

Synthesis of Bismuth Ferrite Nanoparticles by Modified Pechini Sol-Gel Method

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Abstract-Different methods have been adopted for preparing BiFeO₃ nanopowder. Recently, wet chemical methods [1] have received abundant attention. Among the wet chemical methods, the modified Pechini sol-gel method is very cost effective, simple and suitable for synthesis of highly homogenous and very fine crystalline nanopowder. The process is based on the mixing of reactants that oxidize easily, such as metal nitrates, and an organic chelating agent that acts as reducing agent.

Keywords- *Multiferroic Nanoparticles, Pechini Sol-Gel Method, Bismuth Ferrite (BFO)*

I. INTRODUCTION

Multiferroic materials exhibit the coexistence of two or more of the primary ferro-orders such as (anti)ferroelectricity, (anti)ferromagnetism, and/or ferroelasticity in the same phase [1-5]. The combination of ferro-orders in multiferroics means that the different properties interact with each other. This then allows the possibility that one can switch magnetically ordered states using electric fields or vice versa i. e. electrically ordered states using magnetic fields [6]. These materials have attracted considerable research interest due to their potential in device miniaturization and high-density data storage system [7]. It is worth mentioning that multiferroic materials are the most promising materials for spintronic devices such as spin field effect transistors, electrical switching, nanoelectronics, magnetoelectric random access memories (MERAM), high frequency filters and sensors [8, 9]. Among compounds that are multiferroics, BiFeO₃ (BFO) is a paradigmatic and currently the most studied material, because it can exhibit multiferroic properties at room temperature [10]. The multiferroic BiFeO₃ is ferroelectric below TC ~ 1103 K and antiferromagnetic below TN ~ 643 K [11]. The BiFeO₃ have rhombohedral distorted perovskite ABO₃ (A = Bi, B = Fe) structure with space group R3c and lattice parameters a = 5.58 Å and c = 13.87 Å [12-14]. For these properties BFO is one of the prime candidates for room temperature magnetoelectric applications [15]. BFO is found to exhibit weak ferromagnetic properties when the particle size is reduced down to nanoscale [16]. From literature reports it is apparent that the ferroelectric and magnetic properties of BFO could be due to the 'A' site Bi ions and the

'B' site Fe ions respectively [17]. In addition to this, any imbalance in the stoichiometric ratio between Bi, Fe and O ions also influences its multiferroic properties [18]. The investigation on the origin of magnetism in BFO could reveal interesting insights into their magnetic phenomena. BFO demonstrates enhanced magnetic properties through (i) the suppression of its cycloidal antiferromagnetic spin structures and (ii) the formation of antiferromagnetic/ferromagnetic core/shell structures [13]. The magnetic property that occurs due to one of these origins would also influence other properties of BFO. On the other hand, BFO also exhibits visible light driven photocatalytic activities due to its smaller band gap, that currently being explored for applications such for hydrogen production via water splitting and degradation of organic pollutants [19, 20]. Previous investigations revealed that preparation of pure phase BiFeO₃ is a challenge [21-23] due to the formation of different impurity phases, such as Bi₂Fe₄O₉, Bi₃₆Fe₂₄O₅₇ and Bi₂₅FeO₄₀ [24, 25]. Bulk BiFeO₃ also exhibit by serious current leakage problems due to the existence of a large number of charge centers caused by oxygen ion vacancies [26]. These problems limit the use of BiFeO₃ for fabrication of multifunctional devices [6]. In order to reduce leakage current of BFO many attempts have been undertaken, for example: partial substitution of Bi³⁺/Fe³⁺ by ions such as Sm³⁺, Nd³⁺, Gd³⁺, Cr³⁺ etc. and preparation of nanoparticles [11]. Besides as was mentioned earlier BiFeO₃ have a spiral modulated spin structure (SMSS) with an incommensurate long-wavelength period of 62 nm [27]. This spiral spin structure cancels the macroscopic magnetization and prevents the observation of the linear magnetoelectric effect [28]. One of the easiest ways to destroy the SMSS in BFO is the structural modifications or deformations introduced by cation substitutions or doping [11]. Another way is the synthesis of the nanoparticles of BiFeO₃ with a particle size of the order of or smaller than 62 nm [6, 29]. The most widely used techniques for the synthesis of BiFeO₃ nanoparticles are based on different chemical routes such as sol-gel method, combustion synthesis process, sonochemical synthesis process etcetera [6, 29-31]. Therefore, in this investigation, we are interested to prepare BiFeO₃ nanoparticles using the simple wet chemical technique, sol-gel to perturb the SMSS of BFO and to improve their ferroelectric and magnetic properties. Sol-gel method is chosen to prepare nanoparticles because this method

involves molecular level mixing and results in homogeneous material [32].

