MORPHOLOGY-CONTROLLED HYDROTHERMAL SYNTHESIS OF BISMUTH FERRITE USING VARIOUS ALKALINE MINERALIZERS

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The present research reports fabrication of nano- and submicrometer-sized $BiFeO_3$ (BFO) powders from bismuth nitrate and iron chloride by a simple hydrothermal method at 180°C for 16 h in the presence of various MOH mineralizers ($M = K^+$, Na^+ and Li^+). The final products were characterized by X-ray powder diffraction (XRD) and high-resolution transmission electron microscope (HR-TEM). Alkaline mineralizers introduced at suitable concentration have been found to play the key role in the formation of BFO crystallites with certain morphologies and sizes due to cationic radii of mineralizers during the hydrothermal process. A nucleation and crystal growth mechanisms are proposed for the formation of BFO crystallites in the size range of nano and submicrometer.

INTRODUCTION

Recently, multiferroic materials have attracted a great deal of attention due to coexistence of ferroelectricity, ferromagnetism and ferroelasticity in a single compound enabling the development of novel functional materials in the field of information storage, spintronics, multiple-state memories and sensors [1,2]. However, the presence of adequate structural building blocks permitting ferroelectric-type ionic movements, magnetic-interaction pathways for the magnetic order and symmetry conditions are required for the occurrence of ferroelectric and magnetic order in the same material [3]. Among known multiferroics, single-phase $BiFeO_3$ (BFO) with a rhombohedrally distorted perovskite structure is the most interesting candidate, having an antiferromagnetic behavior with a relatively high Neél temperature ($T_N \sim 810°C$) and a ferroelectric behavior with a high Curie temperature ($T_C \sim 810°C$) [4]. BFO is stable in a narrow temperature range, and a number of other phases of Bi and Fe can appear easily if temperature and oxygen partial pressure are not controlled accurately [5]. Although BFO has been studied extensively since its discovery in the 1960s, disadvantages such as presence of high leakage current, impurity phases, low resistivity, small spontaneous polarization, inhomogeneous magnetic spin structure, ferroelectric reliability and high defect density have hindered its practical application.

Till date, an applying various techniques in synthesizing phase-pure BFO has given a chance to overcome those shortcoming and even to get better characteristics. For instance, sonochemical and microemulsion [6], sol-gel [7], solution-combustion [8,9], the soft chemical route [10], co-precipitation [11] and hydrothermal [12] methods have been successfully employed to fabricate BFO with different crystallite sizes and morphologies and avoid the disadvantages of conventional solid state reactions like high preparation temperature, large particle size, wide particle size distribution and aggregation [13]. However, most of them still require a further calcination step at higher temperature (> 400°C).

Compared with the used methods, hydrothermal synthesis has been regarded as a most promising method to produce fine ceramic powders with high crystallinity, high purity, narrow particle size distribution, and controllable microstructure and chemical composition by a closed system operating under low temperature and high pressure. Lately, nanosized BFO has been subjected to intensive scientific study. The authors have applied mineralizer- [14], polymer- [15], and surfactant-assisted [16] hydrothermal and mechanochemical [17] methods in order to obtain nanoscale BFO possessing unique physical properties due to potential quantum confinement effect and low dimensionality in nanocrystallites. Narrow size distribution is essential to exploit the size and quantum confinement effect and tailor nanomaterials with new properties [18].

The role of mineralizers is very important in controlling the dissolution, nucleation and crystallization process under the action of temperature and pressure.

According to Byrappa and Yoshimura [19], the following criteria are generally used to select appropriate mineralizers for hydrothermal synthesis: (1) congruence of the dissolution; (2) sharp change in the solubility with changing temperature or pressure; (3) specific quantitative value of the absolute solubility; (4) the formation of readily soluble mobile complexes in the solution; and (5) specific redox potential of the medium, ensuring the existence of ions. However, the control of the BFO crystal growth under the hydrothermal process using a suitable mineralizer is still a challenging topic for material scientists. Therefore, we have attempted to study the influence of alkaline mineralizers on the crystallization of BFO at 180°C for 16 h.

