

# **SYNTHESIS AND CHARACTERIZATION OF $\text{Zn}^{2+}$ DOPED $\text{Ba}_2\text{TiO}_4$ NANOPARTICLES**

## **A PROJECT REPORT**

*Submitted By*

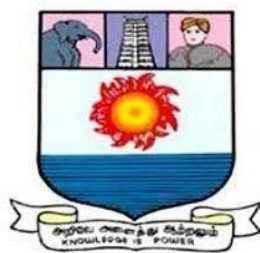
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*In Partial fulfilment of the award of the Degree of*

**MASTER OF SCIENCE**

**IN**

**NANOSCIENCE AND NANOTECHNOLOGY**



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**BONAFIDE CERTIFICATE**

Certified that this project work “**SYNTHESIS AND CHARACTERIZATION OF Zn<sup>2+</sup> DOPED Ba<sub>2</sub>TiO<sub>4</sub> NANOPARTICLES**” is the bonafide work T.SHAJIN (REG.NO. 20203152518218), who carries out the work under my supervision.

Certified further that to the best of my knowledge the work reported here in does not form part of any other thesis on the basis of which a degree or award was conferred on an earlier occasion on this or any other candidate.

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### **DECLARATION**

I hereby declare that the thesis entitled “Submitted by me for the award of the Degtee of **Master of science in Nanoscience and nanotechnology**” is the result of my original and independenr research work carried out under the guidance of **Mrs.M.J.UMA, M.Sc(Nano).,M.Sc(Phy).,B.Ed.,M.Phil.** Assistant Professor Department of Nanoscience and Nanotechnology (SS), S.T. Hindu College, Nagercoil and that it has not been submitted for the award for any Degree, diploma, association, or fellowship of any other Universities of Institution.

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## **PREFACE**

Nanotechnology is the art and science of manipulating matter at the nanoscale to create. It includes making products such as electronic devices, catalysts, sensors, etc. Microwave heating which allows a considerable reduction of the time, has been used in organic chemistry for several decades. In this work, microwave assisted solvothermal method of successfully used for synthesis of  $\text{Ba}_2\text{TiO}_4$  nanoparticles. Here we have to prepare pure and 5wt% and 10wt%  $\text{Zn}^{2+}$  doped  $\text{Ba}_2\text{TiO}_4$  nanoparticles by microwave assisted solvothermal method. The grain size of pure, 5wt% and 10wt%  $\text{Zn}^{2+}$  doped  $\text{Ba}_2\text{TiO}_4$  nanoparticles were determined by PXRD measurements. The electrical properties of  $\text{Ba}_2\text{TiO}_4$  nanoparticles were determined from AC conductivity analysis.

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## LIST OF SYMBOLS AND ABBREVIATIONS

AFM	Atomic Force Microscope
SEM	Scanning Electron Microscope
CNT	Carbon Nano Tube
PXRD	Powder X-Ray Diffraction
AC	Alternating Current
LCR	Inductance Capacitance Resistance
Ba	Barium
Ti	Titanium
Zn	Zinc
Ba <sub>2</sub> TiO <sub>4</sub>	Barium Orthotitanate
$\theta$	Bragg's angle or diffraction angle
$\beta$	Full width of X-ray radiation
JCPDS	Joint Committee Power Diffraction Standard
Cr <sub>2</sub> O <sub>3</sub>	Chromium Oxide
EDAX	Energy Dispersive X-ray Spectroscopy
UV	Ultra violet-Visible Spectroscopy
EDXA	Energy Dispersive X-ray Analysis
NMR	Nuclear Magnetic Resonance Spectroscopy
ICPE	International Conference on Precision Engineering

# **CHAPTER I**

## **INTRODUCTION**

### **1.1 INTRODUCTION OF NANOTECHNOLOGY**

Nanotechnology is defined as fabrication of devices with atomic or molecular scale precision. Devices with minimum feature sizes less than 100 nm are considered to be products of nanotechnology. A nanometer is one billionth of a meter  $10^{-9}$  and is the unit of length that is generally most appropriate marks the nebulous boundary between the classical and quantum mechanical worlds, thus realization of nanotechnology promises to bring revolutionary capabilities. Fabrication of nano machines, nano electronics and other nano devices will undoubtedly solve an enormous amount of the problems faced by mankind today [1].

Two main approaches are used in nanotechnology. In the bottom-up approach materials and devices are built from molecular components which assemble themselves chemically by principles of molecular recognition. In the top-down approach nano objects are constructed from large entities without atomic level control. The impetus for nanotechnology comes from a renewed interest in colloidal science, coupled with a new generation analytical tool such as Atomic Force Microscope (AFM), and the Scanning Tunneling Microscope (STM).

Nanotechnology entails the application of field of science as diverse as surface science, organic chemistry molecular biology micro fabrication etc. Despite the great promise of numerous nanotechnologies such as quantum dots and nano tubes, real commercial application here mainly used advantages of colloidal nanoparticles bulk from such as suntan lotion, cosmetics, protective coatings and stain resistant clothing. Nanotechnology applications in space development sand systems, high performance textile, the agricultural and food, energy [2]. Examples for potential applications of nanotechnology along the value adding chain in the energy sector.

## **1.2 NANOMATERIALS**

A number of physical phenomena become noticeably pronounced as the size of the system decreases. These include statistical mechanical effects, as well as quantum mechanical effects, for examples the quantum size effect where the electronic properties of solids are altered with great reduction in particle size.

This effect does not come into play by going from macro to micro dimensions. However, it becomes dominant when the nano meter size range is reached. This catalytic activity also opens potential risks in their interaction with biomaterials. In Additionally a number of physical-number of physical properties change when compared to macroscopic system. Materials reduced to the nano scale can suddenly show very different properties compared to what they exhibit on a macro scale,

enabling unique applications. A material such as gold, which is scale chemically inert at normal scales, served as a potential chemical catalyst at nano scales.

### **1.3 THE DIFFERENT DIMENSIONS OF NANOMATERIALS**

Nanomaterials are those that have structural components that have at least one dimension less than 100 nanometer. Nanomaterials have different dimensions, the single (or) one dimension double dimension (or) two dimension and three dimension nanomaterials. Example of nano with different dimension is the following [3,4].

#### **One Dimension**

- Surface coatings
- End surface
- Thin films

#### **Two Dimension**

- Carbon nano tubes (or) CNT
- Nano wires
- Inorganic nano tubes

#### **Three Dimension**

- Quantum dots
- Nanoparticles

- Fullerenes
- Precipitates

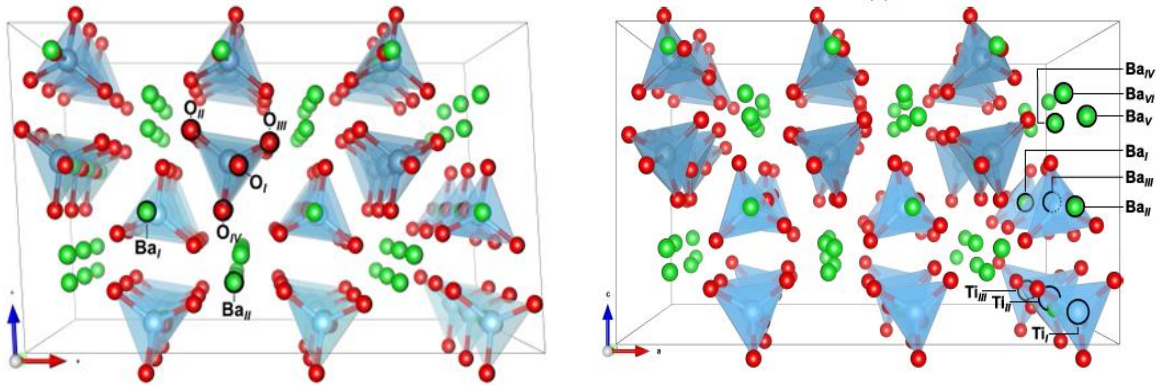
#### **1.4. APPLICATIONS OF NANOMATERIALS**

- ◆ The nanomaterials field includes subfields which develop (or) study materials having unique properties arising from their nano scale dimensions.
- ◆ Interface and colloidal science has given rise to many materials which may be useful in nanotechnology, such as carbon nano tubes and other fullerenes, and various nanoparticles and nano rods. Nanomaterials with fast ion transport are related also to nano ionic's, nano electronics. [5]
- ◆ Nano scale materials are can also be used for bulk applications; most present commercial application of nanotechnology of this flavour.
- ◆ Progress has been made in using these materials for medical application; see nano medicine.
- ◆ Nano scale materials are sometimes used in solar cells which combats the cost of traditional silicon solar cells.
- ◆ Development of applications incorporating semiconductor nanoparticles to be used in the next generation of products, such as display technology, lighting, solar cells and biological imaging; see quantum dots. [6,7]

- ◆ Nanoparticle research is currently an area of intense scientific research, due to a wide application in biomedical, potential and electronic fields. Processing properties and cost issues are pushing down the particle sizes of powders are used in a variety of industries. Fine, ultrafine and nano structured powders are now critical to advancement in numerous applications.

