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Synthesis of Yttrium Doped Bismuth Feraites Nanoparticles by Modified Pechini Sol-Gel Method

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Abstract
Different methods have been adopted for preparing the Yttrium(Y) doped $BiFeO_3$nanopowder. Recently, wet chemical methods 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.

Key words: *Multiferroic nanoparticles; Pechini sol-gel method;Bismuth ferrite (BFO); Yttrium.*

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 (W. Eerenstein *et al.*, 2006). 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. These materials have attracted considerable research interest due to their potential in device miniaturization and high-density data storagesystem (G. S. Lotey *et al.*, 2012). 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 (F. Kagawa *et al.*, 2010). Among compounds that are multiferroics, $BiFeO_3$ (BFO) is a paradigmatic and currently the most studied material, because it can exhibitmultiferroic properties at room temperature (V. V. Lazenka *et al.*, 2012). The multiferroic $BiFeO_3$ is ferroelectric below T_C ~ 1103K and antiferromagnetic below T_N ~ 643K. The $BiFeO_3$ have rhombohedrally distorted perovskite ABO_3 (A = Bi, B = Fe) structure with space group R3c and lattice parameters a = 5.58 Å and c = 13.87 Å (D. P. Dutta *et al.*, 2013). For these properties BFO is one of the prime candidates for room temperature magnetoelectric applications (A. Mukherjee *et al.*, 2014). BFO is found to exhibit weak ferromagnetic properties when the particle size is reduced down to nanoscale (R. Mazumder *et al.*, 2007). 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 (C. Yang *et al.*, 2012). In addition to this, any imbalance in the stoichiometric ratio between Bi, Fe and O ions also influences its multiferroic properties (C. Ederer *et al.*, 2005). 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 cycloidalantiferromagnetic spin structures and (ii) the formation of antiferromagnetic/ ferromagnetic core/ shell structures . 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 (F. Gao *et al.*, 2007).Previous investigations revealed that preparation of pure phase $BiFeO_3$ is a challenge (B. Ahmmad *et al.*) due to the formation of different impurity phases, such as $Bi_2Fe_4O_9$, $Bi_{36}Fe_{24}O_{57}$ and $Bi_{25}FeO_{40}$ (T. Munoz *et al.*, 1985). Bulk BiFeO3also exhibit by serious current leakage problems due to the existence of a large number of charge centers caused by oxygen ion vacancies (G. Arya *et al.*, 2013). These problems limit the use of $BiFeO_3$ for fabrication of multifunctional devices (M. A. Basith *et al.*, 2014). In order to reduce leakage current of BFO many attempts have been undertaken, for example: partial substitution of Bi^{3+}/Fe^{3+} by ions such as Sm^{3+}, Nd^{3+},

Gd^{3+}, Cr^{3+}etc.and preparation of nanoparticles (O. Kurni *et al.*, 2014). Besides as was mentioned earlier $BiFeO_3$ have a spiral modulated spin structure (SMSS) with an incommensurate long-wavelength period of 62 nm (P. Fischer *et al.*, 1980). This spiral spin structure cancels the macroscopic magnetization and prevents the observation of the linear magnetoelectric effect (C. Ederer *et al.*, 2005) One of the easiest ways to destroy the SMSS in BFO is the structural modifications or deformations introduced by cation substitutions or doping (M. A. Basith *et al.*, 2014) Another way is the synthesis of the nanoparticles of $BiFeO_3$ with a particle size of the order of or smaller than 62 nm (T. Park *et al.*, 2007).The most widely used techniques for the synthesis of $BiFeO_3$ nanoparticles are based on different chemical routes such as sol-gel method, combustion synthesis process, sonochemical synthesis process etcetera (J. L. O. Quinonez *et al.*, 2013) Therefore, in this investigation, we are interested to prepare Yttrium (Y) doped $BiFeO_3$ 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 (K. Verma *et al.*, 2012). This method also has an advantages over other chemical methodsbecause of its low cost, generates less carbon residue and easy to prepare (P. Suresh *et al.*, 2014). In this investigation, 10% Yttrium (Y) is substituted in the place of Fe in $BiFeO_3$ because so far there are a large number of reports on the doping effect of Y^{3+} in place of Bi in $BiFeO_3$ nanoparticles (R. Guo *et al.*, 2010) but to the best of our knowledge no reports on the doping of Y^{3+} in place of Fe in $BiFeO_3$ nanoparticles.Y was chosen as a doping element because:

i. The effective magnetic moment of Y^{3+} is large (8.0μB) and the coupling between Y^{3+} and Fe^{3+} can produce improved magnetism.

