

## Optimization of the synthesis of multiferroic bismuth ferrite $\text{BiFeO}_3$ nanopowders by hydrothermal method

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(Received: 23 November 2015, accepted: 29 February 2016)

**Abstract:** Pure phase  $\text{BiFeO}_3$  (BFO) nanopowders were successfully fabricated by a low-temperature hydrothermal synthesis. Effects of the initial KOH concentration and reaction time on the evolution phase of BFO were systematically investigated. The pure BFO was obtained at the temperature of 200 °C by using the KOH concentration of 8M during 6 hours. X-ray powder diffraction (XRD) data refined via Rietveld method indicate that BFO crystallites are in single phase and show a rhombohedra perovskite structure with R3c space group. Differential thermal analysis (DTA) was used to determine the ferroelectric Curie temperature  $T_C$  at ~817.49 °C. FTIR spectroscopy analysis supports the formation of perovskite structure of BFO.

**Keywords:** Multiferroic, bismuth ferrite, hydrothermal synthesis, ferroelectric.

### INTRODUCTION

Multiferroic materials have been widely studied for their potential applications in data storage, sensors and spintronic devices, which show two or more ferroelectric, (anti) ferromagnetic and ferroelastic properties in a certain temperature range [1-3].

Bismuth ferrite is one of promising multiferroics studied materials within a rhombohedrally distorted perovskite structure (Space group R3c). It exhibits a simultaneous coexistence of ferroelectric and anti-ferromagnetic orders parameters with relatively high Curie temperature ( $T_C=830$  °C) and Neel temperature ( $T_N=370$  °C) [4-6]. However, the universal applications of bismuth ferrite are extremely limited due to the difficulty in obtaining single phase BFO. Recently, a variety of wet chemical methods have been introduced to obtain pure BFO materials, such as sol-gel [7,8], co-precipitation [9], microemulsion, thermal annealing [10,11], to name but a few. Still, these methods involve a further high-temperature calcination process at least above 400 °C, which means the higher energy consumption as well as high cost.

Among these manufacturing techniques, hydrothermal methods for obtaining the pure BFO powders require further study because the synthesis of the crystalline ceramic is possible by hydrothermal reaction at a low temperature without addition of calcination step. In the case of BFO, such low processing hydrothermal temperatures prevent the volatilization of reactants and minimize the amount of impurities associated with calcination and ball-milling steps [12].

In this work, single phase BFO powders were prepared at a temperature of 200 °C by hydrothermal method. The phase-formation mechanism under various hydrothermal conditions was investigated and discussed.

### EXPERIMENTAL

The chemical reagents used in this work were bismuth nitrate [ $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ ], iron nitrate [ $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ], nitric acid ( $\text{HNO}_3$ ), and potassium hydroxide (KOH). All of the chemicals have analytical grade purity and were used as received without further purification. Equi-molar

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proportions of  $\text{Bi}(\text{NO}_3)_3$  and  $\text{Fe}(\text{NO}_3)_3$  were dissolved in diluted  $\text{HNO}_3$  and distilled water, respectively. After complete dissolution of the precursors, the solutions are mixed. Then,  $\text{KOH}$  solution was slowly added to the above solution to co-precipitate  $\text{Bi}^{3+}$ , and  $\text{Fe}^{3+}$  ions under constant stirring and a brown precipitate were formed. The precipitate was filtered and washed with distilled water to remove  $(\text{NO}_3)^-$  and  $\text{K}^+$  ions. Then, the precipitate was mixed with  $\text{KOH}$  solution under constant magnetic stirring for 30 min. The suspension mixture was transferred into the stainless-steel Teflon-lined autoclave for the hydrothermal treatment at certain temperature for a period of time. Finally, the autoclave was cooled down to room temperature naturally. The products were filtered, washed with distilled water several times, and then dried at  $90^\circ\text{C}$  for 3 h for characterizations.

