Surfactant Assisted Autocombustion Synthesis Of Bismuth Ferrite

A THESIS SUBMITTED IN PARTIAL FULLFILLMENT OF THE REQUIREMENTS

FOR THE DEGREE OF BACHELOR OF TECHNOLOGY

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MOMATA KISKU
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MOMATA KISKU
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Under the Guidance of

Prof. SUMIT KUMAR PAL

DEPARTMENT OF CERAMIC ENGINEERING

NATIONAL INSTITUTE OF TECHNOLOGY

ROURKELA

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CERTIFICATE

This is to certify that the thesis entitled, **"Surfactant assisted autocombustion synthesis of bismuth ferrite"** submitted by Ms. MOMATA KISKU in partial fulfillment of the requirements of the award of Bachelor of Technology Degree in Ceramic Engineering at the 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.

Prof. Sumit Kumar Pal

Date: 12.05.2009

Dept. of Ceramic Engneering

National Institute of Technology

Rourkela – 769008

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<u>ABSTRACT</u>

In this work, bismuth ferrite powders has been synthesized by glycine nitrate auto-combustion method with addition of ammonium lauryl sulfate (anionic) and triton-X (non-ionic) surfactant. The precursor solutions were prepared from ferric and nickel nitrates. The effects of the surfactant on crystallite size has been investigated by XRD techniques. The results showed that addition of surfactant to the starting solution affected the crystallite size in the final product.

INTRODUCTION

Bismuth ferrite, ($BiFeO_3$, BFO) is one of the very few multiferroic materials with a simultaneous coexistence of ferroelectric with high Curie temperature (Tc = 810-830°C) and antiferromagnetic order (below T_N= 370°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. Therefore multiferroic are rare and it exhibits weak magnetism at room temperature. Although BFO was discovered in 1960, recently there is a renewed interest because of its possible novel applications in the field of radio, television, microwave and satellite communications, audio-video and digital recording and, as permanent magnets. So far, bismuth ferrite powders have been prepared by the solid-state methods (classic [1, 2] and mechanochemical ones [3]) and solution chemistry methods (such as precipitation/co precipitation [4], sol–gel [5, 6] hydrothermal [7] and sonochemical [8]ones). Most of the mentioned procedures need high temperature treatments (>800°C). Due to the requirement of nanosized oxides and in order to avoid bismuth volatilization the developing of low temperature synthesis methods is essential [9]. BiFeO3 structure or properties had been intensively studied [10–18], its practical applications were hampered by the leakage current problems arising out of nonstoichiometry. This is mostly because of the difficulty in obtaining stoichiometric singlephase BiFeO3 materials. It is well known that synthesizing the phase pure BiFeO3 is difficult through the traditional solid-state sintering process. Recently, there have two techniques for successfully preparing the phase pure $BiFeO_3$.

The oxide mixing sintering technique followed by leaching with the dilute nitric acid had been used for synthesizing the phase pure $BiFeO_3$ [19]. However, it resulted in the formation of coarser powders and the process suffered from the poor reproducibility. Another is a rapid liquid phase sintering technique [20], but it needs higher calcinations temperature (880°C) to obtain the phase pure $BiFeO_3$, which means the higher energy consumption and cost. $BiFeO_3$, with its electrical and magnetic ordering has generated interest as a material with application potential. It is expected to form a new type of memory by a combination of ferroelectric and ferromagnetic

properties. During synthesis, the kinetics of formation always leads to a mixture of $BiFeO_3$ as a major phase along with other impurity phases. The task becomes difficult because of the narrow temperature range in which $BiFeO_3$ stabilizes and there are a number of other phases of Bi and Fe, which appear if temperature is not controlled accurately. Preparation of polycrystalline phase-pure BFO is reported to be difficult because of its narrow temperature range of phase stabilization. Various impurity phases have been reported to occur, mainly comprising of $Bi_2Fe_4O_9$, $Bi_{12}(Bi_{0.5}Fe_{0.5})O_{19.5}$ and $Bi_{25}FeO_{40}$[21]. Presence of such impurities results in high leakage in the samples, leading to poor ferroelectric behavior. The most common techniques developed for the formation of phase-pure polycrystalline BFO samples are: (a) forming solid solution of BFO with other ABO_3 type of perovskites such as $BaTiO_3$,[22,23] (b) calcination followed by leaching with nitric acid[24] (c) low temperature thermal treatment[25], (d) rapid liquid phase sintering of BFO and (e) by using rather expensive but ultrapure starting powders of Bi_2O_3 and Fe_2O_3 or with slight deficiency of Bi_2O_3 .

