Low-Temperature Synthesis of Nanosized Bismuth Ferrite by Soft Chemical Route

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The present research describes a simple low-temperature synthesis route of preparing bismuth ferrite nanopowders through soft chemical route using nitrates of Bismuth and Iron. Tartaric acid is used as a template material and nitric acid as an oxidizing agent. The synthesized powders are characterized by X-ray diffractometry, thermogravimetry and differential thermal analysis, infrared spectroscopy, and scanning electron microscopy. The particle size of the powder lies between 3 and 16 nm. In the process, phase pure bismuth ferrite can be obtained at a temperature as low as 400°C, in contrast to 550°C for coprecipitation route. On the other hand, we find that, like solid state reaction route, Pechini's autocombustion method of synthesis generates a lot of impurity phases along with bismuth ferrite.

I. Introduction

NE of the very few magnetoelectrics (ferroelectromagnet/ Seignetomagnet) materials where there is a coexistence of interrelated electric and magnetic dipole structures within a certain temperature range is BiFeO₃ with perovskite structure. BiFeO₃ is ferroelectric ($T_c \sim 1083$ K) and at the same time, antiferromagnetic ($T_n \sim 657$ K). Although BiFeO₃ was discovered in 1960, its applications in electronic industries were hampered because of current leakage problems arising out of nonstoichiometry. Recently, there is a renewed interest in BiFeO₃ because of its possible novel applications¹⁻⁴ in the field of radio, television, microwave and satellite communication, bubble devices, audio-video and digital recording, and as permanent magnets. Incidentally, the synthesis of BiFeO₃ is plagued with problems because of the formation of impurity phases. So far primarily two techniques have been successful in synthesizing phase pure BiFeO₃. In the solid state route⁵ Bi₂O₃ and Fe₂O₃ are reacted at a temperature in the range of 800°-830°C and unreacted Bi₂O₃/Bi₂Fe₄O₉ phases are removed by washing in HNO₃. 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 quite poor. The other technique is to take recourse to simultaneous precipitation/coprecipitation⁶ where solutions of bismuth and iron nitrates are treated with ammonium hydroxide to get hydroxide precipitate. The precipitate needs calcination at a temperature of 550°–750°C to get phase pure BiFeO₃.

In the present communication we report the synthesis of nanosized magnetoelectric bismuth ferrite by a solution evaporation process at a temperature of 400°C. The process is simple, energy saving, and cost effective. We also show that this process

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is superior to the age old Pechini's⁷ autocombustion method of synthesis, where the latter failed to produce phase pure BiFeO₃.

II. Experimental Procedure

Equimolar amounts (0.01*M*) of Bi(NO₃)₃ (3.95 g) and Fe(NO₃)₃ (2.42 g) dissolved in 2 N HNO₃ were taken in a beaker. The parent solutions were standardized for iron and bismuth⁸ as described elsewhere. Tartaric acid in 1:1 molar ratio (3.0018 g) with respect to metal nitrates was added to the solution. The solution was heated under stirring on a hot plate until all the liquids evaporated out from the solution. The temperature of the hot plate was then kept in the range of 150° - 160° C for 1 h. This fluffy green powder was then collected and calcined at different temperatures (300° - 600° C) for 2 h. The yield was 92%. The same procedure was repeated with citric acid in place of tartaric acid and the resultant powder was analyzed.

We also followed Pechini's method of autocombustion to make BiFeO₃. In Pechini's method certain hydroxycarboxylic acids, such as citric acid, form polybasic acid chelates with metal ions and this chelate can undergo polyesterification when heated with a polyhydroxy alcohol to form a polymeric glass which has cations uniformly distributed throughout. Trials have been made to prepare BiFeO₃ with Pechini's autocombustion method using various citrate nitrate ratio.

The powders were characterized by using X-ray diffraction (XRD) (PW 1710, Phillips, Spectries Pvt. Ltd., Amello, Netherlands). The powder morphology was studied using scanning electron microscopy (SEM) (Leo 430i, Carl Zeiss, Germany). Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) of the powders were carried out with Shimadzu (TGA-50) analyzer (Kyoto, Japan). IR spectra of the powders were taken with a Nicolet Model 5PC FTIR (Madison, WI).

III. Results and Discussion

Figure 1 shows the XRD patterns of the synthesized powder prepared via tartarate route, heated in air at different temperatures. The synthesized powder (green powder) is of amorphous nature (Fig. 1(a)). After heat treatment BiFeO₃ phase begins to form, and the phase formation is completed at 400°C. The XRD patterns are in excellent accord with the powder data of JCPDS Card No. 20–169. The particle size of the powders (Table I) were calculated using Scherrer's formula:

$$D = \frac{0.9\lambda}{\beta\cos\theta}$$

where *D* is the average grain size, $\lambda = 1.541^{\circ}A$ (X-ray wavelength), and β is the width of the diffraction peak at half maximum for the diffraction angle 20.