Several modifications to the typical synthesis procedures were employed, with the purpose of investigating the effect of hydrothermal conditions on the phase formation and crystallite morphology. The concentration of  $\text{KOH}$  was varied from 2 to 12 M. The hydrothermal treatments were conducted with duration time ranging from 0 to 10 h at  $200^\circ\text{C}$ . The crystal structure and phase composition of the obtained samples were characterized by x-ray diffraction (XRD) (DRX, D8 ADVANCE, Bruker) in a wide range of Bragg angle  $2\theta$  ( $20^\circ \leq 2\theta \leq 80^\circ$ ) using  $\text{Cu K}\alpha$  ( $\lambda_{1,2} = 1.5406 \text{ \AA}$ ) at room temperature. The x-ray

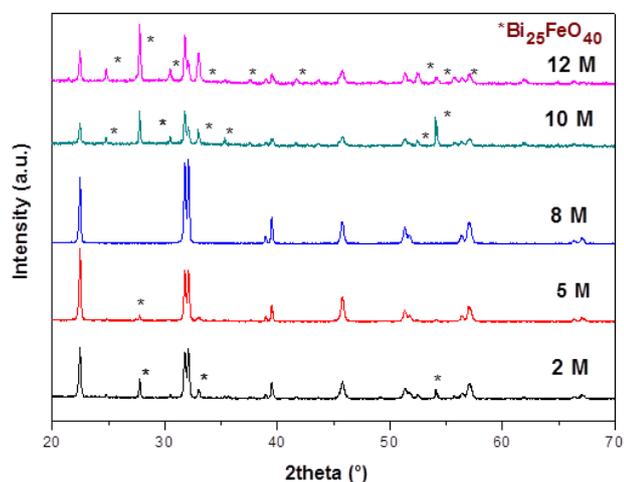
diffraction data was analyzed via Reitveld method using FULLPROF software. Differential thermal analyses (DTA) of the BFO powders were carried out in a Setaram Setsys Evolution TGA-DTA from room temperature to  $900^\circ\text{C}$  under an argon atmosphere with a scanning rate of  $10^\circ\text{C} / \text{min}$ . Fourier Transform Infrared Spectroscopy (FT-IR) measurements were taken with a IR spectrophotometer type CARRY 600 series (from  $400$  to  $4000 \text{ cm}^{-1}$ ).

## RESULTS AND DISCUSSION

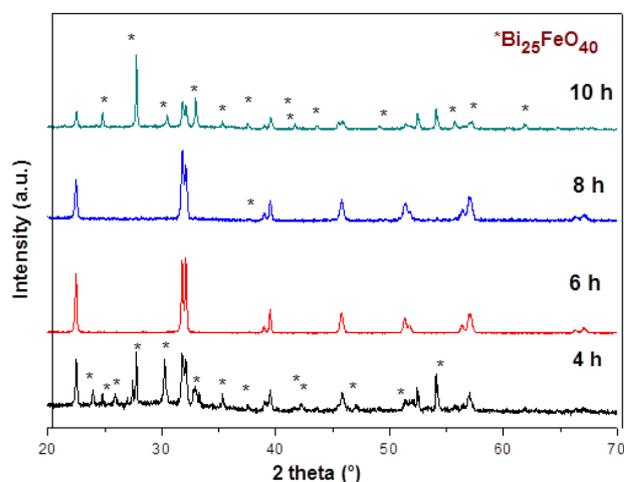
XRD patterns of BFO powders synthesized at  $200^\circ\text{C}$  for 6 hours using different initial  $\text{KOH}$  concentrations of 2, 5, 8, 10 and 12 M represented in **Fig. 1** indicate that only BFO synthesized using 8 M concentration has the pure phase.

However, the presence of  $\text{Bi}_{25}\text{FeO}_{40}$  impurity phase (Sillenite) was detected with the majority BFO phase for samples synthesized with others  $\text{KOH}$  concentration. It was concluded that the suitable amount of  $\text{KOH}$  was beneficial to prevent the formation of impurity phases and therefore promotes the growing of BFO powders into single phase perovskite.

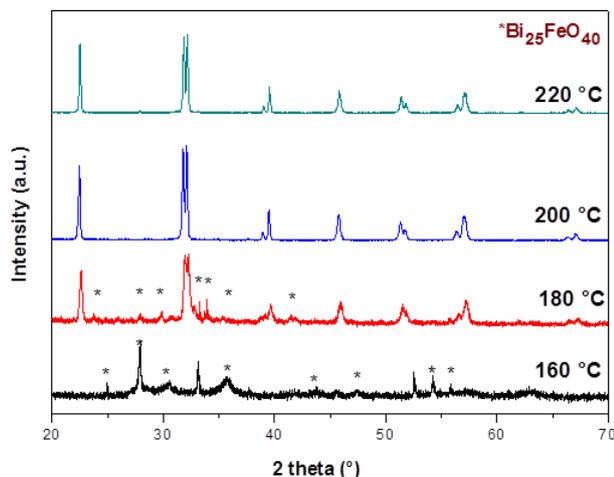
**Fig. 2.** shows XRD patterns of BFO powders synthesized for 4, 6; 8 and 10 h at  $200^\circ\text{C}$  with the optimized  $\text{KOH}$  concentration 8M. The presence of several characteristic peaks at 4 h of  $\text{Bi}_{25}\text{FeO}_{40}$  impurity phase, which completely disappear around 6 hours with the formation of the pure phase, can well be seen. But with increasing the reaction time



