SYNTHESIS AND CHARACTERIZATION OF $BiFeO_3$ BY SOL-GEL METHOD

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DEDICATED TO
MY PARENTS
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CERTIFICATE

I hereby declare that the report entitled **"SYNTHESIS AND CHARACTERIZATION OF BiFe0$_3$ BY SOL – GEL METHOD"** is an authentic record of my own work carried out as Partial fulfillment of the requirements for the award of degree of M.Tech (Materials science and Metallurgical Engineering) at Thapar University, Patiala, under the guidance of Dr. Puneet Sharma (Assistant Professor) during January to July 2011.

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(AKSHAY KUMAR)

ABSTRACT

In the present work multiferroic $BiFeO_3$ (BFO) powder were successfully synthesized by sol–gel method. The calcinations of the powders were carried out at 450^0C, 500^0C and 550^0C. The phase characterization of powders reveals the single phase bimuth ferrite in the sample calcined at 550^0C. Further the single phase bismuth ferrite powder was sintered at 600^0C. The dielectric and *P-E* loop measurement was carried in sintered sample. Dielectric studies in the sintered sample showed that dielectric constant is higher in the lower frequency region and decrease with increase in frequency and become all most constant at higher frequency region. Dielectric losses measurements with respect to frequency clearly reveals that the loss was maximum in the lower frequency region become decrases at higher frequency. *P-E* loop measurement showed no saturation in the samples upto the electric field of 55kV/cm. SEM studies of the sintered $BiFeO_3$ at 600^0C showed the grain size of the order of 68 nm.

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CHAPTER -1

INTRODUCTION

1.1Background of Multiferroics:

Electricity and magnetism were combined into one common discipline in the 19th century, culminating in the Maxwell equations. But electric and magnetic ordering in solids is most often considered separately and usually with good reason the electric charges of electrons and ions are responsible for the charge effects, whereas electron spins govern magnetic properties. There are, however, cases where these degrees of freedom couple strongly. For example, in the new, large field of spintronics, the effects of spins on the transport properties of solids (and vice versa) allow the possibility to control one by the other.

The finding of a strong coupling of magnetic and electric degrees of freedom in insulators can be traced back to Pierre Curie, but the real beginning of this field started in 1959 with a short remark by Landau and Lifshitz in a volume of their Course of Theoretical Physics [1]. "Let us point out two more phenomena, which, in principle, could exist. One is piezomagnetism, which consists of linear coupling between a magnetic field in a solid and a deformation (analogous to piezoelectricity).

The other is a linear coupling between magnetic and electric fields in a media, which would cause, for example, a magnetization proportional to an electric field. Both these phenomena could exist for certain classes of magneto crystalline symmetry [2]. A new twist in this problem was the idea that not only can strong cross-coupling of responses exist in solids (i.e., the appearance of magnetization M in an electric field E, or the inverse effect of electric polarization P generated by the application of magnetic field H), but that there may exist systems in which two types of ordering ferromagnetism, the spontaneous ordering of orbital and spin magnetic moments, and ferroelectricity, the spontaneous ordering of electric dipole moments can coexist in one material in the absence of external electric and magnetic fields. Schmid called these materials as a multiferroics material [3]. Boracites were probably the first known multiferroics [4], and soon several others were either found in nature, or synthesized artificially [5].

The ME effect was demonstrated and studied in the 1960s in Russia [6], and since then, many so called ’multiferroic’ materials have been identified . However, so far the magnitude and operating temperatures of any observed ME coupling have been too small for applications. In fact, the only known multiferroic material of potential practical interest is bismuth ferrite, $BiFeO_3$ which is actually antiferromagnetism below T_N=370^0C and ferroelectric with a high Curie temperature: Tc = 820^0C [7]. As per definition given by Schmid, multiferroics are single phase materials which simultaneously possess two or more primary ferroic properties. Today the term multiferroic has been expanded to include materials which exhibit any type of long range magnetic ordering, spontaneous electric polarization, and/or ferroelectricity.

1.2 Introduction to Multiferroic Materials:

In a ferroelectric material, if the positive and negative electric charges are uniformly separated electric polarization is generated. In multiferroic materials, magnetism and ferroelectricity occur simultaneously and both properties are coupled to each other show in fig1.2. Multiferroic materials can be considered as being materials presenting at least two ferroic states. These ferroic states are ferroelectricity, and ferromagnetism. Thus, as a logical dentition to the term multiferroic, we could use the term multiferroic to any material presenting two of these three properties. However, the most interesting combination was thought to be materials presenting ferroelectricity and ferromagnetism. Hill discussed the conditions required for ferroelectricity and ferromagnetism to be compatible in transition metal oxides, and declared them to be rarely met [8]. Thus, the current trend is that any material presenting simultaneously a polar state and a long range magnetic order is considered as a multiferroic. Multiferroics have been formally defined as materials that exhibit more than one primary ferroic order parameter simultaneously (i.e. in a single phase) [9]. Typical multiferroics belong to the group of the perovskite transition metal oxides, and include rare-earth manganites and ferrites (e.g. $TbMnO_3$, $HoMn_2O_5$, and $LuFe_2O_4$). Other examples are the bismuth alloys $BiFeO_3$ and $BiMnO_3$, and non-oxides such as $BaNiF_4$. In the Hexaferrites $BaMg_{22}Fe_{12}O_{22}$ this compound is part of a class of multiferroics in which the ferroelectric polarization is generated by its unusual magnetic structure. The electric polarization is induced by so-called spin spirals, or cyclic variations in the orientation of the different magnetic moments along the crystal [10].

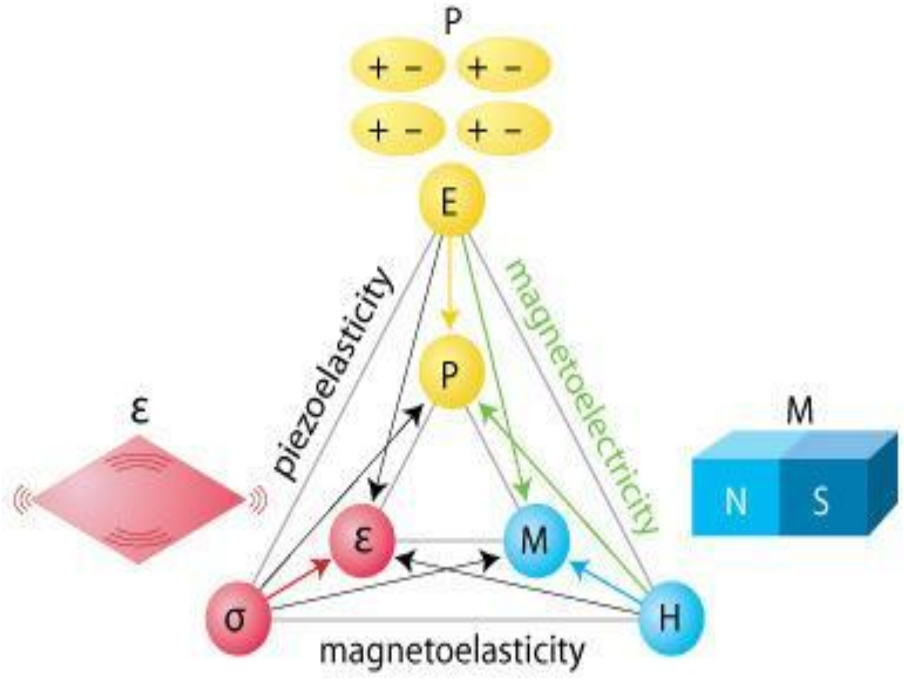

Fig 1.1 Phases exist in Multiferroics[11]

1.3 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 a corresponding localized spin, or magnetic moment. Exchange interactions between the localized moments lead to magnetic order. The situation with ferroelectrics is quite different.

There are several different microscopic sources off erroelectricity, and accordingly one can have different types of multiferroics. Generally, there are two groups of multiferroics. The first group, which can be called type-I multiferroics, contains those materials in which ferroelectricity and magnetism have different sources and appear largely independently of one another, though there is some coupling between them. In these materials, ferroelectricity typically appears at higher temperatures than magnetism, and the spontaneous polarization P is often rather large (of order 10-100μC/cm^2).

Examples are $BiFeO_3$and $YMnO_3$. The second group, which we can call type-II multiferroics, is the relatively recently discovered materials [11] in which magnetism causes ferroelectricity, implying a strong coupling between the two. However, the polarization in these materials is usually much smaller ($\sim 10^{-2} \mu C/cm^2$). Many groups are also investigating composite multiferroics that consist of known magnets and ferroelectrics in the form of multilayer and self-organized nanostructures [12].

