# PROCESSING OF $BiFeO_3$ CERAMICS BY GELCASTING

A

THESIS SUBMITTED IN THE PARTIAL FULFILLMENT OF
THE REQUIREMENT FOR THE DEGREE OF

MASTER OF TECHNOLOGY

IN

CERAMIC ENGINEERING

BY

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DEPARTMENT OF CERAMIC ENGINEERING,
NATIONAL INSTITUTE OF TECHNOLOGY, ROURKELA
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UNDER THE GUIDANCE OF

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2009

# DEPARTMENT OF CERAMIC ENGINEERING
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# ROURKELA-769008

## CERTIFICATE

This is to certify that the thesis on “**Processing of $BiFeO_3$ ceramics by gelcasting”** submitted by **Mr. Shyama Prasad Mohanty**, to the National Institute of Technology, Rourkela in partial fulfillment of the requirements for the award of the degree of **Master of Technology in Ceramic Engineering** is a record of bonafide research work carried out by him under my supervision and guidance. His thesis, in my opinion, is worthy of consideration for the award of degree of Master of Technology in accordance with the regulations of the institute.

The results embodied in this thesis have not been submitted to any other university or institute for the award of a Degree.

**Date** 1st June, 2009

**Prof. Sumit Kumar Pal**
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# ACKNOWLEDGEMENTS

This thesis arose in part of research that has been done in my one year work. By that time, I have worked with a great number of people whose contribution in assorted ways to the research and the making of the thesis deserved special mention. It is a pleasure to convey my gratitude to them all in my humble acknowledgment.

At first, I would like to record my gratitude to **Prof. Sumit Kumar Pal** for his supervision, advice, and guidance. It was his thought, which both of us tried to achieve. I thank you Sir for your help and blessings. I really enjoyed & learned a lot by working with him during the past one year.

I gratefully acknowledge **Prof. S. Bhattacharyya** (H.O.D.), Ceramic Engineering, N.I.T., Rourkela for providing me the necessary facilities in the department.

My sincere thanks go to **Prof. J. Bera, Prof. S.K.Pratihar**, **Prof. B.B.Nayak, Prof. R.Mazumder and Mr. A.Chowdhury** for their constant help, encouragement, inspiration and blessings.

I am very grateful to all the non-teaching members of the department for their help whenever needed in the research work.

I would like to thank, all the research scholars of Ceramic Engineering Department for their help and advice whenever I needed. Special thanks to Saratji, who helped me a lot. I feel guilty if I miss the opportunity to thank my friends, especially Ganesh who helped me a lot in my research work. I thank all of my friends for their support and help.

I would also express my sincere thanks to my parents & family members, for their support, blessings & affection. Without them I wouldn’t have been here to do the work.

Lastly, I owe my deepest gratitude to “God-the super natural power” & all of them, whose blessings are with me.

**Date** 1st June, 2009 ***SHYAMA PRASAD MOHANTY***

# Abstract

An attempt has been made in preparing $BiFeO_3$ articles based on gel casting system. For this purpose, $BiFeO_3$ was synthesized by glycine-nitrate auto combustion route. The powders were calcined between 450-550$^oC$ with different soaking time. Phase pure $BiFeO_3$ was obtained at 550$^oC$ with a soaking time of 2 hours. Phase purity was authenticated by X- ray diffraction technique. Employing BET 5 point method, surface area was measured. The surface area calculated is about 10.36$m^2$/g which is suitable for powder dispersion in gel casting system. Then the phase pure powder was used in gelcasting based on Acrylamide (AM) - N,$N^/$-methylene bisacrylamide (MBAM) premix solution. First, the ratio of AM-MBAM was optimized. Then, stable dispersion of $BiFeO_3$ in that premix solution was also achieved with Triammonium citrate (TAC) as dispersing agent with pH ~9. Then the slurry was gelcasted in humid atmosphere between 50-60$^oC$. The gelcasted bodies have good green strength and free of surface exfoliation defect. Differential scanning calorimetry was employed to study the thermal behavior of green bodies. Gelcasted bodies were first machined in green state and sintered at different temperature between 750-825$^oC$ to obtain the final product. The density of gelcasted body was measured and phases are again identified using X-ray diffraction. It has been observed that with increase in sintering temperature from 750 to 800$^oC$ theoretical density increased from 92.5% to 94%. A small amount of impurity was also present in sintered product.

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# CHAPTER-1

# INTRODUCTION

## 1. Introduction

Magnetism and ferroelectricity are essential to many forms of current technology. Therefore, the quest for multiferroic materials, where these two phenomena are intimately coupled, is of technological and fundamental importance. Multiferroic materials offer the possibility of manipulating the magnetic state by an electric field or vice versa and are of current interest and having potentiality for tunable multifunctional applications, in information storage, such as spintronic devices and sensors [1].

However, the availability of room-temperature, single-phase multiferroics is very limited to result from the unsuitability [2] of the conventional mechanism for cation off centering in ferroelectrics (requiring formally empty *d* orbitals), and the formation of magnetic moments (usually resulting from partially filled *d* orbitals). For ferroelectricity and magnetism to coexist in a single phase, the atoms moving off center to form the electric dipole moment should be different from those carrying the magnetic moment. In magnetic perovskite-structure oxides and related materials, multiferroism is most commonly achieved by making use of the stereochemical activity of the lone pair on the large (*A*-site) cation to provide the ferroelectricity, while keeping the small *B*-site cation magnetic. This is the mechanism for ferroelectricity in the Bi-based magnetic ferroelectrics.

In this regard, Bismuth ferrite ($BiFeO_3$) has recently gained considerable importance both technologically and scientifically. There is existence of both antiferromagnetic and ferroelectric ordering at room temperature in the same phase material, and also magnetoelectric coupling between the two respective order parameters (spin and charge). $BiFeO_3$ materials were reported to be antiferromagnetic below the Neel temperature of $370^{O}C$ and ferroelectric with a high Curie temperature of $830^{O}C$ [3]. $BiFeO_3$ with magnetic $Fe^{3+}$ ions, are ferroelectric. However, it is the Bi ion with two electrons on the 6*s* orbital (lone pair) that moves away from the center-symmetric position in its surrounding oxygen. $BiFeO_3$ has a non-centrosymmetric rhombohedrally distorted perovskite structure with space group R3c.

Till now different processing routes have been examined for synthesis of $BiFeO_3$ such as solid state synthesis routes [4], co-precipitation [5], sol gel [1] etc. It has been reported that one major problem associated with achieving sintered densities above 90% of theoretical density. Other problems include (i) achieving phase pure $BiFeO_3$ and (ii) getting highly resistive $BiFeO_3$ ceramics with low leakage current.

If we think of ceramic processing, shaping is without doubt, the key stage in the manufacturing of any ceramic article, not only because it determines final geometry and thus function, but also, and above all because it has to combine the properties of the raw materials in way that allows the subsequent stages of the production process to be completed successfully.

Among many ceramic process, gel casting has been drawn several attention in processing and optimizing properties of ceramics. Gelcasting is a near-net-shape forming method of advanced ceramic materials. It is used for making high-quality, complex-shaped ceramic parts. The process involves a slurry prepared from ceramic powder and a water based monomer solution which is poured into a mold, polymerized in-situ to immobilize the particles in a gelled part, removed from the mold while still wet, then dried and fired [6,7].

Gel casting also has the following advantages

1. Through gelcasting, article with complex geometries can be produced better than with other methods.
2. It is not limited to use with any particular ceramic powder.
3. Highly dense as well as porous bodies can be manufactured.
4. Gelcasting offers no size limitation. Complex shapes with thin sections as small as 0.2 mm have been gelcasted [8].
5. Excellent green machinability and high green strength.
6. Quickly adapted for use with new materials and new applications.
7. The processing additives are all organic and leave no cation impurities behind in the fired part.
8. Rapid forming cycles and the formed parts requires little machining.
9. Low capital equipment cost.

Though gel casting technique has been severely employed in making structural ceramic components using $Al_2O_3$, $ZrO_2$, SiC etc., now a day's gel casting has also found application in making ferroelectric ($BaTiO_3$)[9], solid oxide fuel cell cathode ($(La_{0.8}Sr_{0.2})_{0.9}MnO_3$) [10] and piezoelectric (lead zirconia titanate)[11] components.

Till now there is no report of making $BiFeO_3$ articles by gel casting method. So it can be an interesting topic to explore and investigate the change in properties of $BiFeO_3$ prepared employing gel casting method. These facts drive an attempt in employing gel casting method in $BiFeO_3$ ceramics preparation.

The present work is mainly focused on achieving more than 90% theoretical density of $BiFeO_3$. In this regard a detailed investigation has been performed in optimizing different parameters which affects gel casting.

First, a phase pure $BiFeO_3$ powder is prepared by auto combustion according to method described in Ref.[12]. The surface area of prepared powders is $10.36 m^2/g$. According to Mark A. Janney [13] surface area of between 5 and 10 $m^2/g$ is a reasonable choice for gelcasting. The gel casting method reported in this work is based on Acrylamide (AM) - $N,N^{/}$-methylene bisacrylamide (MBAM) system. Powders were dispersed in premix solution using Triammonium citrate (TAC) and maintaining the pH of the slurry at 9. Ammonium persulfate (APS) is used as initiator and Tetramethylethylene diamine (TEMED) as catalyst. Gel casted samples have been sintered between 750 to $825^{O}C$. The in-situ formation of $BiFeO_3$ by using $Bi_2O_3$ and $Fe_2O_3$ powders as raw materials has been avoided. This has been done to overcome dispersion problem arising from two different types of powders. It appears that gel casting can be a good alternative way in improving different properties of $BiFeO_3$.

