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# Factors controlling pure-phase multiferroic BiFeO<sub>3</sub> powders synthesized by chemical co-precipitation

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#### 1. Introduction

In recent years, considerable attention has been drawn to multiferroic materials because of their fascinating applications in novel electronic devices [1]. Single-phase BiFeO<sub>3</sub> holds much potential as a multiferroic candidate because magneto-electric coupling occurs even at room temperature-an attribute that endows integrated devices with technological advantage [2]. The use of BiFeO<sub>3</sub>, however, presents a few problems. Avoiding impurities is one of the primary concerns regarding the synthesis of such singlephase multiferroic materials [3]. The impurities are thought to arise from three different causes: First, the evaporation of Bi component occurs easily at the onset of synthesis because of the low decompounded temperature of bismuth salts; this Bi<sub>2</sub>O<sub>3</sub> component appears again in the final production as an impurity. Second, the chemical valence of Fe ion varies in an oxygen-deficient atmosphere; the charge defects with respect to Fe<sup>2+</sup> ions produced in the synthesis are usually related to the large leakage current in BiFeO<sub>3</sub> [4,5]. Third, the synthesis area of single-phase BiFeO<sub>3</sub> in the phase diagram of Bi<sub>2</sub>O<sub>3</sub>-Fe<sub>2</sub>O<sub>3</sub> is very narrow from the view point of thermodynamics, in which two kinds of impurities (Bi<sub>2</sub>Fe<sub>4</sub>O<sub>9</sub> and  $Bi_{25}FeO_{39}$ ) are the usual substitutions for  $BiFeO_3$  [6,7].

The wet-chemical route is feasible for the pure-phase synthesis of  $BiFeO_3$  considering the aforementioned factors [8–10]. For instance, the sol-gel method is able to substantially lower syn-

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#### ABSTRACT

A chemical co-precipitation method is proposed for the synthesis of nano-sized multiferroic BiFeO<sub>3</sub> powders. Pure phase can be obtained by controlling the chemical co-precipitation process, pH level, Bi content, and calcination temperature. The evolutions of phase constitution and structural characteristic of BiFeO<sub>3</sub> powders were investigated by XRD, FT-IR, SEM, and TEM techniques. The slight excess in Bi content plays an important role in the synthesis. The resultant BiFeO<sub>3</sub> powders are of pure phase and have the R3c crystal structure under optimized conditions. The grain size of the BiFeO<sub>3</sub> powders with weak magnetism ranges from 30–40 nm.

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thesis temperature (300–500 °C), reducing impurities to a great extent. Using an oxygen-enriched atmosphere can keep the Fe ion in Fe<sup>3+</sup> form, which minimizes the leakage current of BiFeO<sub>3</sub>. For the preparation of ceramics, liquid phase sintering completed in the solid-state route with a high heating rate (100 °C) can inhibit the production of Bi<sub>2</sub>Fe<sub>4</sub>O<sub>9</sub> and Bi<sub>25</sub>FeO<sub>39</sub> [11].

In this paper, a simple chemical co-precipitation method is proposed for the synthesis of pure single-phase BiFeO<sub>3</sub> powders. The production of impurities can be avoided by controlling the technical parameters using the laws of thermodynamics as bases. The crystallization process of BiFeO<sub>3</sub> is also discussed.

#### 2. Experimental

The reaction precursors were Bi(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O and Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O powders dissolved in nitric acid. To precisely control the chemical precipitation process, we kept pH level constant through synchronized dropping of ammonia (2.5 M) and nitrate solution (2 M). Fig. 1 illustrates this modified method. Fig. 1(a) shows a traditional chemical precipitation process, and Fig. 1(b) shows the modified precipitation process in which a constant pH level is maintained. This modification can ensure homogenous precipitation in the entire process. All of the chemical reagents used were of analytical grade. The final suspension was continually washed until a pH of 7 was obtained. The powders were then filtered, dried, and weighed. Finally, the powders were calcined at various heating schedules.

Thermogravimetric-differential thermal analysis (TG-DTA, STA449C) was conducted with a heating rate of 10 °C/min to investigate the thermal reactions of the powder. The phase structure of the powder was identified using an X-ray diffractometer (Rigaku-D/max-CB, Japan) with CuK $\alpha$  radiation. Fourier transform infrared (FT-IR) spectra were recorded using a Bruker IFS66 v/S spectrometer. The morphology and size distribution of the BiFeO<sub>3</sub> powders were examined by transmission electron microscopy (TEM, CM12). The room-temperature magnetization was measured using a vibrating sample magnetometer (VSM, Lakeshore 7410).