### **1.5 BARIUM TITANIUM OXIDE ( $\text{Ba}_2\text{TiO}_4$ )**

Barium titanium oxide is the white colour precipitate. It has two phases: a low-temperature ( $\beta$ ) phase with  $p2_1/n$  symmetry and a high temperature ( $\alpha$ ) phase with  $p2_1nb$  symmetry [8]. The structure of  $\text{Ba}_2\text{TiO}_4$  is usually among the titanates because its titanium atoms sit in a four-oxygen tetrahedron rather than a six – oxygen octahedron [9]. Barium Titanium Oxides is highly insoluble thermally barium source suitable for glass, optic and ceramic application. However, certain perovskite structured oxides are electronically conductive finding application in the cathode of solid fuel cells and oxygen generation systems. Barium titanium oxide is available in nanopowder.



**Fig. 1.1 Structure of a)  $\beta$  - $\text{Ba}_2\text{TiO}_4$  ( $3 \rightarrow 3 \rightarrow 1$  supercell) and b)  $\alpha$  -  $\text{Ba}_2\text{TiO}_4$  ( $3 \rightarrow 1 \rightarrow 1$  supercell) with Ba, Ti and O ions represented as green, blue and red spheres respectively and  $\text{TiO}_4$  tetrahedra in blue.**

Barium Titanium Oxide is a common electronic ceramic material which shows high dielectric and ferroelectric properties [9]. Due to its high dielectric constant, low dielectric loss and excellent ferroelectric property, it is used in multilayer ceramic capacitors, positive temperature coefficient of resistivity thermistors, dynamic random-access memory. It has been known that high dielectric constant with low dielectric loss and good temperature stability can be attained by the addition of dopants [10].

## 1.6 ZINC OXIDE

Zinc oxide (ZnO) [11,12] is a wide bandgap (3.4 eV at room temperature) semiconductor that is desirable for many applications. It is attractive for forming various forms of nanostructures, such as nanorods, nanowires, and nanobelts [13]. Alloying with MgO or CdO respectively increases or decreases the bandgap energy



of ZnO[14]. Transparent transistors fabricated from ZnO have been reported [15]. With its high exciton binding energy, ZnO is good candidate for room temperature UV lasers [16]. Its large piezoelectric constant is promising for ultrasonic transducers [17]. ZnO is transparent and electrically conductive, making it an ideal material for solar cell windows [18]. One of the major commercial applications of ZnO is the production of varistors [19]. ZnO varistors have high non-ohmic voltage-current characteristics, which originate from grain boundaries between ZnO grains. The mineral form of ZnO can be found in nature and is known as Zincite.

## **1.7 APPLICATIONS**

The exploration of the compounds for commercial purposes has occurred over the past about hundred years in many versions.

Cds materials employed in photo conducting cells to detect radiation in the spectral region which extends from the near infrared gamma radiation. Ba, Cds, CdTe, CdSe and alloys have all been observed to lase under electron beam excitation at low temperature.

Amplification of ultrasonic waves occurs when the drift velocity of optically excited electrons exceeds the velocity of sound in a crystal. The absorption of solar radiation of low energies can be affected by the inclusion of suitable impurities which permit two step optical processes in addition to valence to conduction band transition [20].

## 1.8 PRESENT STUDY

In the present study, we have made an attempt to prepare pure and zinc doped  $\text{Ba}_2\text{Tio}_4$  nanoparticles by microwave assisted solvothermal method. The prepared samples were annealed (pure, 5wt% and 10wt%  $\text{Zn}^{2+}$  doped) at  $600^\circ\text{C}$  and characterized by PXRD and DC conductivity. The results obtained were reported and discussed herein.

## CHAPTER - II

### 2. LITERATURE REVIEW AND METHODS

#### 2.1 LITERATURE REVIEW

A. BEAUGER et al [21] prepared Barium Titanium Oxide concentration is the calcine is less than 1 or 2wt%. For concentration greater than this  $\text{Ba}_2\text{TiO}_4$  inhabits the growth of Barium Titanium Oxide grains, shifts the Curie point towards low temperature, decreases dielectric constant and causes large fluctuations in  $\tan \delta$  curves. After sintering the discs were metalized and connections were welded on each face. The dielectric characteristics of the condenser thus obtained. The frequency range & the relative dielectric constant were measured over the temperature range  $-55^\circ\text{C}$  to  $140^\circ\text{C}$ .

S.J. LEE et al [22] prepared pure and doped Barium Titanium Oxide powders have been synthesized by an ethylene glycol, polymerization complexation route. The Ethylene glycol content affected the crystallization behavior and powder morphology. Barium Titanium Oxide powder requires longer holding times or higher temperature to be crystallized from the amorphous phase. In Barium Titanium Oxide the phase transformation between the low temperature monoclinic symmetry to high temperature orthorhombic symmetry was observed by dilatometry.

ADAM J. M. SLAY et al [23] synthesized  $\text{Ba}_2\text{TiO}_4$  suggests highly unfavorable intrinsic defect formation energies. These studies have shown that the  $\text{Ba}_2\text{TiO}_4$  structure can be described as a series of isolated  $\text{TiO}_4$  tetrahedra separated by Ba ions which occupy 7 and 8 coordinate sites.  $\text{Ba}_2\text{TiO}_4$ , is a hygroscopic material and particularly at elevated temperatures, tends to decompose on contact with humid air.

TAKASHI GOTO et al [24] prepared Ba, TiO, thick films by laser chemical vapour deposition using Ba- and Ti- dipivaloylmethanate precursors. Single - phase  $\text{Ba}_2\text{TiO}_4$ , thick films were obtained at 845-946 K and Ba / Ti source molar ratio 2: 4,  $\text{Ba}_2\text{TiO}_4$ , thick films consisted of truncated grains. Ba; TiO, thick films showed a columnar growth and their deposition rates were 72 and 132 umh, respectively. The total pressure in the chamber was maintained at 400pa. Deposition was conducted for 600 S.

POOJA M. PANCHMATIA et al [25] synthesized  $\text{Ba}_2\text{TiO}_4$ , material is a diverse group of oxometalates with over 50 known crystal structures. It contains isolated or linked tetrahedral structures. Barium titanium oxide has a barium rich Future, studies have suggested that the phase transformation is stable. Temperature can be affected by grain size and impurity effects with some reports showing the lower temperature synthesis routes can stabilise the high temperature orthorhombic

$\alpha'$  - phase. However, over prior work on the barium containing perovskite systems. The undoped  $\text{Ba}_2\text{TiO}_4$  is to be a poor oxide ion conductor.

YOSHINORI SAITO et al [26] synthesized barium titanium oxide by adding barium carbonate to barium titanate.  $\text{Ba}_2\text{TiO}_4$  has a stable phase at high temperatures and it becomes unstable in the temperature range of 1000 ° C or lower.  $\text{Ba}_2\text{TiO}_4$ , can be used as a  $\text{CO}_2$  adsorbent at high temperature. SHAWN O DONNELL et al [27] prepared barium titanium oxide by heating at 1250° C for 2 hour. The thermal stability of  $\text{Ba}_2\text{TiO}_4$ , and the phase transformation between the low temperature monoclinic polymorph and the high temperature orthorhombic polymorph were examined by X - ray diffraction. A martensitic transformation from  $\beta$ - $\text{Ba}_2\text{TiO}_4$ , to  $\alpha$ -  $\text{Ba}_2\text{TiO}_4$  starts at - 100° C and ends at -220° C in the heating process.

## **2.2. PREPARATION OF BARIUM TITANIUM OXIDE NANOPARTICLES**

In this chapter we provide the simple method available for the preparation of nano materials in general, along with the preparation of manganese doped  $\text{Ba}_2\text{TiO}_4$  nanoparticles considered in the present study

## **2.3. SOLVOTHERMAL METHOD**

In solvothermal method a domestic microwave oven is used for the preparation of sample leads to what is generally known as dielectric heating. The frequencies allocated for the solvothermal method are 918MHz and 2.4GHz with the

letter frequency being most often used. The latter is also applied in domestic microwave ovens. [28, 29].