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# CHAPTER-2

# LITERATURE REVIEW

## 2. Literature review

Bismuth ferrite is a multiferroic material which is of great importance due to its wide application in devices like radio, television, microwave and satellite communication, bubble memory devices, audio-video and digital recording, etc [1,2]. In addition to these, due their high sensitivity to ethanol and acetone vapors, bismuth ferrites can also be used as semiconductor gas sensors [3].

### 2.1. Synthesis of $BiFeO_3$

During the past few years, increasing attention has been devoted to BFO thin films. BFO heteroepitaxial films were processed via pulsed laser ablation (PLD) [4] and metal-organic chemical vapor deposition [5] on $SrTiO_3$-single crystal/ $SrRuO_3$ as well as on platinized silicon buffered with a $LaNiO_3$ layer using RF magnetron sputtering [6]. Polycrystalline films were obtained on platinized silicon using sol-gel or PLD routes [7-14].

$BiFeO_3$ has been synthesized by several methods. In the solid state route, [15] $Bi_2O_3$ and $Fe_2O_3$ are reacted at a temperature in the range of $800^O$–$830^OC$ and unreacted $Bi_2O_3/Bi_2Fe_4O_9$ phases are removed by washing in $HNO_3$. The disadvantage of this process lies in the necessity of leaching the unwanted phases using an acid and effectively providing coarser powder and also the reproducibility of the process is poor. Most of the high temperature treatments (>800°C) leads to bismuth volatilization. In order to overcome this problem, low temperature synthesis methods are essential [16]. Ghosh *et al.* [1] have reported the synthesis of bismuth ferrite by a ferrioxalate precursor method with metal ions to oxalic acid ratio 0.5. On calcination at $600^OC$ for 2h, 90% phase pure $BiFeO_3$ was obtained. Szafraniak *et al*. [17] obtained bismuth ferrite nanopowder by mechanochemical synthesis. The method has the advantage over the conventional solid state synthesis since it occurs at room temperature and results in particle size in nanometer scale. Das *et al.* [18] prepared bismuth ferrite powders by sonochemical and microemulsion processes. Though the microemulsion based powders showed slightly better properties with respect to particle size, surface area, and final density, sonochemically prepared powders may be more acceptable considering the ease of preparation and cost effectiveness. Mazumder *et al.* [19] have prepared nanosized powders of $BiFeO_3$ by the glycine combustion synthesis process. A glycine to nitrate ratio of 0.1 has resulted in the formation of nearly phase pure $BiFeO_3$. Saturation magnetization of $\sim 0.4\mu_B$/Fe along with room temperature ferromagnetic hysteresis loop was also observed in the synthesized nanoscale (4–40 nm), whereas multiferroic $BiFeO_3$ in bulk form exhibits weak magnetization (~0.02 $\mu_B$/Fe) and an antiferromagnetic order. Paraschiv *et al*. [16] synthesized bismuth ferrite by using glycine or urea as fuel. In glycine containing system, after annealing at $650^{O}$C, amounts of secondary phases ($Bi_2Fe_4O_9$, $Bi_{36}Fe_2O_{57}$) were also identified beside the $BiFeO_3$ as the major phase. In the case of urea containing system, after annealing at $650^{O}$C only traces of $Bi_2Fe_4O_9$ were detected along with uniformity in shape and size $BiFeO_3$ particles. Bismuth ferrite was synthesized by Farhadi *et al*. [20] using sucrose as a fuel. The main objective of their work was to investigate the activity of $BiFeO_3$ nanopowder as the heterogeneous catalyst for the acetylation reaction. Sol–gel technique [21] followed by leaching was used to prepare single-phase $BiFeO_3$ powders with grain size of 200 nm. Annealing under Ar atmosphere was effective in reducing impurity phases but created large oxygen vacancies and the composition was $BiFeO_{2.75}$ rather than $BiFeO_3$.

### 2.1.1 Problems associated with $BiFeO_3$ ceramics

The major difficulties of making $BiFeO_3$ ceramics are:

(i) Synthesizing phase pure material
(ii) Achieving sintered densities above 90% of theoretical density and
(iii) Getting highly resistive $BiFeO_3$ ceramics with low leakage current.

One of the major problem associated with $BiFeO_3$ synthesis is the formation of unwanted secondary phases. According to Carvalho *et al*. [22] $BiFeO_3$ phase pure compound is very difficult to achieve. Upper or lower calcinations temperatures yielded higher content of the secondary phases $Bi_2Fe_4O_9$ and $Bi_{25}FeO_{39}$. Secondary phases appear due to the kinetics of phase formation. Incidentally, there are only a few reports of making densified and highly resistive $BiFeO_3$ ceramics.

Kumar *et al*. [23] reported the dielectric and ferroelectric properties of $BiFeO_3$ ceramics prepared by solid state route and there was no report about the bulk densities of the samples. The spontaneous polarization of the sample was very low. Wang *et al*. [24] 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 and 4.0 $\mu C/cm^2$, respectively. Pradhan *et al*. [25] followed similar rapid phase sintering, but the percent densification was not reported. In their report the value of the spontaneous and remanent polarizations were only 3.5 and 2.5 $\mu C/cm^2$, respectively. Mazumder et al. [26] achieved 96% of the theoretical density in the sample by spark plasma sintering. Yuan *et a*l. [27] followed the rapid phase sintering technique and synthesized highly resistive and dense (92% of theoretical density) sample by varying the particle size of precursors $Bi_2O_3$ and $Fe_2O_3$ and they reported high spontaneous polarization of their samples.

## 2.2 Gelcasting

In the last decade several consolidation techniques have been investigated with the aim of shaping dense ceramic bodies directly from stable colloidal suspensions [28,29]. These techniques combine advantages such as the microstructural homogeneity provided by colloidal processing and the ability of directly forming complex-shaped ceramic parts. Among many ceramic processing techniques gelcasting has drawn attention of many scientists as well as technologists. Gelcasting is a processing technique, which was first developed in the Metals and Ceramics Division- Ceramic Processing Group at Oak Ridge National Laboratory (ORNL.), Oak Ridge, USA by Mark A Janney and Ogbemi O.Omatete [30]. Now a days gelcasting technique is being utilized in processing structural ceramics as well as electronic ceramics. The main advantages of gelcasting compared to other processes such as slip casting, injection molding, and pressure casting is listed in Table 2.1.

The gelcasting process involves slurry of ceramic powder in a solution of organic monomers which is poured into a mold and then polymerized in situ to form a green body.

**Table 2.1.Comparison of gelcasting process parameters with those for slip casting, injection molding, and pressure casting.**

| **Property** | **Gelcasting** | **Slip casting** | **Injection Molding** | **Pressure Casting** |
|---|---|---|---|---|
| Molding time | 5-60 min | 1-10 hrs | 10-60 sec | 10 min - 5 hr |
| Strength (As-formed) | Moderate to high depending on gel system | Low | High | Low |
| Strength (Dried) | Very High | Low | N/A | Low |
| Mold Materials | Metal, glass, polymer, wax | Plaster | Metal | Porous plastic |
| Binder Burnout | 2-3 hours | 2-3 hours | Up to 7 days | 2-3 hours |
| Molding defects | Minimal | Minimal | Significant | Minimal |
| Maximum Part Dimension | > 1 meter | > 1 meter | ~30cm,<br>1 dimension must be $\leq$1 cm | ~1 meter |
| Warpage during drying/binder removal | Minimal | Minimal | Can be severe | Minimal |
| Thick/thin sections | No problem | Thick section increases time of cast | Problems with binder removal in thick sections | Thick section increases time of cast |
| Particle size | Viscosity goes up as size goes down | Casting time goes up as size goes down | Viscosity goes up as size goes down | Casting time goes up as size goes down |

### 2.2.1 Requirements of gelcasting

The process requirements are a) Monomers and Crosslinkers b) Solvent c) Dispersant d) Additives e) Initiator and Catalyst f) Molding materials

The monomers solution is termed as “Premix solution”. The primary requirement of monomers and crosslinkers is they should be water soluble. At least 20wt% water solubility is required for monofunctional monomer and for difunctional monomers 2 wt% solubility is required, higher solubility is desirable. They undergo a free-radical chain polymerization reaction and the setting is very rapid. The crosslinkers should have at least 2 double bonds [31]. Composition of monomer and crosslinker determines the gel strength, gel stiffness, gel toughness, wet strength, dry strength, green machinability, reactivity. The strength of the gel and the gelcast ceramic increases with increasing total monomer concentration in solution. With increasing ratio of crosslinker to monomer the gel becomes stronger and stiffer [32]. The processing time increases with increasing the monomer to crosslinker ratio [33].Gel formation is shown schematically in Fig.2.1. The monomer is depicted as “M” and the crosslinker is depicted as “X.” Upon the addition of free radicals to the solution, the “M” monomers react to form long chains that are occasionally caused to branch by the incorporation of the “X”. The result is a very high molecular weight polymer that fills space and traps the solvent molecules among its branches. The macroscopic result is a polymer-solvent gel [32].