ii. Y^{3+} (0.90 Å) was used to substitute Fe^{3+} (0.645Å) because of its higher radius, which is expected to create more distortion in $BiFeO_3$ crystal structure and this distortion may enhance electrical polarization (R. Das *et al.*, 2012).

It is reported that ≥ 10% Y doping in $BiFeO_3$ causes a structural transformation from rhombohedral to orthorhombic (G.S. Lotey *et al.*, 2012). Therefore, the Gd doping concentration was chosen as 10% so that crystal structure of the doped samples remain unchanged.

In this present investigation, nominal compositions of $BiFe_{1-x}Y_xO_3$ (x = 0.1) nanoparticles were synthesized by sol-gel method.

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.

Benefits of Sol-Gel method

The various advantages of sol-gel synthesis as the prime method for the production of $BiFeO_3$ are:

- Multi component compounds may be prepared with a controlled stoichiometry mixing sols of different compounds.
- The sol-gel method prevents the problems with co-precipitation, which inhomogeneousbe a gelation reaction.
- Self-purification due to the high exothermic temperatures involvement.
- Synthesis of single phase materials at very low temperatures.
- Simple and cost effective.
- Enables mixing at an atomic level.
- Formation of nanopowder in the desired size and shape with uniform particle size distribution.

Optimizing synthesis route and parameter

The aim of this thesis is to synthesize nanocrystalline $BiFeO_3$with uniform and homogenous particle size distribution. At very beginning conventionalPechini sol-gel route was adopted to synthesize $BiFeO_3$ nanoparticlesusing $Bi(NO_3)_3.5H_2O$ and $Fe(NO_3)_3.9H_2O$ as the initial components, 2-methoxyethanol as the solvent, NH_4OH as pH controller, acetic acid (CH_3COOH) as a chelating agent and ethylene glycol $(OHCH_2CH_2OH)$ as a polymerizing agent.

III. Synthesis Procedure (Pechini sol-gel route)

- Calculated amount of $Bi(NO_3)_3.5H_2$ and $Fe(NO_3)_3.9H_2O$ 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 $(OHCH_2CH_2OH)$ in 1:1 molar ratio were 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).
- The obtained sample was dried in the oven for about 28 hours with two or three intermediate grinding, one after the 1st 12 hours heating and the other two at an interval of 4 hours. The intermediate grinding ensures proper esterification and uniform drying (Figure 1 e).
- The dried gel was then grinded into power in the mortar.
- Finally the powder was grounded to get BiFeO3 nanoparticles (Figure 1f).
- The obtained powder was then annealed for 2 hours at 400°C, 500°C, 550°C and 600°C temperatures. The heating and cooling rate of the furnace were maintained at 3°C/min.