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**Fig. 1.** Schematic of the chemical co-precipitation preparation for BiFeO<sub>3</sub> powder; (a) a traditional co-precipitation process; (b) a homogenous co-precipitation.

#### 3. Results and discussion

#### 3.1. Effect of pH

Fig. 2 shows the TG-DTA curves of the powder prepared by a typical co-precipitation process. The peak near 510 °C corresponds to the crystallization of the BiFeO<sub>3</sub> powder. Thus, to investigate the yield of BiFeO<sub>3</sub> powders as a function of pH, the calcination temperature was set to 550 °C; this was high enough for the crystallization of BiFeO<sub>3</sub> powder in the experiment. Fig. 3 illustrates the XRD patterns of the resultant powders prepared at different pH levels. Two kinds of impurities (Bi<sub>2</sub>Fe<sub>4</sub>O<sub>9</sub> and Bi<sub>2</sub>O<sub>3</sub>) are found in the products. The yield of BiFeO3 powders increases with decreasing pH level. The weight percent of impurities is estimated to be 12% in the sample at pH 9.3. When the solution is at a lower pH level, impurities are slightly reduced and precipitation slowly progresses. This is an indication that homogenous powders of uniform size can be obtained when the solution is at a moderate pH level in the precipitation process. This is also important for the completion of the chemical reaction in the succeeding calcination process (Section 3.4). The influence of pH on BiFeO<sub>3</sub> yield may be related to the evolution of the surface activity of the powders.



**Fig. 3.** XRD patterns of the resultant powders prepared at different pH levels (atomic ratio Bi/Fe = 1:1).

#### 3.2. Effect of Bi content

To further decrease impurities, Bi content (molar ratio) was considered as a means of controlling the co-precipitation process. Fig. 4 illustrates the XRD patterns of the BiFeO<sub>3</sub> powders with different amounts of excess Bi at pH 9.3 and calcination temperature of 550 °C. The BiFeO<sub>3</sub> powders are of pure phase and have the R3c crystal structure when the Bi content has an excess of 3%. The impurities also appear when excess Bi content is larger or smaller than 3% (Fig. 4).

#### 3.3. Crystallization

#### 3.3.1. TG-DTA curve

Fig. 5 shows the TG-DTA curves of the resultant powders prepared under the optimized technical parameters (pH 9.3, Bi content excess of 3%). The endothermic peaks located at 228.5 and 270 °C in the DTA curve are attributed to the decomposition of hydrates and nitrates, which is accompanied by a large weight loss in this stage. A chemical reaction occurs at 481 °C, which corresponds to the crystallization of BiFeO<sub>3</sub> powders. The crystallization temper-



Fig. 2. TG-DTA curves of BiFeO<sub>3</sub> powders prepared by a typical co-precipitation process.



Fig. 4. XRD patterns of BiFeO<sub>3</sub> powders with different amounts of excess Bi at pH 9.3 and calcination temperature of 550 °C.

ature of this optimized BiFeO<sub>3</sub> powder is  $30 \degree C$  lower than that of the powder prepared without optimization. Crystallization temperature is dominated by this chemical reaction, which can be controlled by the pH level and Bi content in the preceding chemical co-precipitation. The small weight loss at  $270-481 \degree C$  is considered the decomposition of remnant nitrates. A ferroelectric–paraelectric phase transition without weight loss is expected to appear at  $829 \degree C$  in the BiFeO<sub>3</sub> powders, as shown in the TG-DTA curve [6,12,13].

#### 3.3.2. FT-IR spectra

Fig. 6 presents the FT-IR spectra of BiFeO<sub>3</sub> powders calcined at different temperatures for 1 h. The spectra agree well with the TG-DTA curves. The peak at  $3420 \text{ cm}^{-1}$  is attributed to the stretching of –OH. Both in the original co-precipitation and  $200 \,^{\circ}\text{C}$ -calcined samples, the peak located at  $1630 \, \text{cm}^{-1}$  indicates the presence of hydrates. In the original co-precipitation sample, the strong peak near  $1380 \, \text{cm}^{-1}$  can be attributed to the vibration of NO<sub>3</sub><sup>-</sup>. When

the calcination temperature increases, the organic bands disappear except for a small remnant of NO<sub>3</sub><sup>-</sup> in the 300 and 400 °C-calcined samples; this is consistent with the TG-DTA results. The broad bands located at 600–400 cm<sup>-1</sup> are generated by the vibration of Fe–O and Bi–O in the amorphous samples. After crystallization, the BiFeO<sub>3</sub> powders show the vibrational Fe–O bands, which stem from the appearance of A<sub>1</sub> and E phonon modes [14]. The peaks at 555 and 420 cm<sup>-1</sup> respectively correspond to the bending vibration of O–Fe–O and stretching vibration of Fe–O, a typical characteristic of BiFeO<sub>3</sub> perovskite with the R3c structure.