1.3.1Type-I multiferroics:

Type-I multiferroics are “older” and more numerous. These are often good ferroelectrics, and the critical temperatures of the magnetic and ferroelectric transitions can be well above room temperature. Unfortunately, the coupling between magnetism and ferroelectricity in these materials is usually rather weak. The materials challenge for this group of multiferroics is to keep all their positive features, but enhance this coupling. As we will see later, the opposite problem exists for type-II multiferroics.One can single out several different subclasses of type-I multiferroics, depending on the mechanism of ferroelectricity in them. We will focus on four of the major subclasses, but there are certainly others.

1.3.1.1 Perovskite types Multiferroic:

Probably the best-known ferroelectrics are the perovskite like $BaTiO_{3,}Pb(ZrTi)O_3$(PZT). Magnetic and other properties of oxides and related compounds, and also many ferroelectrics [13] demonstrates that there seems to be mutual exclusion of magnetism and ferroelectricity in perovskite: Whereas for magnetism one needs partially filled d shells of a transition metal, practically all ferroelectric perovskite contain transition metal ions with an empty d shell, such as Ti^{4+}, Ta^{5+}, W^{6+}. Ferroelectricity in these systems is caused by the off-centre shifts of the transition metal ion, which forms strong covalent bonds with one (or three) oxygen’s, using their empty d states. And somehow, the presence of real d electrons in d^nconfigurations of magnetic transition metals suppresses this process, preventing ferroelectricity in magnetic perovskite. This so called” d^0 vs. d^n problem” was one of the first to be studied theoretically at the beginning of the recent revival of multiferroics [14].

1.3.1.2 Ferroelectricity Due to Lone Pairs:

In $BiFeO_3$, and probably in $BiMnO_3$and $PbVO_3$, $Bi^{3+}$and Pb^{2+}play the major role in the origin of ferroelectricity. In these ions, there are two outer 6s electrons that do not participate in chemical bonds. They are called lone pairs. They have a high polarizability the condition required for ferroelectricity in the classical description. More microscopically one can explain the origin of ferroelectricity in these compounds by ordering of these lone pairs in one direction. Apparently this is what happens in many Bi- and Pb-containing ferroelectrics and multiferroics such as $BiFeO_3$, but it also helps to improve the ferroelectric properties of $Pb\ (Zr_xTi_{1-x})\ O_3$.

In usual perovskite-based ferroelectrics like $BaTiO_3$, the ferroelectric distortion occurs due to the displacement of B-site cation (Ti) with respect to the oxygen octahedral cage. Here the transition metal ion (Ti in $BaTiO_3$) requires an empty “d” shell since the ferroelectric displacement occurs due to the hopping of electrons between Ti “d” and O p atoms. This normally excludes any net magnetic moment because magnetism requires partially filled “d” shells. However, partially filled “d” shell on the B-site reduces the tendency of perovskite to display ferroelectricity .

In order for the coexistence of magnetism and ferroelectricity (multiferroic), one possible mechanism is lone-pair driven[15] where the A-site drives the displacement and partially filled “d” shell on the B-site contributes to the magnetism. Examples include $BiFeO_3$, $BiMnO_3$, and $PbVO_3$ [16]. In the above materials, the A-site cation (Bi^{3+}, Pb^{2+}) has a stereochemically active $6s^2$ lone-pair which causes the 6p (empty) orbital of Bi to come closer in energy to the 2p orbitals of oxygen. This leads to hybridization between the 6p and 2p orbitals and drives the off-centring of the cation towards the neighbouring anion resulting in ferroelectricity.

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1.3.1.3 Ferroelectricity Due to Charge Ordering:

One more mechanism that can lead to ferroelectricity and to type-I multiferroicity can be charge ordering, often observed in transition metal compounds, especially those formally containing transition metal ions with different valence. If, after charge ordering, both sites and bonds turn out to be in equivalent, this can lead to ferroelectricity [17]. Such an order can occur in a compound containing ions of mixed valence and with geometrical or magnetic frustration. These ions form a polar arrangement, causing improper ferroelectricity (i.e. no ionic displacement). If magnetic ions are present, a coexisting magnetic order can be established and may be coupled to ferroelectricity.

Examples: One prominent example for a charge ordered multiferroic is $LuFe_2O_4$, which shows improper ferroelectricity below 330K [18]. The arrangements of the electrons arise from the charge frustration on a triangular lattice with the mixed valence state of Fe^{2+} and Fe^{3+} ions. Ferromagnetic behaviour occurs below 240 K.

1.3.1.4 Geometrically Frustrated Multiferroics:

Geometric frustrated multiferroicity is related to a structural phase transition at high temperature. Several compounds belong to this important class of multiferroics K_2SeO_4, Cs_2Cd_{I4}, and hexagonal $RMnO_3$.These systems are proto-typical multiferroics which can be understood by competition between local interactions on several ion sites. For example, in hexagonal manganites h-$RMnO_3$(R=Ho-Lu, Y), the ferroelectric polarization at high temperature is correlated to lattice distortions through off-centering of ions. Geometric frustration gives rise to novel spin arrangements at low temperature: The spins order in a variety of non-collinear, e.g. (in-plane) triangular to relieve the geometric frustration.

The coexistence of ferroelectric and magnetic order occurs together with a strong coupling between two disparate order parameters. The mechanism of the ferroelectric ordering in hexagonal $RMnO_3$ is still questionable in scientific community and must be understood before a comprehensive picture of multiferroic phenomena in spin frustrated systems can be built. It is still matter of debate whether the geometric distortion is the origin of the electric polarization or whether the off-centring of Mn ions also contributes to the polarization. Physical properties of geometric multiferroics are dominated by the behaviour of the d-shell electrons (e.g. orbitals) and of the rare earth elements with an unfilled f-shell. Hexagonal manganites show the largest deviation from perovskite structure due to the small size of rare-earth ion. Although geometrically frustrated multiferroics exhibit a simple chemistry, they provide a unique set of physical properties, such as rich phase diagrams or multiple frustrations. The strong coupling between ferroelectric and magnetic orders is represented by an anomaly in the static dielectric constant at magnetic phase transitions. Geometric frustrated ferroelectrics are prime candidates for device memory applications.

1.3.1.5 Magnetically Driven Ferroelectricity:

Magnetically driven multiferroics are insulating materials, mostly oxides, in which macroscopic electric polarization is induced by magnetic long-range order. A necessary but not sufficient condition for the appearance of spontaneous electric polarization is the absence of inversion symmetry. In these materials inversion symmetry is broken by magnetic ordering. Such a symmetry breaking often occurs in so-called frustrated magnets, where competing interactions between spins favour unconventional magnetic orders. The microscopic mechanisms of magnetically induced ferroelectricity involve the polarization of electronic orbitals and relative displacement of ions in response to magnetic ordering.

Many multiferroics show the cycloid spiral ordering, in which spins rotate around an axis perpendicular to the propagation vector of the spiral. The induced electric polarization is orthogonal to the propagation vector and lies in the spiral plane. An abrupt change of the spiral plane induced by magnetic field is results in the corresponding rotation of the polarization vector. In $DyMnO_3$ this transition is accompanied by the 600% increase of dielectric constant. The microscopic mechanism of magneto electric coupling in spiral multiferroics involves spin-orbit coupling.

1.3.2 Type-II Multiferroics:

1.3.2.1 Magnetic Multiferroics

The biggest excitement nowadays is caused by the discovery of a novel class of multiferroics in which ferroelectricity exists only in a magnetically ordered state and is caused by particular type of magnetism [19, 20]. For example, in $TbMnO_3$ magnetic ordering appears at T_{N1}=41K, and at a lower temperature, T_{N2}=28K, the magnetic structure changes. It is only in the low-temperature phase that a nonzero electric polarization appears. Similar behaviour occurs in $TbMn_2O_5$.$TbMnO_3$showed that a magnetic field can strongly influence the electric polarization: e.g., in $TbMnO_3$the polarization rotates (or "flops") by $90^o$when a critical magnetic field is applied along a certain direction [19]. In $TbMn_2O_5$[20] the influence o an external field is even stronger: the polarization changes sign with field, and a field alternating between +1.5 and -1.5 Tesla leads to corresponding oscillations in the polarization. Since the discovery of these materials, a number of other type-II multiferroics with strong magneto electric coupling have been discovered and studied.

1.3.2.2 Multiferroic with collinear magnetic structures:

The second group of magnetically driven ferroelectrics are those in which ferroelectricity appears in collinear magnetic structures that are all magnetic moments aligned along a particular axis without the necessary involvement of the spin-orbit interaction. Polarization can appear in these materials as a consequence of exchange striction because the magnetic coupling varies with the atomic positions. The simplest example, found in Ca_3CoMnO_6 [21]. Ca_3CoMnO_6consists of one-dimensional chains of alternating $Co^{2+}$and Mn^{4+}ions. At high temperature the distances between the ions along the chain are the same, the chain has inversion symmetry, and polarization is absent. Magnetic ordering, however, breaks inversion symmetry: the spins form a ↑↑↓↓ type magnetic structure. Due to an exchange striction the distortion of ferro and antiferro bonds (↑↑and↑↓) is different, the material becomes ferroelectric [22].