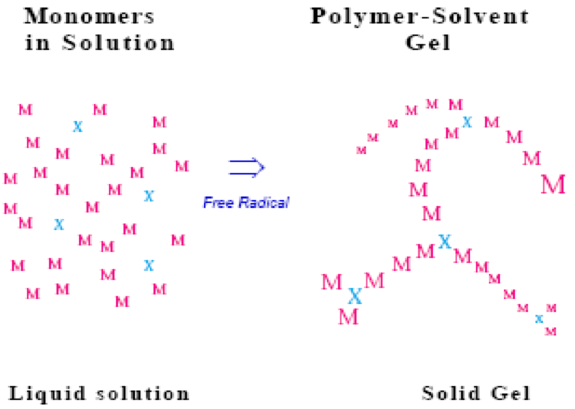

Fig.2.1 Cross linking of monomer-crosslinker in the gel.

The commonly used monomers are Acrylic acid (AA), Acrylamide (AM), Methacrylic acid (MAA) and Methacrylamide (MAM). These monomers are often combined with crosslinker N,N$^{/}$-methylene bisacrylamide (MBAM). Poly(ethylene glycol) diacrylate [PEGDA], Poly(ethylene glycol) dimethacrylate [PEGDMA] are also reported as crosslinking agent [34].

### 2.2.2 Factors affecting gelcasting

The key factors gelcasting technique are the homogenization and dispersion of the powder in the premix solution and the stability of the suspension, which are determined by attractive and repulsive forces, whose behavior is directly dependent on the zeta potential of the powders. pH also helps in better dispersion [35]. It happens due to better dissociation of the dispersant in the alkaline medium. Milling is done to prepare homogeneous slurry. The slurry should be flowable in nature. The entrapped air in the slurry leaves pores in the casted parts, which results in flaws and reduced mechanical properties. So, deairing is done prior to casting. Excess deairing may lead to liquid loss by evaporation and affect the slurry properties [30]. Initiator is added for free-radical chain polymerization reaction. Catalyst is used to generate free radicals from initiator and enhance the polymerization reaction. Gelation takes place at 40-80$^{O}$C. The gelation reaction proceeds in two stages - initiation and propagation. The initiation interval is often called the "idle" stage because there is no macroscopic evidence that a reaction is occurring. That is, the viscosity of the solution or slurry does not increase and no heat is generated, as happens later during the propagation stage. Drying should be done at high relative humidity to avoid defects in the dried parts [31]. After drying the organic material remaining in the gelcast part is typically between 2-6 wt %.

The success of gelcasting technique also depends on the following factors

1. Choice of solvent.
2. Surface area of powders.
3. High solid loading
4. Dispersing agent
5. Initiator and catalyst
6. Mold materials

Water is the most widely used solvent because it is easily available, cheapest solvent, most of the materials are soluble in it, ecofriendly and most ceramists prefer to work in water [31]. Alcohol is also reported in some cases [36].

Attaining higher solid loading in the slurry depends on the powder system. For example in case of alumina 70 vol % solid loading in slurry can be attained but 40 to 45 vol% solid loading can be attained in case of silicon nitride. A target surface area of powder is between 5 and 10 $m^2/g$ [37]. The powder must be milled to break down hard agglomerates that were formed during calcining. Sometimes conditioning may be needed before making slurry if a high solids loading is to be obtained.

Next to powder selection is choice of dispersant. For a powder to become well dispersed; it must be wet by the solvent, the particles must become separated from one another, mixed with the solvent system and they must remain separated and not reagglomerate. Polyelectrolyte species are widely used as dispersing agents. These materials can impart electrostatic and steric stabilization to a given colloidal dispersion. Tong *et al.* [38] have discussed the 3 states of dispersant which is depicted in Fig. 2.2. The dispersant capability can exert well, when the state of dispersant in the surface of the particles is in saturated adsorption state, both unsaturated adsorption and over-saturated adsorption are bad to the dispersing of particles in the solvent.

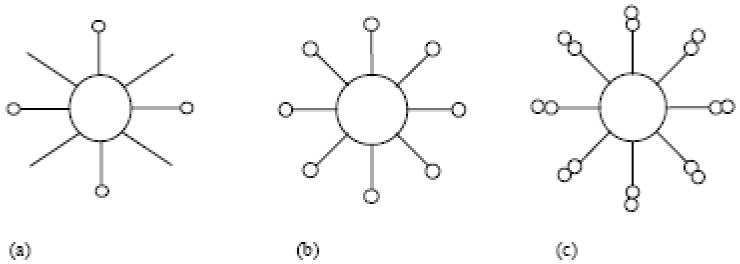

Fig.2.2 The state of dispersant in the surface of the particles (a) Unsaturated adsorption, (b) saturated adsorption, (c) over-saturated adsorption.

Triammonium citrate (TAC), Lactic acid, poly (acrylic acid) and poly (methacrylic acid) derivatives are also used as dispersing agents.

Initiator forms free radicals which help in free-radical chain polymerization reaction. Some of the initiators are Ammonium persulfate (APS), Azobis [2-(2-imidazolin-2-yl) propane] HCl (AZIP) and Azobis (2-amidinopropane) HCl (AZAP) [36]. Tetramethylethylene diamine (TEMED) is frequently added to catalyze the breakdown of the APS, therefore accelerate the polymerization and crosslinking reaction. The processing time decreases with increasing the concentration of initiator and catalyst. Defoamers are sometimes added to aid in bubble removal. Some additives are also added to modify the surface properties and avoid surface exfoliation. Polyethylene glycol is used to solve the purpose [39].

Molds for gelcasting are non-porous in nature and can be made from several materials like metals, glass, wax, and plastics [31]. Glass provides a smooth surface which helps in easy release of gelled parts. Poly vinyl chloride (PVC) forms a thin ungelled layer which acts as a lubricant surface. Mold release agents are used to adjust the interaction of the slurry with the mold surface. These include waxes, oils, greases, polymer dispersions, polymer resin solutions, oils, fatty acids and fatty acid derivatives, inorganic powders, or sometimes combinations of the above [32].

Among the several gelcasted materials, the most studied material is $Al_2O_3$. Gelcasting of microporous alumina membrane substrate in tubular and planar configurations have been performed by Prabhakaran *et al.* [40] using high amount of urea–formaldehyde as gelling agent. They achieved porosity >70% where as literature shows that porosity of membrane substrates prepared by several methods is <50%. Mao *et al.* [41] used epoxy resin as gelling agent and optimized the slurry with a solid loading of 80 wt% for gelcasting.

Macroporous nanocrystalline YSZ was fabricated by gelcasting [42]. There are also reports on $Al_2O_3/ZrO_2$ [43] where porosity varies from 6% to 50% by gelcasting using polystyrene (PS) as pore-forming agent. In case of non-oxide ceramics, SiC slurry with 50 vol. % solid loading was gelcasted with sintering assistants, $Al_2O_3$ and $Y_2O_3$ [44]. Porous silicon carbide/silicon nitride composite ceramics have been developed by gelcasting [45].

Chen *et al.* [46] performed aqueous gelcasting of hydroxyapatite. They investigated the effects of the dispersant, pH values on the dispersing ability of HA powder and the rheological behavior of the slurries. Gelcasting was studied on fused silica glass powder [47]. It is better than slipcasting process where segregation always occurs and results in density deviation.

In case of electroceramic materials, either phase developed powder has been gelcasted or insitu development of phase has taken place in the casted material on sintering. Santacruz *et al.* [48] gelcasted nano-$BaTiO_3$ powders. They used agar as gelling agent. They achieved solids loadings as high as 80 wt%. Guo *et al.* [35] extend the gelcasting technology for the fabrication of piezoelectric ceramics. They investigated the colloidal chemistry of PZT powders in aqueous solution, the rheological behavior of the PZT suspension and the influence of dispersants on the rheology of the suspension and on the electrical properties of the gelcast PZT samples. Zhou *et al.* [49] gelcasted lead free piezoelectric ceramics. They performed aqueous gelcasting for $0.94Bi_{0.5}Na_{0.5}TiO_3$–$0.06BaTiO_3$ (BNBT6). Lin *et al.* [50] applied gelcasting to fabricate protonic ceramic membrane fuel cells. The anode, cathode were gelcasted. In this case, insitu development of phase has been achieved. Zhang *et al.* [51] also developed insitu phase in Lanthanum Strontium Manganite (LSM) which is used as solid oxide fuel cell cathode.

### 2.2.3 Problems solved in gelcasting

One of the major problems associated with gelcasting techniques is surface exfoliation. The surface exfoliation problem was solved by Li *et al.* [39] and they studied the effect of polyethylene glycol on of SiC green bodies prepared by gelcasting. Liya et al. [43] investigated the factors influencing surface exfoliation in $Al_2O_3$–$ZrO_2$ green bodies prepared by gelcasting. They observed that the temperature gradient and oxygen can inhibit the polymerization of AM/MBAM monomer and lead to surface exfoliation of the green bodies. This can be solved by eliminating temperature gradient and removing $O_2$ to solidify the ceramic slurry at a high temperature. Nitrogen atmosphere is helpful to solve the problem. During drying structural and residual stresses develop in the material which causes defects, such as cracking, bending and other malformations. Zheng *et al.* [52] studied the drying and sintering characteristics of gelcast $BaTiO_3$-based ceramic parts. They have used the liquid desiccant method for drying of $BaTiO_3$-based semiconducting ceramic gelcast parts.