It is only recently that microwave irradiation has been used in the synthesis of inorganic nanoparticles and keeps showing rapid growth in its application to material science. Compared with conventional heating methods, the solvothermal method presents a more rapid and simultaneous environment for the formation of nanoparticles due to fast homogeneous heating effects of microwave irradiation. Therefore, the solvothermal method has advantages for short reaction times, high energy efficiency and the ability to induce the formation of particles with small size, narrow size distribution and high purity.

## **2.4. MATERIALS USED**

Analytical reagent AR grade Barium acetate, titanium tetrachloride, urea and manganese acetate, along with distilled water were used for the preparation of pure  $\text{Ba}_2\text{TiO}_4$  nanoparticles.

## **2.5. PREPARATION OF PURE AND $\text{Zn}^{2+}$ DOPED (5wt% and 10wt%)**

### **$\text{Ba}_2\text{TiO}_4$ .**

The analytical reagent barium acetate, titanium tetrachloride, manganese acetate, urea and distilled water were used for the preparation of barium oxide nanoparticles. First we prepared the pure  $\text{Ba}_2\text{TiO}_4$  nanoparticles, barium acetate,

titanium tetrachloride and urea were taken in the molecular ratio 1: 3 and dissolved in 100ml of distilled water. The white colour precipitate was obtained. The colloidal precipitate was cooled to room temperature naturally and washed several times with double distilled water and then with acetone to remove the organic impurities. The sample was then filtered and dried in atmospheric air and collected as a yield [30]. The collected samples were further annealed at 600°C for 1hr. The annealed samples were collected as yield.

$$\text{Yield percentage} = \frac{\text{product mass}}{\text{sum of reactants}} \times 100$$

## **2.6. REACTION MECHANISM**

The reaction mechanism of microwave assisted synthesis of nanoparticles is summarized as below. First the strong complexation between barium acetate, titanium tetrachloride and urea lead to the formation of barium titanium urea. Secondly the barium titanium urea complexes undergo thermal decomposition under microwave irradiation to be produced at nanoparticles. The reaction mechanism of manganese acetate and urea in the solution to produce the manganese acetate urea complex decomposes at a given temperature under auto generous pressure produced by microwaves. Water acts as both reaction media and dispersion media which can effectively absorb and stabilize the surface of the particle and favour the production of small size nanoparticles.

In order to improve the ordered the prepared samples were annealed at 600° C for One hour. The annealed samples were used for characterization studies. The required amount of the substance (A) was estimated by using the formula.

$$A = \frac{MXV}{1000}$$

Where,

M is the molecular weight of the substance

X is the concentration in molar units.

V is the volume of the solvent 100ml in the present work.

The reactions were found to be fast in the three samples and highly yielding with microwave the mass of the product nano powders prepared were measured accurately. The yield percentage was calculated using the relation.



## **CHAPTER – III**

### **3. INSTRUMENTATION TECHNIQUES**

#### **3.1. POWDER X - RAY DIFFRACTION**

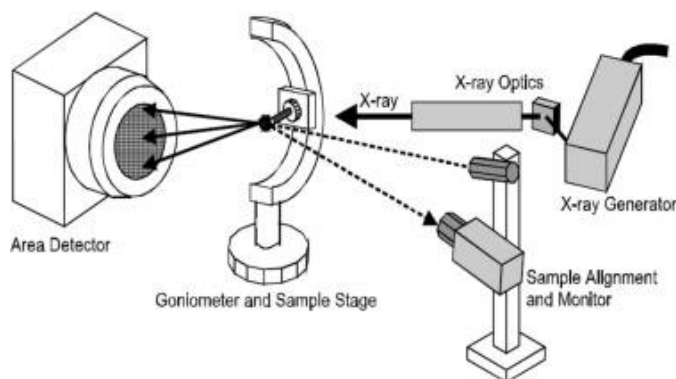
X - ray powder diffraction is a rapid analytical technique primarily used for phase identification of a crystalline material and can provide information on unit cell dimensions. The analyzed material can provide information on unit cell dimensions.

X - ray diffraction is based on constructive interference of monochromatic x rays and a crystalline sample. These x - rays are generated by a cathode ray tube, filtered to produce monochromatic radiation collimated to concentrate and directed towards the sample. The interaction of the incident rays with the sample produces constructive interference when condition satisfy Bragg's law ( $n\lambda = 2d \sin \theta$ ). The Law relate the wavelength of electromagnetic radiation to the diffraction angle and the lattice spacing in the crystalline sample. [31] These diffracted x - rays are then detected, processed and counted. By scanning the sample through range of  $2\theta$  angle all possible diffraction direction of the lattice should be attained due to random of the powdered material. Typically, this is achieved by comparison of d - spacing with standard reference pattern.

Powder x - ray diffraction is a scientific technique using x - ray, neutron, or electron diffraction on powder or microcrystalline samples for structural

characterization of materials. An instrument dedicated to performing such powder measurement is called a powder diffractometer. Powder diffraction stands in contrast to single crystal diffraction techniques, which work best with a single, well-ordered crystal. A diffractometer produces waves at a known frequency, which is determined by their source. [32,33]

X - ray diffractometer consists of three basic elements x - ray tube, a sample holder and an x - ray detect. X - rays are generated in a cathode tube by heating a filament to produce electrons, accelerating the electron towards the target by applying a voltage and bombarding the target material with electrons. Filtering by foils or crystal monochromator is required to produce monochromatic x - rays needed for diffraction when the geometry of the incident x - rays impinging the samples satisfies the Bragg equation constructive interference occurs. A detector records and processes this x - ray signal and converts the signal to a count rate which is then output to a device such as printer or computer monitor.[33]



**Figure 3.1 Powder X-ray diffraction**

The geometry of an x - ray diffractometer is such that the sample rotates in the path of the collimated x - ray beam at an angle while the x - ray detector is mounted on an arm collected the diffracted x - rays and rotates at an angle of  $2\theta$ .

### **3.1.1 APPLICATION OF PXRD**

X- ray powder diffraction is most widely used for identification of unknown crystalline materials. Determination of unknown solid is critical to studies in geology, environmental science, material science, engineering and biology [24].

- Characterization of crystalline materials.
- Determination of unit cell dimension.
- Measurement of sample purity.

With specialized techniques XRD can be used to

- ◆ Determination of crystal structures using rietveld refinement.
- ◆ Identification of model amount of minerals, characterize thin film samples.
- ◆ By determining dislocation density and quality of the film by rocking curve measurements. Measuring super lattices in multilayered epitaxial structures [25].
- ◆ Make textural measurements such as the orientation of grains in polycrystalline samples.
- ◆ Determining lattice mismatch between film and substrate and interfering stress and strain.

- ◆ Determining the thickness, roughness and density to the film using glancing incidence x - ray reflectivity measurement.

### **3.2. AC CONDUCTIVITY**

Every material has a unique set of electrical characteristics that are dependent on its dielectric properties. Accurate measurements of these properties can provide scientists and engineers with valuable information to properly incorporate the material into its intended application for more solid designs or to monitor a manufacturing process for improved quality control. A dielectric materials measurement can provide critical design parameter information for many electronics applications. For example, the dielectric loss of a cable insulator, the electrical impedance of a substrate, or the frequency of a dielectric resonator can be related to its dielectric properties [26].

Dielectric and magnetic characteristics of ceramic materials are of increasing importance in the field of solidstate electronics and modem communication devices. Ferroelectrics have vast applications from microwave to radio frequencies due to their importance. An important property of these materials is their high dielectric constant and high electrical resistance compared to normal dielectric materials [27]. The dielectric constant is the ratio of the permittivity of a substance to the permittivity of free space. As the dielectric constant increases, the electric flux density increases, if all other factors remain unchanged. The conductivity of a

polycrystalline ceramic material is complex in nature. The real part of the conductivity ( $\sigma$ ), called the polarization conductivity, is a function of frequency and temperature. It is supposed to follow power law as [28].