In the case of Ca_3CoMnO_6, exchange striction arises from transition metal ions with a different valence ($Co^{2+}$and Mn^{4+}). One can, however, get the same effect even for identical magnetic ions, when one takes into account that the exchange in transition metal oxides usually occurs via intermediate oxygen's and depends on both the distance between the metal ions and the metal-oxygen-metal bond angle. In $RMnO_3$perovskite where R is a small rare earth, the Mn magnetic order in the basal plane is of the type ↑↑↓↓. As proposed by Sergienko,Sen, and Dagotto [23], exchange striction in this case can cause the oxygen ions to shift perpendicular to the Mn-Mn bonds, which produces a polarization along the direction of the shift.

1.4 Synthesis of Multiferroics Material by Different Route:

- Solid state reaction method
- Hydrothermal Method
- Chemical route Method
- Sol- Gel Method
- Co- precipitation Method
- Autocombustion Method

1.4.1 Solid State Reaction:

A solid state reaction is also called as conventional ceramic route method is a synthesis method used for the preparation of polycrystalline ceramic materials. The procedure for synthesis of materials is described as follows:The reactants are ground and mixed usually in an agate mortar and pressed into pellets.

- The pellets are then heated in a chosen atmosphere at temperatures 1000-1500 ^{0}C, or close to molten point of the sample.
- The heating and mixing is repeated until a homogeneous product formation is complete or when the crystallinity of the material is sufficient.

The complete procedure is summarized in Fig 1.5 (i) The reaction rate is limited by nucleation of the product phase and diffusion of ions through the newly formed product layer.Therefore the reaction is promoted by a large surface area which is increased by repeated grinding and mixing and by elevated

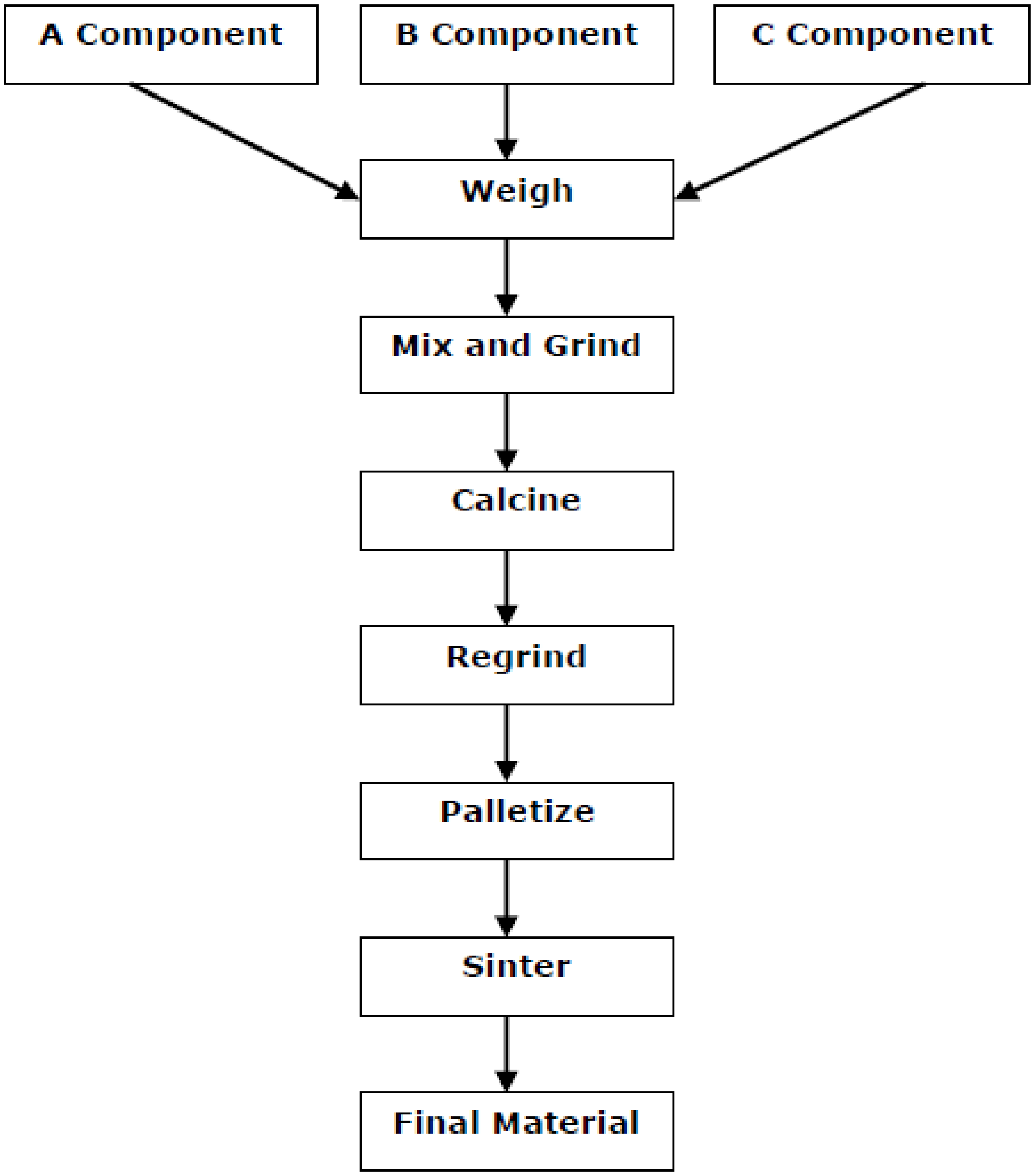

Fig.1.2 sample preparation solid state reaction

1.4.2 Hydrothermal Method:

Hydrothermal method is also termed as hydrothermal synthesis. This method can be used for the synthesis of single crystal depends on the solubility of minerals in hot water under high pressure. For hydrothermal research a high temperature pressure apparatus called "autoclave" is needed. This method involves H_2O both as a catalyst and occasionally as a component of solid phases in the synthesis at elevated temperature (>100^0C) and pressure (a few atmosphere). The material we have to prepare by hydrothermal method must have accurate known composition, homogeneous, pure and fine. In the series of low temperature techniques the hydrothermal method is very versatile for the synthesis of nano phase materials. The synthesis reaction were carried out in a temperature range of 100^0C to 1000^0C or more and pressure range is 1 atmosphere to several thousand atmosphere, the reactions can be carried out in water hence this method is known as “Hydrothermal Method”.

The important advantages of this method are mentioned as:

- With small increase in temperature kinetics of, reactions are greatly enhanced.
- New meta stable products formed.
- High purity products are formed from impure feed stocks.
- This method is cost effective because no precipitants are needed in many cases.
- Minimization of pollution due to closed system conditions and reagents are recycled.

There are few differences between hydrothermal method and other techniques for preparation of powders and processing.

- Powder is directly formed from solution.
- The powder may be anhydrous, crystalline or amorphous depends only on producing of hydrothermal powder temperature.
- It is possible to control particle size by hydrothermal temperature.
- It is possible to control particle shape by starting materials.
- It is also possible to control chemical, composition stiochiometry etc.
- For many cases powder do not need calcinations and milling process.

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1.4.3 Pechini Method (Polymeric Precursor Method):

The polymeric precursor method is also called as pechini method. This method involves complexing of cations in an organic media makes use of low cost precursors and resulting in a homogeneous ion distribution at molecular level. During the synthesis a formation of a polyster resin, during the thermal decomposition of organic material no segregation of cations was observed. This polymeric precursor method has many advantages such as:

- The possibility to work in aqueous solutions with high stiochiometry control.
- Lower temperature process and cost effective technique because of inexpensive precursors and equipments.

1.5.4 Sol Gel Method:

The sol-gel method is also known as wet chemical method or chemical solution deposition. This method has been employed for fabrication of materials such as metal oxide starts from a chemical solution that reacts to produce colloidal particles (sol). A sol is the dispersion of solid particles (~0.1%1μm) in a liquid where only Brownian method suspends the particles. A gel is a state where both liquid and solid are dispersed in each other which presents a solid network containing liquid components.

The sol -gel coating process usually consists of four steps:

- The desired colloidal particles once dispersed in a liquid to form a sol.
- The deposition of sol solution produces the coatings on the substrates by spraying, dipping or spinning.
- The final heat treatments pyrolyze the remaining organic or inorganic components and form an amorphous or crystalline coating.

This sol-gel method consist of two distinct reactions such as hydrolysis of the alcohol groups and condensation of resulting hydroxyl groups. This technique is very much cheap and low temperature technique which allows a fine control on the products chemical composition even in small quantity of dopants like organic dyes and rare earth metals can be introduced in the sol and end up in the final product finely dispersed.