EXPERIMENTAL

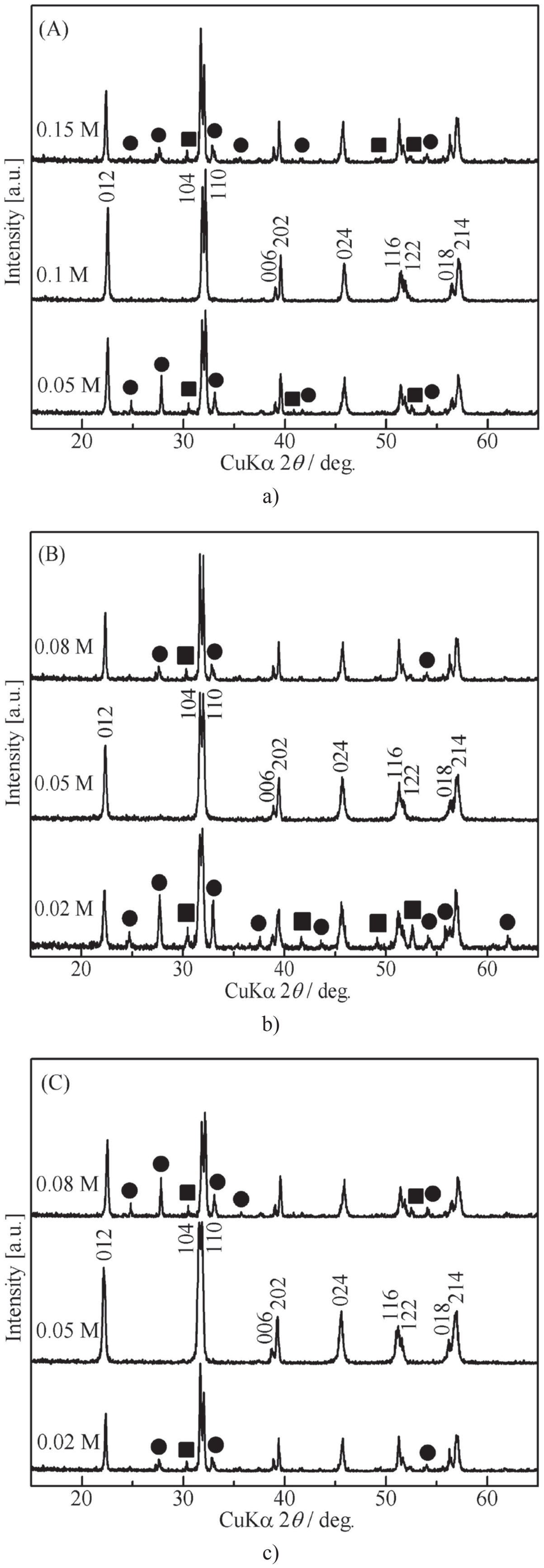
The chemical reagents used in the present work were bismuth nitrate [$Bi(NO_3)_3{\cdot}5H_2O$], iron chloride ($FeCl_3{\cdot}6H_2O$), potassium hydroxide (KOH), sodium hydroxide (NaOH) and lithium hydroxide (LiOH) (Shanghai Chemistry Company). All source chemicals were analytical grade purity and used as received without further purification. In a typical procedure, equimolar amount (0.02 M) of $Bi(NO_3)_3{\cdot}5H_2O$ and $FeCl_3{\cdot}6H_2O$ were carefully weighted in stoichiometric proportion. $Bi(NO_3)_3{\cdot}$ ${\cdot}5H_2O$ was dissolved in 10 ml ethylene glycol (EG) with continuous stirring (solution A) and $FeCl_3{\cdot}6H_2O$ was dissolved in 10 ml distilled water (solution B). Then, the solution B was slowly added into the solution A under vigorous stirring for 15 min. 13.2 M aqueous solution of ammonia (NH_3) was slowly dropped into the homogenous solution to adjust its pH > 10 by constant stirring, and a brown-colored precipitate was formed. The precipitate was filtered and repeatedly washed with distilled water to remove NO_3^- and Cl^- ions. The suspension was transferred into a 40 ml Teflon-lined stainless steel autoclave and mineralizer solutions were then added with a filling capacity of 70%. Potassium hydroxide (KOH), sodium hydroxide (NaOH) and lithium hydroxide (LiOH) were utilized for the preparation of mineralizer solutions. The hydrothermal treatment was subsequently carried out for the different concentrations (0.02-0.15 M) of the mineralizers at a reaction temperature of 180°C for 16 h under autogenous pressure. After the autoclave was cooled down naturally to room temperature, the final products in the autoclave were filtered out and washed with distilled water and absolute ethanol several times to remove residual soluble salts and unreacted ions. The obtained powders were dried at 80ºC for 5 h before characterization.