Bismuth ferrite ($BiFeO_3$) nanopowder was prepared by the novel combustion technique using glycine as a fuel. This method is fast, high yielding, clean, safe, cost effective, compatible with the substrates and very suitable for practical organic synthesis. Two bismuth ferrite potential precursors systems, namely $Fe(NO_3)_3 \cdot 9H_2O$ – $Bi(NO_3)_3$. $9H_2O$ – glycine with different metal nitrate/organic compound molar ratios have been investigated in order to evaluate their suitability as $BiFeO_3$ precursors. The presence into the precursor of both reducing (glycine) and oxidizing (NO_3–) components modifies dramatically their thermal behavior comparative with the raw materials, both from the decomposition stoichiometries and temperature occurrence intervals points of view. Also, the thermal behavior is dependent on the fuel nature but practically independent with the fuel content. The fuel nature influences also some characteristics of the resulted oxides (phase composition, morphologies). In the case of the oxides prepared using urea as fuel, a faster evolution toward a single phase composition with the temperature rise is evidenced, the formation of the BiFeO3 perovskite phase being completed in the temperature range of 500–550°C.

Surfactants are wetting agents that lower the surface tension of a liquid, allowing easier spreading, and lower the interfacial tension between two liquids. Surfactants reduce the surface tension of water by adsorbing at the liquid-gas interface. They also reduce the interfacial tension between oil and water by adsorbing at the liquid-liquid interface. Many surfactants can also assemble in the bulk solution into aggregates. Examples of such aggregates are vesicles and micelles. The concentration at which surfactants begin to form micelles is known as the critical micelle concentration or CMC. When micelles form in water, their tails form a core that can encapsulate an oil droplet, and their (ionic/polar) heads form an outer shell that maintains favorable contact with water. When surfactants assemble in oil, the aggregate is referred to as a reverse micelle. In a reverse micelle, the heads are in the core and the tails maintain favorable contact with oil. Soft ferrites are largely used in electronics and telecommunication industries. In order to improve the magnetic properties of this material non-conventional methods are widely studied. Some of these methods are: co-precipitation, hydrothermal, sol–gel and sol–gel auto-combustion [26], [27] and [28]. Addition of cationic surfactant with hydrophilic head and hydrophobic tail into the solution results in formation of reverse micelles. Placing the aqueous ions inside these micelles can be effective in controlling the nucleation and growth of the particles. Due to the existence of surfactant, the surface tension of solution is also reduced, which reduces the energy of the formation of the new phase [29]

In the present work the synthesis of bismuth ferrite by a simple combustion technique, using as starting system $Fe(NO_3)_3 \cdot 9H_2O$ – $Bi(NO_3)_3$. $9H_2O$ as oxidizer and glycine as fuels and two different surfactants i)Triton X, ii)ALS has been performed. The powder was obtained by calcination at a temperature of 500^oC and 550^oC. The phase has been identified by by XRD techniques.

LITERATURE REVIEW

Carmen et. al. has reported the Synthesis of nanosized bismuth ferrite (bifeo3) by a combustion method starting from Fe(NO3)3·9H2O–Bi(NO3)3·9H2O–glycine or urea systems(*Journal of Thermal Analysis and Calorimetry, Vol. 94 (2008) 2, 411–416*)

According to him combustion method may represent a suitable route in the synthesis of nanosized $BiFeO_3$ at temperatures lower than 650°C. The fuel nature, glycine or urea strongly influences the thermal behavior of the precursors and some characteristics of the resulted oxides (phase composition, morphologies). Starting from glycine containing system, after annealing at 650°C, amounts of secondary phases ($Bi_2Fe_4O_9$, $Bi_{36}Fe_2O_{57}$) were also identified beside the BiFeO3 major phase. The particles of the obtained $BiFeO_3$ present a non-homogenous morphology being strongly interconnected in a kind of three-dimensional, porous skeleton. In the case of urea containing system, after annealing at 650°C only traces of $Bi_2Fe_4O_9$ were detected along with uniform, as shape and size $BiFeO_3$ particles. The fuel content may influence the particle size and the reduction of Fe^{3+} to Fe^{2+} of BFO. Thus, further transmission electron microscopy (TEM) and Mossbauer investigations are required in order to determine the particle average size and the presence/absence of Fe^{2+} into $BiFeO_3$ powders prepared by the combustion method

Sushmita Ghosh et.al reported low temperature synthesis of bismuth ferrite nanoparticles by a ferrioxalate precursor method(*Materials Research Bulletin 40 (2005) 2073–2079*)

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.