a

b

c

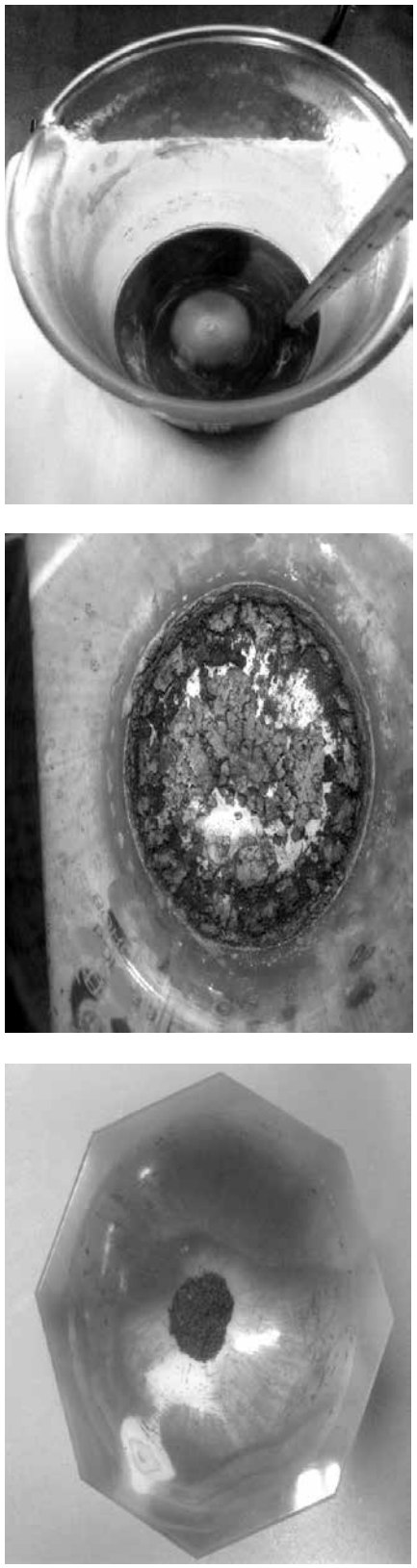


Figure 1: Synthesis steps a) Dissolving components with 4hours continuous stirring b) Solution after pH control c) Solution during heating at about 70°C to 80°C d) Onset of a thin gel like layer e) Dried gel after oven heating f) After final grinding.

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

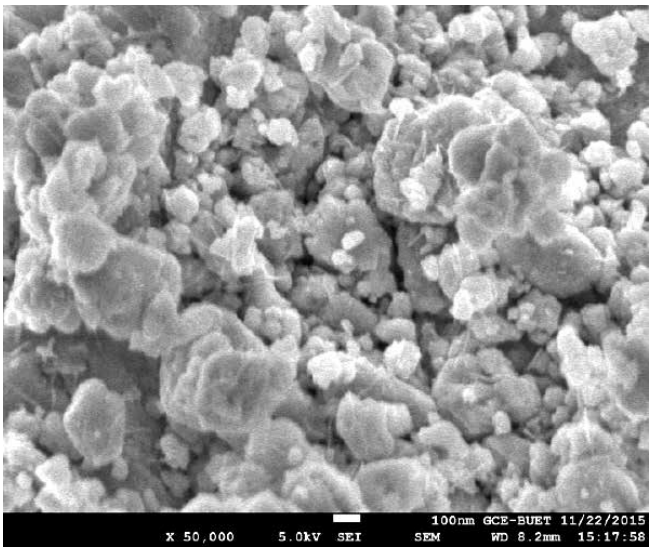
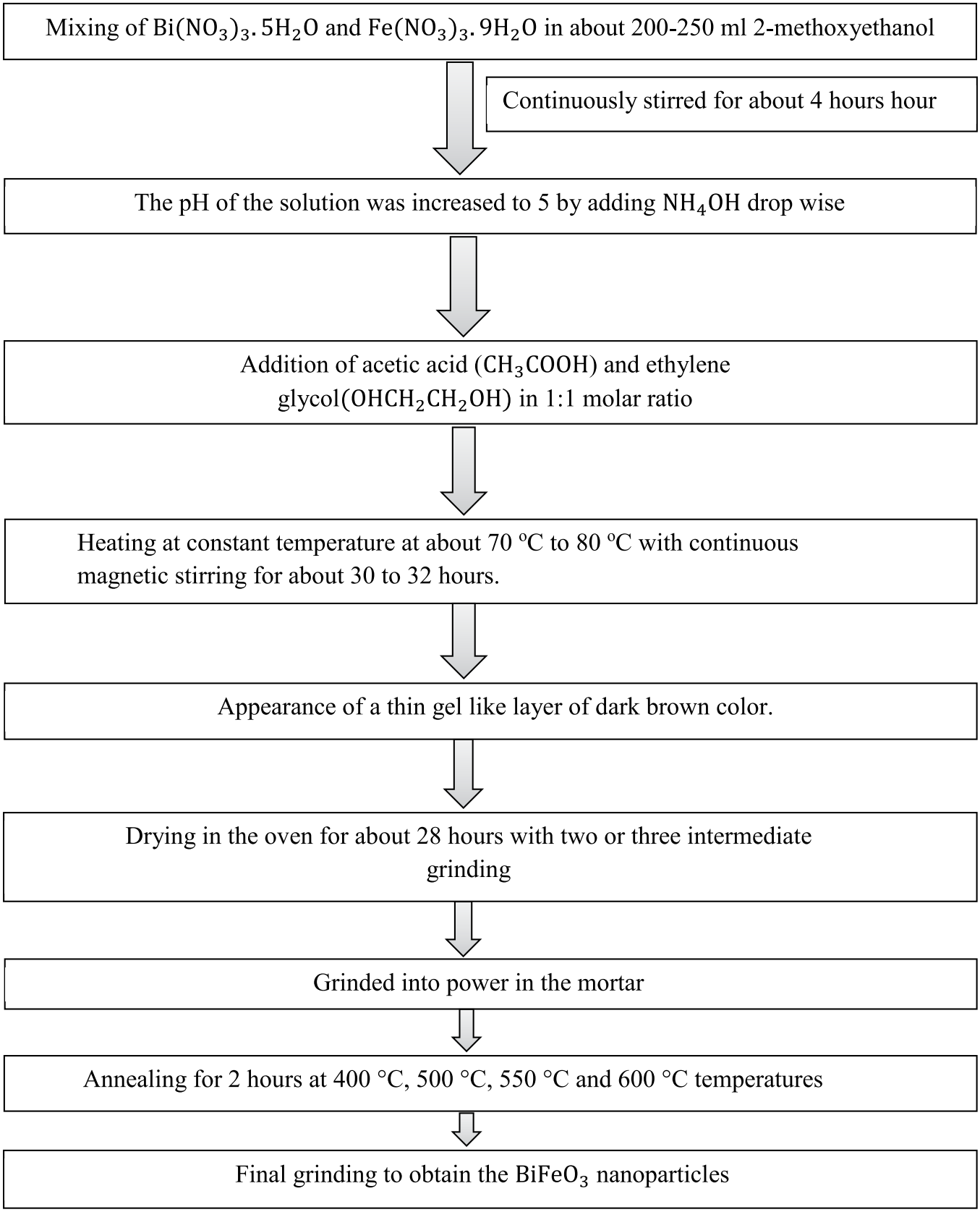