#### 3.3.3. Phase constitutions

The XRD patterns of the BiFeO<sub>3</sub> powders calcined at different temperatures for 1 h are shown in Fig. 7. Below 450 °C, the diffraction patterns are from the amorphous phase. The powders crystallize when the annealing temperature is higher than 450 °C [Fig. 7(b)], but have remnant  $Bi_2O_3$  both in 450 and 600 °C-



Fig. 5. TG-DTA curves of BiFeO<sub>3</sub> powders prepared by a homogenous co-precipitation process at pH 9.3 and 3% excess Bi.



Fig. 6. FT-IR spectra of BiFeO<sub>3</sub> powders calcined at different temperatures for 1 h.



**Fig. 7.** XRD patterns of BiFeO<sub>3</sub> powders calcined at different temperatures for 1 h (a) at room temperature ~425 °C; (b) at 450–600 °C, the Rietveld analysis of the 550 °C-calcined sample is shown in the figure; the inset (right) shows the patterns of other samples.



Fig. 8. TEM image of BiFeO<sub>3</sub> powder.

calcined samples\_XRD Rietveld analysis indicates that no secondary phase is observed in 500 and 550 °C-calcined samples. After subtracting background contribution, the crystallinity of BiFeO<sub>3</sub> powders calcined at high temperatures can be calculated as follows [15]:

$$Cr = \frac{\int_{0}^{\infty} I_{Cr}^{corr}(2\Theta) \sin^{2}(\Theta) \cos(\Theta) d(\Theta)}{\int_{0}^{\infty} (I_{Cr}^{corr}(2\Theta) + I_{am}^{corr}(2\Theta)) \sin^{2}(\Theta) \cos(\Theta) d(\Theta)}$$
(1)

where  $\Theta$  is the diffraction angle,  $I_{Cr}^{corr}$  is the corrected scattering intensity from the crystalline phase, and  $I_{am}^{corr}$  denotes the corrected scattering intensity from the amorphous phase. In the 500 °Ccalcined sample, the crystallinity of the BiFeO<sub>3</sub> powder is estimated as 88.5% according to Eq. (1). The BiFeO<sub>3</sub> powder prepared at 550 °C is of pure phase and has the *R*3*c* crystal structure.

The grain size of the BiFeO<sub>3</sub> powder was determined from the integrated width of the diffraction peak using the Scherrer equation [16].

$$\left(\frac{\delta}{\tan\theta}\right)^2 = \frac{K\lambda}{L_{hkl}} \left(\frac{\delta}{\tan\theta\sin\theta}\right) + 16\left(\frac{\Delta d}{d_{hkl}}\right)^2 \tag{2}$$

where  $\delta$  is the integrated width of diffraction peak, *K* is a constant (usually equal to 1),  $L_{hkl}$  denotes the size of (hkl) normal direction,  $\lambda$  is the wavelength,  $\theta$  represents the diffraction angle,  $d_{hkl}$  is the interplanar distance, and  $\Delta d$  is the average deviation caused by stress. The value of  $K\lambda/L_{hkl}$  provides the grain size of nanoparticles. We used the (010) and (110) peaks to calculate grain size. Two factors, i.e., "apparatus width" and the  $K_{\alpha 2}$  line of the target, must be taken into account to extract the integrated widths of the diffraction peaks. The calculated grain sizes of the BiFeO<sub>3</sub> powders prepared at 500 and 550 °C are 31 and 38 nm, respectively. The TEM image of the BiFeO<sub>3</sub> powder with an irregular morphology is shown in Fig. 8. The size of the BiFeO<sub>3</sub> powder obtained from the TEM image is slightly larger than that obtained from the XRD calculations; this is due to the soft agglomeration of the powder.