So, it can be concluded from literature review that

1. Synthesis of phase pure and high density $BiFeO_3$ is a subject of research interest.
2. Gelcasting can offer high density, so employing this technique for preparation of $BiFeO_3$ ceramics should be explored.
3. Optimization of different factors is key to success for gelcasting technique.

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# CHAPTER-3

# OBJECTIVE

## 3. Objective

Based on literature review it is evident that till now no attempt has been made in preparing $BiFeO_3$ ceramics by gelcasting method. So the prime focus of this present work is to investigate the applicability of gelcasting method in preparing $BiFeO_3$ ceramics. In gelcasting method different processing parameters varies with different powder morphology and success of gelcasting lies in optimizing those parameters.

So the objectives of the present work mostly lies in optimizing different aspects starting from phase pure powder preparation to optimizing sintering temperature and time of gelcasted body, which are as follows

1. Preparation of phase pure $BiFeO_3$ powder by glycine-nitrate auto-combustion route.
2. Optimization of calcining temperature and time for powder from auto-combustion.
3. Phase identification of $BiFeO_3$ powder to ensure purity.
4. Surface area measurement of powder to find suitability for gelcasting.
5. Optimization of monomer to crosslinker ratio.
6. Preparation of well dispersed and flowable slurry using a dispersing agent and adjusting the pH value of slurry.
7. Optimization of solid loading in the slurry.
8. Gelcasting of slurry in a humid atmosphere and observation of defects arising during the gelcasting process and observation of green stage machinability.
9. Optimization of sintering temperature and time for gelcasted bodies.
10. Measurement of density by Archimedean principle and phase identification in sintered body.

# CHAPTER-4

# EXPERIMENTAL PROCEDURE

## 4. Experimental procedure

In the present work $BiFeO_3$ powders were synthesized by Glycine-nitrate combustion route & then the phase pure powders were gelcasted.

### 4.1 Powder Preparation

#### 4.1.1 Estimation of $Fe_2O_3$

$Fe(NO_3)_3$ solution was prepared by dissolving $Fe(NO_3)_3.9H_2O$[Merck, Pure] in deionized water. The solution was filtered to remove impurity and the clear solution was collected. 3 ml of this clear solution was taken and to it 2-3 drops of AAC buffer was added to get a precipitate. Then it was filtered through Whatman-41 filter paper followed by washing with hot water. Then the precipitate was taken in a pre-weighed platinum crucible and fired at $1000^{O}C$ for 1 hour. After firing the platinum crucible was again weighed. The difference in weight was the amount of iron oxide in 3 ml of solution.

#### 4.1.2 Glycine-nitrate combustion synthesis

0.25M $Bi(NO_3)_3$ solution was prepared by dissolving $Bi(NO_3)_3.5H_2O$ [S.D.Fine Chem.Ltd., AR] in nitric acid solution. Stoichiometric amount of $Bi(NO_3)_3$ solution and $Fe(NO_3)_3$ solution was mixed together in a beaker. Then Glycine [Qualigens] was added keeping glycine to nitrate ratio of 0.1 according to ref [1]. The solution was placed on the hot plate. The temperature of the hot plate was then kept in the range of $80–90^{O}C$ and the solution was continuously stirred with help of a magnetic stirrer. Dehydration of the homogeneously mixed solution during heating caused the development of a viscous gel. Then the gel got self ignited on further heating. This ignition product ash was voluminous and fluffy in nature. The ash was grounded with agate mortar and powder was calcined at various temperatures from 450 to $550^{O}C$ with soaking time varying from 1 to 2 hours.

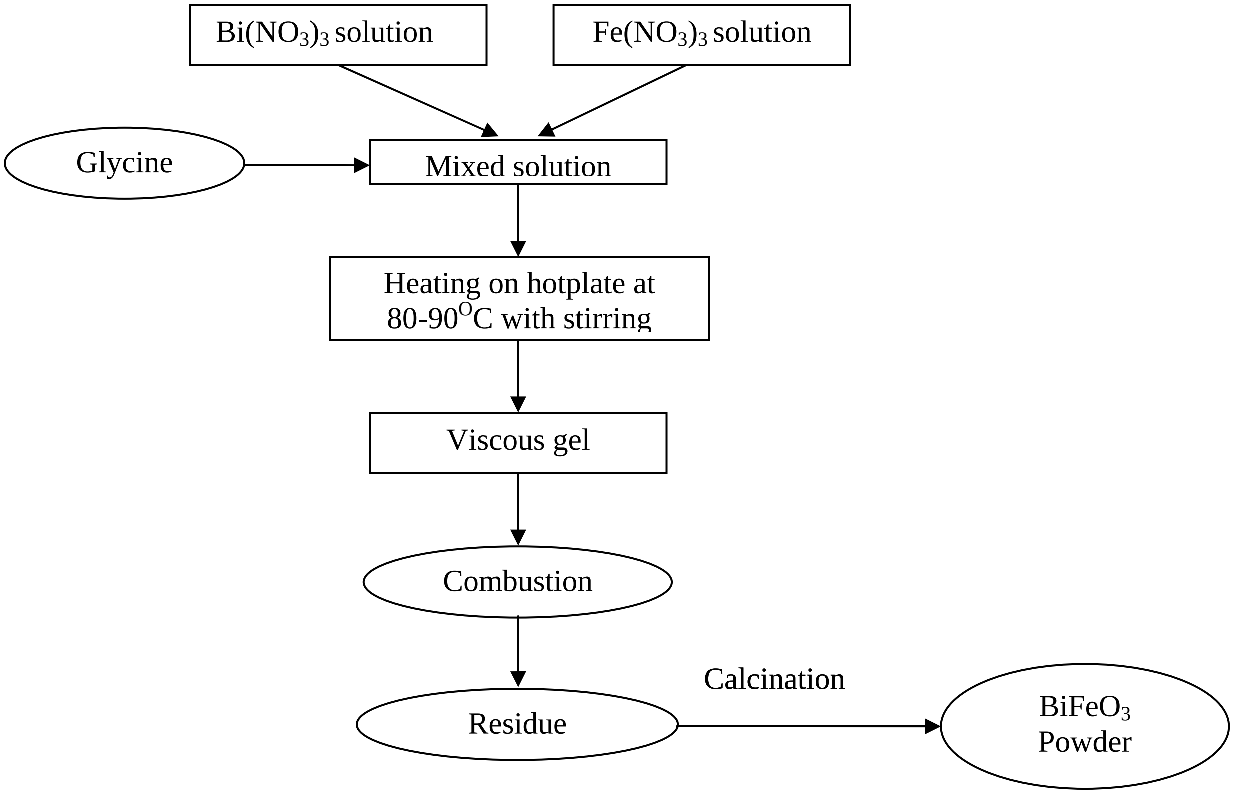

Fig.4.1 Flowchart for the Combustion synthesis of $BiFeO_3$

### 4.1.3 Phase identification

The phases developed in calcined powder was identified using X-ray diffraction technique (Philips PAN analytical, Netherland) using Ni filter and with Cu $K_\alpha = 1.54\ A^O$ radiation. The generator voltage and current was set at 35 KV and 30mA respectively. The samples were scanned in the 2θ ranges 20 to $60^O$range in continuous scan mode. The scan rate was $0.04^O$/sec. Phases present in the sample has been identified with the search match facility available with Philips X'pert high score software.

The crystallite size of the calcined powders was calculated from X-ray line broadening using the Scherrer's equation as follows:

$$t = \frac{0.9\lambda}{\mathrm{B}\cos\theta} \tag{4.1}$$

Where, t = crystallite size,

λ = wavelength of the radiation,

θ = Bragg's angle and B = full width at half maximum

## 4. 2 Powder characterization

### 4.2.1 Particle Size Analysis

In order to find out the particles size distribution, the $BiFeO_3$ powder was dispersed in water and then sonicated by ultrasonic processor [Oscar Ultrasonic] to break the agglomerates. Then particle size was measured using computer controlled particle size analyzer [ZETASIZER, Nanoseries (Malvern Instruments Nano ZS)].

### 4.2.2 Powder surface area measurement

The powders were dried in oven at $100^{O}C$ for 12 hours before analysis. BET surface area was measured using 5 point method by AUTOSORB 1, Quantachrome. The average particle size was estimated by assuming all the particles to have the same spherical shape and size. The average particle diameter, D (in nm), is given by:

$$D = \frac{6000}{\mathrm{S_{sp}} * \rho} \tag{4.2}$$

where "$S_{sp}$" is the specific surface in sq.m/g of the sample and "ρ" is the true density in g/cc

## 4.3 Gelcasting of $BiFeO_3$ Powder

For gelcasting, Acrylamide ($C_2H_3CONH_2$, AM) [S.D.Fine, LR] was used as the monomer, N,N$^{/}$-Methylene bisacrylamide ($(C_2H_3CONH)_2CH_2$, MBAM) [SRL,AR] as a cross-linker, N,N,N$^{/}$,N$^{/}$- tetramethylethylenediamine (TEMED) [SRL] as a catalyst, and Ammonium persulphate (APS) [Qualigens] as an initiator. Triammonium citrate (TAC) [S.D.Fine, AR] was used as dispersant.

