Raju, Y. S. Zhao, A. K. Cheetham and C.N. R. Rao, "Solid State Commun", V. 122, p.49, 2002.

**[84]** S. Niitaka, M. Azuma, M. Takano, E. Nishibori, M. Takata, M. Sakata, "Solid StateIonics", V.172, p.557,2004.

[**85**]N. A. Hill and K. M. Rabe, "First – principles investigation of ferromagnetism and ferroelectricity in Bismuth manganite", Phys. Rev. B 59, 8759, 1999.

[**86**]KeertiChhabra," Preparation And Characterization Of (1-x)BiFeO3 – xNiFe2O4 (x=0, 0.3) Composite", M.Sc. thesis, Thapar University, India,2012.

[87]Zumdahl, Steven S,"Chemical Principles" 6th Ed. Houghton Mifflin Company. p. A22. ISBN 0-618-94690-X,2009.

[88]M.W.Barsoum, "Fundamentals of Ceramics", McGraw-Hill company,

Inc., New York, 1997.

[89] Z. Simasa, and A. M. Victor, IEEE, Transition of magnetic, Vol.

24, No. 2, p. 1910-1916, 1988.

[90] M. A. Ahmed, and M. A. El Hiti, J Phys. III France, Vol. 5, p. 775-781, 1995.

[91] D. Elkong; Egypt J. Sol, Vol.23, p. 137-146, 2000.

**[92]** P.J.Harrop, "Dielectrics", England by page Bros (Nor wich ) Ltd, Nor wich , First published, PP.(3-6), 1972.

[93]James D. Patterson, Bernard C. Bailey, "Solid State Physic Introduction to the Theory", Springer-Verlag BerlinHeidelberg ,2007, p.(509), 2007.

[94]Jalle, "An outline of polymer chemistry", Oliver and Boyed, Ltd, 1974.

[95]M.C. Lovell, A.J. Aery, and M.W. Vernon, "Physical properties of materials", New York ,1976.

[96]R.A. Levy, "Principle of solid state physics", 4th edition, Academic press ,1976.

[97] H. Frohlich, "theory of dielectrics", 1st edition, Oxford University Press. 1958.

**[98]** S. Borowitz, and A. Beiser, "Essentials of Physics", 2nd edition, Addison-Wesley publishing Company, 1971.

[99] William D. Callister, Jr., "Materials science and engineeringanintroduction". John Wiley & Sons, p.(702-709), 2007.

[100] Brian S. Mitchell, "An Introduction To Materials Engineering And Science", A John Wiley& Sons, Inc, P.(99-100), 2004.

[101]Mailadil. t. Sebastian, "dielectric materials for wireless communication", Elsevier, 2008.

[**102**]Dr .SobhiS.al-Rawi 'DrShakerShaker 'DrMaolod Y.Hassan" 'Solid StatePhysics ", Ministry of Higher Educationand Scientific Research, University of Mosul ' p.(329-399), 1988. [103]L. L. Hench, J. K. West, "Principles of Electronic Ceramics", Wiley, New York ,p.189, 1990.

[104]K. Zadeh, B. Fry, "Nanotechnology-Enabled Sensors", springer, Australia, 2008.

[105]C.Raab, M. Simko, U. Fiedeler, M. Nentwich, A. Gazso, "Production of nanoparticles and Nanomaterials", Institute of technology assessment of the austrian academy of sciences, No. 006en ,2011.

[**106**]Gustau Catalan and James F. Scott, "Physics and Applications of Bismuth Ferrite", Adv. Mater., Vol. 21, p.2463–2485, 2009.

[107] Kiselev, S.V.; Ozerov, R.P., Zhdanov, G.S.. "Detection of magnetic

order in ferroelectric BiFeO3 by neutron diffraction", Soviet physics-

Doklady, Vol. 7, No. 8, p.742-744, 1963.

[108]Spaldin , Nicola A.;Cheong,Sang-wook,Ramesh,Ramamoorthy,

"Multiferroics :Past ,Present , and future", Physics Today, Vol.63, No.10, p.38, 2010.

[109]Chu,YH;L.W.Martin ,M B .Holcomb and R .Ramesh,"Controlling magnetism with multiferroics", Materials Today ,Vol.10,No. 10,p.16-23,2007.

[**110**]Seidel, J. et.al, "Conduction at domain walls in oxide multiferroics", Nature Materials, Vol.8 ,No. 3 ,P.229- 234, 2009.

[111]Ghosh,Sushmita; Dasgupta, Subrata,Sen, Amarnath,SekharMaiti,Himadri," Low-Temperature Synthesis of Nanosized Bismuth Ferrite by Soft Chemical Route", J. Am. Ceram Soc., Vol.88, No.5,P. 1349-1352,2005.
[112] Han,J.-T.;Huang,Y.-H.,Wu,X.-J.,Wu,C.-L.,Wei,W.,peng,B., Huang , W. and Goodenough,J.B.," Tunable Synthesis of Bismuth Ferrite with Various Morphologies", Advanced Materials, Vol.18,No. 16,P.2145-2148,2006.