II. SOL-GEL METHOD

The sol-gel process may be described as:

“Formation of an oxide network through polycondensation reactions of a molecular precursor in a liquid”.

A sol is a stable dispersion of colloidal particles or polymers in a solvent. The particles may be amorphous or crystalline. An aerosol is particles in a gas phase, while a sol is particles in a liquid.

A gel consists of a three-dimensional continuous network, which encloses a liquid phase, in a colloidal gel, the network is built from agglomeration of colloidal particles. In a polymer gel the particles have a polymeric sub-structure made by aggregates of sub-colloidal particles. Generally, the sol particles may interact by Vander Waals forces or hydrogen bonds. A gel may also be formed from linking polymer chains. In most gel systems used for materials synthesis, the interactions are of a covalent nature and the gel process is irreversible. The gelation process may be reversible if other interactions are involved.

III. BENEFITS OF SOL-GEL METHOD

The various advantages of sol-gel synthesis as the prime method to produce BiFeO_3 are:

- Multi component compounds may be prepared with a controlled stoichiometry mixing sols of different compounds.
- Simple and cost effective.
- Enables mixing at an atomic level.
- Distribution. At very beginning conventional Pechini sol-gel route was adopted to synthesize BiFeO_3 nanoparticles using $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ as the initial components, 2- methoxyethanol as the solvent, NH_4OH as a pHcontroller, acetic acid (CH_3COOH) as a chelating agent and ethylene glycol ($\text{OHCH}_2\text{CH}_2\text{OH}$) as a polymerizing agent.

IV. OPTIMIZING SYNTHESIS RUTE AND PARAMETER

The aim of this thesis is to synthesize nanocrystalline BiFeO_3 with uniform and homogenous particle size. The sol-gel method prevents the problems with co- precipitation, which inhomogeneous be a gelation reaction.

- Self-purification due to the high exothermic temperature's involvement.

- Synthesis of single-phase materials at very low temperatures.

V. SYNTESIS PROCEDURE (PECHINI SOL-GEL ROUTE)

- Calculated amount of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were initially taken into a beaker with about 200-250 ml 2-methoxyethanol as the solvent.
- Then the solution was magnetically stirred for about 4 hour until all the components get dissolved and the clear solution was obtained (Figure 1a).
- Then the pH of the solution was increased to around 5. It was done by adding NH_4OH drop wise and the color of the solution turned to blackish red and finally to nontransparent whitish red color (Figure 1b).
- Afterwards acetic acid (CH_3COOH) and ethylene glycol ($\text{OHCH}_2\text{CH}_2\text{OH}$) in 1:1 molar ratio was added to the solution sequentially.
- After that the solution was heated at constant temperature at about 70°C to 80°C with continuous magnetic stirring for about 30 to 32 hours (Figure 1c).
- At the end almost all the solvent got evaporated and the solution got thicker and thicker. Finally, a thin gel like layer of dark brown color appeared (Figure 1d).

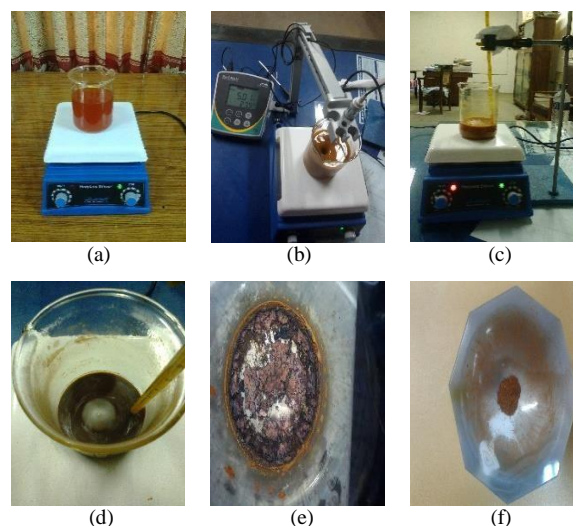


Figure 1. Synthesis steps a) Dissolving components with 4hours continuous stirring b) Solution after pH control c) Solution during heating at about 70°C to 80°C d) Onset of a thin gel like layer e) Dried gel after oven heating f) After final grinding.