1.4.5 Auto combustion Route:

One of the most widely used and useful method of preparation of ABO3is theCombustion synthesis route using a fuel. The fuel used may be glycine ,citric acid or urea. The precursor materials used for the synthesis of ABO_3 by auto combustion route are ANO_3 and BNO_3 solutions with a certain concentration level. Combustion synthesis is becoming one of the most popular methods for the preparation of a wide variety of materials, .The main advantage of using this technique is due to the simplicity, the broad applicability range, the self-purifying feature due to the high temperatures involved, the possibility of obtaining products in the desired size and shape. This method is rapidly emerging as one of the most-convenient methods for the preparation of oxide materials. An aqueous solution of a redox system constituted by the nitrate ions of the metal precursor, acting as oxidizer, and a fuel like urea, glycine, citric acid or many others is heated up to moderate temperatures and, upon dehydration, the strongly exothermic redox reaction develops, which is generally self-sustaining and provides the energy for the formation of the oxide. Among the various wet chemical processes, the combustion route is found to be simple and cost effective for the synthesis of homogeneous, very fine, crystalline nanopowders without the intermediate decomposition and calcinations steps which other conventional synthesis routes would require.

The process is based on the mixing of reactants that oxidize easily, such as metal nitrates, and an organic fuel acting as a reducing agent. An external heat supply is needed to initiate the ignition of the mixture leading to a self-sustainment of an exothermic redox reaction. In this technique, based on the principles of the propellant chemistry, a thermally induced redox reaction takes place between an oxidant and a fuel. Many types of combustion synthesis exist which differ mainly in the physical state of the reactants or in the combustion modality. By combustion-based methods it is possible to produce monophasic nanopowders with homogeneous microstructure, at lower temperatures or shorter reaction times, if compared with other conventional methods like solid-state synthesis or nitrate method.The various advantages of adopting combustion synthesis as the prime method for the production of $ABO_3$are.

- Self-purifying feature due to the high temperatures involved,
- The possibility of obtaining products in the desired size and shape.
- Simple and cost effective. Homogeneous, very fine crystalline nanopowders without the intermediate decomposition and calcinations steps which other

1.5 Bismuth Ferrite:

Bismuth ferrite, ($BiFeO_3$, BFO) is one of the very few multiferroic materials with a simultaneous coexistence of ferroelectric with high Curie temperature (T_c = 810-830 ^{o}C) and antiferromagnetic order (below T_N= 370 ^{o}C) parameters in perovskite structure. However, these two ordering parameters are mutually exclusive in principle because ferroelectricity and magnetism require different filling states of d shells of transition metal ions. Empty d shells mainly exist in ferroelectricity, while partially filled d shells are required in magnetism.

1.6 Structure of Multiferroics:

Multiferroics materials exhibits perovskite structure as shown in figure 1.3the general formula of multiferroics materials is $ABO_{3,}$where A, B are cations and O(anions) is oxygen which are situated at octahedron site of the lattice. A occupy the corner of the lattice occupy the centre. The some of the important perovskite type multiferroics are $TbMnO_3$, $BiFeO_3$ and $BiMnO_3$.

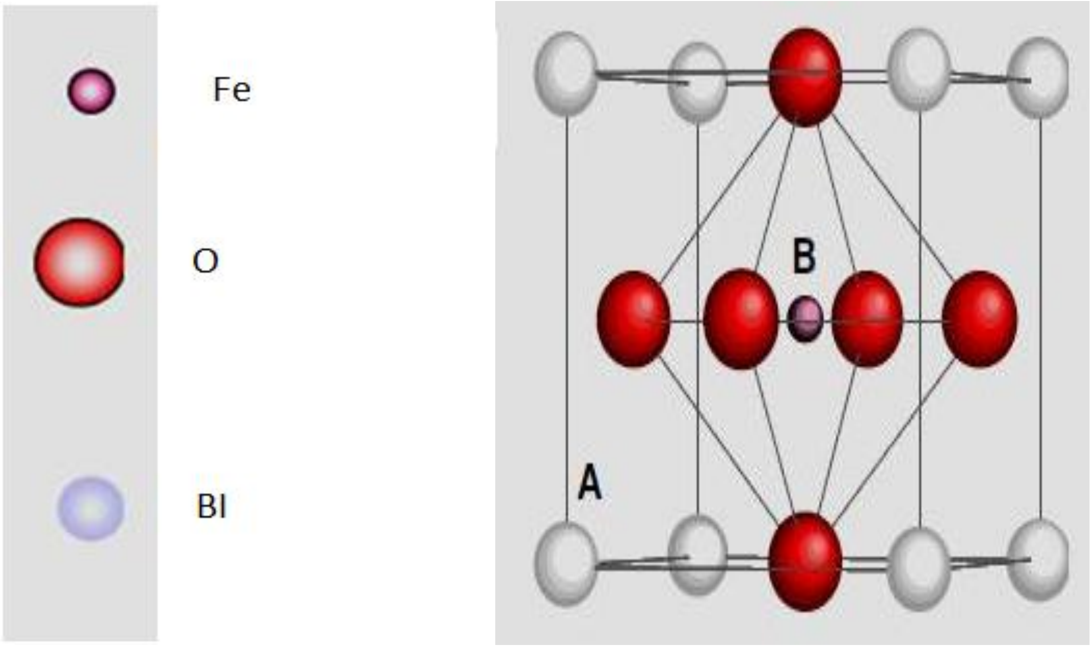

Figure 1.3 The perovskite structure the small B cation (bi) is at the centre of an octahedron of oxygen anions (red). The large A cations (gray) occupy the unit cell corners**.**

1.7Applications:

Multiferroic materials have many applications in bulk form as well as in nano form in electronic devises. Now a day the coating of multiferroics material is being used for better application. Multiferroic composite structures in bulk form are explored for high-sensitivity ac magnetic field sensors and electrically tunable microwave devices such as filters, oscillators and phase shifters (in which the ferri, ferro or antiferromagnetic resonance is tuned electrically instead of magnetically [25]. In multiferroic thin films, the coupled magnetic and ferroelectric order parameters can be exploited for developing magneto electronic devices.

These include novel spintronics devices such as tunnel magneto resistance (TMR) sensors and spin valves with electric field tunable functions. A typical TMR device consists of two layers of ferromagnetic materials separated by a thin tunnel barrier (~2 nm) made of a multiferroic thin film [26]. In such a device, spin transport across the barrier can be electrically tuned. In another configuration, a multiferroic layer can be used as the exchange bias pinning layer. If the antiferromagnetic spin orientations in the multiferroic pinning layer can be electrically tuned, then magneto resistance of the device can be controlled by the applied electric field [27]. One can also explore multiple state memory elements, where data are stored both in the electric and the magnetic polarizations.

CHAPTER 2

LITRETURE REVIEW

Multiferroics materials have recently gained a considerable attention due to it multifunctional device application and underlying new physics. Among the class of multiferroics, $BiFeO_3$ is one of the widely investigated important materials due to it ferroelectric and magnetic transition temperature well above room temperature, which gives the possibility of RT multiferroics. In past years, large efforts have been made to get strong FE and FM polarization together. Researcher has done a considerable work on the processing and microstructral aspect on the properties of $BiFeO_3$. Effect of substitution has been thoroughly investigated on the structural, electric and magnetic properties. In this chapter the important work carried out in last few years related to synthesis of $BiFeO_3$ by sol-gel method and effect of processing condition on the properties has been reviewed.

Y. Duan *et al* 2004[28] A series of $BiFeO_3$ nanopowders were prepared by the sol-gel process. X-ray diffraction analysis shows that their rhombohedral crystal symmetry remains unchanged. However, as the particle size decreases, the edge length of the unit cell increases markedly and the angle between the edges deviates increasingly from 60°. Magnetic measurements show obvious weak ferromagnetism. The magnetization and magnetic susceptibility increase with decreasing particle size. Mössbauer studies reveal that the spin canting angles in the smaller particles are bigger and have a wider distribution. The magnetic structure in these particles is a complicated uncompensated antiferromagnetic spin arrangement.

Jong Kuk Kim *et al.*2005[29] High purity multiferroic $BiFeO_3$ (BFO) powders were synthesized by sol–gel process using bismuth nitrate and iron nitrate as sources.The BFO powders annealed at 600 ^{0}C in nitrogen environment were mainly composed of a rhombohedral $BiFeO_3$ phase (R-phase) with a minor impurity phase of Bi_2O_3. A pure BFO R-phase has been obtained by leaching out the minor Bi_2O_3 phase using diluted nitric acid. A reversible phase transformation of the BFO R-phase has been detected at 836 ^{0}C by a differential thermal analysis. The powders of BFO R Phase exhibits a uniform feature with the particle size of ∽200 nm. The dielectric constant of the BFO R-phase is measured to be ∽15 in the frequency range of 10^4∽10^6 Hz at room temperature.

