

# Effect of Temperature on Structural and Electrical Properties of Bismuth Ferrite Nanoparticles Prepared By Sol Gel Method

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**ABSTRACT:** Bismuth ferrite nano particles were prepared by sol-gel route using solutions of iron nitrate and bismuth nitrate. The produced powder was dried at 150°C for 2 h and then calcined at various temperatures for 2 h as well. XRD was used to study the structure of BiFeO<sub>3</sub> nanoparticles, it is found that the grain size were about 12.8, 39.9 and 47.6 nm as calculated using Scherrer equation for samples calcined at 450 °C, 500 °C and 550 °C for 2 h respectively, this explain that grain size increase with increase in temperature and XRD too showed that besides the formation of single phase BiFeO<sub>3</sub> an impurity phase was also observed. From diagnosis of samples, we found that BiFeO<sub>3</sub> have rhombohedral structure. Scanning electron microscope (SEM) surface morphology study indicated a better homogeneity with fine grain morphology besides the formation of single phase BiFeO<sub>3</sub> an impurity phase. Less impurity phases was found in sample calcined at 450 °C. Atomic force microscope (AFM) declare that it has homogenous particle distribution and coarseness of surface with change of particles to spherical form with dimension of 1.21 nm, also Granularity Cumulation Distribution Report for same sample found that average diameter is equal to 45.31 nm. Finally the electrical properties results of BiFeO<sub>3</sub> such as the dielectric constant, tangent loss and electrical resistivity and conductivity were studied at different applied frequencies.

**KEYWORDS:** Bismuth Ferrite nanoparticle, Sol-gel, Magnetic Materials, Nanomaterial's, Multiferroic.

## I-INTRODUCTION

Bismuth ferrite, BiFeO<sub>3</sub> (BFO) is one kind of ferrite, a magnetic materials which have combined electrical and magnetic properties, being discovered in 1960, recently there is a renewed interest because of its possible novel applications in the field of radio, television, microwave and satellite communications, audio-video, digital recording and, as permanent magnets. BFO is a well-known multiferroic at room temperature having para- to ferro-electric transition temperature (T<sub>c</sub> ~ 1103 K) and a G-type antiferromagnetic transition at T<sub>N</sub> ~ 643 K [1]. Multiferroic BFO nanostructures exhibit interesting magnetic and optical properties because of nano scale size effects.

BFO powders have been prepared by the solid-state methods [2,3] and mechano-chemical ones [4] and solution chemistry methods such as precipitation / coprecipitation [5], sol-gel [6,7], alkali metal ions-assisted controllable synthesis hydrothermal method [8] and sonochemical ones [9].

Most of the mentioned procedures need high temperature treatments (>800°C). Due to the requirement of nanosized oxides and in order to avoid bismuth volatilization the developing of low temperature synthesis methods is essential.

Previous studies have demonstrated that synthesis of bismuth Ferrites nanoparticles through a traditional solid-state method produces poor reproducibility and causes formation of coarser powders as well as Bi<sub>2</sub>O<sub>3</sub>/Bi<sub>2</sub>Fe<sub>4</sub>O<sub>9</sub> and other impurity phases [8,9], however, these approaches have certain short comings such as impurities in the final products [10].

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S.Ghosh et al. [11], used low temperature synthesis of bismuth ferrite nanoparticles by a ferrioxalate precursor method, the synthesis route is simple, energy saving and cost-effective, this work showed that the reaction of  $\text{Bi}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  results in the formation of multiphase products. Low temperature synthesis is used by Jie Wei et al., [12] to produce pure BFO nanoparticles by ethylenediaminetetraacetic acid complexing sol-gel process, as a novel approach.

In 2009, M.Kisku [13], synthesized bismuth ferrite by glycine nitrate auto-combustion with addition of two different types of surfactant namely ammonium lauryl sulfate and Triton X. In 2010, R.Pandu et al. [14], studied effect of sintering temperature on structural and electrical properties of  $\text{BiFeO}_3$  multiferroics at low temperature by using sol gel technique. In 2011, Chun Lin Fu et al. [15] prepared  $\text{BiFeO}_3$  powders by sol gel process and calcined at different temperatures. After calcining at  $600^\circ\text{C}$  for 1h, XRD spectra has the emergence of several sharp diffraction peaks, compared with the standard XRD spectrum of the crystal  $\text{BiFeO}_3$ .