The FESEM image of the synthesized particles by using the above-mentioned route and chemicals are shown below:

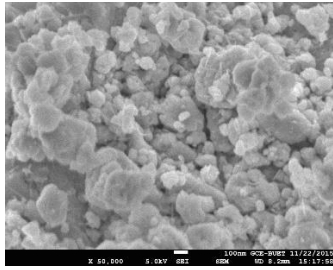


Figure 2. FESEM image of BiFeO₃ (400 °C)

From the FESEM image it can be seen that, the particles are mostly agglomerated and not homogeneous in size. These are actually not the desired size and distribution of the synthesized nanoparticles. In order to get homogeneous and required size nanoparticles, the synthesis route was changed. In this new route, deionized water was used as solvent and citric acid as chelating agent. Because previous literature reports that, citric acid is stronger chelating agent than acetic acid and by using deionized water as solvent and citric acid as chelating agent it is expected to get homogeneous and small size nanoparticles [35].

VI. NEW SYNTHESIS PROCEDURE (MODIFIED PECHINI SOL-GEL ROUTE)

- Stoichiometric proportion of Bi(NO₃)₃.5H₂O and Fe(NO₃)₃.9H₂O were initially dissolved in 400 ml deionized water with an individual concentration of 0.025M.
- The solution was stirred for about half an hour to obtain a clear solution.
- When the solution was transparent, 0.02 mole of C₆H₈O₇ as the chelating agent was added to the solution to complex the metal cations (Figure 3a).
- The solution was then stirred and heated at 70-75 °C for 8-10 hours to form a transparent blackish-red sol (Figure 3b).
- Afterwards appropriate amount of ethylene glycol was added to the solution as polymerization agent.
- The resultant solution was heated at 70-75 °C to initiate the polymerization reaction and a few minutes later a gel was formed with vigorous boiling and fuming (Figure 3c).
- The gel was dried at 100°C for 24 hours in a functional oven to obtain fluffy green xerogel (Figure 3d).
- The xerogel samples were then grounded into powder and annealed at 400-600 °C (the heating and cooling rate were maintained at 3°C /min.) for 2 hours using a functional furnace in static air (Figure 3e).
- Finally, the powders were grounded to get BiFeO₃ nanoparticles (Figure 3f).

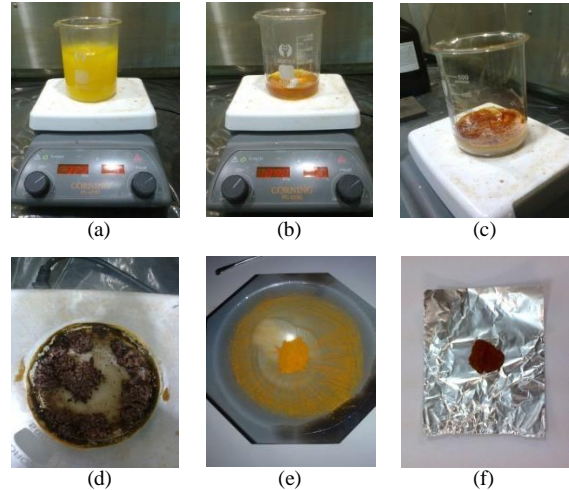


Figure 3. Synthesis steps a) mixing raw materials into deionized water, b) formation of sol, c) formation of gel, d) precursor xerogel, e) ground xerogel, f) annealed BiFeO₃ powder.

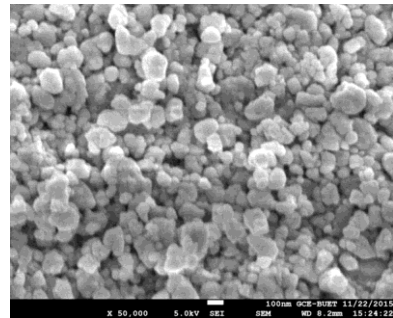


Figure 4. FESEM image of BFO (400 oC)

From the FESEM image in figure 4, it can be seen that, the particles are not so much agglomerated and not homogeneous in size. These are the desired size and distribution of the synthesized nanoparticles. And the average particle size of BiFeO₃ nanoparticle is 94 nm.

VII. CONCLUSION

The FESEM images of the synthesized powder by following this new route clearly demonstrated the formation of very fine homogenous and nearly spherical nanoparticles with very little agglomeration effect. And hence we inferred the new route and parameters are optimum to synthesize BiFeO₃ nanoparticles with desired size and shape.

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