**3.2 Fig. LCR meter**

The AC electrical measurements were carried out using a conventional two probe setup. The powdered samples were pelletized using a hydraulic press by applying a pressure of about 4 tones. Graphite coating was given to the flat surfaces of pellets to make it more conductive. Before taking the measurement the pellets were annealed in the holder assembly up to 150<sup>0</sup> C in order to remove the moisture content. Agilent LCR meter was used to measure the capacitance (C) and the dielectric loss factor ( $\tan \delta$ ) in the temperature range of 40 -150<sup>0</sup> C with an accuracy of  $\pm 1^0$  C. The measurements were done while cooling Air capacitance ( $C_{\text{air}}$ ) was measured maintaining the dimensions equal to that of the pellet. Variation of air

capacitance with temperature was negligible hence it was measured only for the room temperature. The dielectric constant ( $\epsilon_r$ ) Was calculated using the relation [29].

$$\epsilon_r = C_p / C_{air}$$

The AC electrical conductivity of samples was calculated using the relation

$$\sigma_{ac} = \omega \epsilon_0 \epsilon_r \tan\delta$$

Where,  $\omega$  is the angular frequency, ( $\omega = 2\pi f$ ;  $f=100\text{Hz}$  to  $1\text{MHz}$ )

$\epsilon_0$  is the permittivity of free space ( $8.854 \times 10^{-12} \text{ F/m}$ ),

$\epsilon_r$  is the dielectric constant,

$\tan\delta$  is the loss tangent.

AC conductivity measurements are widely used to overcome certain difficulties in measurements. Among these are polarization effects in ionic conductors and electrolytes, barriers at internal surfaces and contact resistance. Assuming that the sample is represented by a parallel combination of capacitance and resistance, the values of series resistance and capacitance then describe the unknown directly. A voltage is applied to two flat plates immersed in the solution, and the resulting current is measured from Ohm's Law, the conductance= current / voltage. Actually there are many practical difficulties. Use of voltage would soon

deplete the ions near the plates, causing polarization, and a higher actual resistance.

This can mostly be overcome by using ac voltage [30].

## CHAPTER IV

### RESULT AND DISCUSSION

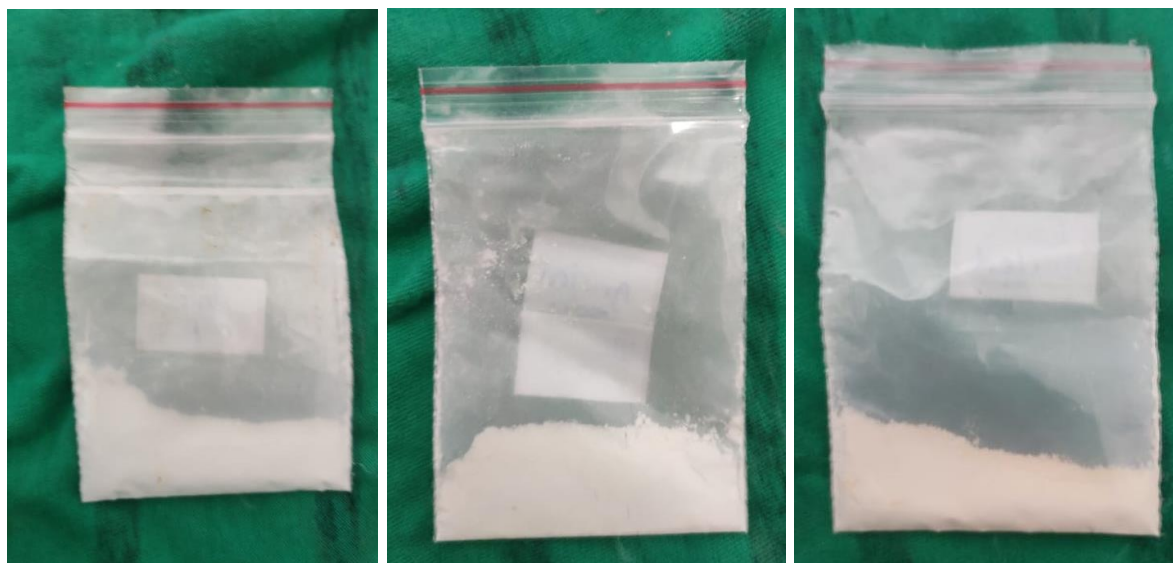
#### 4.1 COLOR AND PHOTOGRAPH OF PREPARED NANOPARTICLES

There are number of methods available for the synthesis of nanomaterials such as sol - gel, solid state reaction, precipitation, and microwave assisted solvothermal method. Among these methods, microwave assisted solvothermal technique is a simple, rapid and versatile method for the synthesis of nanoparticles. The average time taken to prepare all the samples in the present study was observed to be 15 to 18 minutes. The reactions were found to be fast with the microwave. The colloidal form of samples were collected and washed with distilled water for five times and then with acetone. The photographs of prepared samples were shown in the Figure 4.1. The colors of the prepared samples were noted. By this method high quality, fine white color nano powder has been obtained. Then the prepared nanoparticles were annealed 600<sup>0</sup>C temperature. There is a small change in the color of the proposed samples. Table 4.1 shows the colors for the prepared samples. Fig 4.1 Photograph of the prepared samples From left (i) as prepared Ba<sub>2</sub>TiO<sub>4</sub>, (ii) 5% Zn<sup>2+</sup> doped (iii) 10% Zn<sup>2+</sup> doped Ba<sub>2</sub>TiO<sub>4</sub>

**Table 4.1 Reaction time, yield percentage and colour**



Name of the sample	Reaction time (min)	colour	Yield percentage
Pure Ba <sub>2</sub> TiO <sub>4</sub>	17	white	12.34
5wt% Zn <sup>2+</sup> doped Ba <sub>2</sub> TiO <sub>4</sub>	15	Pale brown	10.80
10wt% Zn <sup>2+</sup> doped Ba <sub>2</sub> TiO <sub>4</sub>	10	Brown	10.91



**Figure 4.1 Photographs of Pure Ba<sub>2</sub>TiO<sub>4</sub>, 5wt% Zn<sup>2+</sup> doped Ba<sub>2</sub>TiO<sub>4</sub>, nano particle and 10%wt Zn<sup>2+</sup> doped Ba<sub>2</sub>TiO<sub>4</sub> nano particles**

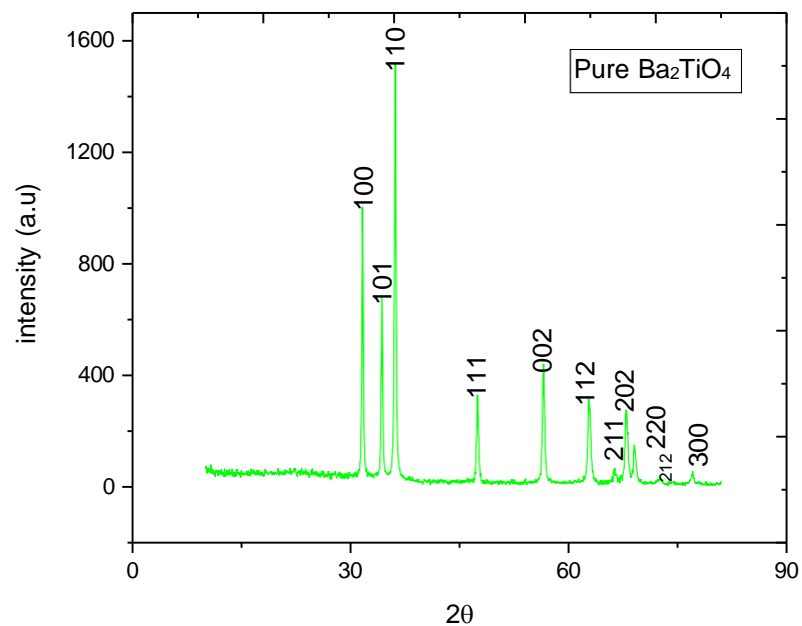
## 4.2 PXRD ANALYSIS

The PXRD pattern of pure  $\text{Ba}_2\text{TiO}_4$ , 5wt% and 10wt% Zinc doped nanoparticles are provided in figures 4.3-4.5. All the different peaks present in the PXRD pattern pure  $\text{Ba}_2\text{TiO}_4$  nanoparticles can be indexed using the data available in the JCPDS file (50-0626). From the PXRD pattern, the average crystallite sizes were determined by the Scherer formula and the lattice parameter were determined. From the indexed PXRD pattern the structure of the prepared pure  $\text{Ba}_2\text{TiO}_4$  nanoparticles were found to be monoclinic. The obtained grain sizes are shown in table 4.2.