In 2011, G.Biasotto et al. [16], have done a novel synthesis of perovskite bismuth ferrite nanoparticles, by microwave assisted hydrothermal method to obtain crystalline bismuth ferrite nanoparticles at temperature of  $180^\circ\text{C}$ . In 2012, S.Layek and H. C. Verma [17], studied magnetic and dielectric properties of multiferroic  $\text{BiFeO}_3$  nanoparticles by a novel citrate combustion method. BFO nanoparticles with average crystallite size of about 50nm have been prepared by using metal nitrates and citric acid. In 2013, H. Y. Dai et al. [18], synthesised bismuth ferrite ( $\text{BiFeO}_3$ ) ceramics by the solid-state reaction method followed by rapid liquid phase sintering. The effect of sintering atmosphere ( $\text{N}_2$ , air and  $\text{O}_2$ ) on the structure and electrical properties of  $\text{BiFeO}_3$  multiferroic ceramics were investigated. In 2014, Dengzhou Yan et al, [19], Studied structural and phase transition of  $\text{BiFeO}_3$  particles prepared by hydrothermal method and the verification of crystallization-dissolution-crystallization mechanism, they show the optimal synthesis temperature of  $\text{BiFeO}_3$ .

The aim of the present work is to study the sol-gel synthesis route of BFO and investigate its structural and electrical properties with temperature.

## II-MATERIALS AND METHODS

**2.1 Materials Used** : Analytical grade bismuth Nitrate,  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ , iron Nitrate,  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ , nitric acid ( $\text{HNO}_3$ ) and citric acid ( $\text{C}_6\text{H}_8\text{O}_7$ ) were used with out further purification.

**2.2 Preparation method**: Bismuth ferrite powder was prepared by mixing two previously prepared nitrate acid solutions of 0.2 M so that the ratio of Bi : Fe is one. The solution was then heated at ( $65-70^\circ\text{C}$ ) with constant stirring for two hours. Then at the end of the reaction a fluffy mass (gel) was obtained which is then converted to brown-black powder when heated in an oven for 2 hour at a temperature of  $150^\circ\text{C}$ . Finally this powder was calcinated in a furnace at different temperature ( $450, 500$  and  $550^\circ\text{C}$ ), to obtain the crystallized bismuth Ferrite nanoparticles with controllable sizes.

**2.3 Apparatus** : The X-ray diffraction pattern were recorded using XRD-6000 with  $\text{CuK}\alpha$  ( $\lambda=1.5406\text{\AA}$ ) with accelerating voltage of 220/50HZ which is produced by SHIMADZU company.

Scanning electron microscope used in imaging the nanoparticles was a VEGA/EasyProbe 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., Libušina triad.

LCR meter type Agilent impedance analyzer of USA origin operating at frequency of ( $50\text{Hz}-5\text{MHz}$ ) was used to measure all electrical properties such as resistivity, conductivity, dielectric constant and tangent loss.

Digital Instruments, Veeco Metrology Group SPM \_AA 3000, AFM contact Mode, Angstrom, Advanced, Inc., VSA. was used for further investigation of BFO surface structures.