#### 3.3.4. Magnetism

Fig. 9 shows the typical M-H loop of the BiFeO<sub>3</sub>; weak magnetism can be observed in the powder. Bulk BiFeO<sub>3</sub> is a G-type



**Fig. 9.** Typical M-H loop of BiFeO<sub>3</sub> powder at room temperature. The inset is an enlarged part of the loop between -2 kOe and 2 kOe.

antiferromagnet at room temperature and does not exhibit magnetism in the M-H curve. The weak magnetism can be attributed to the size effect of the nano-sized BiFeO<sub>3</sub> powder, which differs from the linear M-H relationship in BiFeO<sub>3</sub> ceramics [17,18].

#### 3.4. Discussion

The nano-sized powder prepared by homogenous precipitation was subjected to the nucleation and growth of nano-sized particles. The pH level of the Bi–Fe solution plays an important role in the "homogenous" nucleation and growth of Bi(OH)<sub>3</sub> and Fe(OH)<sub>3</sub> particles. The corresponding chemical reactions are as follows:

$$Bi^{3+} + 3OH^{-} \rightarrow Bi(OH)_{3}\downarrow; Fe^{3+} + 3OH^{-} \rightarrow Fe(OH)_{3}\downarrow$$
(3)

In this study, "homogenous" has two connotations: the balance between the nucleation and growth of Bi(OH)<sub>3</sub> and Fe(OH)<sub>3</sub> for maintaining sufficiently small precipitated particles, which should keep the pH level low; and the precipitation of Bi(OH)<sub>3</sub> proceeding slowly to keep pace with that of Fe(OH)<sub>3</sub>, which should keep the pH at a constant level. The modified co-precipitation route proposed in this study is a feasible solution for achieving this homogenous process. Through this homogenous co-precipitation, the precipitated powders exhibit phase stability and have no secondary phase in the calcination process, as shown in Fig. 7(a). The structural characteristic of BiFeO<sub>3</sub> in the amorphous phase can be observed from the original precipitated powder in the 425 °C-calcined sample. The peak broadening in these samples is generated by the diffraction of amorphous-phase BiFeO<sub>3</sub>. No substantial changes are observed in the broadened peaks except for the width and intensity. This phase stability can be considered essential to inhibiting the production of impurities during the calcination process at low temperatures.

The phase constitution varies with further increase in calcination temperature. The appearance of very small amounts of Bi<sub>2</sub>O<sub>3</sub> and Bi<sub>2</sub>Fe<sub>4</sub>O<sub>9</sub> in the 450 °C-calcined sample [Fig. 7 (b)] indicates that the powder undergoes a solid-state reaction between Bi<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub>, as shown by the exothermic peak in Fig. 5. This chemical reaction also marks the crystallization of BiFeO<sub>3</sub>. The 500 and 550 °C-calcined samples are phase-pure and possess the *R*3*c* structure. As Carvalho and Tavares pointed out, however, the decomposition of BiFeO<sub>3</sub> shows one-dimensional kinetics, and BiFeO<sub>3</sub> is not stable even at low temperatures (500–600 °C) [19]. In this study, two aspects can be analyzed as the causes of impurity reduction: First, the excess Bi content can effectively compensate for the evaporation of Bi component in the chemical reaction during the calcination process. Second, from a thermodynamics perspec-

tive, the fast chemical reaction between  $Bi_2O_3$  and  $Fe_2O_3$  needs excess Bi to serve as the driving force because the R3c phase of BiFeO<sub>3</sub> has no solvus line in the  $Bi_2O_3$ -Fe<sub>2</sub>O<sub>3</sub> phase diagram. Furthermore, the phase diagram shows that the slight excess in Bi content can reduce the production of  $Bi_2Fe_4O_9$  because a chemical reaction between the Bi-rich phase and  $Bi_2Fe_4O_9$  may occur. Thus, the slight excess in Bi content may play a fundamental role in the preparation of pure-phase nano-sized BiFeO<sub>3</sub> powders.

When the calcination temperature was increased further, BiFeO<sub>3</sub> began to decompose because of its unstable thermodynamic character. Small amounts of Bi<sub>25</sub>FeO<sub>39</sub> can be observed in the 600 °C-calcined sample.

#### 4. Conclusions

Multiferroic BiFeO<sub>3</sub> powders were synthesized through a simple chemical co-precipitation route. The slight excess in Bi plays an important role in the chemical co-precipitation synthesis of nanosized BiFeO<sub>3</sub> powders. The resultant BiFeO<sub>3</sub> powders with weak magnetism are of pure phase and have the *R3c* crystal structure.

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