SYNTHESIS OF MULTIFERROIC $BiFeO_3$ MATERIAL BY AUTOCOMBUSTION TECHNIQUE

A THESIS SUBMITTED IN PARTIAL FULFILMENT
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By

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CERTIFICATE

This is to certify that the thesis entitled *"Synthesis of Multiferroic* $BiFeO_3$ *Material by autocombustion technique "* submitted by Mr. Binit Kumar Agrawal in partial fulfilment of the requirements for the award of Bachelor of Technology Degree in Ceramic Engineering at National Institute of Technology ,Rourkela (Deemed University) is an authentic work carried out by him under my supervision and guidance.

To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other University / Institute for the award of any Degree or Diploma.

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Contents

Chapter 1

General Introduction

1.1 Multiferroic Materials

Multiferroic materials, which are a class of materials that yield simultaneous effects of ferroelectricity, ferromagnetism, and antiferromagnetism in the same material, offer a wide opportunity for potential applications in information storage, spintronic devices and sensors. Multiferroic have been formally defined as materials that exhibit more than one primary ferroic order parameter simultaneously in a single phase. Magnetism and ferroelectricity are involved with local spins and off-centre structural distortions, respectively. These two seemingly unrelated phenomena can coexist in certain unusual materials, termed multiferroics. Multiferroics, sometimes called magnetoelectrics, possess two or more switchable states such as polarization, magnetization or strain. These compounds present opportunities for potential applications in information storage, the emerging field of spintronics, and sensors. Although there are a number of materials that possess both ferroelectricity and magnetism, it may be surprising that there need not necessarily be a large coupling between them.

Despite the possible coexistence of ferroelectricity and magnetism, a pronounced interplay between these properties has rarely been observed . This has prevented the realization of multiferroic devices offering such functionality. Typical multiferroics belong to the group of the perovskite transition metal oxides, and include rare-earth manganites and -ferrites (e.g. $TbMnO_3$, $HoMn_2O_5$, $LuFe_2O_4$). Other examples are the bismuth alloys $BiFeO_3$ and $BiMnO_3$, and non-oxides such as $BaNiF_4$ and spinel chalcogenides, e.g. $ZnCr_2Se_4$. These alloys show rich phase diagrams combining different ferroic orders in separate phases. Apart from single phase multiferroics, composites and heterostructures exhibiting more than one ferroic order parameter are studied extensively. Some examples include magnetic thin films on piezoelectric PMN-PT substrates and Metglass/PVDF/Metglass trilayer structures. Besides scientific interest in their physical properties, multiferroics have potential for applications as actuators, switches, magnetic field sensors or new types of electronic memory devices.

Multiferroism and Symmetry

Each multiferroic property is closely linked to symmetry. The primary ferroic properties can be characterized by their behavior under space and time inversion. Space inversion will reverse the direction of polarization P while leaving the magnetization M invariant. Time reversal, in turn, will change the sign of M, while the sign of P remains invariant.

	Space Invariant	**Space Variant**
Time Invariant	Ferroelastic	Ferroelectric
Time Variant	Ferromagnetic	Ferrotoroidic

Magnetoelectric multiferroics require simultaneous violation of space and time inversion symmetry. In $BiFeO_3$, off-centering of ions gives rise to an electric polarization, while at a lower temperature additional magnetic ordering breaks time-reversal symmetry.

In general, a variety of mechanisms can cause lowering of symmetry resulting in multiferroicity as described below.

Charge Ordered

Mechanism:

A possible origin for a multiferroic state is charge ordering. 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 330 K. 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. Ferrimagnetic behavior occurs below 240 K.

In addition, charge ordered ferroelectricity is suggested in Fe_3O_4 and $(Pr,Ca)MnO_3$

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_2CdI_4, 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 or Kagomé structures in order 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-centering of Mn ions also contributes to the polarization.

Physical properties of geometric multiferroics are dominated by the behavior of the d-shell electrons (eg-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.