## III - RESULTS AND DISCUSSION

### 3-1 XRD analysis

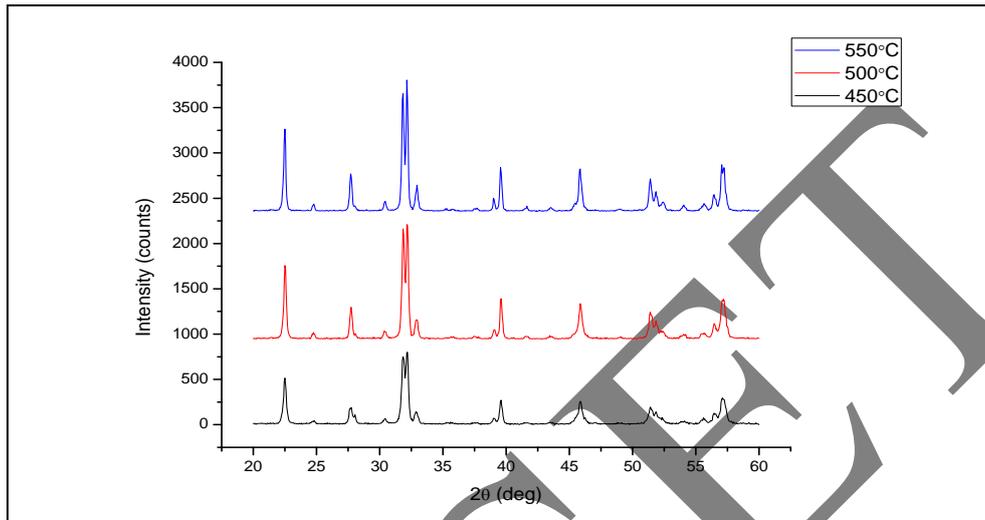
The XRD spectra of  $\text{BiFeO}_3$  calcined at  $450, 500$  and  $550^\circ\text{C}$  are shown in fig.(1). The prominent peaks in the plot are indexed to various (hkl) planes of BFO. The sample calcined at  $450^\circ\text{C}$  seem to have only impurity phase but

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samples calcined at 500 and 550°C are both having two impurity phases BiFeO<sub>3</sub>. In sample heated at 450°C, phases Bi<sub>25</sub>FeO<sub>4</sub> with BiFeO<sub>3</sub> and its have less peak compared with other sample, but in sample treated at 500 and 550°C appear to have (Bi<sub>3.43</sub>Fe<sub>0.57</sub>O<sub>6</sub> and Bi<sub>25</sub>FeO<sub>4</sub>) with BiFeO<sub>3</sub> only peaks of Bi<sub>3.43</sub>Fe<sub>0.57</sub>O<sub>6</sub> is less.

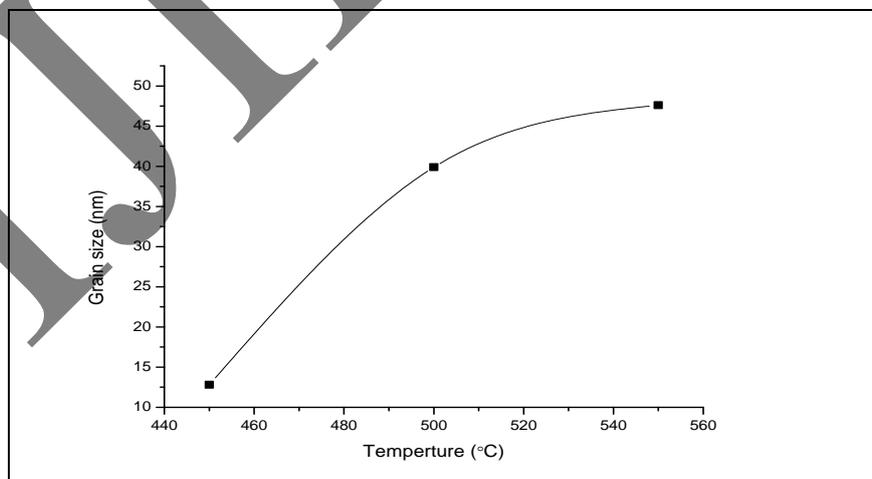


**Fig (1):** The XRD spectra of BiFeO<sub>3</sub> calcined at 450, 500 and 550°C.

The average grain size of ferrites samples was determined from the most intense X-ray line broadening using Scherrer's equation [20]:

$$D = 0.9 \lambda / \beta \cos \theta$$

Where, D is the grain size,  $\lambda$  is the wavelength of the radiation,  $\theta$  is the Bragg's angle and  $\beta$  is the full width at half maximum (FWHM). [21]. The grain size calculated from Scherrer equation are (12.8, 39.9 and 47.6 nm) for sample calcined at the described temperatures respectively.