Saied Farhadi et.al reported through Bismuth ferrite (BiFeO3) nanopowder prepared by sucrose-assisted combustion method: A novel and reusable heterogeneous catalyst for acetylation of amines, alcohols and phenols under solvent -free conditions.(*Journal of Molecular Catalysis A: Chemical)* of developing an efficient catalytic procedure for acetylation of various amines, alcohols and phenols by use of nano-size BiFeO3 as recyclable heterogeneous catalyst under

Solvent-free mild reaction conditions. Among the various substrates studied, acetylation of anilines and primary aliphatic amines proceeded rapidly. The BiFeO3 catalyst was easily prepared and reusable without loss of activity. To our knowledge, this is the first report of catalytic acetylation on a perovskite-type mixed oxide.

Jie Wei et.al has has reported the low-temperature synthesis of $BiFeO_3$ nanoparticles by ethylenediaminetetraacetic acid complexing sol–gel process (Materials Research Bulletin 43 (2008) 3368–3373):

He has successfully prepared the pure BiFeO3 nanoparticles by a simple method using EDTA as the chelating agent. Compared with the traditional solid-state sintering process, the pure BiFeO3 was attained at a much lower temperature (600 8C) 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 our 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 at a low temperature via an EDTA complexing sol–gel process

EXPERIMENTAL

Bismuth ferrite powder was synthesized by a solution evaporation route. 0.25 M Bi (NO3)3 and 0.25 M Fe (NO3)3 solution prepared by dissolving in dilute nitric acid. These two solutions were mixed in a beaker. To this Glycine with mole ratio 0.1 with respect to nitrate was added to the above solution. The surfactant added was with the mole ratio of 0.05 with respect to metal. Surfactants used were (i) Triton X, (ii) ALS (ammonium lauryl sulfate)

This solution was then heated on a hot plate under continuous stirring condition to its boiling temperature until all the liquid evaporated. There was an immense evolution of brown fumes, towards the end of the reaction a fluffy brown mass was obtained at the base of the beaker. Then the powder was calcined at 500°C and 550°C. Then the crystallite size of the powders was calculated by Scherrer formula.

FLOW CHART

```
┌──────────────┐                                    ┌──────────────┐
│ Bi(NO₃)₃     │────────────────┐                  │ Fe(NO₃)₃     │
│ solution     │                │                  │ solution     │
└──────────────┘                ▼                  └──────────────┘
                         ┌──────────────┐
┌──────────────┐         │   Mixed      │          ┌──────────────┐
│ Glycine      │────────▶│  solution    │◀─────────│ Surfactant   │
└──────────────┘         └──────────────┘          │              │
                                │                   │ a .Triton X  │
                                │                   │              │
                                ▼                   │ b. ALS       │
                    ┌──────────────────────┐        └──────────────┘
                    │ Combustion on hot-plate│
                    │ with   stirring        │
                    └──────────────────────┘
                                │
                                ▼
                    ┌──────────────────────┐
                    │ Fluffy brown powder is │
                    │ obtained               │
                    └──────────────────────┘
                                │
                                ▼
                    ┌──────────────────────┐
                    │ Calcined at 500°C and  │
                    │ 550°C (1Hr)            │
                    └──────────────────────┘
                                │
                                ▼
                    ┌──────────────────────┐
                    │       BiFeO₃           │
                    └──────────────────────┘
```