A premix solution containing 10 wt% AM and MBAM was prepared. The ratio between AM and MBAM was kept at 20:1 and 15:1. To optimize the dispersant and pH suspension was prepared using 1 vol% powder. The dispersant amount was first varied from 0.5-3.5 wt% of powder. Then pH was varied from 7-11. Relative suspension height was observed to evaluate the slurry stability. Then the slurry was prepared using premix solution & phase pure $BiFeO_3$ and TAC powder. Triammonium citrate (2.5 wt% of powder) was added to disperse the powder in slurry. The pH of the slurry was adjusted to 9 by adding $NH_4OH$ solution. The solid loading achieved was 32.5 vol%. 1-Butanol [SRL, AR] was added as defoamer. Mixing was done to obtain homogeneous slurry and then, it was de-aired in vacuum to remove entrapped bubbles. To the slurry TEMED, ammonium persulphate (1 wt% of organic monomers) was added and mixed. Then the slurry was casted into a glass mold and gelled at 50-60$^{O}$C in high relative humid condition. After gelation, the circular plate was removed from mold, dried in oven at 80-90$^{o}$C. Fig 4.2 shows flow chart of gelcasting system. The gel casted samples were cut into small pieces in green stage and then samples were subjected to DSC measurements and sintering.

### 4.3.1 Thermal decomposition behavior of the dried green gelcasted body

Thermal decomposition behavior of the gelcasted green body has been studied using Netzsch, STA 449C. The DSC/TG patterns were collected as a function of temperature up to 750$^{O}$C under $N_2$ atmosphere. The heating rate was 10$^{O}$C/min in $N_2$ atmosphere.

### 4.3.2 Sintering

The gelcasted samples were sintered at various temperatures between 750 to 825$^{O}$C. The soaking time was 2 hours. During sintering the samples were kept at 550$^{O}$C for 2 hours the complete burn out of organic binders.

### 4.3.3 Density measurement

Density of sintered samples was determined by Archimedes principle. Kerosene was used as the immersion liquid. Density was calculated using the following equation

$$BD = \frac{D * \rho_s}{W - S} \qquad (4.3)$$

Where, D= Dry weight of the sample.

W= Weight of the sample in air, including kerosene in open pores

S= Weight of sample suspended in kerosene

$\rho_s$= Density of kerosene

### 4.3.4 Microstructure Analysis

Microstructure of powders, green gelcasted samples and sintered samples were observed using Scanning Electron Microscope (JEOL -JSM 6480LV).

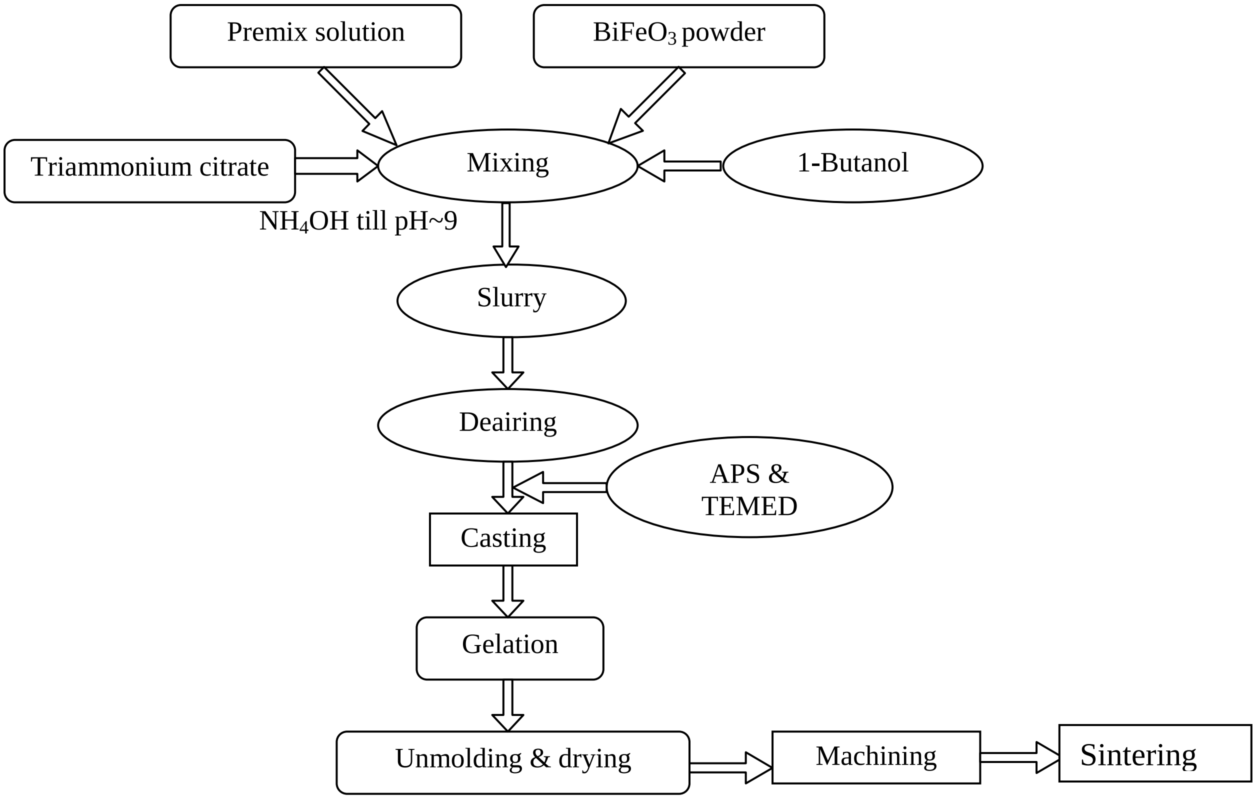

Fig. 4.2 Flowchart of the gelcasting process.

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# CHAPTER-5

# RESULTS AND DISCUSSION

## 5. Results and discussion

### 5.1 Phase analysis of calcined $BiFeO_3$ powder

$BiFeO_3$ powder was synthesized by glycine nitrate route keeping glycine: nitrate ratio 0.1 according to ref [1]. Then the powders were calcined at 500°C and 550°C for 1 hour. Fig 5.1 shows X-ray diffraction pattern of samples calcined at 500°C and 550°C for 1 hour. The XRD profiles were compared with JCPDS- 74-2493. It was observed that phases were not fully developed. It was also observed that the relative intensity of peaks also increased when calcining temperature was increased from 500°C to 550°C. However, there is no trace of secondary phases present in the samples. Then the powder was calcined at 550°C for 2 hours. Fig. 5.2 shows X-ray diffraction pattern of $BiFeO_3$ powders calcined at 550°C for 2 hours. It was again compared with JCPDS - 74-2493. It has been observed that phases were fully developed with no trace of impurity. Fig 5.3 shows changes in intensity when calcinations time increased from 1 hour to 2 hours.

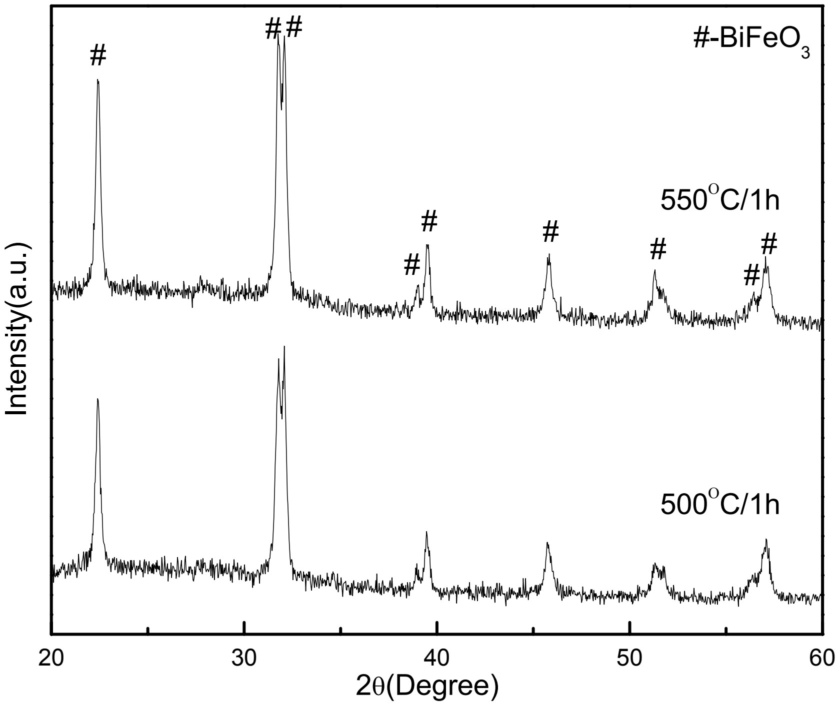

Fig 5.1 XRD patterns of samples calcined at 500°C and 550°C for 1 hour.