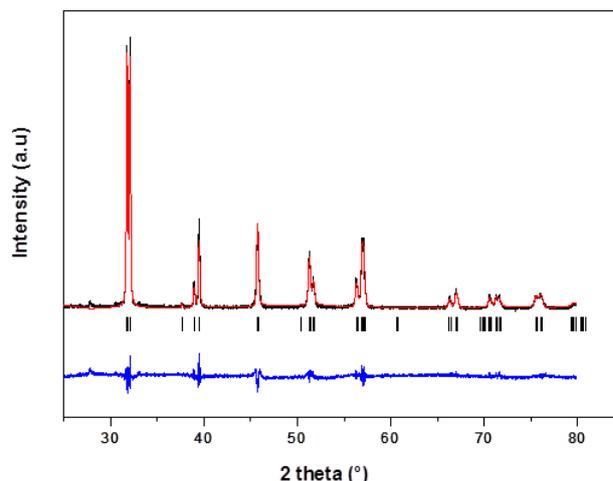
**Fig. 1.** XRD patterns of  $\text{BiFeO}_3$  powders synthesized at  $200^\circ\text{C}$  for 6 h using different  $\text{KOH}$  concentrations of 2, 5, 8, 10 and 12M.



**Fig. 2.** XRD patterns of  $\text{BiFeO}_3$  powders synthesized at  $200^\circ\text{C}$  for 4, 6, 8 and 10 h, using 8 M  $\text{KOH}$  concentration.



**Fig. 3.** XRD patterns of BiFeO<sub>3</sub> powders synthesized at 160, 180, 200 and 220 °C for 6 h using 8 M KOH concentration.



**Fig. 4.** Rietveld refined XRD spectra of BiFeO<sub>3</sub> sample synthesized at 200 °C for 6 h using 8 M KOH concentration.

to 8 h, Bi<sub>25</sub>FeO<sub>40</sub> phase reappears at low trace that becomes majority by going to 10 h. Those results indicated that the product component was changed with reaction time and it was found that 6 h was the favorable time to obtain BFO pure phase.

Only BFO powders synthesized at 200 °C by using the KOH concentration of 8M during 6 hours can be indexed as BFO pure phase with a perovskite structure with R3c space group according to the powder data of PCW 2.3 [13, 14].

**Fig. 3.** represents XRD patterns of BFO samples obtained at 160, 180, 200 and 220 °C in 6 h with 8 M of KOH concentration. For the optimized reaction time and KOH concentration, the phase evolution from Sillenite Bi<sub>25</sub>FeO<sub>40</sub> to perovskite BiFeO<sub>3</sub> could be achieved again by increasing reaction temperature  $\geq 200$  °C. It concluded that the formation of second phase was favored at

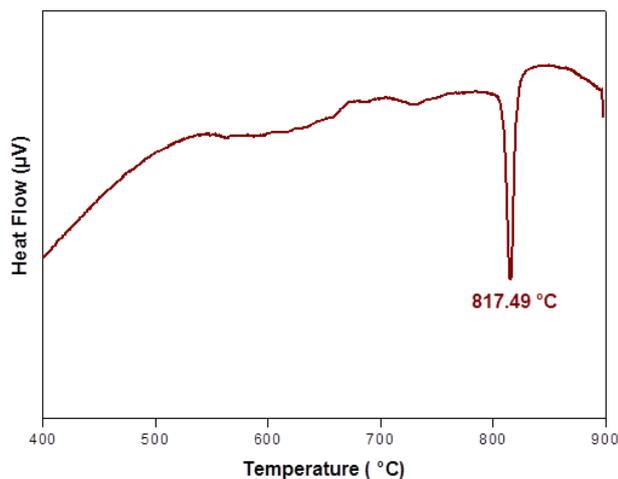
lower temperatures, whereas higher reaction temperature was required to form pure BFO crystallites.