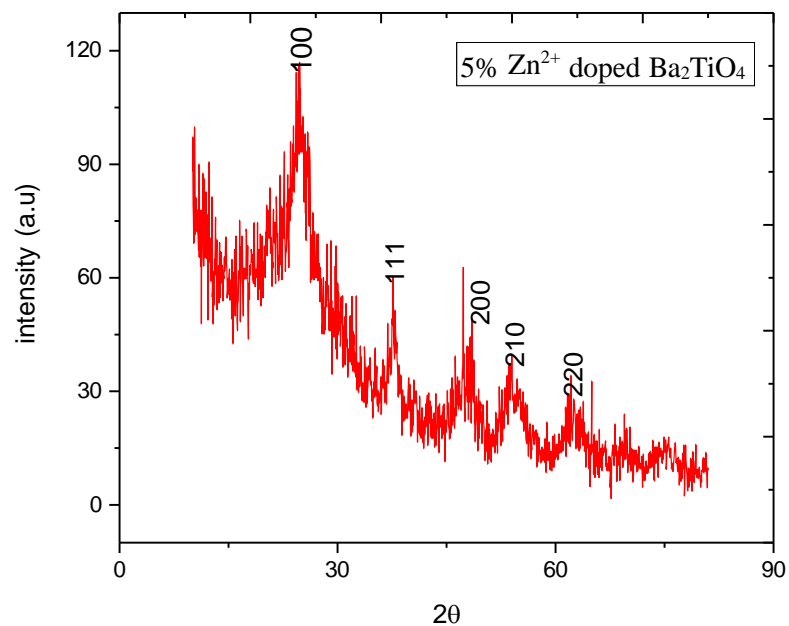
X-ray diffraction (XRD) is a powerful technique used to uniquely identify the crystalline phase present in materials and to measure the structural properties (strain state, grain size, epitaxy, phase composition, preferred orientation and defect structure) of these phases. XRD is also used to determine the thickness of thin films and multi layers and atomic arrangements in amorphous materials (including polymers) and at interfaces. The study of crystal structure by X-ray diffraction was discovered in the year 1912 by Bragg. X-ray diffraction method is widely used for characterization of composite materials.

**Table 4.2 Particle size of prepared nanoparticles**

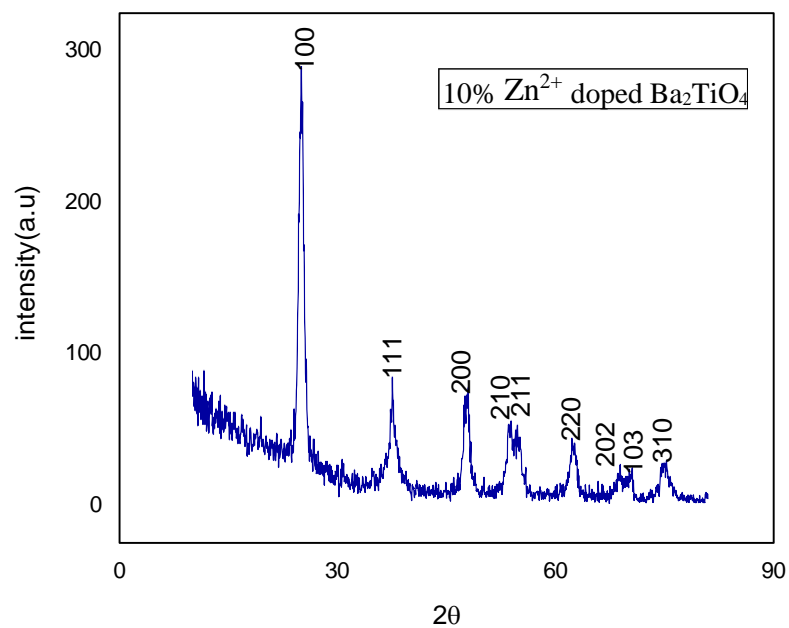
Name of the Sample	Particle size from PXRD (nm)
Pure Ba <sub>2</sub> TiO <sub>4</sub>	31.69
5wt% Zn <sup>2+</sup> doped Ba <sub>2</sub> TiO <sub>4</sub>	23.61
10wt% Zn <sup>2+</sup> doped Ba <sub>2</sub> TiO <sub>4</sub>	13.93



**Figure 4.2 PXRD pattern of pure Ba<sub>2</sub>TiO<sub>4</sub> nanoparticles.**



**Figure 4.3 PXRD pattern of 5.0wt% Zn<sup>2+</sup> doped Ba<sub>2</sub>TiO<sub>4</sub> nanoparticles.**



**Figure 4.4 PXRD pattern of 10wt% Zn<sup>2+</sup> doped Ba<sub>2</sub>TiO<sub>4</sub> nanoparticles.**

### 4.3 AC CONDUCTIVITY MEASUREMENT

The behavior of electrical parameters such as dielectric constant, dielectric loss factor and AC electrical conductivity with respect to frequency and temperature is shown in figures 4.5-4.7. It was observed that for all the prepared samples. The AC conductivity increases with increase in temperature and decreases with increase in frequency.

The variation of AC electrical conductivity with frequency and temperature are shown in figures 4.5-4.7. It was observed that for all the prepared samples the AC electrical conductivity increases with increase in temperature and frequency. Here the AC electrical conductivity increases with frequency and hence the mechanism of conduction in the prepared samples is localized conduction mechanism. Also the conduction process was due to small polaron hopping since the conductivity increases with frequency. The conductivity of the material is low at low temperatures because the mobility of ion is very low at low temperatures.

The observed values of AC electrical parameters such as dielectric constant ( $\epsilon_r$ ), dielectric loss ( $\tan \delta$ ) and Ac conductivity are shown in Tables 4.3-4.5.

**Table 4.3 AC conductivity of pure Ba<sub>2</sub>TiO<sub>4</sub> nanoparticles**

<b>Temperature</b>	<b><math>\sigma_{ac}</math> (<math>10^{-7}</math> mho/m)</b>				
	<b>100Hz</b>	<b>1KHz</b>	<b>10KHz</b>	<b>100KHz</b>	<b>1MHz</b>
40	1.02	1.37	2.39	7.45	36.2
50	1.2	1.70	3.89	9.88	38.1
60	1.52	2.16	4.57	11.7	48.5
70	2.1	2.80	5.28	15.6	56.2
80	2.2	2.96	5.75	17	64.8
90	2.28	3.11	5.88	18.5	68.5
100	2.48	3.22	6.25	19.4	78
110	2.53	3.39	6.28	19.6	83.2
120	2.7	3.60	6.46	20	88.1
130	3.13	3.97	6.82	20.5	89.5
140	3.46	4.29	7.22	21.2	92.8
150	4.16	4.95	8.08	22.6	98.7

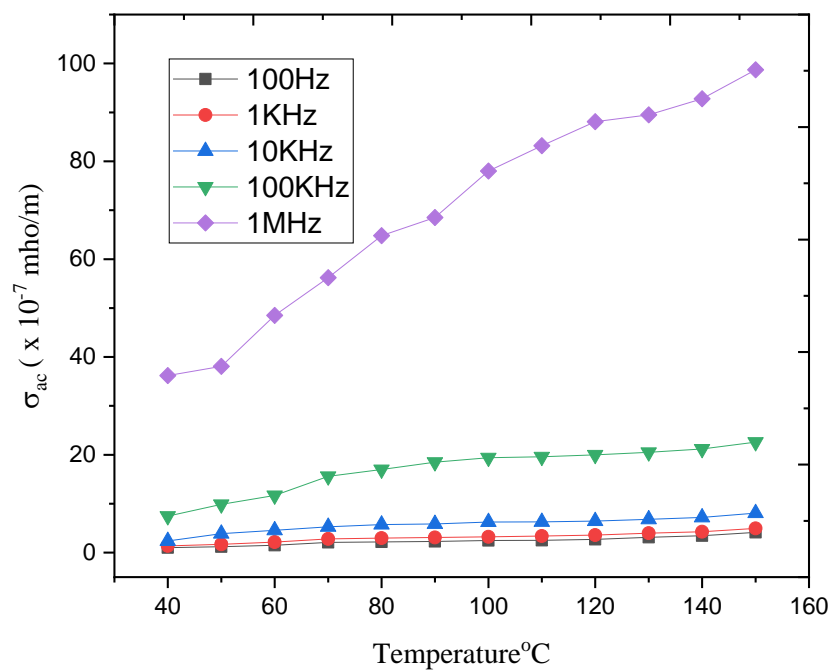
**Table 4.4 AC Conductivity for 5wt% of Zn<sup>2+</sup> doped Ba<sub>2</sub>TiO<sub>4</sub> nanoparticles**