**Fig (2) :** Explain the relation between grain size and calcination temperature.

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Figure (2) demonstrate the relation between grain size of prepared ferrites nanoparticles and calcinations temperatures, it indicates that the particle size increases with temperatures.

### 3-2 Scanning Electron Microscopy (SEM) analysis:

The scanning electron microscope (SEM) used to study the surface morphology, from it we 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[22].Fig. (3) explain the SEM images for samplescalcined at 450 °C, 500 °C and 550 °C.

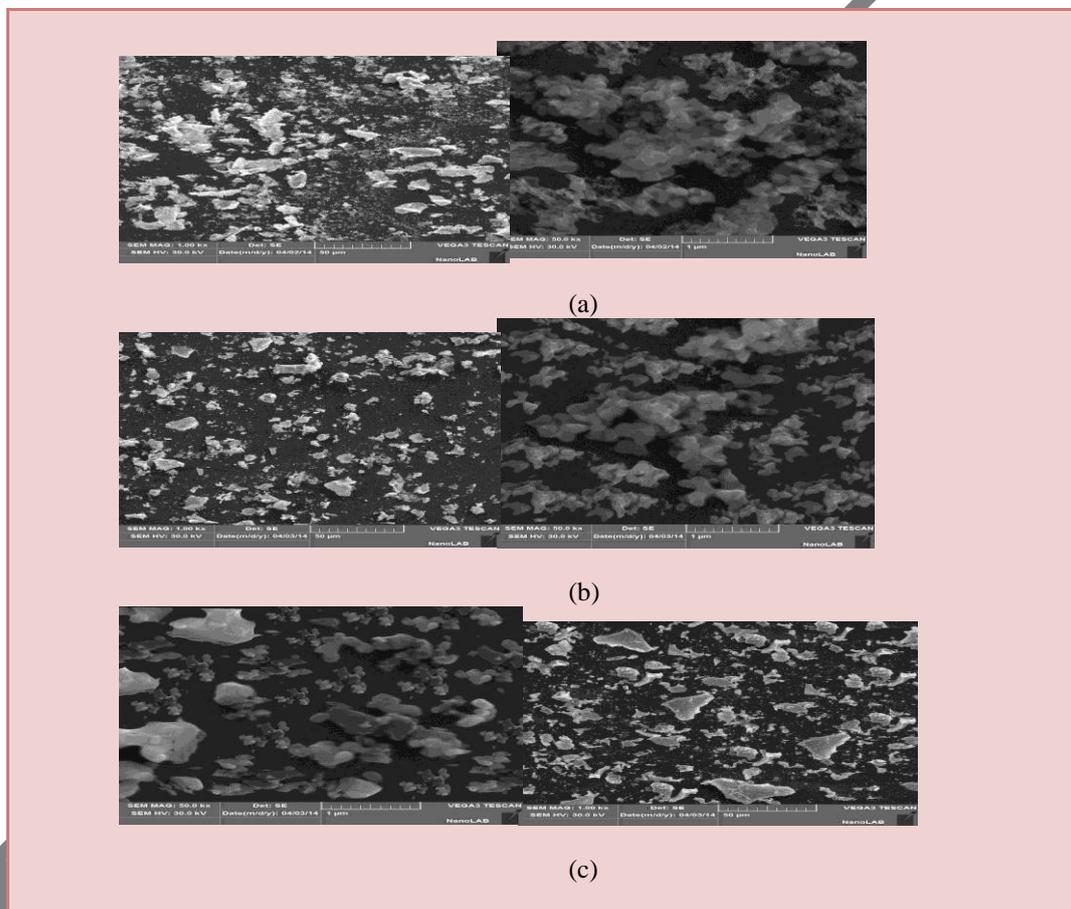
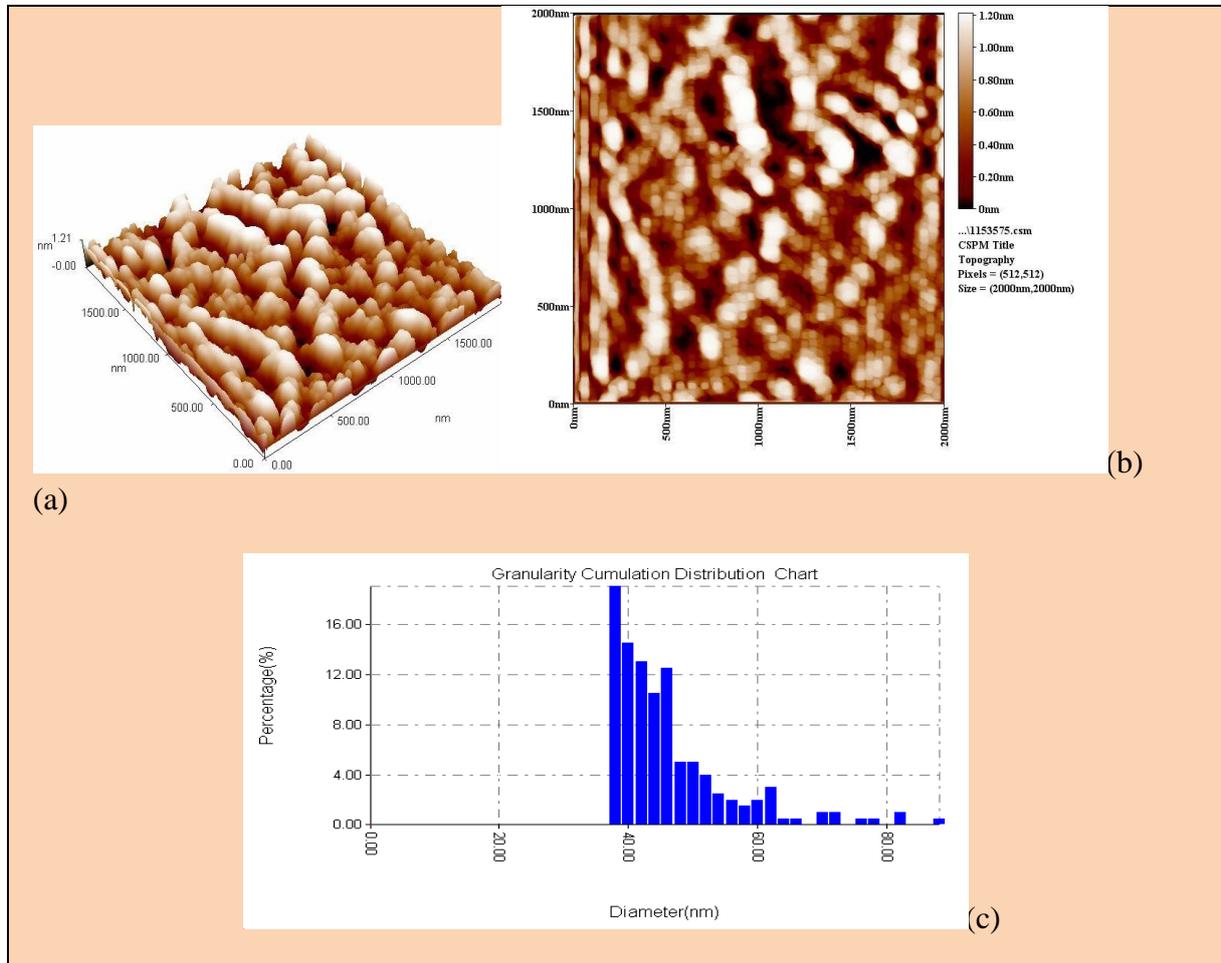


Fig.(3): Explain SEM images for bismuth ferrites nanoparticles calcined (a) 450°C, (b) 500°C and (c) 550°C.

### 3-3 Atomic force microscopy (AFM) analysis:

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 [23]. The Digital Instruments, Veeco Metrology Group SPM\_AA 3000, AFM contact Mode, Angstrom, Advanced, Inc., VSA. was used for further investigation of BFO surface structures.