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 favor 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 cycloidal 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 results in the corresponding rotation of the polarization vector. In DyMnO3 this transition is accompanied by the 600% increase of dielectric constant (the giant magnetocapacitance effect. The microscopic mechanism of magnetoelectric coupling in spiral multiferroics involves spin-orbit coupling.

E-type Antiferromagnet (I.e. ortho-$HoMnO_3$): In the presence of strong uniaxial anisotropy, competing interaction can stabilize a *periodic collinear spin arrangement of the up-up-down-down* type. Such a spin modulation commensurate with the structural or charge modulation can induce electric polarization via exchange striction mechanism that does not require spin-orbit coupling.

Lone pair multiferroics

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 perovskites to display ferroelectricity.

In order for the coexistence of magnetism and ferroelectricity (multiferroic), one possible mechanism is lone-pair driven where the A-site drives the displacement and partially filled “d” shell on the B-site contributes to the magnetism. Examples include $BiFeO_3$, $BiMnO_3$, $PbVO_3$. In the above materials, the A-site cation (Bi3+, Pb^{2+}) has a stereochemically active $6s^2$ lone-pair which causes the Bi 6p (empty) orbital to come closer in energy to the O 2p orbitals. This leads to hybridization between the Bi 6p and O 2p orbitals and drives the off-centering of the cation towards the neighboring anion resulting in ferroelectricity.

Applications of Multiferroic Material

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 antiferro-magnetic resonance is tuned electrically instead of magnetically.

In multiferroic thin films, the coupled magnetic and ferroelectric order parameters can be exploited for developing magnetoelectronic devices. These include novel spintronic 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. 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 magnetoresistance of the device can be controlled by the applied electric field. One can also explore multiple state memory elements, where data are stored both in the electric and the magnetic polarizations.

Among all the multiferroic materials studied so far, BiFeO3 (BFO) that exhibits the coexistence of ferroelectric and antiferromagnetic (AFM) orders has received great attention due to its high ferroelectric Curie point (TC∼1103 K) and the antiferromagnetic (AFM) Néel point (TN∼647 K) . BFO is one of the prime candidates for room-temperature magneto electric applications. Multiferroic have potential for applications as actuators, switches, magnetic field sensors or new types of electronic memory devices.

1.2 Introduction

Bismuth Ferrite ($BiFeO_3$) is an attractive material exhibiting multiferroism at room temperature, which is ferroelectric (TC = 820–850°C) and anti-ferromagnetic (TN=370–380°C). **$BiFeO_3$** is an inorganic chemical compound with a perovskite structure. It is one of the most promising lead-free piezoelectric materials by exhibiting multiferroic properties at room temperature. Multiferroic materials exhibit ferroelectric or anti-ferroelectric properties in combination with ferromagnetic and antiferromagnetic properties in the same phase. The multiferroics with a coupling of at least two of the possible three orders (or degrees) of freedom viz., ferromagnetic (or antiferromagnetic), ferroelectric (or antiferroelectric), and ferroelastic are rare in nature as transition metal ions with active *d* electrons tend to reduce the off-center distortion necessary for ferroelectricity.