- $Bi(NO_3)_3$ solution
- $Fe(NO_3)_3$ solution
- Glycine
- Mixed solution
- Surfactant
  a .Triton X
  b. ALS
- Combustion on hot-plate with   stirring
- Fluffy brown powder is obtained
- Calcined at $500^{o}C$ and $550^{o}C$ (1Hr)
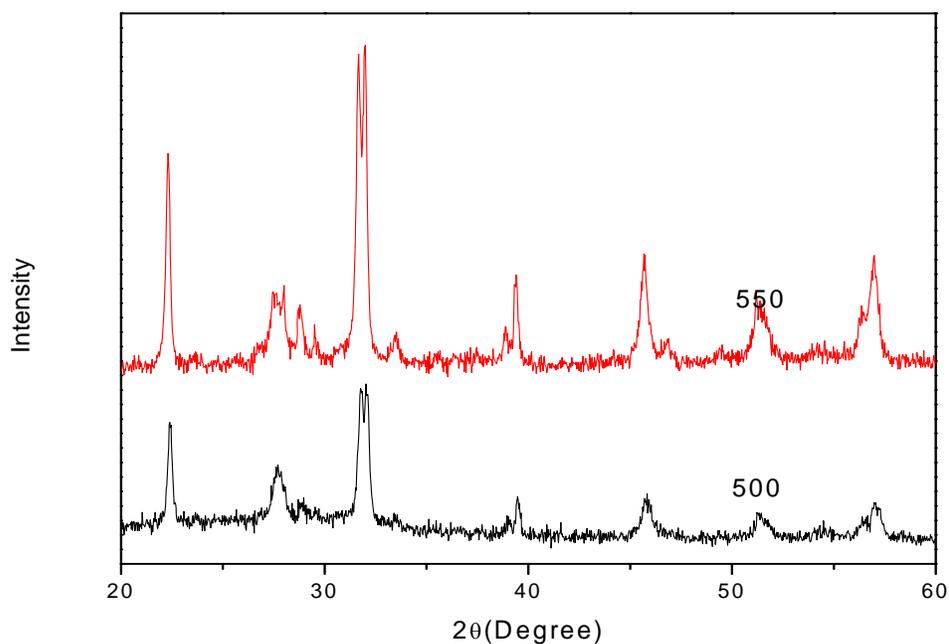- $BiFeO_3$

RESULT AND DISCUSSION

Fig (a) : XRD pattern of $BiFeO_3$ with ALS as surfactant

Fig(a) shows XRD pattern of $BiFeO_3$ prepared via auto-combustion with ALS (Ammonium Lauryl Sulfate) as anionic surfactant. It has been observed that $BiFeO_3$ are fully developed at 550^oC with some impurities. A crystallite size for the sample prepared at 550^oC is 37.35nm.
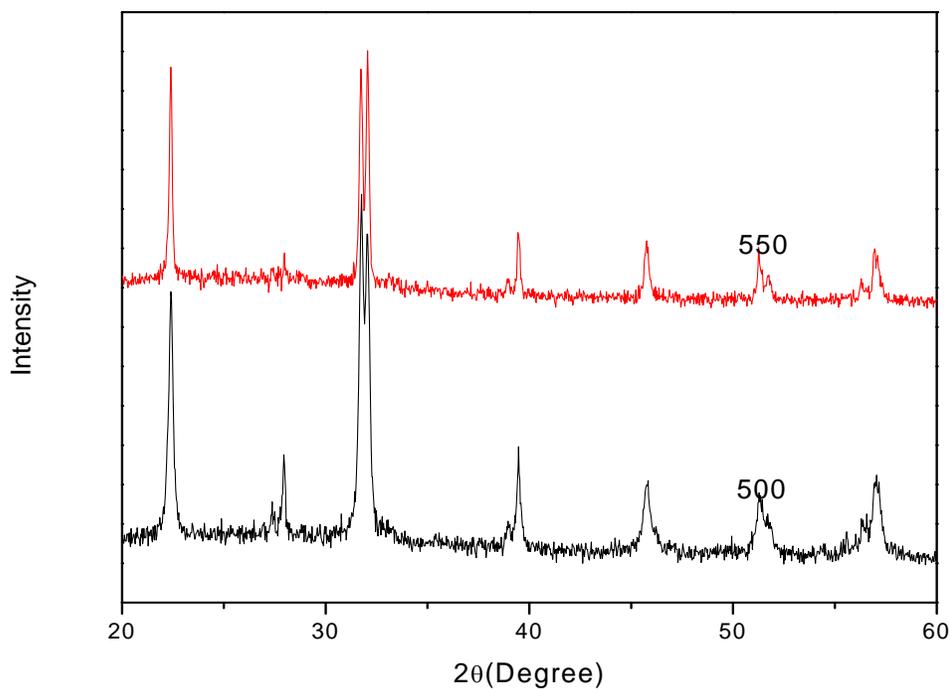
Fig (b) : XRD pattern of $BiFeO_3$ with Triton X as surfactant

Fig (b) shows XRD pattern of $BiFeO_3$ prepared via auto-combustion with Triton X as non- ionic surfactant. It has been observed at 500^oC, there is a considerable amount of impurity which disappears when sample is heat treated at 550^oC and at 550^oC phase pure $BiFeO_3$ is obtained. The calculated crystallite size in this case is 62.86nm.

CONCLUSION

BiFeO$_3$ is prepared via auto-combustion synthesis using 2 different type of surfactant namely ALS (Ammonium Lauryl Sulfate) and Triton X. It has also been observed that Triton X is more suitable in preparing phase pure BiFeO$_3$ at 550°C. But the crystallite size are greater than the sample prepared with ALS.

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