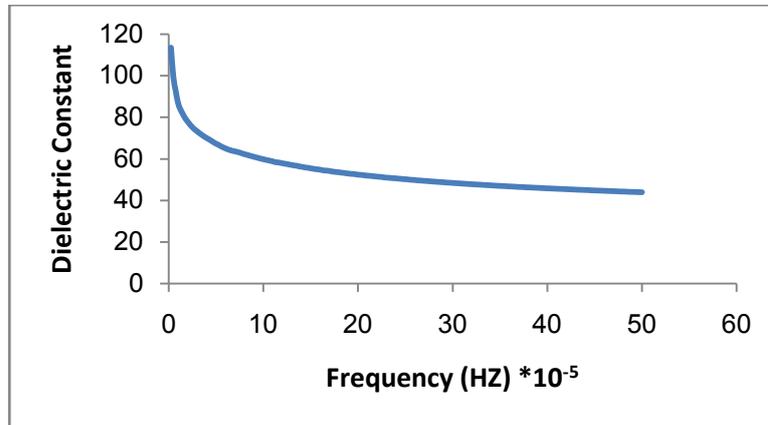
**Fig (4): Explain AFM for sample calcined at 450°C.**

Figure (4) explain images of AFM for sample calcined at 450°C with area (size=2000nmX2000nm) and analytical ability (pixels=512,512). Where fig (4-a) is a picture of AFM in three dimension(3D), it explain structural shape for grains and infig (4-b) is the picture of AFM in two dimension(2D), the estimated average roughness is 0.303nm and estimated RMS (root square mean) is 0.349nm and finally fig (4-c) represents granulometry cumulation distribution chart where it is used to calculate average particles diameter which was calculated to be 45.31 nm.

### 3-4 Electrical properties

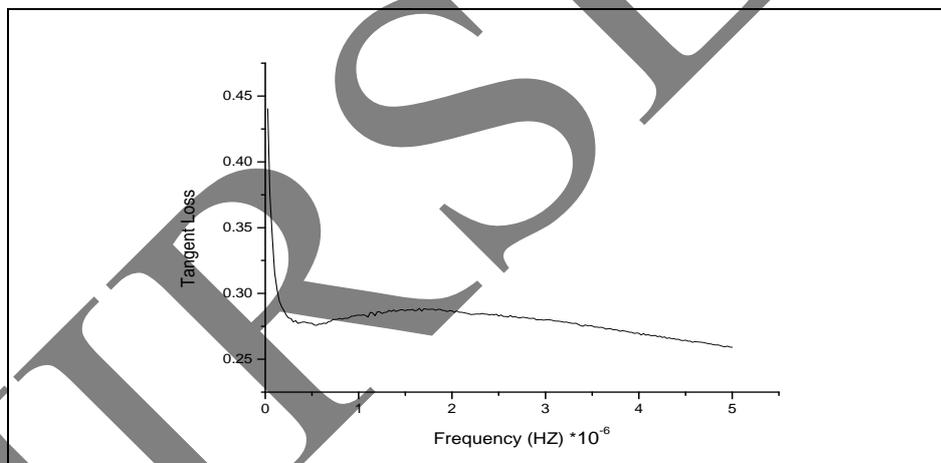
#### Dielectric properties

Fig.(5) Shows the dielectric constant measurements with respect to frequency in the region of (50Hz-5MHz) of BiFeO<sub>3</sub> pellets produced using PVA as a binder and applying pressure of 5 ton/cm<sup>2</sup> and sintered at 450°C and using LCR meter. It was found that dielectric constant was higher in the lower frequency region. It decreases with further increase in frequency and becomes almost constant at higher frequency region. Such behaviour is seen because at low frequencies all types of polarization contribute. As the frequency is further increased only electronic and ionic polarisation contributes which is the reason for the decrease in the dielectric constant [24].