$BiFeO_3$ is the most interesting in the family of a very few single-phase multiferroics because of its high phase transition temperatures (Curie temp1083K and Neel temperature□675 K). Several techniques have been employed in synthesizing **$BiFeO_3$** In the solid state route **Bi_2O_3** and **Fe_2O_3** are reacted at a temperature in the range of 800–830 ◦C and unreacted **$Bi_2O_3/Bi_2Fe_4O_9$** phases are removed by washing in **HNO_3**. Another technique is simultaneously precipitaton , where a solution of bismuth nitrate and iron nitrate is treated with ammonium hydroxide to get a hydroxide precipitate. The precipitate needs calcination at a temperature in the range of 550–750 ◦C to get phase pure **$BiFeO_3$**. In another approach nanosized **$BiFeO_3$** particles have been prepared by a solution evaporation (tartaric acid template) technique at a temperature as low as 450 ◦C. It can also be prepared through co-precipitation (700 ◦C), sonochemical (450 ◦C) and autocombustion (400 ◦C) routes.Incidentally, there are only a few reports of making densified and highly resistive **$BiFeO_3$** ceramics. Mahesh Kumar et al. [8] reported the dielectric and ferroelectric properties of **$BiFeO_3$** ceramics where **$BiFeO_3$** was prepared by solid state route and there was no report about the bulk densities of the samples. The spontaneous polarization of the samplewas very low.Wang et al. [9] showed that a rapid liquid-phase sintering of **$BiFeO_3$** can result in 92% of relative density and gave rise to spontaneous and remanent polarization of 8.9,4.0_C/cm2, respectively. Pradhan et al. [10] followed similar rapid phase sintering, but the percent densification was not reported. In the later case, the spontaneous and remanent polarizations were only 3.5 and 2.5_C/cm2, respectively instead of earlier reported [9] high values. Recently, Yuan et al. [11] followed rapid phase sintering technique and synthesized highly resistive and dense (92% of theoreticaldensity) sample by varying the particle size of precursors **Bi_2O3** and **Fe_2O3** and they reported high spontaneous polarization of their samples.

The various methods which are generally employed for the synthesis of $BiFeO_3$ are

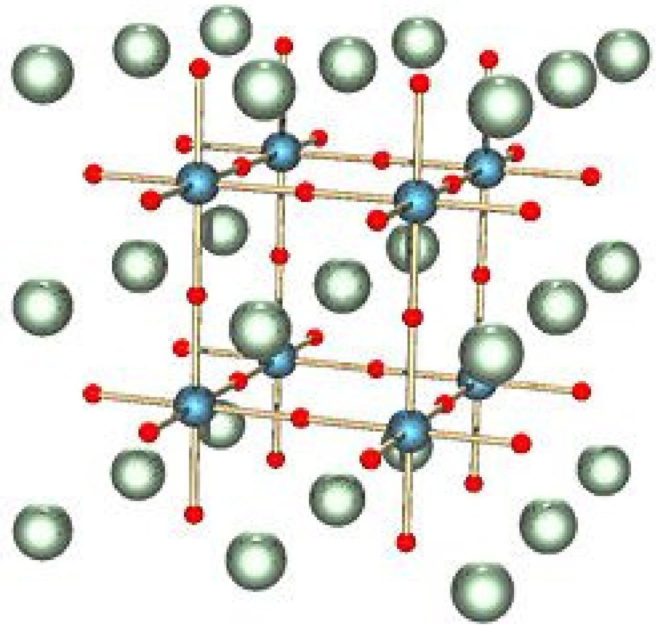
- Solid state reaction Method
- Coprecipitation Method
- Autocombustion Method

1.3 Characteristics

The co-existence of ferroelectricity and ferromagnetism and their coupling with elasticity provide an extra degree of freedom in the design of new functional sensors and multistate devices. Due to its multiferroism, an electric field can induce change in magnetization and an external magnetic field can induce electric polarization. This phenomenon is known as the magneto electric effect (ME) effect and materials exhibiting this effect are called magneto electrics or seignetto magnets. Further proof of it being ferromagnetic is that it produces a hysteresis loop during ferroelectric characterization. The ability to couple to either the electric or the magnetic polarization allows an additional degree of freedom in device designs.

One of the major drawbacks of $BiFeO_3$ material is the leakage current arising out of its nonstoichiometry. This is mostly because of the difficulty in obtaining stoichiometric single-phase $BiFeO_3$ materials. Therefore it allows current to pass through when a high voltage is applied. Attempts to improve the electrical properties have been made by doping it with rare earth elements such as lanthanum (La), samarium (Sm), gadolinium (Gd), terbium (Tb) and dysprosium (Dy) etc. The dopant can be at the A site or the B site. A site being the edges of the perovskite cell and the B site being the centre of the perovskite cell.