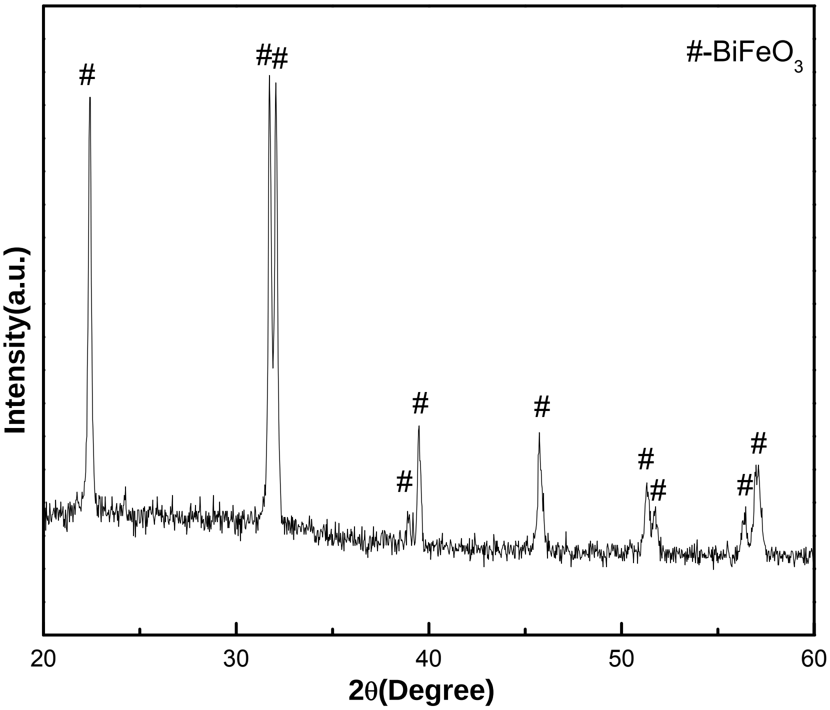

Fig.5.2 XRD pattern of $BiFeO_3$ powder calcined at $550^{O}C$ for 2 hours

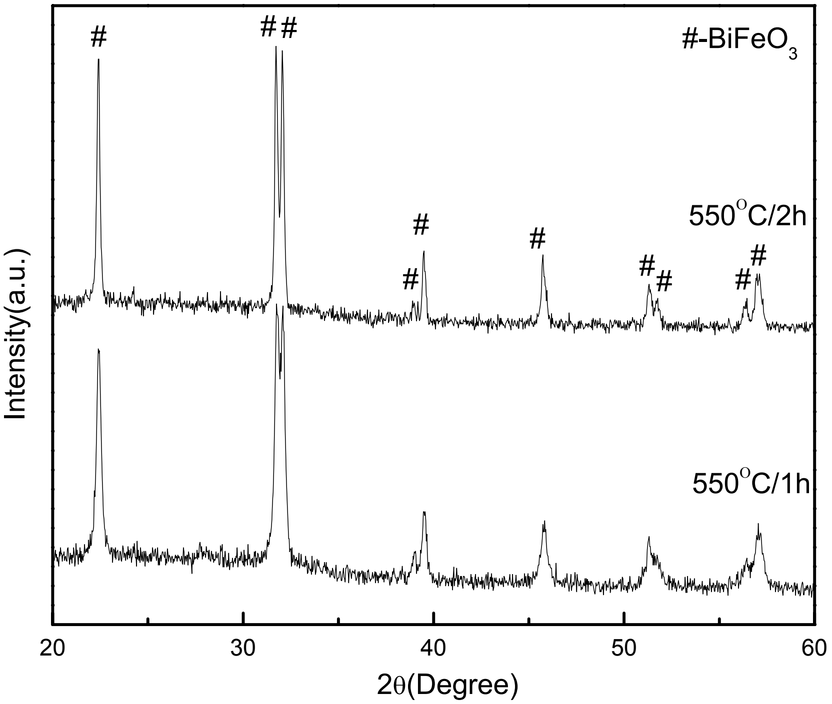

Fig.5.3 XRD patterns of $BiFeO_3$ powder calcined at $550^{O}C$ for 1 hour and 2 hours.

The average crystallite size was calculated by using Scherrer's formula (Equation 4.1). Table 5.1 shows the variation of crystallite size with increasing temperature. It has been observed that crystallite size increases with increasing temperature. However, the crystallite size did not change when samples were calcined for 2 hours at 550$^{O}$C.

**Table 5.1 Variation of crystallite size with calcination temperature and time.**

| **Calcination** | **Average crystallite size(nm)** |
|---|---|
| 500$^{O}$C/1h | 52.9 |
| 550$^{O}$C/1h | 85.1 |
| 550$^{O}$C/2h | 85.1 |

## 5.2 Particle size distribution of calcined $BiFeO_3$ powder

Fig.5.4 shows the particle size distribution of $BiFeO_3$ powder calcined at 550$^{O}$C. The particle size distribution shows that around 30 volume percent of particles are in between 0.2-0.5μm range.

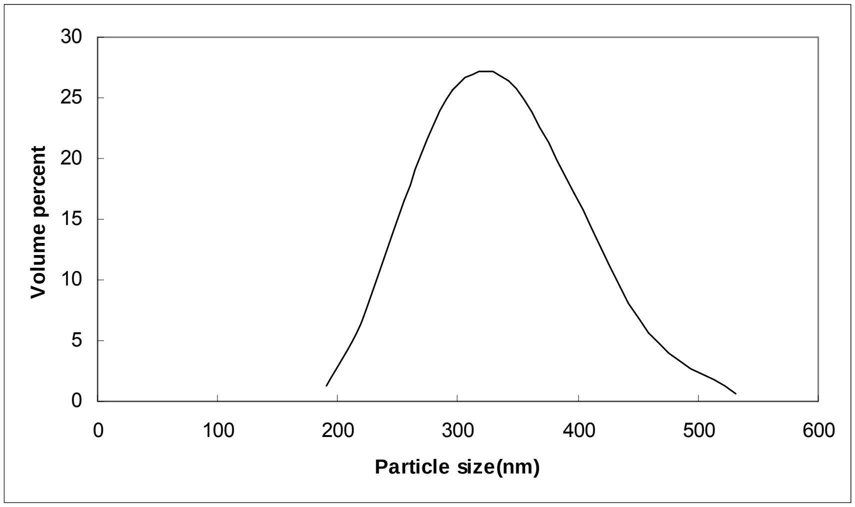

Fig.5.4 Particle size distribution curve of calcined $BiFeO_3$ powder

### 5.3 Surface area of measurement calcined $BiFeO_3$ powder

Surface area of phase pure calcined powders were measure using BET 5 points method. First time the measured surface area was 10m$^2$/g. The surface area was again measured to check the reproducibility and consistency of the result. Surface area measured next time was 10.72m$^2$/g. The average of the two results was taken for consideration which was 10.36m$^2$/g. According to Mark A. Janney [2] particles with surface area with 5 –10m$^2$/g is suitable for gelcasting. The average particle size calculated using equation (4.2) is 69.36nm. The density of the calcined powders obtained by combustion route was found to be 8.13 g/cc which is 97.4% of theoretical density.

### 5.4 Microstructure of calcined $BiFeO_3$

Fig 5.5 shows the microstructure of the calcined powder. It has been observed that particles are highly agglomerated and flaky in nature.

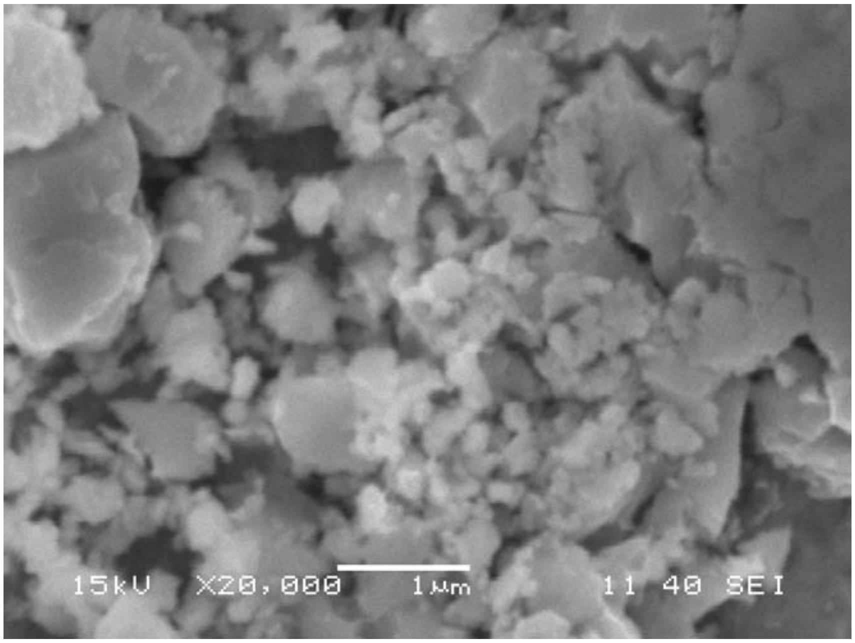

Fig.5.5 SEM image of calcined powder

### 5.5 Dispersion study of $BiFeO_3$ powders in aqueous medium

Dispersion behavior was studied by relative suspension height method. 1vol% of $BiFeO_3$ powders were dispersed in water using TAC as dispersing agent. The amount of TAC was varied from 0.5 – 3.5 wt%. TAC generally gives good dispersion in alkaline medium. Then pH was adjusted to 7, 9 and 11. Samples were kept for 24 hours. It was observed stability of dispersion was improved with increase in TAC amount up to 2.5 wt% of TAC. With 2.5% of TAC the sedimentation height was minimum at pH= 9. There is no considerable change in 3 and 3.5 wt%. So the initial amount of TAC was fixed at 2.5 wt%.