V. Fruth *et al.*2005[30] Owing to their peculiar characteristics, bismuth oxides are used in various domains, such as microelectronics, sensor technology, optical coatings, transparent ceramic glass manufacturing, etc. Bismuth oxide system exhibit high oxide ionic conductivity and have been proposed as good electrolyte materials for application, such as solid oxide fuel cell (SOFC) and oxygen sensor. Antimony doped and undoped Bi_2O_3 films were deposited onto glass substrate from bismuth nitrate and antimony precursor solutions. As chelating agent polyethyleneglycol (PEG) was used and the above-mentioned precursor solutions were sufficiently viscous. In the present paper, the formation of different phases belonging to Bi–O system during thermal treatments of the Bi-based films is investigated by means of spectroscopic ellipsometry (SE), polarising microscope observation, X-ray diffractometry (XRD), and infrared spectrometry (IR). The thickness and the porosity of the films were evaluated. These preparation techniques, differing mainly in precursor materials and method of deposition, lead to different quality of the resulting films.

Sushmita Ghosh *et al.*2005[31] reported low temperature synthesis of bismuth ferrite nanoparticles by a ferrioxalate precursor method that a simple low temperature synthesis route for preparing $BiFeO_3$ nanopowders through a solution evaporation method. Oxalic acid is used here as the chelating agent. Compared to the conventional solid-state reaction process and co precipitation method, $BiFeO_3$ phase can be formed at a much lower temperature through ferrioxalate precursor method. Further, the oxidation of ferrioxalate precursor by HNO_3 was accompanied by the evolution of various gases (such as CO_2, NO_2 and water vapor) and the gas evolution helped the product to obtain a fine grain structure. Oxalic acid and nitric acid present in the solution play the key role for the synthesis of $BiFeO_3$ at a low temperature.

Hongri Liu *et al.*2006[32]Several methods have been used to prepare ferroelectromagnetic $BiFeO_3$ films. In this paper, we adopted a sol–gel process to fabricate $BiFeO_3$ films on indium tin oxide (ITO)/glass substrates. X-ray diffraction pattern indicated that the samples are randomly oriented. Cross section scanning microscopy showed that the thicknesses of both films were about 1.2 Am and no apparent diffusion between the $BiFeO_3$ films and ITO/glass substrates. Remnant polarization of 2.0 and 1.75 AC/cm2 were identified by the measuring of electric hysteresis loops for the films annealed at 500 and 600 ^{0}C respectively at an applied field of 108 kV/cm. Dielectric property and loss factor were investigated as a function of frequency. In addition, magnetism was detected at 77 K..

Chao Chen, Jinrong Cheng *et al.*2006[33] A low-temperature hydrothermal synthesis route was utilized to fabricate single-phase $BiFeO_3$ (BFO) crystallites. Effects of the initial KOH concentration, reaction temperature and duration time on the phase evolution, the particle size and morphologies of BFOcrystallites were systematically investigated. X-ray diffraction results indicated that perovskite BFO crystallites have been synthesized at the temperature of 200^{0}C using the KOH concentration of 4M. Scanning electron microscopy observation revealed a homogeneous size distribution of submicron BFO powders. The ferroelectric Curie temperature of our hydrothermal BFO crystallites was determined to be 825^{0}C by differential thermal analysis. The hydrothermal reactions to form crystalline BFO powders were discussed based on the dissolution–crystallization process.

W. N. Su *et al.* 2007[34] Synthesized the $BiFeO_3$ ceramics by sol-gel method (BFO-1) and high-pressure synthesis (BFO-2). X-ray diffraction showed that these ceramics are almost of single phase. It is difficult to observe a ferroelectric loop of BFO-1 even at an electric field of 6kV/cm. Compared to BFO-1, the high-pressure synthesized one has higher resistivity, higher density, and better crystallization. Under an applied electric field of 120kV/cm, the values of remnant polarization and the coercive field are 46μC/cm^2 and 73kV/cm, respectively. At room temperature, a magnetic hysteresis loop with enhanced magnetization was observed in BFO-2.

V. A. Khomchenko *et al.* 2007[35] Developed the $Bi_{1-x}AxFeO_3$ ceramics (A=Ca, Sr, Pb) by conventional mixed oxide route. The crystallographic structure of all samples is characterized by the rhombohedral symmetry (space group R3c). The existence of switchable ferroelectric polarization is verified by piezoresponse force microscopy. Magnetic properties of Ca and Sr-doped ceramics are found to reproduce the antiferromagnetic behavior of undoped $BiFeO_3$ without any enhancement of the magnetization. On the contrary, Pb-doped compound demonstrates appearance of a weak ferromagnetism. It is thus shown that Pb doping of $BiFeO_3$ is a promising way for preparing multiferroic materials.

V. Fruth *et al.*2007[36]This paper describes a simple low-temperature synthesis method of preparing bismuth ferrite thin films by a wet chemical route, using bismuth and iron nitrates and two chelating agents (citric acid and polyvinyl alcohol). The films were layer by layer deposited on substrate (silica glass) using the dip-coating technique. The thickness of the layers were controlled by viscosity of the solutions and withdrawing speed parameters. After specific annealing, in air, the samples were characterized by scanning electron microscopy SEM, spectroelipsometry SE, X-ray photoelectron spectroscopy XPS, Raman spectroscopy. A more thoroughly control of the processing parameters seems to be essential in obtaining BiFeO3 thin films. Solution chemistry variations (differences in precursor type) can have a significant impact on the film properties.

Qing-hui Jiang *et al.*2008[37]BiFeO3 was synthesized using a sol– gel process, i.e., so-called Pechini method, as evidenced by X-ray diffraction pattern. Optimal conditions for the synthesis of single-phase BiFeO3 ceramics were obtained. This Pechini technique developed in this work is expected to be useful in synthesis of doped BiFeO3 or BiFeO3-based solid solution. Conventional sintering and spark plasma sintering processes were used to fabricate BiFeO3 ceramics. Ferroelectric and magnetic loops were measured at room temperature. The ceramic sample shows a stable dielectric constant and low loss tangent between 100 Hz and 10 MHz.

Jie Wei *et al.*2008[38] This paper reports the synthesis and characterization of multiferroic BiFeO3 nanotubes. Perovskite BiFeO3 nanotubes with outer diameters 150–190 nm were synthesized by a facile sol–gel template method. The photoabsorption of BiFeO3 nanotubes was characterized by UV–visible diffuse reflectance spectrometry. The BiFeO3 nanotubes show weak ferromagnetism at room temperature, unlike the antiferromagnetic order in bulk BiFeO3, reflecting the grain size-confinement effect on the magnetic ordering of BiFeO3.

M. Thrall *et al.* 2008[39] Synthesized the multiferroic $BiFeO_3$ by using both vacuum and argon atmospheres. The synchrotron X-ray powder diffraction investigation on pressed pellets of the starting powders of Bi_2O_3 and Fe_2O_3 were carried out up to the final formation of $BiFeO_3$. The difference in the transformation temperature of monoclinic Bi_2O_3 to cubic Bi_2O_3 was found to be 650°C and 700°C when samples were sintered in a vacuum and argon environments, respectively. It was found that this reaction was 75% complete before the multiferroic product began to form. In both cases it was found that the quantity of Fe_2O_3 was unaffected by increasing temperature until after the transition of monoclinic to cubic Bi_2O_3 had reached its maximum value. After this transition the quantities of cubic Bi_2O_3 and Fe_2O_3 were found to decrease at very similar rates yielding the final $BiFeO_3$ structure. An SEM study of the bulk microstructure of the $BiFeO_3$ product showed a poor densification due to incomplete reactions between the remaining Bi_2O_3 and Fe_2O_3.

Jia-Huan Xu *et al.*2009[40] Bismuth ferrite ($BiFeO_3$) nanopowders were synthesized by a sol–gel method at the temperature as low as 450 °C. The obtained sol was transparent and homogenous when the mixture ionic concentration was properly controlled with the help of ethylene alcohol.

De-Chang Jia *et al.*2009[41]Bismuth ferrite powders were synthesized by a simple sol–gel method at the temperature as low as 450 °C. Single phase $BiFeO_3$ powders with a rhombohedral perovskite structure were fabricated after Bi–Fe gels were calcined at 450–650 °C. Atomic ratio of Bi to Fe is approximately 1:1 for $BiFeO_3$ powders, as determined by energy dispersive X-ray spectrometer. $BiFeO_3$ powders show weak ferromagnetism at room temperature and strong size-dependent magnetic properties, which is different from the linear $M–H$ relationship in $BiFeO_3$ ceramics. Dielectric anomaly at round 330 °C near the magnetic transition point corresponds to the antiferromagnetic to paramagnetic phase transition, indicating the coupling between polarization and magnetization in $BiFeO_3$ powders. A reversible ferroelectric phase transformation of $BiFeO_3$ powders has been detected at 827 °Cby a differential thermal analysis.