1.4 Structure



$BiFeO_3$ material has got a rhombohedrally distorted perovskite structure ($a = b = c =$ 5.63 A°, $\alpha = \beta = \gamma = 59.4^0$) at room temperature. .A perovskite is any material with the same type of crystal structure as calcium titanium oxide ($CaTiO_3$), The general chemical formula for perovskite compounds is ABX_3, where 'A' and 'B' are two cations (Bi and Fe) of very different ionic radii. The 'A' atoms are larger than the 'B' atoms. The ideal cubic-symmetry structure has the B cation in 6-fold coordination, surrounded by an octahedron of anions, and the cation in 12-fold cuboctahedral coordination. The relative ion size requirements for stability of the cubic structure are quite stringent, so slight buckling and distortion can produce several lower-symmetry distorted versions, in which the coordination numbers of A cations, B cations or both are reduced.

(Structure of a perovskite. The chemical formula is of the form "ABX_3". The red spheres are X atoms (usually oxygen), the deep blue spheres are B-site atoms (usually a smaller metal cation, such as Ti^{4+}), and the green spheres are the A-site atoms (usually a larger metal cation, such as Ca^{2+}).

1.5 Doping in $BiFeO_3$

In an attempt to get improved properties, there are also a fewreports on doped BiFeO3. Li et al. [12] reported the crystal structure,electronic structure and magnetic properties of Sr-doped

BiFeO3. Sr-doping increases the oxygen vacancy concentration and $Bi_{1-x}Sr_xFeO_3$ behaves like an antiferromagnet and weak ferromagnet simultaneously. Palkar [13] studied the effect of Mn doping on structural, ferroelectric and magnetic properties of La-modified BiFeO3. Ferroelectric properties are not affected by Mn substitution but a small enhancement in magnetization is observed.Jun et al. [14] prepared highly resistive BiFeO3 ceramics by Nb doping and studied their electric and magnetic properties. They reported a very low remanent polarization of 0.15_C/cm2. Jiang et al. [15] prepared La-doped BiFeO3 by Pechini method followed by conventional sintering. The dissipation factor reduced to 1%, which is highly desired for potential applications. However, the reported polarization value was very low and the microstructure revealed appreciable porosity.

Bi1−*x*Pb*x*FeO3 ceramics have been prepared by a simple simultaneous precipitation technique followed by the conventional sintering process. The sintered density and dielectric property improved with Pb addition. Typical non-lossy ferroelectric loops (in contrast to lossy loop of BiFeO3) have been observed in the Bi1−*x*Pb*x*FeO3 ceramics at room temperature. Pb-doped BiFeO3 powders can be synthesized by simultaneous precipitation method and their dielectric and ferroelectric properties are investigated after sintering in air. Bulk densities up to 93% of theoretical density can be achieved with Pb-doping. The dielectric and ferroelectric properties also improves.

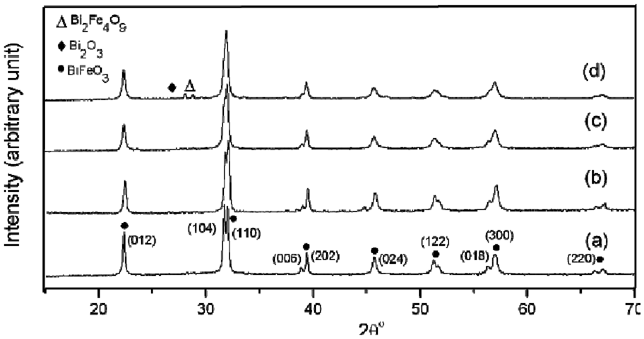


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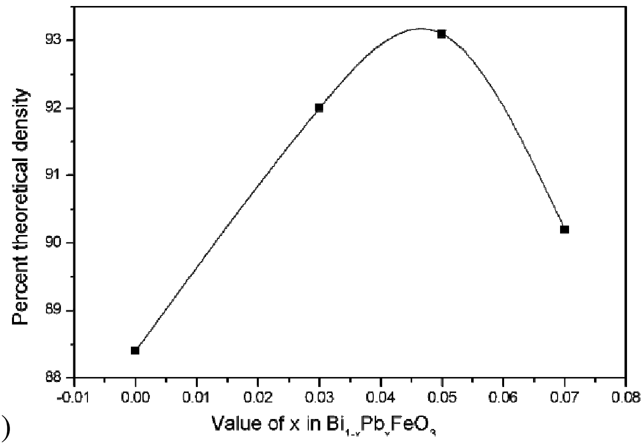
Fig. 1. X-ray diffraction patterns of (a) BiFeO3, (b) Bi0.97Pb0.03FeO3, (c) Bi0.95Pb0.05FeO3, and (d) Bi0.93Pb0.07FeO3.