### 5.6 Optimization of AM: MBAM ratio

The green strength of gelcasted body depends on amount of crosslinker and monomer. Higher is the amount of crosslinker better is the green strength. So for the present study 10 wt% of two premix solutions having AM:MBAM ratios 15:1 and 20:1 were prepared. The TAC amount was fixed at 2.5 wt% and pH 9 was maintained in both the cases. It was observed that maximum solid loading was attained in the solution where AM:MBAM ratio was 15:1 compared to AM:MBAM ratio 20:1. Apart for this, some surface cracks were generated where AM:MBAM ratio was 20:1. During green machining, samples having AM:MBAM ratio 20:1, could not withstand with cutting speed. On the other hand, for the samples having AM:MBAM ratio 15:1 shows some improved surface property and good green strength and excellent machinability at green stage. Those samples were also free of surface exfoliation. It clearly indicates that with increase in crosslinker concentration green strength, surface property and machinability improves.

The maximum solid loading achieved with AM:MBAM ratio was 32.5 volume %. With increase in amount of TAC from 2.5 wt% to 3 and 3.5 wt%, solid loading did not improve, slurry become too viscous to be poured and it may be due to hygroscopic nature of TAC. Therefore, the AM: MBAM ratio was optimized to 15:1 for gelcasting of the $BiFeO_3$ powders. Fig 5.6 shows microstructure of gelcasted green body. Microstructure exhibits different particles are held together by crosslinkers.

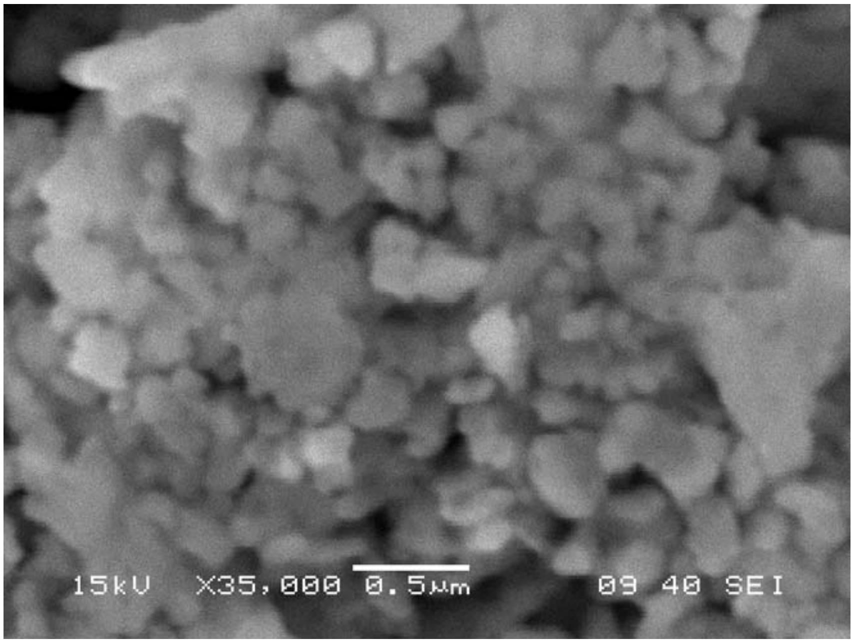

Fig. 5.6 Microstructure of gelcasted green body.

### 5.7 Thermal analysis of the gelcasted green bodies

Fig. 5.7 shows the DSC/TG plot of the green body. The weight loss below 300°C was attributed to the removal of physically bound water. The amount of loss was 2.7%. The second major weight loss occurred between the temperature range from 300°C to 520°C. The weight loss in this region is 7% which was due to the removal of polymeric substances. A stable weight is attained for the green body at about 520°C. The total weight loss was about 9.7%. After 520°C there is no weight loss observed. The exothermic peak around 650°C may be due to decomposition of $BiFeO_3$ into $Bi_2Fe_4O_9$ and $Bi_{25}FeO_{39}$ [3].

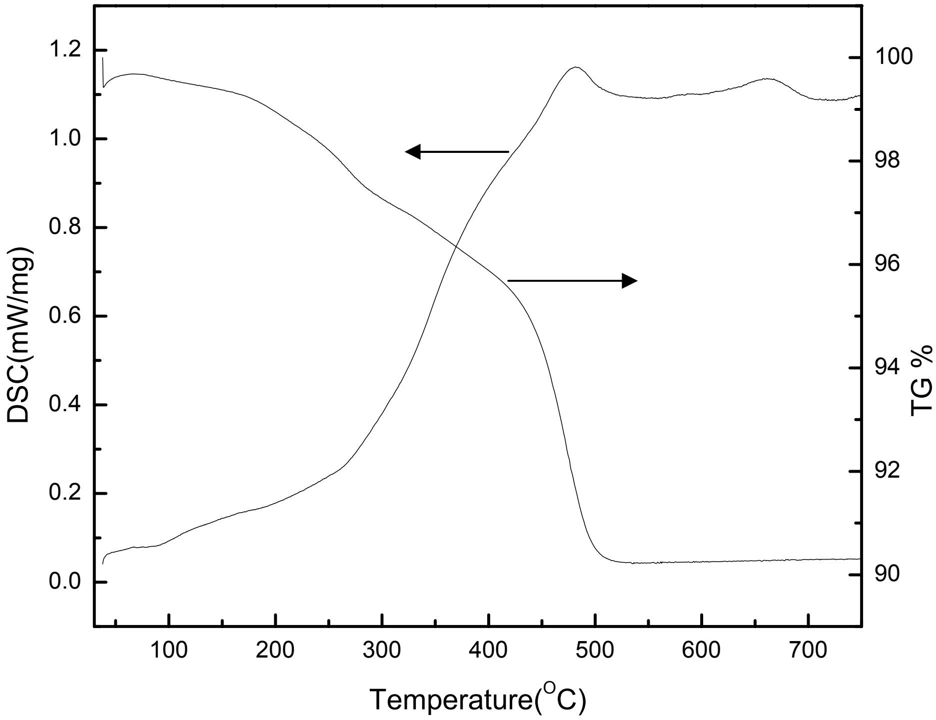

Fig.5.7 DSC/TG plot of the dried gelcast material

### 5.8 Sintering of samples

From TG curve of green gelcasted body it has been observed that the complete burnout of organic polymers completes at 520$^{O}$C. So during sintering samples were kept at 550$^{O}$C for 2 hours. Then samples were sintered at 750$^{O}$C, 800$^{O}$C and 825$^{O}$C with soaking time of two hours in each case. The relative densities of the samples sintered at 750$^{O}$C & 800$^{O}$C with 2 hours of soaking period were 92.5% & 94% respectively.

### 5.9 Phase analysis of the sintered samples

Fig.5.8 shows the comparison of calcined powder and sample sintered at 750$^{O}$C for 2 hours XRD pattern. There are secondary phases ($Bi_2Fe_4O_9$ & $Bi_{25}FeO_{39}$) in the sintered sample along with the $BiFeO_3$ phase. In the samples sintered at 800$^{O}$C for 2 hours similar secondary phases was also observed which is depicted in Fig.5.9. There is no existence of $BiFeO_3$ phases in the samples sintered at 825$^{O}$C.These phases developed by decomposition of $BiFeO_3$ due to its lower thermodynamic stability. It is evident from DSC graph of green gelcasted samples that the formation of secondary phases started at $650^{O}C$. X-ray diffraction patterns also shows the presence of secondary phases in the sintered samples. Thermogravimetric analysis of green gelcasted body shows that there is a total weight loss of 7% due to organic polymer decomposition. This amount is quite high where as others have reported the weight loss due to organic polymers within 2-5%. The exothermic decomposition of organic polymers may be helping the formation of secondary phases. High organic content indicates that solid loading is not maximized. Now this solid loading depends on efficiency of dispersing agents. It can be concluded that use of TAC is not suitable for achieving maximum solid loading.

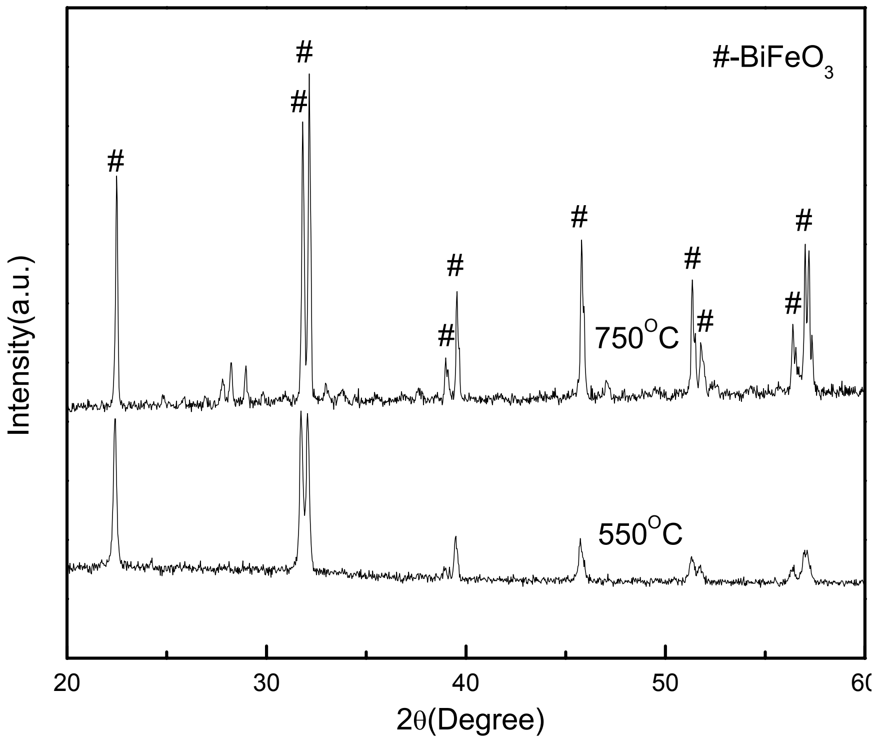

Fig. 5.8 XRD patterns of gelcast material sintered at $750^{O}C/2h$ and powder calcined at $550^{O}C/2h$.