The phase structure of the as-synthesized $BiFeO_3$ powders was characterized by X-ray powder diffraction with monochromated CuKα radiation (λ = 1.5406 Å) at 40 Kv and 50 Ma (Dmax-3C, Rigaku, Japan). The transmission electron microscope (TEM), high-resolution transmission electron microscope (HR-TEM) and selected area electron diffraction (SAED) images of the final products were observed using a JEOL 200 CX TEM (Tokyo, Japan,) with acceleration voltage of 300 Kv.

RESULTS AND DISCUSSION

The XRD patterns of $BiFeO_3$ powders synthesized at 180°C for 16 h with different initial concentrations of KOH (a), NaOH (b) and LiOH (c) are illustrated in Figure 1. Obviously, the XRD patterns present the formation of the phase pure BFO by a mild hydrothermal treatment with appropriate concentration of the mineralizers. Diffraction peaks of BFO correspond well with the reported data (PDF Card No. 86-1518). The diffraction patterns of BFO have been readily indexed as a rhombohedrally distorted perovskite structure with space group *R3c* and lattice parameters *a* = 5.577 Å and *c* = 13.862 Å. However, the formation of impurity phases, Bi_25FeO_{40} (PDF Card No.46-0416) and $Bi_2Fe_4O_9$ (PDF Card No.20-0836), was observed when the concentrations of alkaline solutions were either low or high. It can be elucidated that the strong base of OH^- might favor the formation of Bi–O–Bi bridges between the non-bridging structural hydroxyl groups in the alkaline hydrothermal process [12]. Suitable concentrations of the mineralizers were advantageous to avoid impurity phases and to grow single-phase BFO crystallites. A consumption of a higher KOH concentration (0.1 M) for the formation of BFO is related to the high cationic radius. In fact, higher cationic radii of the mineralizers require higher concentrations for the minimum and consequently for full crystallization.

The images of the transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HR-TEM) and selected area electron diffraction (SAED) of the final products prepared by the hydrothermal process at 180°C for 16 h are shown in Figure 2. As displayed in Figure 2a-c, BFO powders have laminar with irregular shape (a), rectangle (b) and rod-like (c) crystallites in the range of nano and submicrometer due to the influence of KOH, NaOH and LiOH, respectively. It is confirmed that the diminution of the particle size of final products decreases according to the following sequence of decreasing cationic radii of basic mineralizers: 200 ± 10 nm in KOH (1.38 Å) > 120 ± 5 nm in NaOH (1.02 Å) > 64 ± 3 nm in LiOH (0.75 Å). In Figure 2c, rod-like BFO crystallites with width of ca. 200 nm and length of ca. 64 nm were observed. According to previous data [20], the nanoparticles would aggregate vertically by the driven force that can be attributed to the local stress and the decrease of the surface-free energy. Some adjacent submicron particles joined with each other to form laminar morphology of BFO powders when hydrothermal process was performed using KOH (Figure 2a). It is well known that the physical and chemical



a)

b)

c)