Figure 1 shows the XRD patterns of pure BiFeO3 and Bi1−*x*Pb*x*FeO3 (x = 0.03, 0.05 and 0.07) samples. No impurity phase or excess PbO phase was detected up to x = 0.05. For x = 0.05, small amounts of $Bi_2Fe_4O_9$ and Bi_2O_3 were formed as impurity phases.From DSC study, it is found that pure BiFeO3 showed a sharp endothermic peak corresponding to antiferromagnetic to paramagnetic transition at373 ◦C, but with Pb addition there was no sharp transition. The absence of a sharp peak and a broad transition point out towards local inhomogeneity, probably in the nanoscale.



(Fig 2)

Fig. 2 shows the variation of bulk densities of the sintered pellets with Pb addition. In the present study, the maximum in density (□93.5%) was achieved for *x* = 0.05. Further addition of Pb (*x* = 0.07) lowered the bulk density.

Interestingly, with Pb-doping the grain size decreased drastically. Probably, Pb-doping, up to a certain level, inhibits grain growth and helps in densification . To understand this behavior,we have to first note that in $BiFeO_3$, small amounts of Fe2+ ions and oxygen vacancies exist . Incidentally,$BiFeO_3$ shows p-type conductivity , which can be understood by considering the substitution of a small amount Fe2+ ions in Fe3+ positions (acceptor doping of Fe3+ by Fe2+) When PbO is added significantly with respect to pure BiFeO3 after Pb-doping.

1.6 Summary of Literature Review

- The synthesis of $BiFeO_3$ can be done using a variety of techniques
- The most simple and cost effective method of synthesis of $BiFeO_3$ is by autocombustion route where reaction time is less.
- monophasic nanopowders with zero impurity level at lower temperatures can be prepared by autocombustion route.
- The fuel/oxidant ratio has clearly the most intense influence on the structural and morphological properties of the powders.Therefore the quantity of fuel will play a crucial role in the synthesis of powder.
-

1.7 Objective of the Present Study

The main objective is to produce $BiFeO_3$ which must have the following characteristics :

I. Synthesizing phase pure material,
II. Achieving sintered densities above 90% of theoretical density
III. Getting highly resistive $BiFeO_3$ ceramics with low leakage current.
IV. Achieving good piezoelectric and dielectric properties

Chapter 2

Experimental Work

2.1 Autocombustion Route

One of the most widely used and useful method of preparation of BFO is the combustion synthesis route using a fuel.The fuel used may be glycine ,citric acid or urea.the precursor material used for the synthesis of BFO by autocombustion route are $BiNO_3$ and $FeNO_3$ 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 tchnique 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/or calcination steps which other conventional synthesis routes would require. The process is based on the mixing of reactants that oxidize easily, such asmetal 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 BFO 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 calcination steps which other conventional synthesis routes would require
- monophasic nanopowders at lower temperatures or shorter reaction times

2.2 Procedure

Bismuth ferrite was prepared by a novel combustion method using glycine as the fuel. The procedure adopted are