B Bhushan *et al.*2009[42]Substrate-free pure-phase $BiFeO_3$ (BFO) nanoparticles doped with alkaline earth metals (Ba, Sr and Ca) have been synthesized by a sol–gel route and their thermal, optical, dielectric and magnetic properties are discussed. The characteristic structural phase transitions of BFO nanoparticles are found to occur at much lower temperatures. A reduction of the Neel temperature has been observed in the doped samples in comparison with the pristine one, whereas the band gap shows a reverse trend. Iron was found to be only in the Fe3+ valence state in all the doped samples. Magnetoelectric coupling is seen in our samples. Weak ferromagnetism is observed at room temperature in all of the doped and undoped BFO nanoparticles with the largest value of coercive field 1.78 kOe and saturation magnetization 2.38 emu g−1 for Ba and Ca doped BFO nanoparticles, respectively.

S. Vijayanand *et al.*2009[43] Single phase nanocrystalline $BiFeO_3$ of average crystallite size ∽25 nm with very high magnetization at room temperature is synthesized by an autocombustion method. Magneticmeasurements above room temperature show deviation between field cooled and zero field cooled magnetization below 645 K, the Néel temperature (T_N) of the bulk material, indicating intrinsic nature of ferromagnetism. However, observation of a broad magnetic transition above T_N of $BiFeO_3$ and extended up to 800 K suggests the presence of Fe_3O_4 as a possible magnetic impurity phase. Evidence for the presence of Fe_3O_4 is obtained from detailed analysis of the powder x-ray diffraction pattern.

A. Hardy *et al.*2009[44] Phase pure $BiFeO_3$ powders are synthesized by an entirely aqueous solution–gel route, starting from water soluble Fe(III) nitrate or citrate, and Bi(III) citrate as precursors. In order to obtain stable solutions, which transform to homogeneous gels upon drying, the pH is adjusted to 7 and a citric acid content equimolar to the metal ions is selected. The presented synthesis allows very low temperature (400 °C) crystallization of $BiFeO_3$ together with a secondary phase, as shown by high temperature XRD. This parasitic phase remains up to high temperatures, where decomposition of BiFeO3 is observed from 750 °C onwards, and $Bi_2Fe_4O_9$ is formed. However, optimization of the furnace treatment, considering anneal temperatures and heating rates showed that phase pure $BiFeO_3$ can be obtained, with the heating rate being the crucial factor (5 °C/min).

Ratnakar Pandu *et al.*2010[45] Polycrystalline samples of $BiFeO_3$ are synthesized at low temperature using sol-gel technique. From the XRD analysis it is seen that crystallite size increases and the strain in the crystallites decreases with increasing sintering temperature. As the crystallite size increases with increasing temperature the lattice parameter (a_R) decreases. SEM micrographs show that the samples are homogeneous. It is also confirmed from the SEM micrographs that the grain size increases with increasing sintering temperature. Analyzing the SEM micrographs it can be concluded that the particle size follows the Gaussian distribution. Ferroelectric to paraelectric transition temperature (Tc) is detected by DTA analysis, which shows that the Curie temperature of pure $BiFeO_3$ is 814°C which is very close to the ideal value (827°C) found by dielectric measurement.

Fusheng Wen *et al.*2010[46] Multiferroic $BiFeO_3$ nanoparticles and ceramics have beensuccessfully prepared by Sol-Gel method and following high-pressure synthesis. The denser samples, good crystallization and crystal structure deformation have been obtained via high-pressure synthesis proved by XRD, SEM and Raman spectra. The enhanced magnetization of high-pressure samples attributes to crystal structure deformation; moreover, the enhanced dielectric loss of high-pressure samples results from good crystallization. The better microwave absorption properties can be obtained by high-pressure synthesis, and the minimum reflection loss elevates from -13 dB at 12.4 GHz to -17 dB at 11.2 GHz. It means that the high-pressure synthesis can effectively improve microwave absorption properties of multiferroic materials.

Kyoung Sun Kim *et al.* 2010[47] The influence of processing parameters on phase formation and particle size of hydrothermally synthesized $BiFeO_3$ powders was investigated. $BiFeO_3$ powder was synthesized by dissolving bismuth nitrate and iron nitrate in KOH solution at temperatures ranging from 150 to 225°C. X-ray diffraction patterns and scanning electron microscopy observation indicated that rod-like a Bi_2O_3

phase was formed at initial stage of reaction and dissolved into ions to form thermodynamically stable $BiFeO_3$ phase. Single-phase perovskite $BiFeO_3$ has been formed using a KOH concentration of 8M at a temperature of$\leqslant 175^0$C in a 6 h reaction period. $BiFeO_3$ particle growth was promoted by lowering the KOH concentration, or increasing the duration time or reaction temperature. The effects of processing conditions on the formation of crystalline $BiFeO_3$ powders were discussed in terms of a dissolution–precipitation mechanism. The magnetization of the $BiFeO_3$ powders at room temperature showed a weak a ferromagnetic nature.

Chaudhuri *et al.*2010 [48] bismuth ferrite nanoparticles were synthesized using the solvothermal method without the help of any mineralizer. The shape of the particles was changed by changing the synthesis temperature during solvothermal process. The as-prepared samples were characterized by an X-ray powder diffractometer (XRD), scanning electron microscope (SEM), thermal analyzer and vibrating sample magnetometer (VSM). It was observed that the change in solvent also led to the variation of the shape of the particles. Spindle, plate, cylindrical and hexagonal shapes were obtained. The particles showed antiferromagnetic nature within the measured temperature range of $80K \leq T \leq 300$ K.

CHAPTER 3

EXEPERIMENTS PROCEDURE

Bismuth ferrite, BiFeO3 was prepared by Sol-gel method .The raw material used for experiments were bismuth nitrate pentahydrate [$Bi(NO_3)_3.5H_2O$] with 98% purity and iron nitrate non hydrate[$Fe(NO_3)_3 9H_2O$] with 98% purity. Bismuth nitrate pentahydrate (5 mol% excess) and iron nitrate non hydrate were mixed with mole ratio of 1:1 and dissolved in 2- methoxyethnol after the solution was transparent it continues stirring one hours at room temperature after one hour strring added crtric acid ($C_6H_8O_7$) as a chelating agent and acetic acid. Then resulting solution was transparent, blackish red and clear. Futher, solution was heated at temperature 80^0C on a hot plate under continuous stirring condition until all the liquid evaporated. There was an immense evolution of brown fumes, towards the end of the reaction a fluffy brown mass (Gel) was obtained at the base of the beaker. The obtained gel was calcined at 450^0C, 500^oC and 550^o C. independently with holding time of 4 hours with heating and cooling rate maintained at 5^0C per minute. Phase identification of the annealed powders was carried out by X-ray diffraction instruments X'Pert Pro-Panlytical. Further the powder was pressed into pellets of 10 mm diameter die under 10 ton/cm^2 pressure using hydraulic press. The pressed pellets were sintered 600^0C temperature for two hours. For dielectric and P-E loop measurements, the sintered pellets were coated on both sides by Ag paste. The dielectric measurements were carried out by the instruments LCR meter Agilent 4284A (frequency range 20Hz to 1MHz) and the P-E loop of the pellets were carried out by the scan Agilent 4284A(frequency range 20Hz to 1MHz) .The scanning electron microscopy the samples were carried out using SEM model JEOL JSEM 6510VL. Before SEM the samples were made conducting by sputtering of Au-Pd layer of thickness 10 nm approximately. Fig. 3.1 shows the flow diagram of the processing and characterization of the samples.