Figure 1. XRD patterns of the BFO powders synthesized at 180°C for 16 h using different concentrations of KOH (a), LiOH (b) and NaOH (c). Key: ● = Bi25FeO40, ■ = $Bi_2Fe_4O_9$.

properties of the solvent can influence the solubility, reactivity and diffusion behavior of the reagents and the intermediate. Ethylene glycol used in the present work is an excellent capping agent and good dispersive medium for the starting materials, which may also play a critical role in the nucleation and growth of BFO crystallites with different morphologies.

The typical HR-TEM images of the as-synthesized BFO, recorded from the edge of the crystallites, are shown in Figure 2d-f. The crystal lattice fringes are clearly observed, and average distance between the neighboring fringes is 0.396 nm, corresponding to the (012) plane of a rhombohedral phase BFO crystal. It suggests that the BFO crystal formed with a preferred growth orientation. The SAED patterns (Figure 2g-i) taken on the samples exhibit well-ordered and linearly arranged spots giving good agreement with the rhombohedral structure of BFO, which further confirms the results of XRD and HR-TEM images.

The formation processes of BFO in the hydrothermal system can be assigned to two stages: first, $Bi(NO_3)_3$ and $FeCl_3$ transformed into hydroxides in a relatively short time, then formed $Fe(OH)_3$ and $Bi(OH)_3$ subjected to mineralizers (KOH, NaOH and LiOH) attack to dissolve and react at high temperature and pressure. Finally, insoluble BFO powders precipitated from supersaturated hydrothermal fluid. The formation mechanism can be ascribed according to the following chemical reactions:

$$Bi(NO_3)_3{\cdot}5H_2O + C_2H_6O_2 \rightarrow [Bi(C_2H_5O_2)]^{2+} + 3NO_3^- + H^+$$

$$FeCl_3{\cdot}6H_2O \rightarrow [Fe(H_2O)_6]^{3+} + 3Cl^-$$

$$[Bi(C_2H_5O_2)]^{2+} + [Fe(H_2O)_6]^{3+} + 5NH_3 \rightarrow$$
$$\rightarrow 5NH + C_2H_6O_2 + Bi(OH)_3 + Fe(OH)_3$$

$$Fe(OH)_3 + Bi(OH)_3 \xrightarrow[\text{mineralizer } (M = K^+,\ Na^+ \text{ and } Li^+)]{\substack{\text{hydrothermal treatment} \\ \text{at } 180^{\circ}\text{C for 16 h using MOH}}} BiFeO_3.$$

From these formulae, it was found that the reaction between $Bi(OH)_3$ and $Fe(OH)_3$ in the presence of various basic mineralizers is very important, and the morphology and crystal size are strongly dependent on the cationic radii of mineralizers. According to Chen et al., the dissociation of bismuth and iron hydroxides and the formation of ionic complexes might prevent the growth of BFO crystallites and limit the size of BFO particles [12]. The formation mechanism of BFO crystallites can be expressed as a dissolution, nucleation, and crystallization of the starting materials under hydrothermal conditions.

CONCLUSIONS

In the present work, nano- and submicrometer-sized BFO powders with different morphologies have been successfully fabricated from bismuth nitrate and iron

