

A Facile Route to the Synthesis of BiFeO₃ at Low Temperature

Ting Liu,[‡] Yebin Xu,^{†,§} Shangshen Feng,[¶] and Jingyuan Zhao[§]

[‡]Wuhan National Laboratory for Optoelectronics, School of Optoelectronic Science and Engineering, Huazhong University of Science and Technology, Wuhan, Hubei 430074, China

[§]Institute of Optoelectronic Science and Engineering, Huazhong University of Science and Technology, Wuhan, Hubei 430074, China

[¶]College of Physics and Electronic Engineering, Taizhou University, Linhai, Zhejiang 317000, China

A facile sol-gel methodology based on the glycerol-gel reaction was used to prepare single-phase BiFeO₃ crystallites. The particle size and morphologies of BiFeO₃ crystallites were characterized by field-emission scanning electron microscope and transmission electron microscope. X-ray diffraction results indicated that single-phase and well-crystallized BiFeO₃ has been synthesized at the temperature as low as 400°C. In present work, single-phase BiFeO₃ can be formed at lower temperature and less organics is required, furthermore, the process is simple and easy to control.

I. Introduction

Compounds exhibiting simultaneously electric and magnetic dipoles are available in nature or have been synthesized in the laboratory.¹ BiFeO₃ is one of the few materials, which exhibits simultaneously ferroelectric ($T_C \approx 830^{\circ}$ C) and antiferromagnetic ordering ($T_N \approx 370^{\circ}$ C).² Because of this magnetoelectric coupling, BiFeO₃-based systems may be used to develop novel applications in the field of radio, television, microwave and satellite communication, bubble memory device, audio-video, and digital recording, etc.³⁻⁶ The synthesis procedure for this material is problematic as it is very difficult to obtain the pure phase because the temperature stability range of single-phase BiFeO₃ is very narrow.^{7.8} As a conventional preparation technique, solid-state reactions based on oxides and carbonates of metal components have been used, with thermal treatments around 800° – 830° C, but unreacted Bi₂O₃/Bi₂Fe₄O₉ was present and was removed by washing with HNO₃.⁹

A variety of wet chemical methods were also used to synthesize BiFeO₃. Phase-pure BiFeO₃ can be synthesized at low temperature via a hydrothermal process; however, pressure is required.^{10–12} The microemulsion technique, ¹³ ferrioxalate precursor method,¹⁴ solution combustion method,¹⁵ and citrate method¹⁶ can only obtain nearly phase-pure BiFeO₃ and traces of a bismuth-rich secondary phase of silenite type were observed. The sol–gel methods based on ethylene glycol (EG),^{17,18} some carboxylic acids with and without EG^{19–21} were used successfully to prepare single-phase BiFeO₃. We successfully synthesized BiFeO₃ by polyvinyl alcohol (PVA) route at 400°C.²² We also find an interesting phenomenon; it appears that OH group is favor for the formation of BiFeO₃ and the effect of COOH group is just contrary. We guess that it is possible to synthesize pure BiFeO₃ with a new complexing agent that has more OH groups and less COOH groups, but no experimental proof was provided. As we known, glycerol has three hydroxyl groups and no COOH groups, and it can form complexes with many metal ions. Therefore, maybe glycerol is a new complexing agent to prepare pure BiFeO₃. In this paper, glycerol route was used to prepare BiFeO₃ and well-crystallized BiFeO₃ has been synthesized at the temperature of 400° - 600° C.

II. Experimental Procedure

BiFeO₃ sample was synthesis by a sol-gel process using glycerol (C₃H₈O₃). Bi₂O₃ powders, Fe(NO₃)₃ · 9H₂O, glycerol, and nitric acid were used as the starting ingredients. Bi₂O₃ powders (4 mol% excess) were dissolved in nitric acid solution to obtain Bi(NO₃)₃ solution. Glycerol was added to Bi(NO₃)₃ solution with stirring at the temperature of 70°C, then stoichiometric $Fe(NO_3)_3 \cdot 9H_2O$ was added. During the process, the mol ratio of metal ion to hydroxyl groups in glycerol (M/-OH) was 1:1.5. With continuous heating at 70°C under constant stirring to evaporate superfluous water, the volume of the solution decreased and the solution viscosity increased continuously. A gel was formed with evolution of NO_x gas resulting from decomposition of nitrate ions. Throughout the process, no signs of precipitation were observed. Then, the sample was removed from the hot plate and heated in an oven at 220°C for 2 h. The resulting mass was slightly ground into a fine powder and BiFeO₃ precursor was obtained. Finally, the precursor was calcined at 350°-600°C for 2 h in static air to obtain BiFeO₃ powder.