FLOW CHART

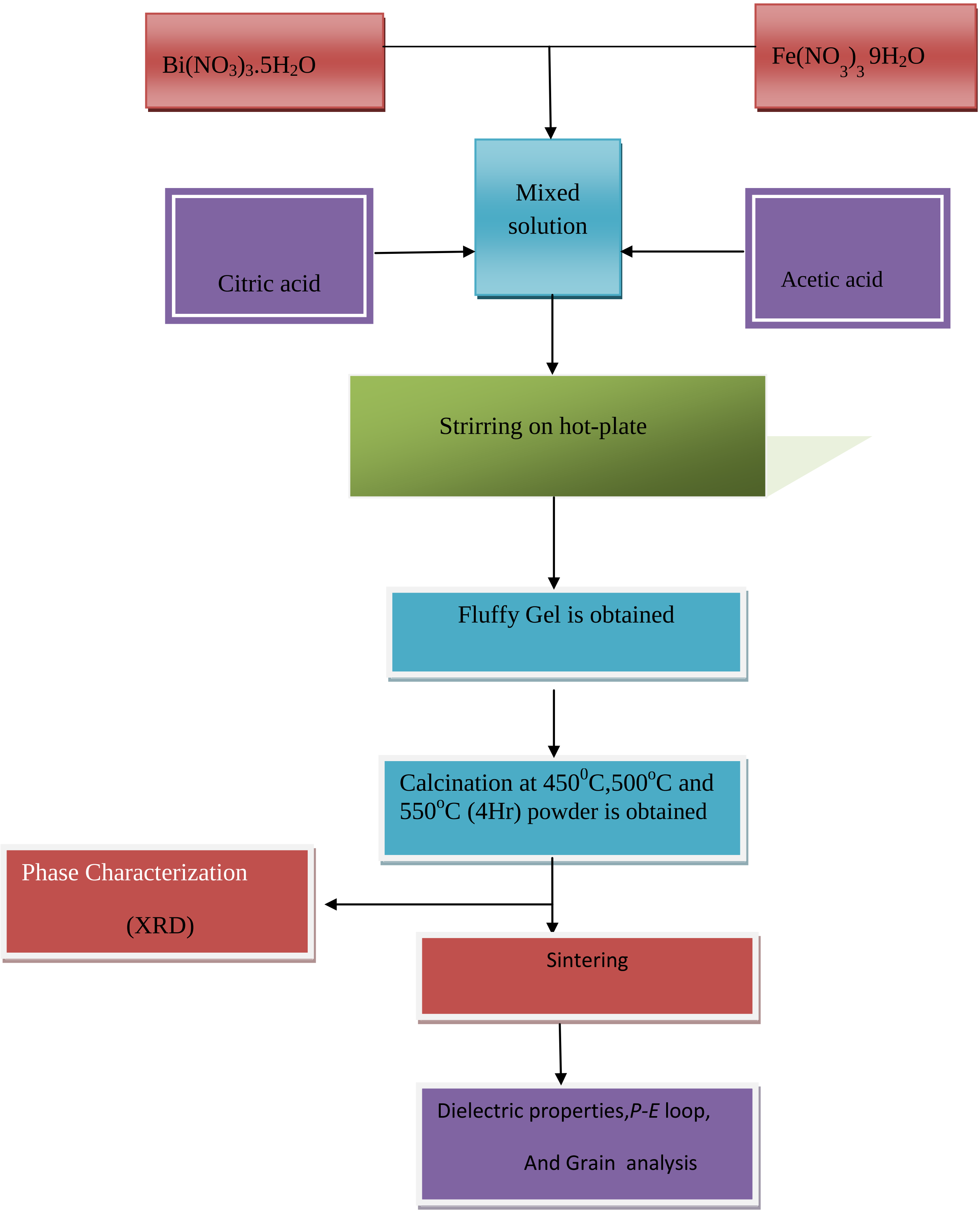

FIG.3.1 FLOW CHART

CHAPTER 4

RESULTS AND DISCUSSION

4.1 XRD Analysis:-

Fig. 4.1 Shows the XRD pattern of $BiFeO_3$ powder calcined at different temperature 450^0C, 500^0C and 550^0C respectively. It evident from the figure(4.1) Show that sample calcined at 450^0 C single phase shows peaks of BiFeO3 (JCPDS 86-1518) along with the $Bi_{25}FeO_{40}$impurity phase(JCPDS 46-01416)With increasing temperature to 500^oC the intensity of $BiFeO_3$ (JCPDS 86-1518) phase increases with two impurity phase of $Bi_2Fe_4O_9$ (JCPDS 74-1098) and $Bi_{30}Fe_2O_{37}$ (JCPDS 42-0181) are found. Further increasing the temperature to 550^oC Single phase $BiFeO_3$ with minor impurity are found.

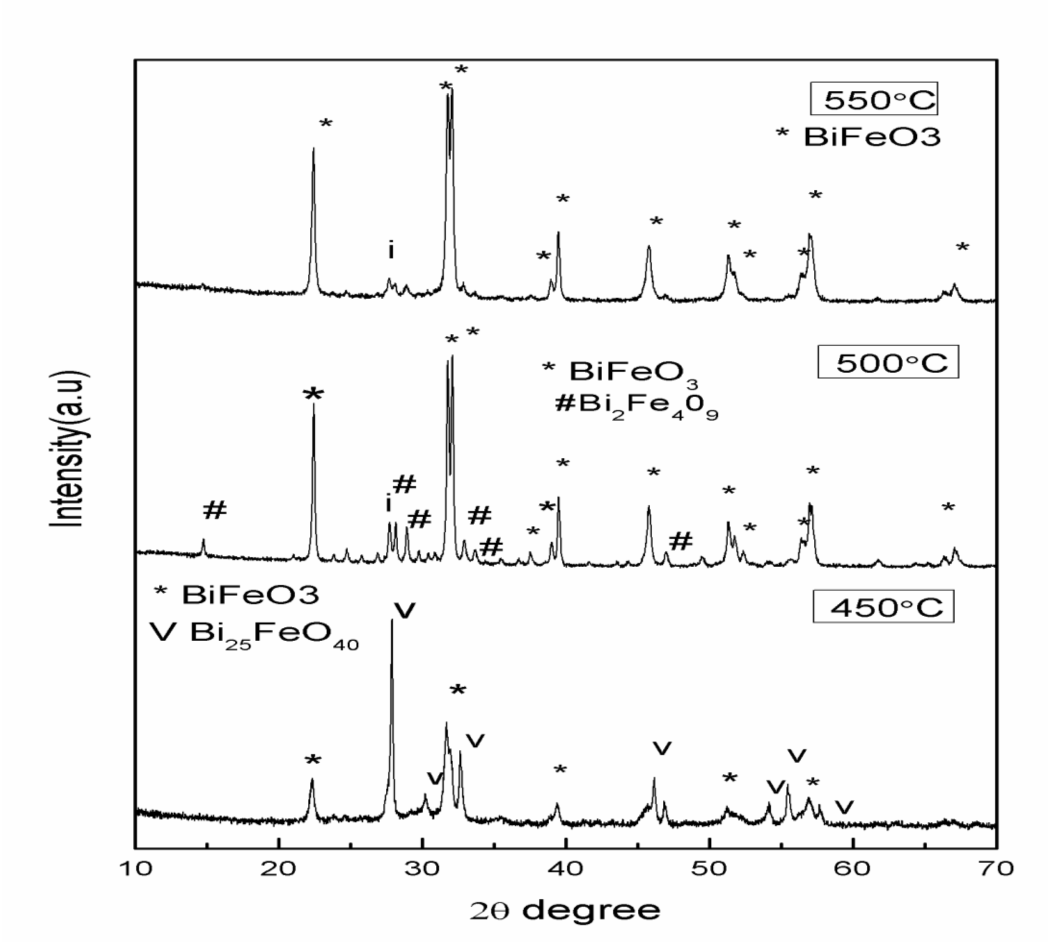

Fig. 4. 1XRD patterns of $BiFeO_3$ powders calcined at various temperatures.

Table 1. shows the crystalline sizes of powder calcined at 450^0C, 500^0C and 550 ^{0}C.The crystalline size increase with temperature up to 500^0C. Sample calcined at 550 the crystallite size decreases this could be attributed to recrystallization of the grains

Table 4.1 Crystallite size of the calcined powders

TEMPERATURE ^{0}C	CRYSTALLITE SIZE(nm)
450^0C	44.23
500^0C	68.16
550^0C	56.146

4.2 P-E Loop measurements

Fig. 4.2 shows the room temperature P-E loop measurement of the sample sintered at 600°C The maximum field is applied was 55kv/cm. It clear from the graph that sample do not show saturation. This is due to the semiconducting nature of BiFeO3 which causes leakage current in the sample.

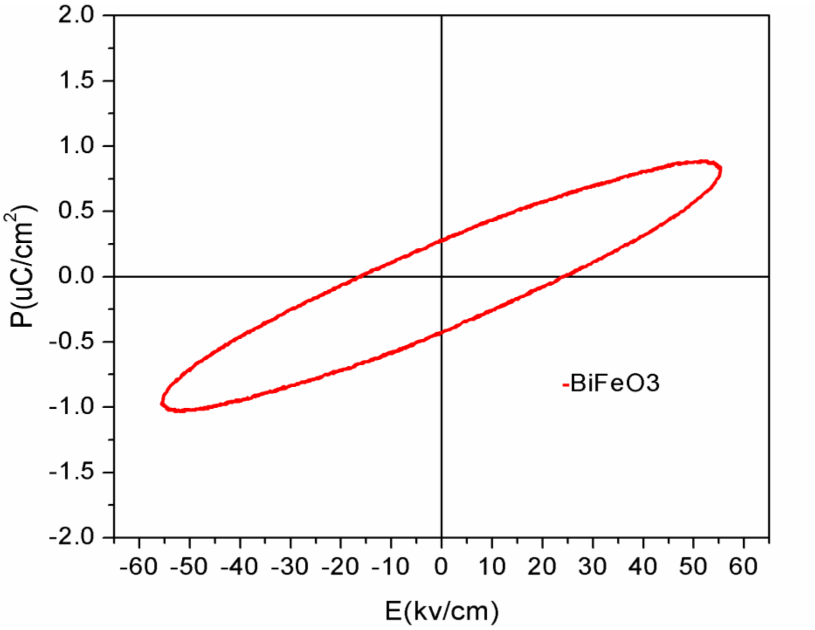

Figure 4.2 : P-E Loop of the pure $BiFeO_3$.