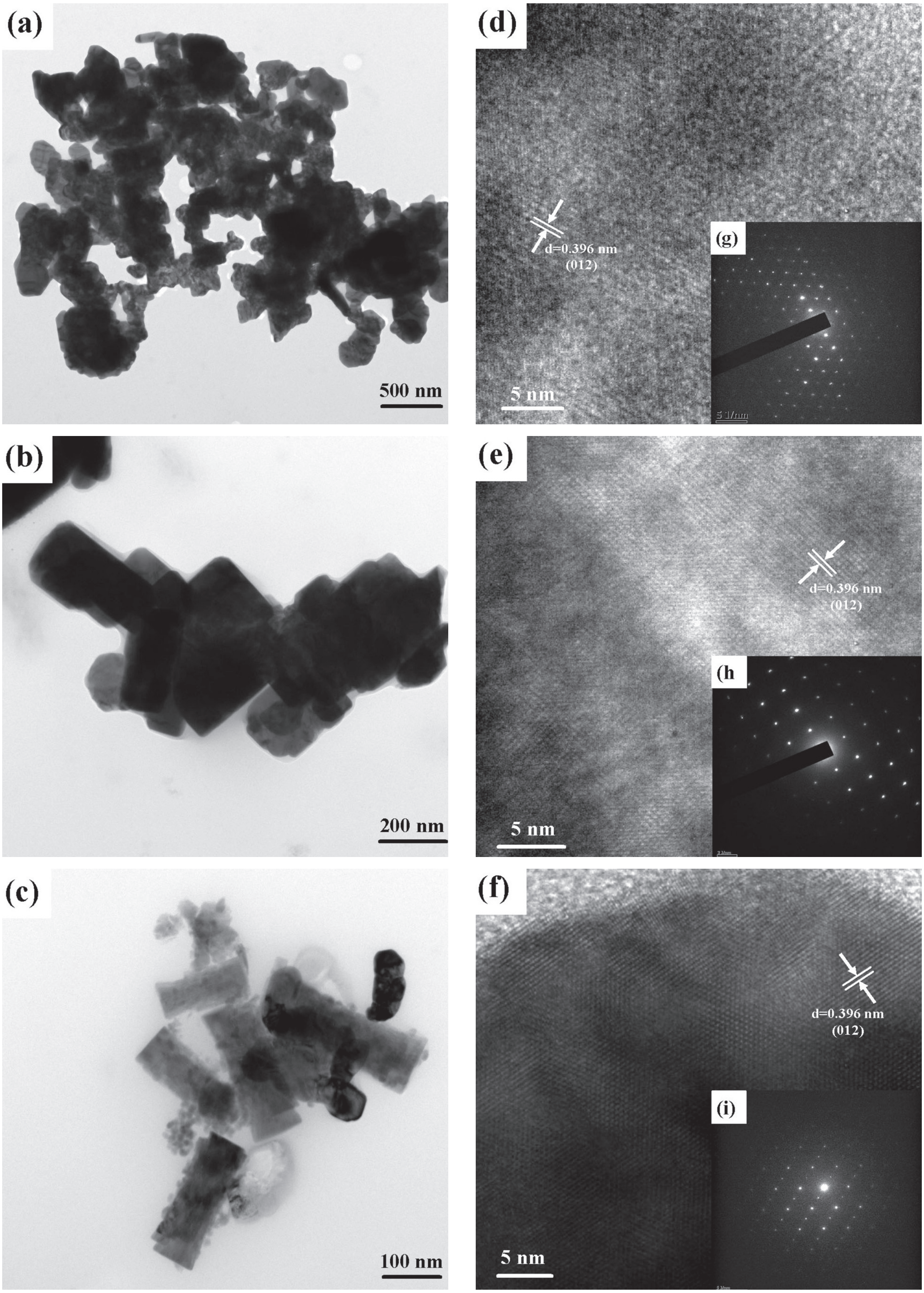


Figure 2. The TEM, HRTEM and SAED images of the BFO powders synthesized at 180°C for 16 h using KOH (a, d and g), NaOH (b, e and h) and LiOH (c, f and i), respectively.

chloride by a hydrothermal method at 180°C for 16 h using MOH mineralizers (M = K^+, Na^+ and Li^+). Alkaline mineralizers have a great effect on the morphologies and sizes of BFO crystallites due mainly to cationic radii of mineralizers during the hydrothermal process. A possible formation mechanism of BFO crystallites in the presence of various mineralizers was proposed.

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