To further analyze the structural transformation, the measured X-ray diffraction data were simulated with Rietveld refinement program. The Rietveld method is used to refine a theoretical line profile until it matches the measured profile based on least squares approach. The difference between the measured and simulated XRD patterns for BiFeO<sub>3</sub> powders synthesized at 200 °C for 6 h using 8 M KOH concentrations was shown in **Fig. 4**.

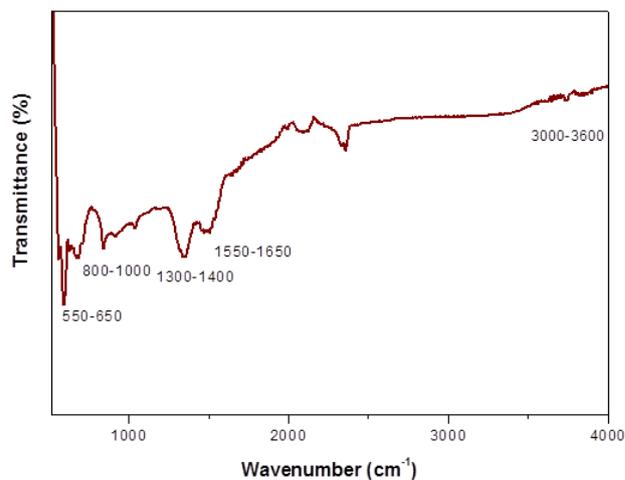
**Table I** presents the crystal structure parameters and profile R-factors derived from the Rietveld refinement program [15]. The small R-values of refinements (Rwp and Rp) suggest that the best fits are observed between the simulated and measured values of XRD patterns.

**Table I.** Refined structure parameters of BiFeO<sub>3</sub> sample synthesized at 200 °C for 6 h using 8 M KOH concentration.

Crystal structure	Lattice parameters	Atoms	x	y	z	Profile R-factors %
R3c	a=b=5.580 Å	O	0.116	0.321	0.101	Chi2: 3.12 Bragg R-factor: 3.02
	c=13.875 Å	Fe	0	0	0	
	d=8.347	Bi	0	0	0.218	
	c/a=2.486					
	$\alpha = \beta = 90.00^\circ$					
	$\tilde{\alpha} = 120.00^\circ$					



**Fig. 5.** DTA curve of BiFeO<sub>3</sub>.



**Fig. 6.** Room temperature FTIR spectra of BiFeO<sub>3</sub> powders.

The DTA curve, shown in **Fig. 5**, reveals an endothermic peak around 817.49 °C, which resulted from the ferroelectric to paraelectric phase transformation in BFO. The Curie temperature of 817.49°C was in good agreement with the previous reports and this was one of evidences of the ferroelectricity nature of our hydrothermal BFO samples [16-18].

Fourier transformed infrared (FTIR) spectra corresponding to crystalline BFO powders derived from the hydrothermal reaction is presented in **Fig. 6**. The strong absorptive peaks around 400-600 cm<sup>-1</sup> were attributed to the Fe-O stretching and bending vibration, being characteristics of the octahedral FeO<sub>6</sub> groups in the perovskite compounds. Another band which appeared between 800-1000 cm<sup>-1</sup> characterized the metal-oxygen band and confirmed the formation of highly crystalline phase R3c of BFO [19-22].

The Absorbance band around 1384 cm<sup>-1</sup> was due to the presence of trapped nitrate groups NO<sub>3</sub><sup>-</sup> [23]. The wide band around 3000-3600 cm<sup>-1</sup> was the result of the antisymmetric and symmetric stretching of bond H<sub>2</sub>O and OH<sup>-</sup> groups, while the band at 1550-1650 cm<sup>-1</sup> corresponding to the bending vibrations of H<sub>2</sub>O [24-25].

## CONCLUSIONS

In the present work, the influence of the different mineralizer concentrations along with duration time on the phase formation of BiFeO<sub>3</sub> powders, which are synthesized by hydrothermal method, was investigated and the optimal conditions to

retain pure monophasic BFO were 200°C during 6 h using 8 M KOH concentration. The perovskite R3c phase of our powders was confirmed and the ferroelectric Curie temperature T<sub>C</sub> was determined. This work will be followed by a magnetic properties study of BFO (variation of remanent magnetization as function of the applied magnetic field and temperature).

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