Figure2: FESEM image of $BiFeO_3$ (400°C)

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.

Flow Chart of Synthesis Procedure



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 homogeneousand small size nanoparticles (M. Hasan *et al.*, 2016)

IV. New Synthesis Procedure (modified Pechini sol-gel route)

- Stoichiometric proportion of $Bi(NO_3)_3.5H_2O$ and $Fe(NO_3)_3.9H_2O$ 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 $C_6H_8O_7$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 xero gel (Figure 3d).
- The xero gel 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 $BiFeO_3$ nanoparticles (Figure 3f).

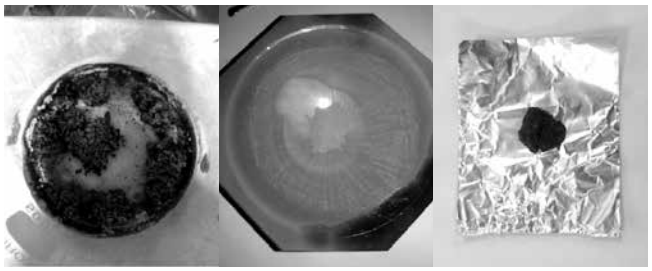


Figure 3: Synthesis steps a) mixing raw materials into deionized water, b) formation of sol, c) formation of gel, d) precursor xerogel, e) ground xerogel, f) annealed $BiFeO_3$ powder.