- precursor was prepared in aqueous solution from metal nitrates and glycine.Solutions of 0.2 M $Bi(NO_3)_3$ and 0.2M $Fe(NO_3)_3$ were prepared.As $Bi(NO_3)_3$ is insoluble in water,it was first dissolved in HNO_3.
- 50 ml of both the solutions were then properly mixed in a beaker.
- Glycine/nitrate ratio as taken as 0.1.The appropriate amount of glycine was then added to the above solution and the mixture was stirred until complete dissolution occurred.
- Then, the mixture was heated and evaporated on a hot plate with stirring till it became a dark viscous resin. Continuous heating leads to the auto-ignition of dried resin with the evolution of large quantities of gases.
- The brownish color ash obtained after combustion was analyzed for perovskite-type BiFeO3 phase.
- The whole process was over after 30 min, but the time between the actual ignition and the end of the reaction was less than 20 s.
- After the combustion is over in chamber,it is further heated for 5-10 minutes to allow complete combustion of material.
- After cooling,it is taken out of chamber and grinding is done to achieve finer powder.
- After that,powder was calcined at 450 C for 6 hour The crystal structure of the synthesized powder was characterized

2.3 Calculation:

Calculation of metal nitrate content

From $Fe(NO_3)_3$: 50 ml 0.2 M solution of $Fe(NO_3)_3$contains-(0.2/20)*3=0.03 mole of NO_3

From $Bi(NO_3)_3$: 50 ml 0.2 M solution of $Bi(NO_3)_3$ contains-(0.2/20)*3=0.03 mole of NO_3

From HNO_3: 250 ml solution contain- 60 ml HNO_3

50 ml solution contain -12 ml HNO_3

NO_3 from HNO_3=(12*0.7*1.41)/63=0.188 mole of NO_3

Total NO_3content=.03+0.03+0.188=0.248 mole

Since G/N=0.1

So glycine content=0.0248 mole

Amount of glycine=0.0248*75.05=1.8612 gm

So the final composition of precursor is

- $Bi(NO_3)_3$=50 ml
- $Fe(NO_3)_3$=50 ML
- Glycin=1.8612 gm

Using Citric acid as fuel

Here Metal content/Citrate content=1

Calculation of metal content

From $Fe(NO_3)_3$: 50 ml 0.2 M solution of $Fe(NO_3)_3$contains-(0.2/20)*1=0.01 mole of Fe
From $Bi(NO_3)_3$: 50 ml 0.2 M solution of $Bi(NO_3)_3$ contains-(0.2/20)*1=0.01 mole of Bi
Total metal content=0.01+0.01=0.02 mole
Since M/C=1,

So, C=0.02 mole=0.02*210.14=4.2028 gm

2.4 Choice of fuels:

Physicochemical properties of the oxidepowders synthesized by combustion processes mainly depend on the nature and amount of fuel used. In order to identify the suitable fuel for the synthesis of $BiFeO_3$, there are various organic fuels such as urea, citric acid, glycine and sucrose which are available. Among them, glycine is the best fuel and resulted in the formation of pure and nano-size $BiFeO_3$ powder. As an easy-obtained product, glycine is low-cost compared with other organic fuels.

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F/O ratio may have some effect on the morphology of the powders calcined at 1000 ◦C, without affecting their phase composition, For example, in FE samples a very low surface area was measured at F/O = 1.2, which increased for F/O = 2 and decreased slightly again for higher F/O values. Although the interpretation of this trend is still not clear, it is in agreement with the correspondent trend of the agglomeration degree with F/O, according to the fact that for higher agglomeration degrees lower surface areas are obtained Another example of the effect of F/O ratio on the morphology is the large particle size (540 nm) and non-homogeneous texture observed for CE powders prepared at F/O = 1, which is probably caused by the BaCO3 precipitation occurred before the gel formation. In general, low F/O ratios mean low cost and low organics to burn out, although, high F/O values seem more pertaining. Nevertheless in some cases high F/O ratios may affect the phase composition of the final powders, as for CO samples, where some phase segregation occurred for F/O = 4. A possibleThe F/O ratio has an important effect on the formation temperature of perovskite-type structure as shown in for FE samples: for F/O = 2 almost 100 wt.% perovskite is present after calcination at 600 ◦C for 5 h, whereas, at higher F/O values,the diffraction peak of the perovskite-type structure almost disappears and longer calcinations times at the same temperature or higher temperatures are necessary in order to obtain the perovskite-type structure. Explanation of this result can be related on one side with the dependence of the phase segregation with pH described for CO.