<b>Temperature</b>	<b><math>\sigma_{ac}</math> (10<sup>-7</sup> mho/m)</b>				
	<b>100Hz</b>	<b>1KHz</b>	<b>10KHz</b>	<b>100KHz</b>	<b>1MHz</b>
40	0.0782	0.283	0.597	2.02	16
50	0.0794	0.297	0.64	2.32	17.7
60	0.0833	0.317	0.659	2.41	19.5
70	0.0982	0.334	0.691	2.55	19.8
80	0.117	0.347	0.806	2.72	20.2
90	0.162	0.374	0.897	3.14	20.9
100	0.204	0.408	0.99	3.28	21.4
110	0.211	0.484	1.09	3.43	21.6
120	0.245	0.56	1.21	4.24	21.8
130	0.266	0.646	1.35	4.66	23
140	0.336	0.876	1.88	8.71	32.22
150	0.429	1.09	2.14	9.45	34.5

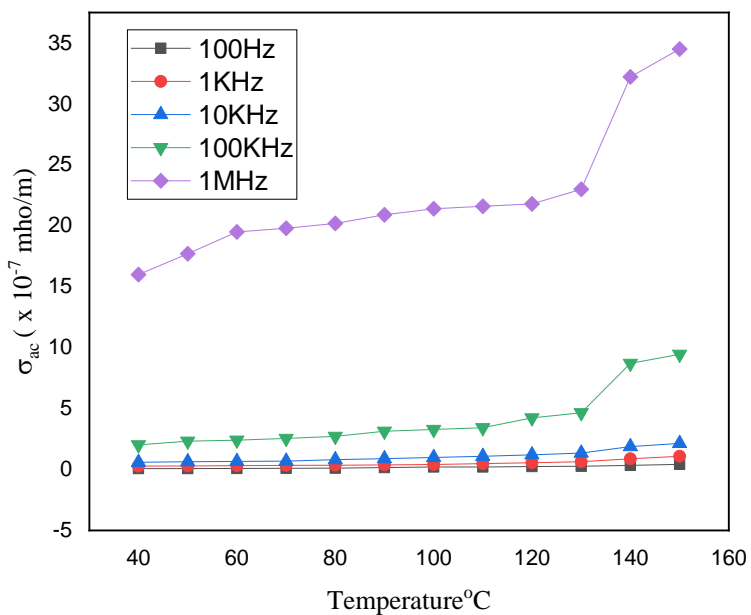
#### 4.5 AC conductivity for 10wt% Zn<sup>2+</sup> doped Ba<sub>2</sub>TiO<sub>4</sub> nanoparticles

Temperature	$\sigma_{ac}$ (10 <sup>-7</sup> mho/m)				
	100Hz	1KHz	10KHz	100KHz	1MHz
40	0.0168	0.173	0.485	1.92	12
50	0.0194	0.208	0.612	2.03	12.9
60	0.0224	0.219	0.646	2.21	13.6
70	0.024	0.243	0.763	3.25	15.6
80	0.0269	0.267	0.812	3.53	16.4
90	0.0285	0.283	0.82	3.54	16.6
100	0.0312	0.297	0.823	3.53	17.8
110	0.0447	0.312	0.84	3.75	18.8
120	0.0514	0.338	0.908	3.91	19
130	0.0452	0.345	0.94	3.97	19.4
140	0.0619	0.356	1.40	5.39	20.6
150	0.0774	0.378	2.31	5.66	21.3

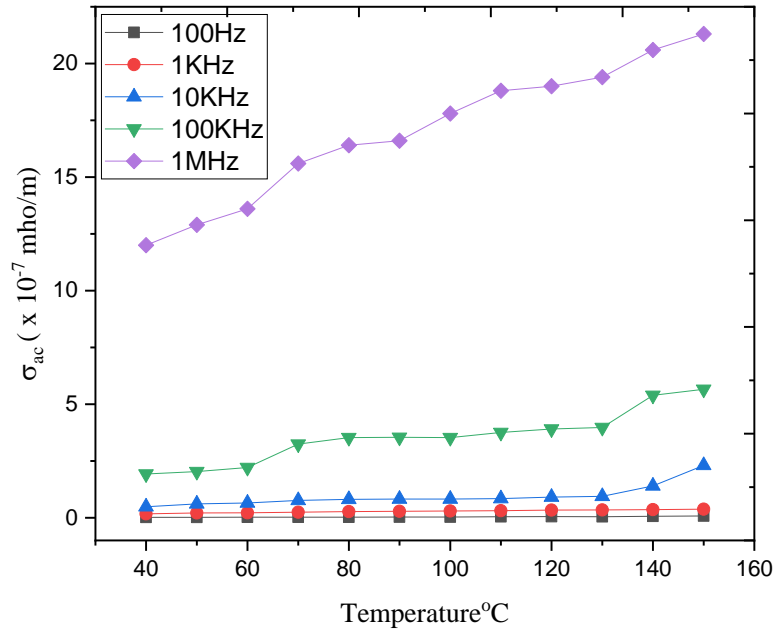




**Figure 4.5 AC electrical conductivity for pure Ba<sub>2</sub>TiO<sub>4</sub> nanoparticles**



**Figure 4.6 AC electrical conductivity for 5wt% of Zn<sup>2+</sup> doped Ba<sub>2</sub>TiO<sub>4</sub> nanoparticles**



**Figure 4.7 AC electrical conductivity for 10wt% of Zn<sup>2+</sup> doped Ba<sub>2</sub>TiO<sub>4</sub> nanoparticles**

**Table4.6. Dielectric constant for pure Ba<sub>2</sub>TiO<sub>4</sub> nanoparticles**

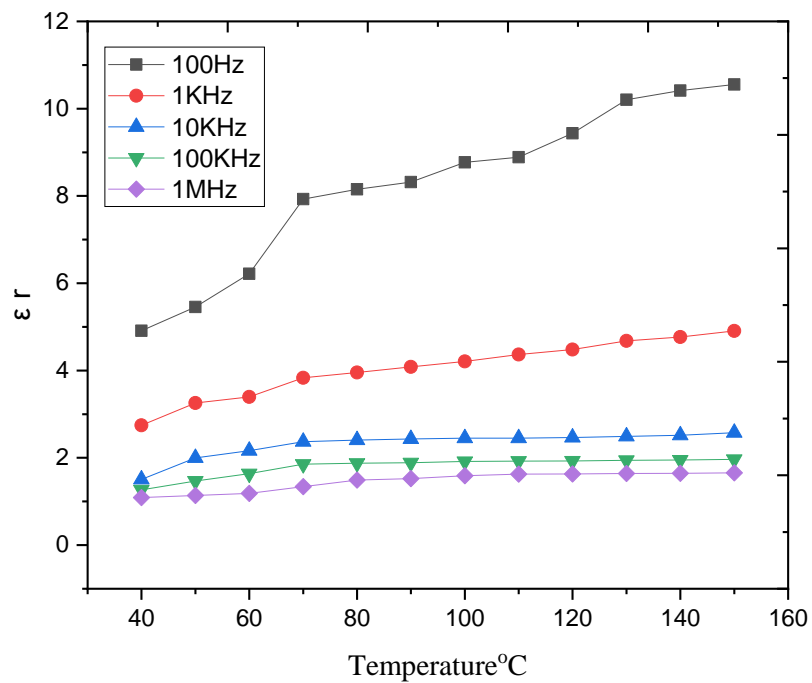
Temperature	100 Hz	1KHz	10KHz	100KHz	1MHz
40	4.912186	2.744615	1.506876	1.26647	1.088615
50	5.456061	3.257778	1.996562	1.467213	1.138835
60	6.216614	3.397391	2.16251	1.638552	1.184607
70	7.929581	3.833257	2.369583	1.854291	1.34106
80	8.151313	3.956702	2.40608	1.876263	1.489994
90	8.316316	4.084933	2.432246	1.886747	1.522816
100	8.768906	4.207209	2.4499	1.915581	1.590448
110	8.886606	4.368654	2.451869	1.925458	1.62827
120	9.434873	4.480589	2.464283	1.9298	1.629153
130	10.20562	4.680691	2.490448	1.941572	1.640853
140	10.41276	4.76979	2.51758	1.950494	1.646173
150	10.55491	4.909147	2.576786	1.965326	1.654496