Thermogravimetric (TG) analysis (Diamond TG/DTA, PerkinElmer Instruments, Waltham, MA) was used to monitor the decomposition and pyrolysis of the precursor at a heating rate of 10°C/min in static air. Fourier transform infrared spectroscopy (FT-IR, Vertex 70, Bruker Optik GmbH, Ettlingen, Germany) was used to determine the chemical bonding of the BiFeO₃ precursor and powders. The phases were identified by powder X-ray diffraction (XRD) using CuKa radiation (Bruker D8 Advance). Field-emission scanning electron microscopy (FESEM, Sirion 200, FEI Inc., Eindhoven, the Netherlands) and transmission electronic microscopy (TEM, Analytical Transmission Electron Microscope, H-600 STEM/EDX PV9100, Hitachi, Chiyoda-ku, Tokyo, Japan) were used to observe the grain size and the morphology of BiFeO₃ powders. Raman scattering spectra were measured at room temperature using a Raman spectrometer (Renishaw RM-1000, Gloucestershire, U.K.) with a radiation of Ar⁺ laser at 514.5 nm. Magnetic properties were measured using quantum design physical property measurement system (Quantum Design, San Diego, CA).

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[†]Author to whom correspondence should be addressed. e-mail: xuyebin@yahoo.com



Fig. 1. TG curve of BiFeO₃ precursor.

III. Results and Discussion

Figure 1 shows the TG curve of the BiFeO₃ precursor powder. The weight loss (12.1%) in the temperature range between room temperature and 500°C could be assigned to dehydration of the precursor, the decomposition of nitrate and the carbonization and volatilization of glycerol. No more weight loss was observed in the temperature range from 500° to 700°C. The later XRD patterns show that single-phase BiFO₃ was completely crystallized into perovskite phase at 400°C. The TG curve shows a weight loss until 500°C, maybe this is due to a delay of weight loss, because the sample for XRD analysis was calcined at 400°C for 2 h, but the sample in TG analysis is heated at 10°C/min without holding.

Figure 2 shows the FT-IR spectra obtained from the precursor and prepared BiFeO₃ powders at different temperature. For the BiFeO₃ precursor, the broad absorption band in the range of 3372 cm^{-1} is assigned to O–H stretching. The bands in the frequency at 1704 and 1633 cm⁻¹ were assigned to the asymmetric COO⁻ stretching vibrations.^{23,24} There is no COO⁻ in glycerol molecules; however, some hydroxyl groups of glycerol molecules can be oxidized to COO⁻ by the excess HNO₃. The bands located at around 1385, 1040, and 795 cm⁻¹ indicated the existence of nitrate ions.^{18,21,24} The absorption features at 443 and 553 cm⁻¹ are, respectively, attributed to the Fe–O stretching and bending vibrations, being characteristics of the octahedral FeO₆ groups in the perovskite compounds.^{25,26} For precursor heated at 400° and 600°C for 2 h, all the organic peaks are seen to disappear.



Fig. 2. FT-IR spectra of BiFeO₃ precursor and powders calcined at 400° and 600° C.



Fig. 3. XRD patterns of BiFeO₃ precursors and powders calcined at various temperatures for 2 h.

Figure 3 shows the XRD patterns of the BiFeO₃ precursor and powders calcined at 350°-600°C for 2 h. The precursor is XRD amorphous, as is characterized by the broad continuum. At 350°C, some weak XRD peaks showed up in addition to the continuum, which correspond to reflections from BiFeO3. Heating the precursors to 400°C yields pure rhombohedral BiFeO₃ with a perovskite structure, and the XRD patterns are in excellent accord with ICCD file 86-1518. The XRD analysis did not show any formation of Bi₂O₃ or Fe₂O₃ or any other impurity phases of bismuth ferric oxide such as Bi₂Fe₄O₉, Bi₂₄Fe₂O₃₉, and $Bi_{25}FeO_{40}$. Increasing the calcination temperature to 500° and 600°C, the diffraction peaks become stronger and sharper, reflecting greater crystallization. No other significant changes are observed and all diffraction lines could be indexed to the rhombohedral structure of BiFeO₃. Therefore, single-phase BiFeO₃ was completely crystallized into the perovskite phase at a temperature as low as 400°C. The average crystallite sizes of the synthesized powders are also determined according to the X-ray line-broadening of the (012) diffraction peak using Scherrer's equation: $D = 0.89\lambda/B \cos \theta$, where D is the crystallite size; λ is the X-ray wavelength (0.15406 nm for CuK α); B is the corrected FWHM of the diffraction peak; and θ corresponds to the diffraction angle. The average crystallite size was about 96 and 338 nm for the powders calcined at 400° and 600°C, respectively.

To get further insight on the structural variation of BiFeO₃ samples, a Raman study was also carried out, as shown in Fig. 4.



Fig. 4. Raman spectra of BiFeO₃ powders calcined at 400° and 600°C.



Fig.5. FESEM micrographs of BiFeO3 powders calcined at 400°C (a) and 600°C (b) for 2 h.