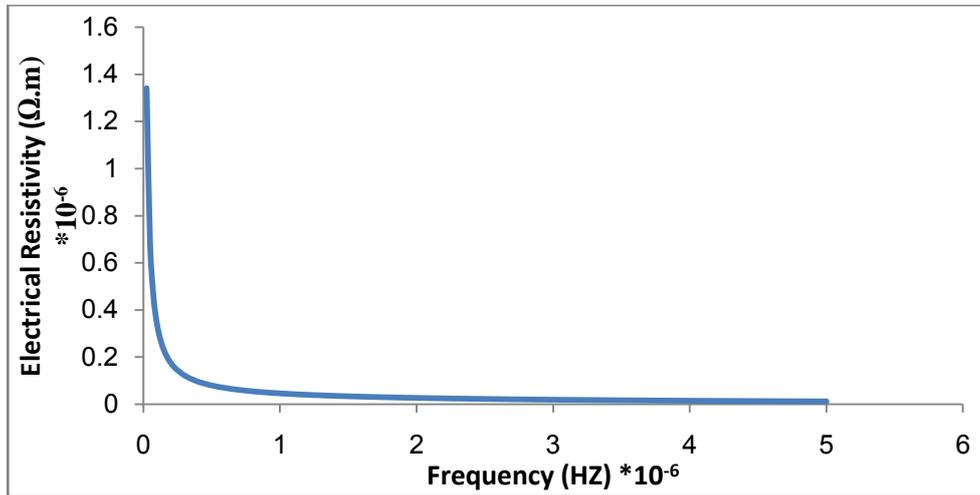
**Fig (5):** Explain the variation of dielectric constant with applied frequency.

The dielectric constant decrease with increase of frequency so this encouraged that BiFeO<sub>3</sub> can be used in insulator application for both lower and higher frequencies.



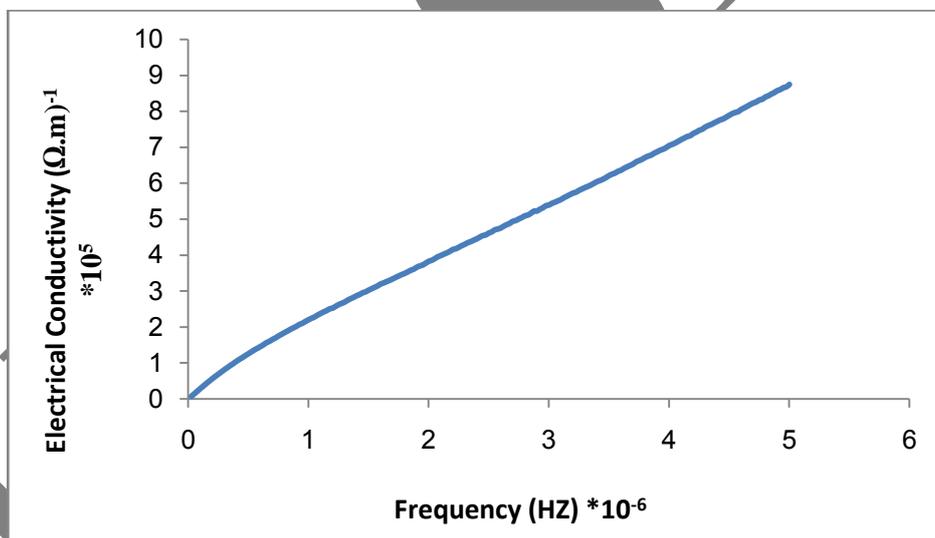
**Fig(6)** Variation of dielectric loss with applied frequency.

Also fig.(6) show that tangent loss decrease with increase frequency so that BiFeO<sub>3</sub> thus prepared caused in dielectrics materials applications.



**Fig.(7) Relation between electrical resistivity and applied frequency.**

Figure (7) show the electrical resistivity decrease with increase of frequency applied so that BiFeO<sub>3</sub> can be used in high frequency applications devices.



**Fig.(8) Relation between electrical conductivity and applied frequency.**

We can see from figure (8) also that electrical conductivity increases with increase of frequency. So from figs.7 and 8 one can conclude the possibility of use to these materials in high frequency device applications.

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