[113]S. Feldbauer," Advances in Powder Metal Sintering Technology", Abbott Furnace Company, St. Marys, PA 15857. [114]T. Theivasanthi and M. Alagar ,"X-Ray Diffraction Studies of Copper Nano powder", Department of Physics, PACR Polytechnic College, India,2010.

[115]B. D. Cullity, "Elements of X-Ray Diffraction", 2nd Ed, Addision-Wesley.INC. ,1978.

[**116**] "Solid State Physics X-ray Scattering III: Debye-Scherrer Method", Physics ,340, spring (3), 2012.

[117]Wang .J.; B.Neaton ,H.Zheng,V.Nagarajan ,S.B.Ogale , B.Liu, D.,

Viehland, V. Vaithyanathan , D.G. Schlom , U.V. Waghmare, N.A. Spaldin ,

K.M.Rabe ,M.Wutting and R.Ramesh,"Epitaxial BiFeO3 Multiferroic

Thin film Heterostructures", Science, Vol.299, No. 5613, P.1719-1722, 2003.

[118]Rye A. Johnson, "growth characterization of RF magnetron sputtered  $BiFeO_3$  on epitaxial  $SrTiO_3$ ", B.Sc. thesis, Texas State University-San Marcos, 2013.

[**119**]Zeches ,R.J.; Rossell,M.D.,Zhang,J.X.,Hatt,A.J., He,Q., Yang , C.-H.,Kumar,A.,Wang ,C.H.,Melville ,A.,Adamo , C.,Sheng , G., Chu,Y.-H.,Ihlefeld ,J.F.,Ederer,C., Gopalan , V., Chen ,L.Q., Schlom ,D,"Strain – Driven Morphotropic phase Boundary in BiFeO<sub>3</sub>", Science , Vol.326 , No. 5955, P.977-980, 2012.

[120]A.Lagashettya,V.Havanoorb,S.Basavarajab,S.D.BalajiA.Venkatara manb," Microwave-assisted route for synthesis of nanosized metal oxides", Science and Technology of Advanced Materials,Vol. 8,p. 484–493, Elsevier Ltd,2007.

[121] C. W.Chu, "Science new", Vol.148, No. 12, P.183, 1995.

[122] Kazuo Nakamoto, "Infrared and Raman spectra of inorganic and coordination compounds", 4<sup>th</sup> edition, Marquette university, 1986.

[123]"Zinc-manganese ferrites", Ph.D. Thesis, Andhra University, Waltair, 1981.

[124] Smart, L. E.; Moore, E. A," Solid State Chemistry", CRC: New York, 2005.

[**125**]B.Tareev, "Physics of dielectric materials", Mir publishers, Moscow, P.(101-145, 174-202), 1979.

أن زيادة درجة الحرارة ربما ساعدت على نمو وكبر الدقائق لكنها بقت ضمن حدود النانو أشكال مجهر القوة الذرية بينت ان حجم الدقائق صغيرة جدا ومتجانسة وضمن حدود النانو.

كوناً أن الشوائب تؤثر على الخواص الكهربائية لفيرايت البزموث لذلك تم فحص الخواص الكهربائية باستخدام جهاز LCR meter فقط للنموذج بدرجة C° 450 وبإضافة 5% من الكهربائية باستخدام جهاز LCR meter فقط للنموذج بدرجة C° 450 وبإضافة 5% من كحول البولي فينيل كرابط له . حيث كانت قيم ثابت العزل 113.42 الى 43.93 للتردد من KHZ للتردد من 5MHZ المى 55 KHZ الى 25 KHZ ، هذا يدل على ان ثابت العزل يقل بزيادة التردد. قيم المقاومية الكهربائية كانت من 1.3x0  $\Omega$  من 1.3x0 من 25 KHZ الى 25 KHZ ، هذا يدل على ان ثابت العزل يقل بزيادة التردد. قيم المقاومية على ان ثابت العزل يقل بزيادة التردد. قيم المقاومية معلى الكهربائية كانت 50 MHZ ، هذا يدل على ان ثابت العزل يقل بزيادة التردد. قيم المقاومية على ان المقاومية الكهربائية تقل بزيادة التردد فيم التوصيلية الكهربائية كانت 50 SMHZ ، هذا يدل على ان المقاومية الكهربائية تقل بزيادة التردد. قيم التوصيلية الكهربائية كانت 50 SMHZ ، هذا يدل على ان المقاومية الكهربائية تقل بزيادة التردد. قيم الموصيلية الكهربائية كانت 50 SMHZ ، هذا يدل على ان المقاومية الكهربائية تقل بزيادة التردد. قيم التوصيلية الكهربائية كانت 50 SMHZ ، هذا يدل على ان المقاومية الكهربائية الكهربائية الكهربائية الكهربائية معن 20 SMHZ ، هذا يدل على ان التوصيلية الكهربائية الكهربائية الكهربائية ، وريادة التردد. قيم التوصيلية الكهربائية كانت 50 SMHZ ، هذا يدل على ان التوصيلية الكهربائية تزداد بزيادة التردد من 25 KHZ ، هذا يدل على ان التوصيلية الكهربائية ، مذا يدل على ان التوصيلية الكهربائية من 20 SMHZ ، هذا يدل على ان التوصيلية الكهربائية من 25 SMHZ ، هذا يدل على ان التوصيلية الكهربائية من 20 SMHZ ، هذا يدل على ان التوصيلية الكهربائية من 20 SMHZ ، هذا يدل على ان التوصيلية الكهربائية من 20 SMHZ ، هذا يدل على ان 1.3 SMHZ المود من 25 SMHZ ، هذا يدل على ان 25 SMHZ ، هذا يدل على ان 30 SMHZ ، هذا يدل على ان 40 SMHZ ، هذا يدل على ان 40 SMHZ ، هذا يدل على ان 40 SMHZ ، من 20 SMHZ ، هذا يدل على ان 40 SMHZ ، هذا يدل على ان 40 SMHZ ، هذا يدل على 10 SMHZ ، هذا يدل على ان 40 SMHZ ، هذا يدل على 10 SMHZ ، هذا يدا على ان 40 SMHZ ، هذا يدل على ان 40 SMHZ ، هذا يدل على 10 SMHZ ، هذا يدل على 10 SMHZ ، هذا يدل على 10 SMHZ ، ما 20 SMHZ ، هذا يدل على 10 SMHZ ، ما