**Table 4.7 Dielectric constant for 5wt% doped Ba<sub>2</sub>TiO<sub>4</sub> nanoparticles**

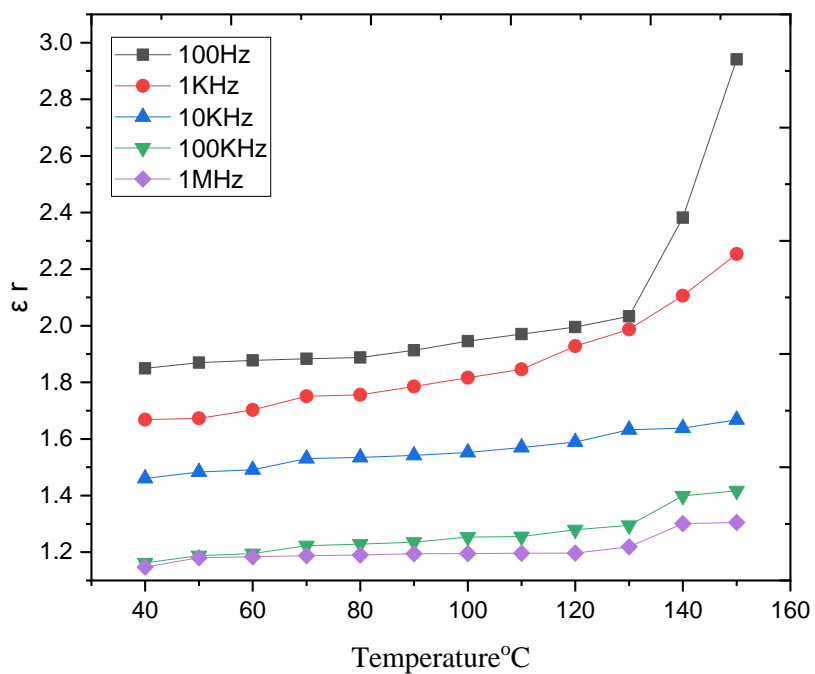
<b>Temperature</b>	<b>100 Hz</b>	<b>1KHz</b>	<b>10KHz</b>	<b>100KHz</b>	<b>1MHz</b>
40	1.849384	1.667991	1.460415	1.162427	1.147601
50	1.869721	1.672662	1.483322	1.187855	1.180147
60	1.877527	1.702992	1.491192	1.19511	1.183969
70	1.883421	1.751031	1.530911	1.222776	1.187837
80	1.887932	1.755953	1.534556	1.228748	1.190165
90	1.913147	1.785471	1.541799	1.235093	1.194332
100	1.945295	1.816589	1.552226	1.253523	1.195151
110	1.970592	1.84596	1.569806	1.255109	1.196221
120	1.995146	1.927943	1.589143	1.279626	1.196717
130	2.033199	1.986566	1.632306	1.29451	1.219044
140	2.381921	2.106179	1.638149	1.398601	1.300719
150	2.941114	2.253306	1.667694	1.416983	1.304999

**Table 4.8 Dielectric constant for 10wt% doped nanoparticles**

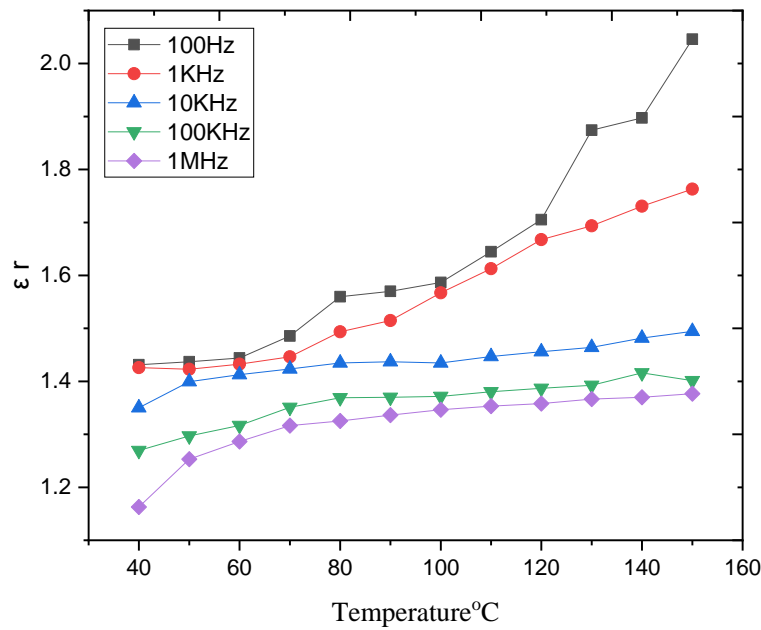
<b>Temperature</b>	<b>100 Hz</b>	<b>1KHz</b>	<b>10KHz</b>	<b>100KHz</b>	<b>1MHz</b>
40	1.431419	1.426065	1.350142	1.269513	1.162847
50	1.436902	1.422836	1.399305	1.29681	1.253126
60	1.444149	1.432543	1.412779	1.316636	1.286362
70	1.485632	1.446442	1.423536	1.350939	1.316341
80	1.55976	1.493719	1.434841	1.369108	1.325169
90	1.570076	1.514876	1.4371	1.369956	1.336393
100	1.58666	1.567214	1.434621	1.371508	1.346337
110	1.644616	1.612594	1.446882	1.380345	1.353271
120	1.705239	1.667637	1.45598	1.38704	1.3581
130	1.874265	1.693787	1.464103	1.392532	1.36651
140	1.897417	1.730741	1.481596	1.416174	1.369865
150	2.045987	1.762987	1.494365	1.401357	1.376611



**Figure 4.8 Pure  $\text{Ba}_2\text{TiO}_4$  nanoparticles**



**Figure.4.9 5wt%  $\text{Zn}^{2+}$  doped nanoparticles**



**Fig. 4.10 10wt% doped**

**Table 4.9 Dielectric loss pure Ba<sub>2</sub>TiO<sub>4</sub> nanoparticles**

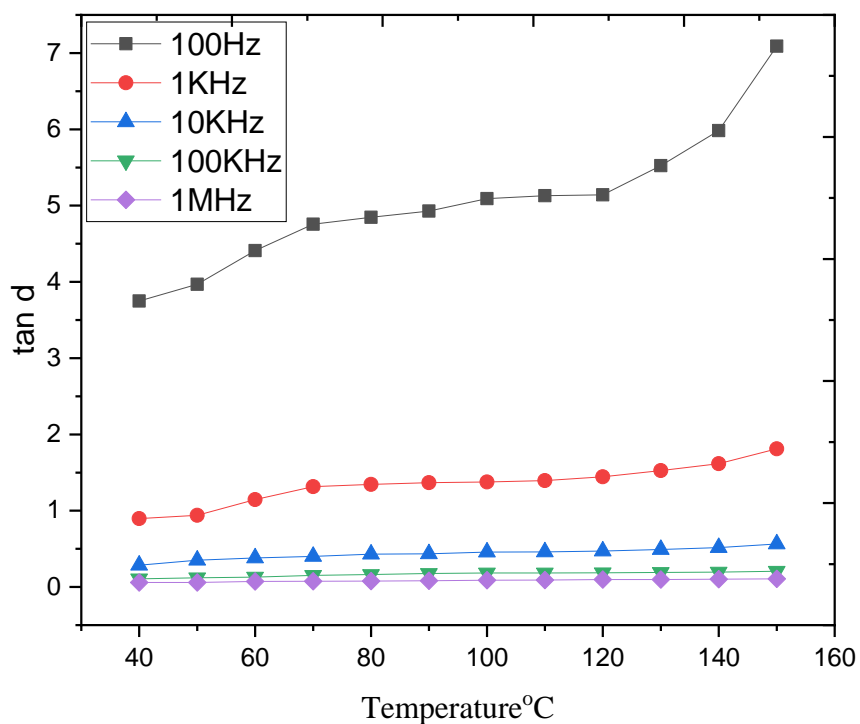
Temperature	100Hz	1KHz	10KHz	100KHz	1MHz
40	3.7496	0.8965	0.2848	0.1058	0.0598
50	3.9687	0.9386	0.3504	0.1211	0.0602
60	4.4109	1.14565	0.3802	0.1289	0.0737
70	4.7568	1.3157	0.4011	0.1512	0.07535
80	4.8463	1.3449	0.4297	0.16298	0.078254
90	4.92863	1.36848	0.43483	0.17591	0.08092
100	5.09098	1.37576	0.458643	0.182597	0.088187
110	5.1302	1.39471	0.46046	0.183564	0.091925
120	5.1417	1.44426	0.471558	0.186561	0.097271
130	5.52349	1.525555	0.492563	0.190046	0.098135
140	5.98309	1.61676	0.515628	0.195482	0.101425
150	7.08929	1.81207	0.564009	0.2069	0.107347