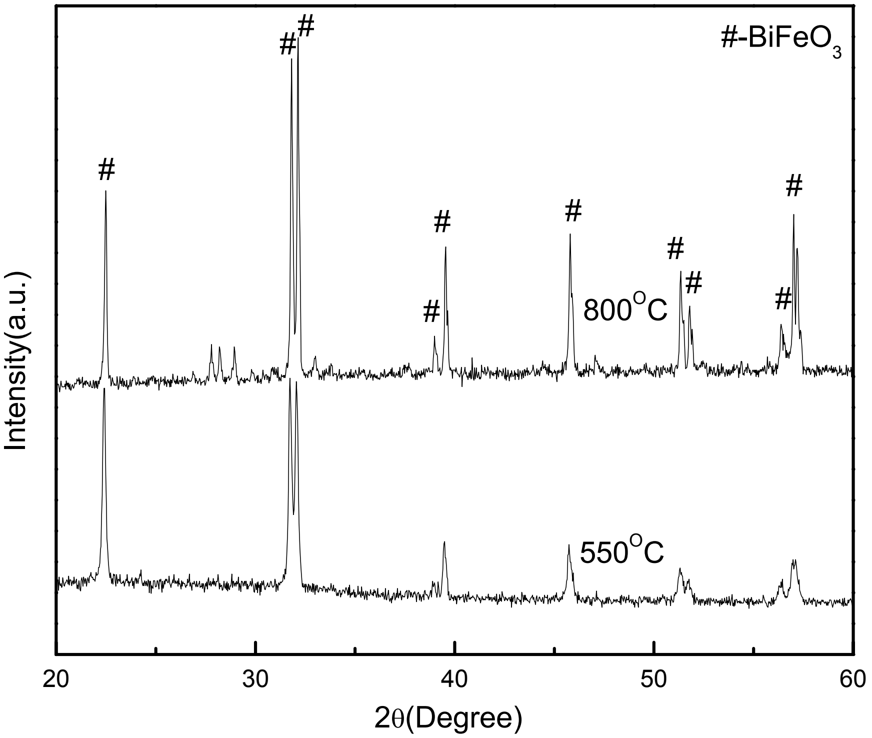

Fig. 5.9 XRD patterns of gelcast material sintered at 800°C/2h and powder calcined at 550°C/2h.

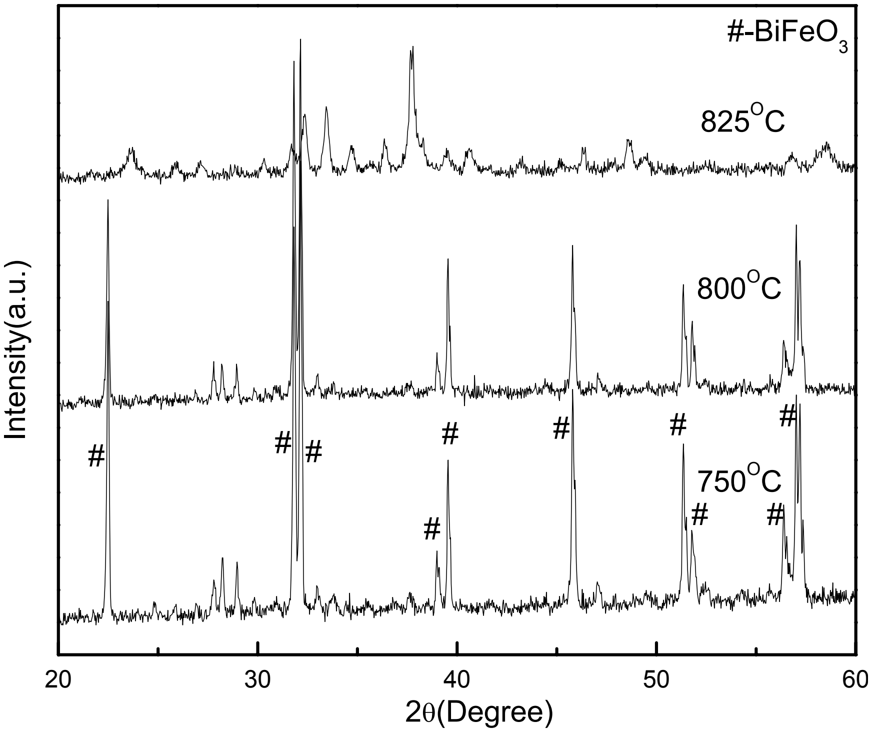

Fig. 5.10 XRD patterns of gelcast material sintered at 750°C/2h, 800°C/2h and 825°C/2h

### 5.10 Microstructure analysis of the sintered samples

Fig 5.11 (a) & (b) shows microstructure of sintered gelcasted body sintered at 800$^{O}$C and 750$^{O}$C respectively. It is evident from the microstructure with increase in sintering temperature from 750$^{O}$C to 800$^{O}$C pores have been removed which leads to more dense microstructure.

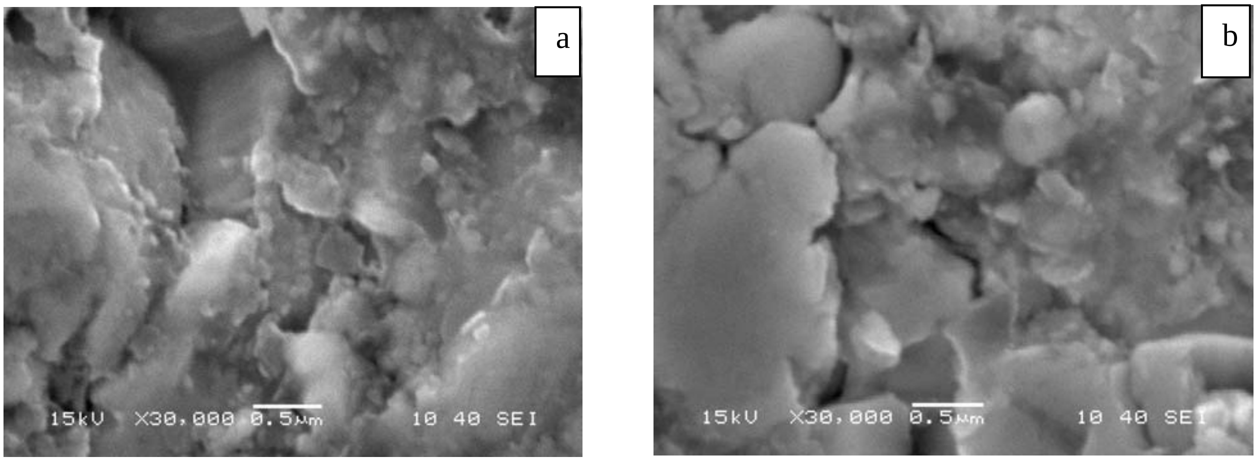

Fig.5.11 SEM microstructure of samples sintered at a) 800$^{O}$C b) 750$^{O}$C.

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# CHAPTER-6

## CONCLUSIONS

## 6. Conclusions

It can be concluded from the present study that gelcasting can be an alternative method in preparing highly dense $BiFeO_3$ ceramics. It has been observed that due to the high organic content in the green body secondary phases has been developed in the sintered body. To overcome this problem high solid loading during slurry preparation is necessary which eventually reduces the organic content in the gelcasted body. The success of high loading depends on powder surface area and characteristics of dispersing agent. The surface area of calcined powder was $10.36 m^2/g$ which is suitable for gelcasting process. However, the hygroscopic characteristics of Triammonium citrate prevents high solid loading in the slurry. The maximum solid loading attained is 32.5% with Triammonium citrate as dispersing agent. It has been also found that AM:MBAM ratio =15:1 is suitable for gelcasting of $BiFeO_3$ ceramics. This ratio gives excellent green strength and machinability to gelcasted $BiFeO_3$. In the present work it has been observed that with increase in sintering temperature from 750 to $800^{O}C$ the density of sintered samples increased from 92.5 to 94% of theoretical density.

# CHAPTER-7

# FUTURE WORK

## Future work

Future plan involves the following aspects

1. The effect of polyacrylate based dispersant on solid loading.
2. An increase in solid loading of $BiFeO_3$ in slurry.
3. Synthesis of impurity free and high resistive $BiFeO_3$ ceramics by gelcasting.
4. Detailed rheological property study.
5. Electrical and magnetic property measurement.
6. Gelcasting of nano sized $BiFeO_3$ powders.