الخلاصة

في هذه الدر اسة مساحيق فيرايت البزموث النانوية (BiFeO<sub>3</sub>) ، حضرت بالطريقة الكيميائية الحديد (المحلول – جل) . وقد استخدمت نترات البزموث Bi (NO<sub>3</sub>)<sub>3</sub>.5H<sub>2</sub>O) ، حضرت بالطريقة الكيميائية (المحلول – جل) . وقد استخدمت نترات البزموث Bi (NO<sub>3</sub>)<sub>3</sub>.9H<sub>2</sub>O ونترات الحديد (NO<sub>3</sub>)<sub>3</sub>.9H<sub>2</sub>O) وحامض النتريك HNO<sub>3</sub> ونترات الحديد مسحوق فيرايتي ذات دقائق نانوية . الجل المنتج جفف بدرجة C<sup>6</sup>H<sub>8</sub>O<sup>7</sup> ولمدة ساعتين ثم بعد ذلك مسحوق فيرايتي ذات دقائق نانوية . الجل المنتج جفف بدرجة C<sup>8</sup> (Soc, 450°C, 500°C, 500°C) لمدة ساعتين أبضا.

الخواص التركيبية والكهربائية للمساحيق النانوية ل BiFeO<sub>3</sub> درست بإستخدام العديد من القياسات مثل (حيود الاشعة السينية(XRD) - الاشعة تحت الحمراء تحويل فورير (FTIR) -المجهر الالكتروني الماسح(SEM) - مجهر القوة الذرية(AFM) - جهاز قياس الخواص الكهربائية والعزلية باستخدام (LCR meter) ). حيث أظهر فحص حيود الأشعة السينية أن الجل المجفف كان غير متبلور، ولكن بعد عملية الكلسنة بدرجة C<sup>°</sup> 350 أصبح متبلور .

بعد تحليل كافة القمم التي ظهرت باستخدام حيود الاشعة السينية لكل النماذج المكلسنة وجد أن هناك العديد من الشوائب تظهر مع البزموث فيرايت أحادي الطور، حيث إن النموذج بدرجة 450°C يعتبر افضل نموذج حيث كان البزموث فيرايت احادي الطور القمة الرئيسية مع ظهور قمم صغيرة تعود الى اطوار شائبة وكان الطور الشائب الظاهر فقط طور واحد لكن النموذج بدرجة 2°700 يعتبر أسوأ نموذج بالرغم من أن البزموث فيرايت كان القمة الرئيسية إلا أن هناك الكثير من الاطوار الشائبة لذلك لم ندرس خصائص هذا النموذج.

كذلك من حيود الأشعة السينية وبإستخدام معادلة ديباي-شيرار تبين أن الحجم الحبيبي كان nm(12.5-12.8-39.9-47.6) للنماذج بدرجات (2°°C, 500°C, 500°C, 350°C) على التوالي . هذا يدل على أن الحجم الحبيبي يزداد بزيادة درجة الحرارة. من خلال المجهر الالكتروني الماسح للبزموث فيرايت تبين بإن حجم الحبيبات أقل من nm 100 وكذلك لاحظنا



جمهورية العراق وزارة التعليم العالي والبحث العلمي جامعة ديالى كلية العلوم /قسم الفيزياء

تحضير ودراسة الخصائص التركيبية والكهربائية لمساحيق فيرايت البزموث النانوية.

رسالة مقدمة الى مجلس كلية العلوم – جامعة ديالى وهي جزء من متطلبات نيل درجة الماجستير علوم في الفيزياء



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2014م

**A** 1436