4.3 Measurements of Dielectric Properties:

Fig. 4.3 Shows the room temperature dielectric constant measurements with respect to frequency in the range of 20Hz to 1MHz of $BiFeO_3$ sample sintered at 600°C using LCR meter. It was found that dielectric constant was higher in the lower frequency region it shows maximum value i.e. 91.5 at 70Hz frequency. Dielectric constant decrease with further increase the frequency and become all most constant at higher frequency region. Such behaviour may attributed to space charge polarization in the sample.

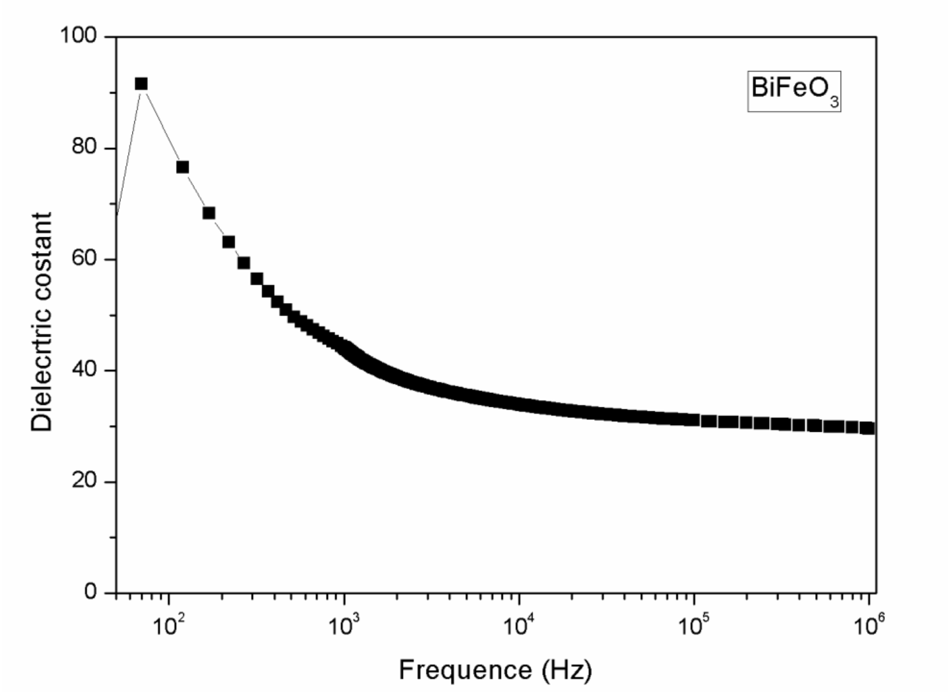

Figure 4.3: Dielectric constant in $BiFeO_3$ at room temperature.

Fig 4.4 Shows the dielectric losses corresponding loss factor for the system is presented in fig 4.5.we observed that loss are maximum in the lower frequency region become low at higher frequency.

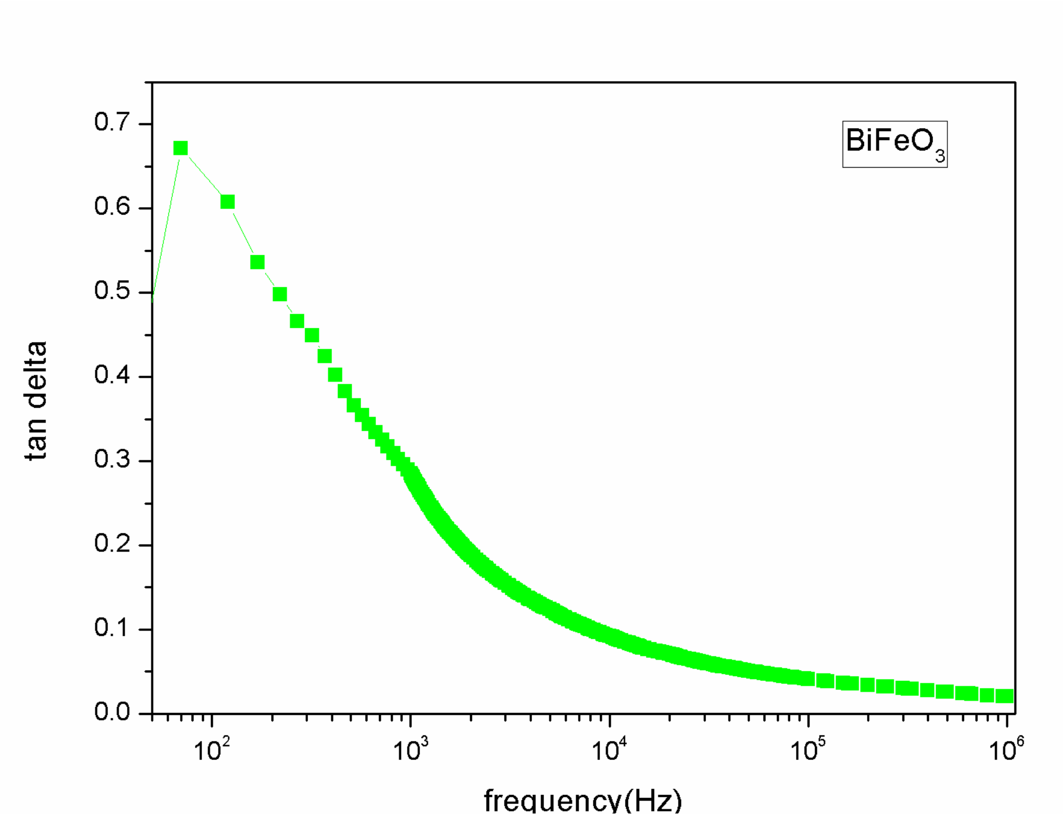

Figure 4.4: Dielectric losses in pure BiFeO$_3$.

4.4 SEM studies

Fig.4.5 shows the scanning electron micrographs of sintered pellets of BiFeO3 at 25,000x magnification. It is clear from SEM micrograp that grain posses spherical symmetry with well uniformity. The average grain size of is found to be 68 nm, which is higher than crystallite size of calcined powders. This shows that some grain growth has taken place during sintering.

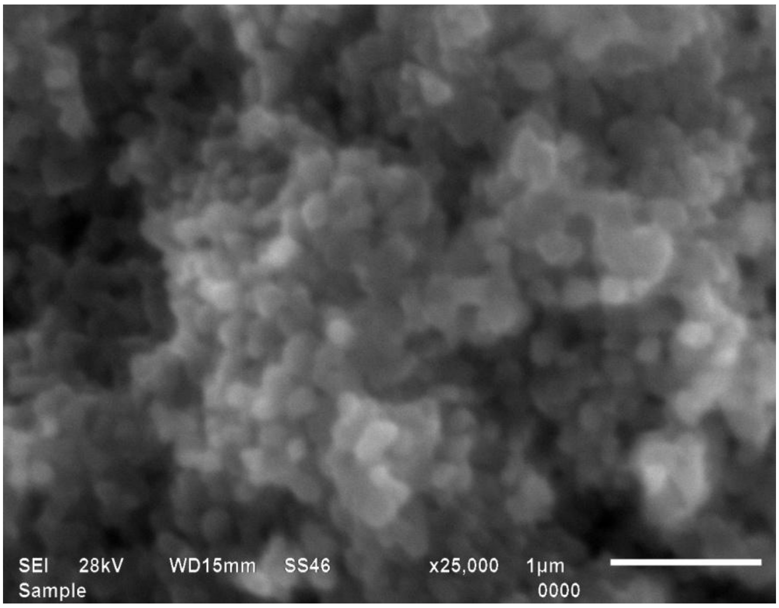

Figure 4.5: SEM imege of $BiFeO_3$.

CONCLUSION

The aim of my present work is the synthesis and characterization of Bismuth ferrite nano particles by sole gel method followed by dielectric, polarization and microstructural studies of sintered sample.

- The single phase bismuth ferrite ($BiFeO_3$) has been successfully prepared by Sol- gel method.
- The phase investigation showed that single phase is formed in the sample calcined at 550
- Dielectric studies in the sintered sample showed that dielectric constant is higher in the lower frequency region and decrease with increase in frequency and become all most constant at higher frequency region. Dielectric losses measurements with respect to frequency clearly reveals that for $BiFeO_3$ loss was maximum in the lower frequency region become low at higher frequency.
- *P-E* loop measurement showed no saturation in the samples upto the electric field of 55kV/cm. This is due to the leakage current.
- SEM studies of the sintered $BiFeO_3$ at 600C showed the grain size of the order of 68 nm.

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