Eleven fundamental Raman modes can be seen in each spectrum. According to the former literature, the peaks at 139, 172, and 220 cm⁻¹ are the A₁ modes, and the other peaks are related to the E modes of BiFeO₃ molecules.^{27–29} Our Raman spectra are in good agreement with that of previously reported data.^{17,27–29} On the other hand, with increasing calcinations temperature to 600°C, the intensity of the 139 cm⁻¹ peak increases. The increase in peak intensity of this normal A₁ mode is indicative of the enhancement in the contribution of the Bi-O1 vibrational mode, which might be caused by lattice distortions and changed spin–phonon coupling in as-prepared BiFeO₃ nanoparticles.¹⁷ Increasing calcinations temperature, the peak at 615 cm⁻¹ shift to 605 cm⁻¹, and the intensity decreases obviously. Maybe it is related to the particle size.

Figure 5 shows the FESEM micrographs of BiFeO₃ powders calcined at 400° and 600°C for 2 h. The powders calcined at 400°C are found to be agglomerates of some small particles with diameters of about 100 nm. On increasing calcinations temperature to 600°C, the particle size is growing larger obviously. Figure 6 represents the typical TEM image of BiFeO₃ powders calcined at 400°C for 2 h. As can be seen, the powder comprises nanoparticles with an average size about 100 nm. The particle sizes calculated from the XRD peak widths by Scherrer's equation agree with those from TEM and FESEM. The powder produced is also very agglomerated which could be due to the small amount of organics.

The magnetic hysteresis loops of BiFeO₃ powders calcined at 400° and 600°C are shown in Fig. 7. Weak ferromagnetism is observed with corresponding coercivity about $H_c \approx 732$ Oe and $H_c \approx 110$ Oe for sample clacined at 400° and 600°C, respectively. The magnetization does not saturate even at high fields of



Fig. 6. TEM image of BiFeO₃ precursor calcined at 400°C.

30 kOe. With calcination temperature increasing from 400° to 600° C, corresponding coercivity and magnetization are decreased, consistent with other report.¹⁷

Many authors reported the synthesis of BiFeO₃ via sol–gel method^{14,16–22} and the results were listed in Table I. EG, PVA, and glycerol monomer contain only OH group but not COOH group, pure BiFeO₃ can be synthesized easily.^{17,18,22} Single-phase BiFeO₃ can also be obtained with tartaric acid and malic acid.¹⁹ With EG as polymerizing agent, pure BiFeO₃ can be obtained from citrate and maleic precursor,²⁰ but not from malonic acid and succinic acid¹⁹ precursors. From Table I, we can see that OH group is favor for the formation of BiFeO₃ and the effect of COOH group is just contrary. It is unclear what the reason could be.

Glycerol is a triple alcohol and can form complexes with many metal ions.³⁰ Phase pure BiFeO₃ powders were successfully prepared at 400°C. This formation temperature is the same as that in PVA route,²² but is lower than that in other sol–gelbased method.^{17–21} Furthermore, no intermediate phases were observed. The role of glycerol was attributed to generate a highly viscous and stable mixture solution, which prohibited the aggregation of Bi and Fe and favored the formation of BiFeO₃ phase. Besides low formation temperature, another



Fig. 7. Magnetic hysteresis loops of BiFeO₃ powders calcined at 400° and 600° C. The inset shows an enlarged view of the curve for samples calcined at 600° C.

 Table I.
 The Relationship Between Pure BiFeO₃ and Complexing Agent

	ОН по. 3 2 1		COOH no. 0 0 0	Pure BiFeO ₃ $\sqrt[4]{}$	Reference Present work Liu <i>et al.</i> ²² Park and colleagues ^{17,18}
Glycerol PVA EG					
			Without EG	With EG	
Tartaric Malic Citric Maleic [†]	2 1 1 0	2 2 3 2	\checkmark \checkmark × ×		Selbach and colleagues ^{19,21} Selbach <i>et al.</i> ¹⁹ Jiang and colleagues ^{16,20} Selbach <i>et al.</i> ¹⁹

Selbach et al.19 2 Succinic 0 \times × Selbach et al.19 2 Malonic 0 × × Ghosh et al.¹⁴ ? 2 Oxalic 0 Х

[†]Contain one C = C. $\sqrt{}$, obtain pure BiFeO₃; ×, do not obtain pure BiFeO₃; ?, no report; PVA, polyvinyl alcohol; ethylene glycol; EG, ethylene glycol.

advantage of present method over other successful sol-gel synthesis methods is less organics that are used in the preparation. For example, in order to obtain 1 mol BiFeO₃ via glycerol route, only 92 g organics is required. For EG method,¹⁷ tartaric method,²¹ malic method¹⁹ and PVA method,²² the corresponding organics weight is 2640, 300, 268, and 132 g, respectively. With EG as polymerizing agents, required organics weight becomes higher further.^{19,20} Obviously, the present method has a higher weight ratio of the ceramic powders to the organics. Compared with PVA method, glycerol is liquid and the dissolution procedure is omitted, so it is more convenient.

IV. Conclusion

A facile glycerol route was used to synthesize $BiFeO_3$ powders. Pure and well-crystallized $BiFeO_3$ powders were obtained at the temperature of 400° – $600^{\circ}C$, without any intermediate phases. The process is simple and easy to control; furthermore, singlephase $BiFeO_3$ can be formed at lower temperature and less organics are required.

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