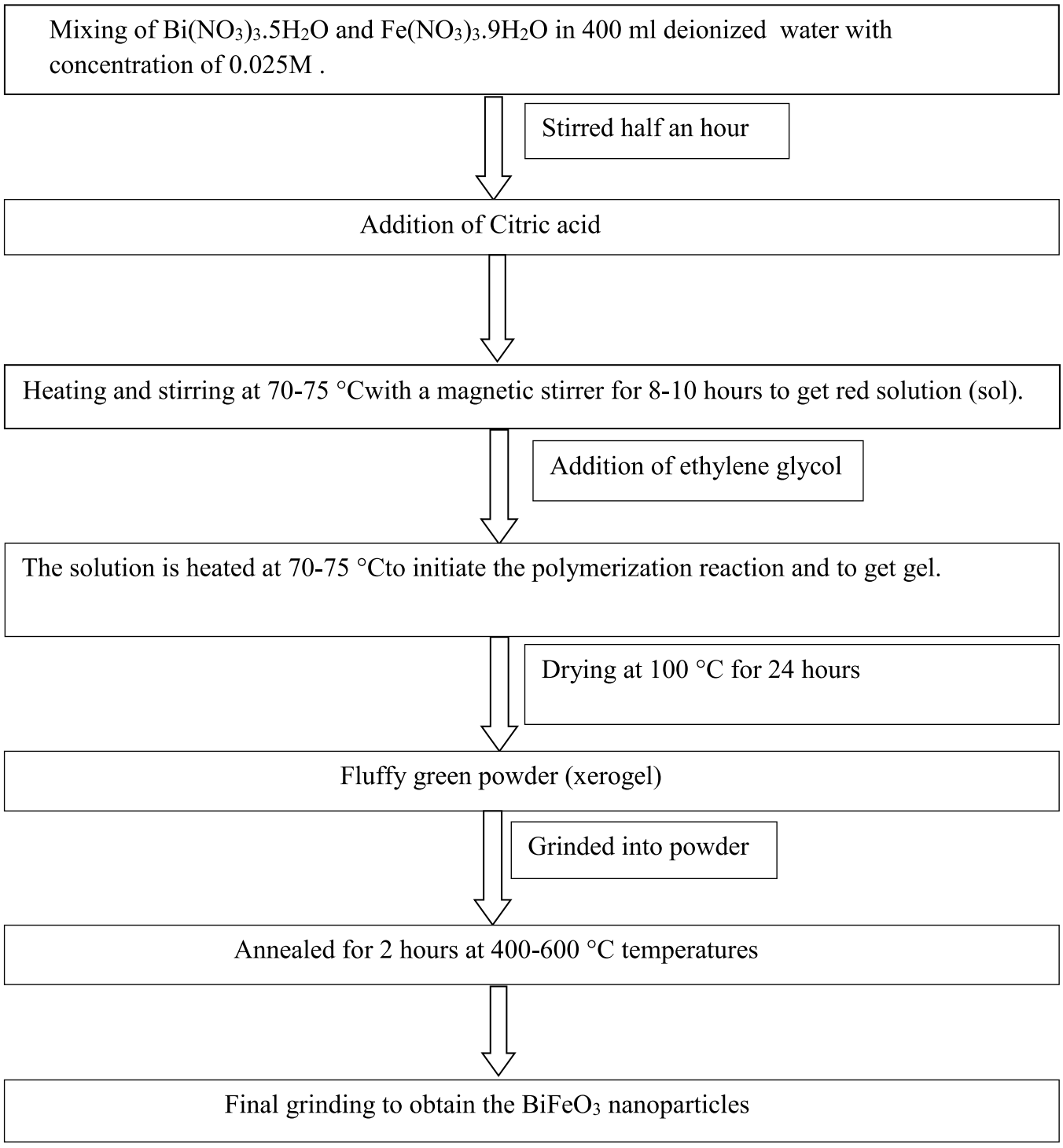
V. Synthesis of Gd doped $BiFeO_3$ nanoparticles

The synthesis process of the Y doped BFO powders was quite similar to the synthesis of pure BFO powder, except that there is an addition of rare earth metal(Y) into the Bi-Fe ionic solution before the heating process.

VI. 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 $BiFeO_3$ nanoparticles with desired size and shape.

New flow Chart of Synthesis Procedure



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