**Table4.10. Dielectric loss for 5wt% Zn<sup>2+</sup> doped Ba<sub>2</sub>TiO<sub>4</sub> nanoparticles**

<b>Temperature</b>	<b>100Hz</b>	<b>1KHz</b>	<b>10KHz</b>	<b>100KHz</b>	<b>1MHz</b>
40	1.3754	0.3057	0.07354	0.0312	0.02512
50	1.3823	0.31962	0.07762	0.0351	0.02704
60	1.4154	0.33512	0.07952	0.0362	0.02957
70	1.6345	0.34312	0.08124	0.0375	0.030038
80	1.70032	0.355786	0.09453	0.0398	0.030503
90	2.19806	0.376522	0.10466	0.0457	0.03141
100	2.2857	0.404185	0.11471	0.0471	0.032157
110	2.30946	0.471483	0.12463	0.0492	0.032556
120	2.37432	0.52247	0.13641	0.0596	0.0327
130	2.47171	0.585105	0.14824	0.0648	0.033892
140	2.53507	0.748073	0.206064	0.112089	0.044509
150	2.62147	0.87402	0.23043	0.119993	0.047499

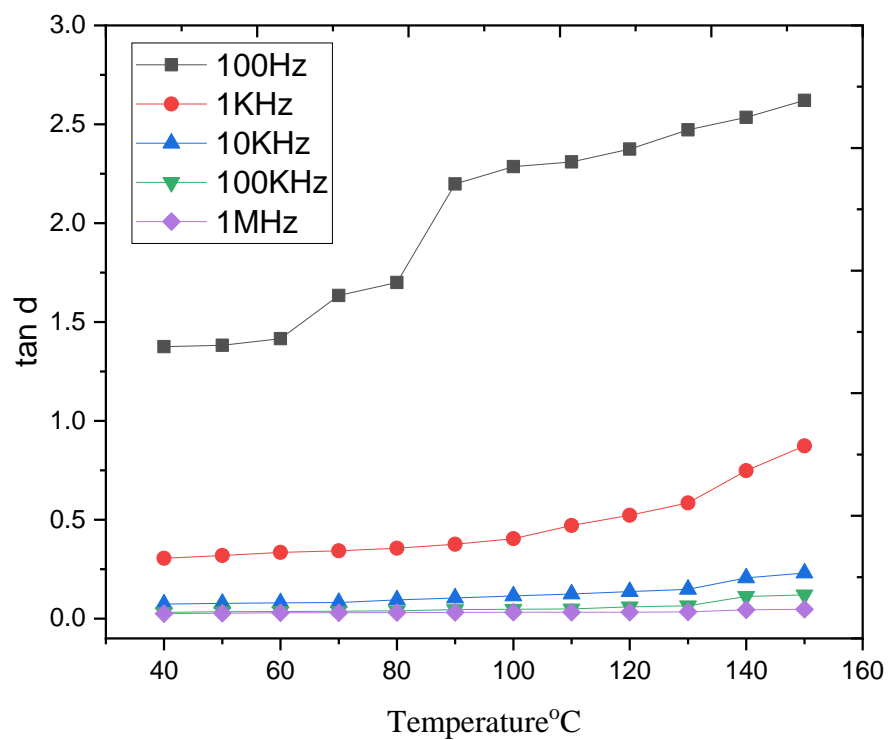
**Table 4.11. Dielectric loss for 10wt% doped  $\text{Zn}^{2+}$  nanoparticles**

Temperature	100Hz	1KHz	10KHz	100KHz	1MHz
40	0.2353	0.2251	0.0652	0.0291	0.01711
50	0.2654	0.2609	0.07957	0.0301	0.01802
60	0.2987	0.2709	0.08163	0.0312	0.0183
70	0.30986	0.2882	0.092912	0.04321	0.01996
80	0.32176	0.308537	0.093728	0.046401	0.020739
90	0.3431	0.309496	0.094519	0.046503	0.020907
100	0.35317	0.310017	0.095005	0.046301	0.022442
110	0.43342	0.320287	0.096159	0.048919	0.023571
120	0.48919	0.335379	0.10331	0.050669	0.023771
130	0.542667	0.337379	0.106336	0.051309	0.024286
140	0.58665	0.34053	0.156259	0.068433	0.025703
150	0.680527	0.355591	0.25581	0.072642	0.026423

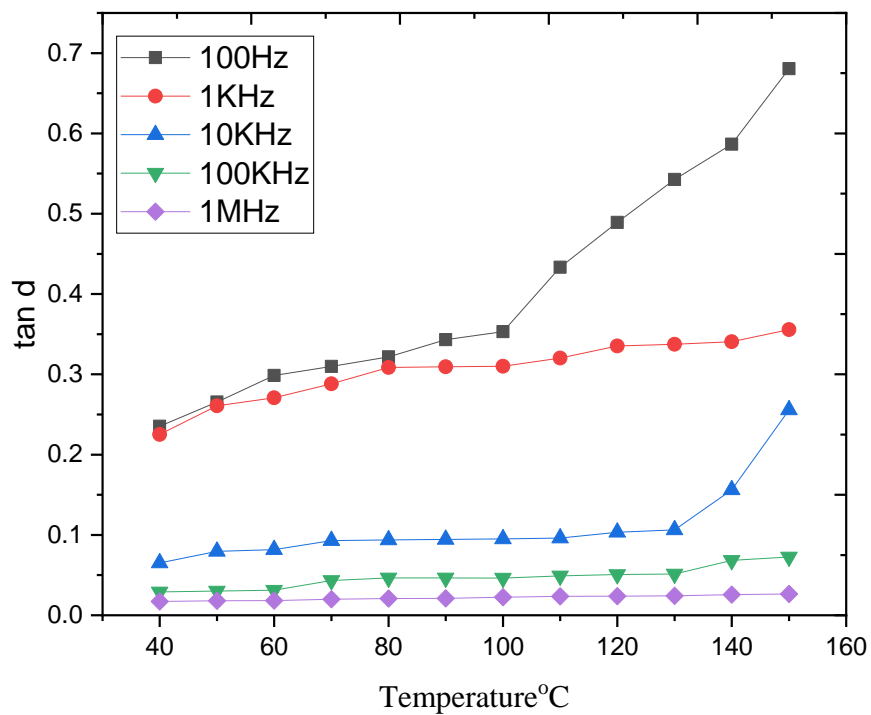


**Figure. 4.11 Dielectric loss pattern for Pure  $\text{Ba}_2\text{TiO}_4$  nanoparticles**





**Fig. Dielectric loss pattern for 5wt% Zn<sup>2+</sup> doped nanoparticles**



**Fig. Dielectric loss pattern for 10wt% Zn<sup>2+</sup> doped nanoparticles**

## **CHAPTER V**

### **SUMMARY AND CONCLUSION**

Nanoscience and Nanotechnology is an interdisciplinary area of research and it is interfacing with various scientific disciplines like physics, chemistry, biology, material science and engineering. Nanomaterials are used as safer and efficient product in agriculture, industry, medicine, transport and communication.

In the present study, pure  $\text{Ba}_2\text{TiO}_4$  nanoparticles were prepared by simple solvothermal method with a domestic microwave oven. The prepared samples were characterized by making Powder x - ray diffraction (PXRD) and AC electrical measurements.

The identity of the material was confirmed and the crystalline size was determined by using Debye - Scherrer's formula. The PXRD patterns indicate the nano crystalline nature of the prepared samples also indicate that the prepared samples were monoclinic in structure. Particle size of 31.69nm, 23.61nm, 13.93nm for pure, 5wt%, 10wt% respectively.

The prepared samples were pelletized and dielectric measurements were carried out for various temperatures with various frequencies 100Hz, 1 KHz, 10 KHz, 100 KHz and 1 MHz. The dielectric parameter viz. Dielectric constant and dielectric loss factor increase with increase in temperature and decrease with

increase in frequency. The AC electrical conductivity values have been found to be increase with increase in temperature and frequency. The major application of  $\text{Zn}^{2+}$  doped  $\text{Ba}_2\text{TiO}_4$  nanoparticles are used in electro-optical devices, dielectric amplifiers, varistors, pyroelectric sensors, micro-capacitors, and piezoelectric devices are the included applications.

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