2.5 Safety condition

The auto-combustion reaction can be explosive, yielding a high flame which quickly propagates through the reactant mixture. Therefore, safety becomes more and more important when many grams of powder have to be prepared by auto-combustion synthesis, as observed by other authors. Moreover, if the combustion reaction is more explosive, more powder is displaced from the combustion beaker and the product is thus lost. Even if the combustion reaction takes place very calmly, without flame production, only 80% of the product can be recovered at low F/O ratios, because some of the very fluffy powder flies away with the combustion gases. At F/O = 0.8, where the intensity of the process is decreased, a 90% of recovery can be attained.

For these reasons, in this work, special care has been taken in the identification of the safety conditions.it is described that the combustion intensity decreases with F/O ratio and changes with the phase composition of the chemical mixture. Another important point is the material of the combustion beaker. On this respect, by comparing three combustion reactors made of different materials (sintered alumina,Pyrex glass and stainless steel) and by fixing all the other parameters, results show that sintered alumina reactor displays the highest combustion intensity, whereas stainless steel reactor displays the lowest one. This trend has been associated with the different dispersion capacity of the three materials. In summary,when this is possible, higher F/O ratios, lower pH values and combustion reactors with higher heat dispersion capacity are recommended in order to conduct safely the combustion.

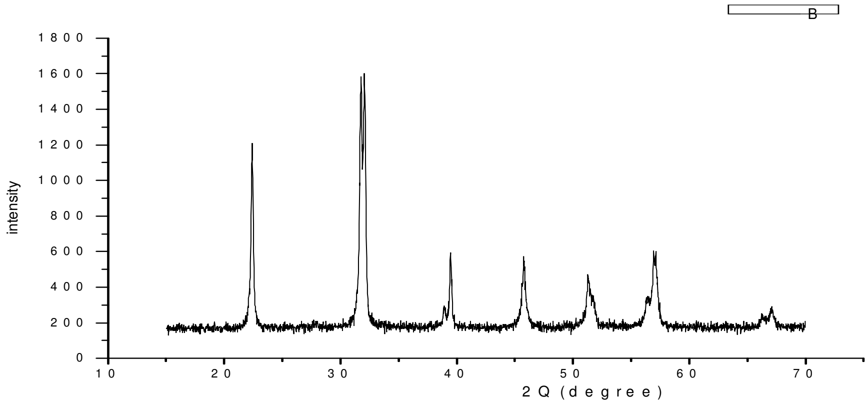
Chapter 3

Result and Discussion

3.1XRD Analysis

Compared with the traditional solid-state sintering process, the pure BiFeO3 was attained at a much lower temperature (600 C) without formation of other phase impurities. Moreover, prepared BiFeO3 nanopowders have a better homogeneity and fine grain morphology in this case. BiFeO3 nanopowders present the same Neel temperature (TN) and ferroelectric Curie temperature (TC) as those of bulk BiFeO3, which reveals the multiferroic properties of the BiFeO3 nanoparticles. The BiFeO3 nanoparticles show a weak ferromagnetic order at room temperature, which should be attributed to the size-confinement effects of the BiFeO3 nanostructures. The heterometallic polynuclear complexes forming in the solution are the key reason for synthesizing pure BiFeO3 powder.

The fuel/oxidant ratio has clearly the most intense influence on the structural and morphological properties of the powders.Low fuel/oxidant ratios are recommended in some cases in order to avoid segregation of the dopant and to obtain powders with small particle size. Nevertheless, high fuel/oxidant ratios may be considered a better choice, in order to avoid dangerous flame production and massive powder volatilization. Low pH and the use of stainless steel beakers are two other recommended conditions which decrease the explosivity of the combustion reaction .The fuel/oxidant ratio should be carefully selected in order to avoid precipitation of the most insoluble compounds or segregation of the dopant. Moreover, high fuel/oxidant ratio increase the formation temperature of the perovskite-type structure.The crystal structures of the BFO ceramics were determined by x-ray diffraction XRD, at a scan rate of 4 deg/min. The figure below shows the XRD patterns of powders calcined at 450 °C .



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