Figure 2 shows the SEM micrographs of the powder. The TG curve (Fig. 3) of the uncalcined powder depicts a very small weight loss up to 700° C (0.71%), which is because of the presence of trapped nitrates (as also confirmed from IR dip (Fig. 4)⁹

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Fig.1. X-ray diffractograms of bismuth ferrite powders (a) green (b) calcined at 400°C (c) calcined at 500°C and (d) calcined at 600°C.

at 1384 cm⁻¹). No evidences of other coordinated or free carbonaceous matter in IR spectra indicate the completion of oxidation of the organics, during the evaporation process. Differential thermal analysis (Fig. 5) up to 700°C at a scan rate of 10° C/min shows a phase change at 384°C which is the Neel temperature of BiFeO₃.⁴ DTA of the sample was also carried out in nitrogen atmosphere and the same result is obtained.

When the synthesis process is repeated with citric acid in place of tartaric acid, BiFeO₃ is formed as a minor phase only (Fig. 6); the major phases are β -Bi₂O₃, BiO, Fe₂O₃, Bi₂₅FeO₄₀, Bi₄₆Fe₂O₇₂. The Pechini's method⁷ of auto-ignition also generated a lot of

impurity phases like Bi_2O_3 , $Bi_2Fe_4O_9$, $Bi_46Fe_2O_{72}$ (Fig. 7).

The uniqueness of tartaric acid as a chelating agent in synthesizing $BiFeO_3$ probably resides in the formation of heterometallic polynuclear complexes in the solution, where reacting metal atoms come in close proximity. This occurs because of the

Table I. Particle Size of the BiFeO₃ Powders

Calcination temperature (°C)	Particle size (nm)
Green	3.288
300	3.425
400	11.013
500	16.513
600	16.507



Fig. 2. Scanning electron microscopy micrograph of the $BiFeO_3$ powder after calcination at 400°C.



Fig. 3. Thermogravimetric analysis curve of green BiFeO₃ powder.

presence of two carboxylate and two hydroxyl group with proper orientation to form a polynuclear complex, which breaks on heating in the presence of concentrated HNO₃ leading to the formation of bismuth ferrite. Similar structure of bismuth tartarate complex^{10,11} (Fig. 8) shows that nine coordinated¹² bismuth environment and involve bidentate interactions with three alkoxide/carboxylate (five-membered ring) and one carboxylate (four-membered ring) of four different tartarate ligands. Consequently, in the present case bismuth centers are bridged by the ligands to give coordination polymeric arrays supplemented by hydrogen bonding between ligands and with water. Such types of polymeric arrays of bismuth and iron alternately may form the heterometallic polynuclear polymeric arrays, which on decomposition in presence of nitric acid give rise to the reaction product.



Fig. 4. IR spectra of green bismuth ferrite powder.



Fig.5. Differential thermal analysis curve of $BiFeO_3$ (calcined at 600°C) powder.



Fig. 6. X-ray diffractogram of BiFeO₃ powder synthesized using (a) tartaric acid calcined at 600° C, (b) citric acid calcined at 600° C, hundred intensity or next intense peaks are marked.



Fig.7. X-ray diffractogram of BiFeO₃ powder synthesized using Pechini's method calcined at 400°C, hundred intensity or next intense peaks are marked.



Fig. 8. Nine coordinated Bismuth tartarate showing bidentate interactions with carboxylate groups of four tartarate ligands.



Fig. 9. Bismuth citrate dimeric complex.

The tridentate chelation¹⁰ by citrate is available from X-ray crystallographic reports. The complex of Bismuth (III) with a tridentate tetra-anionic citrate ligand adopts a well-defined dimeric arrangement imposed by chelate coordination of the pendant carboxylate moiety to a neighboring bismuth centre (Fig. 9). Because of the dimeric nature of the complex (in contrast to polymeric arrays for tartaric acid), the possibility of formation of Bi(III)-Fe(III) heteronuclear arrangement has not become predominant. This resulted in the formation of impurity phases via citrate method. This is also true for the Pechini's route in the present case. Also it is conceived that during autoignition process, the higher temperature and an excess of carbonaceous materials lead to the formation of impurity phases. Such impurity phases are always observed during the solid-state synthesis of BiFeO₃. However the detailed mechanism under the reaction conditions must be further studied.

IV. Conclusion

A simple method has been invented to prepare $BiFeO_3$ nanopowders using tartaric acid as the chelating agent. Compared with the conventional solid-state reaction process and coprecipitation method, $BiFeO_3$ phase can be formed at a much lower temperature without formation of any intermediate phase and therefore a better homogeneity and fine grain size are obtained. Tartaric acid and nitric acid present in the solution play the key role for the synthesis of $BiFeO_3$ at a low temperature.

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