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Synthesis of pure phase $BiFeO_3$ powders in molten alkali metal nitrates

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Abstract

Pure phase $BiFeO_3$ powders were successfully synthesized in molten alkali metal nitrates (KNO_3–$NaNO_3$) at 500 °C. The as-prepared $BiFeO_3$ had a rhombohedral structure which was studied using X-ray diffraction. The plate-like morphologies were investigated through scanning electron microscopy and transmission electron microscopy. The average length and width of $BiFeO_3$ plates were 400 and 200 nm, respectively. Furthermore, the mechanism of formation of $BiFeO_3$ was also discussed through X-ray diffraction, thermogravimetry, differential thermal analysis and mass spectrometry.

Keywords: A. Powders: chemical preparation; B. Platelets; D. Perovskites

1. Introduction

Recently, multiferroics have engendered increasing interest because of their many potential applications for micro- or nano-electronic devices, magnetic storage elements and interesting fundamental physics [1,2]. The term "multiferroic" means coexistence of ferroelectric and magnetic ordering in one single phase or multiphase materials. However these two ordering parameters are mutually exclusive in principle because ferroelectricity and magnetism require different filling states of d shells of transition metal ions. Empty d shells mainly exist in ferroelectricity, while partially filled d shells are required in magnetism [3]. Therefore multiferroics are rare. As one kind of very few multiferroics, $BiFeO_3$ has simultaneous ferroelectric ($T_c \sim 820$–850 °C) and G-type antiferromagnetic ($T_N \sim 370$ °C) behaviors at room temperature, with a distorted perovskite structure [4,5]. In the past decades, although many efforts have been made to synthesize $BiFeO_3$, it is difficult to avoid the formation of impurities such as $Bi_2Fe_4O_9$ and $Bi_{25}FeO_{40}$. In the conventional solid-state reaction [6,7], the impurities are removed by leaching with dilute nitric acid. However, the disadvantages of the method lie in poor reproducibility and presence of coarse powders. Furthermore, some soft chemical routes, such as hydrothermal synthesis [8–10], sol–gel [11,12] and microemulsion [13], have been applied to prepare pure $BiFeO_3$. However, so far, to the best of our knowledge, there are few reports on the preparation of pure $BiFeO_3$ using molten salts.

Molten salts are effective ionic liquid media for preparing inorganic materials [14,15]. Although Chen et al. [16] have made pure $BiFeO_3$ in NaCl–Na_2SO_4 molten flux, the synthesis temperature is high up to 800 °C and the formation temperature range for pure phase is quite narrow. In this paper, pure phase $BiFeO_3$ powders were synthesized in molten KNO_3–$NaNO_3$ at 500 °C. No impurities were formed when the temperature was up to 550 °C.

2. Experimental

All chemical reagents were analytical grade purity without any further purification. Typically, $Bi(NO_3)_3\cdot 5H_2O$, $Fe(NO_3)_3\cdot 9H_2O$ and tartaric acid were dissolved in 100 ml 1 M HNO_3 to form a clear solution. After stirred for 30 min, the solution was evaporated in a rotary evaporator (Heidolph VV2011) at about 75 °C for 2 h. The granular precursor was then easily collected. The nitrates (KNO_3/$NaNO_3$ = 51:49) and the as-prepared precursor were mixed in a weight ratio of 30:1, and then ground in a mortar for 30 min. The mixture was transferred to a crucible and calcined at different temperatures in a furnace for 4 h. After reaction, the product was washed and

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filtered by deionized water and anhydrous ethanol for several times and then dried at 60 °C for 6 h.

The phase composition of the unwashed solidified melts and the as-washed synthesized powders were characterized by X-ray diffraction (XRD, Model D/MAX-RB, Rigaku Co., Tokyo, Japan) with Cu Kα radiation (λ = 1.5418 Å), over the scanning range of 10–60°. The morphology of $BiFeO_3$ powders was studied by field emission scanning electron microscopy (FESEM, Model JSM-6700F, JEOL, Tokyo, Japan) and field emission transmission electron microscopy (FETEM, Model JEM-2100F, JEOL, Tokyo, Japan). Thermogravimetric analysis (TG), differential thermal analysis (DTA) and mass spectrometry (MS) were carried out using a thermal analyzer (STA-429C, Netzsch, Bavaria, Germany) and a mass spectrometer (ThermoStarTM, Balzers, Balzers, Liechtenstein), respectively, at the heating rate of 10 °C/min in Ar atmosphere. Fourier transform infrared (FTIR) spectra of $BiFeO_3$ were taken with an IR spectrophotometer (Nicolet 380, Thermo Electron Corporation, Madison, WI, USA).

3. Results and discussion

The XRD patterns of the samples synthesized in molten KNO_3–$NaNO_3$ at different temperatures are presented in Fig. 1(a)–(f). At 250 °C, only $Bi_2O_2CO_3$ was detected in the as-washed sample (Fig. 1(b)). During the synthesis of $BiFeO_3$, the tartaric acid is a chelating agent which participates in the formation of metallic complexes in the solution [17]. $Bi_2O_2CO_3$ may arise from the decomposition of the precursor of $BiFeO_3$ comprising such metallic complexes when heated in the molten nitrates. The composition of the unwashed solidified melts calcined at 250 °C was also studied by XRD (Fig. 1(a)). It is shown that the water soluble $KFeO_2$ and insoluble $Bi_2O_2CO_3$ coexist in the unwashed sample. Other phases except KNO_3 and $NaNO_3$ are not found within detection limits. The $KFeO_2$ was removed by washing the solidified melts and only $Bi_2O_2CO_3$ was left. It can be presumed that $KFeO_2$ and $Bi_2O_2CO_3$ are the intermediates during the formation of $BiFeO_3$. With the increase of reaction temperature, the $BiFeO_3$ phase begins to appear (Fig. 1(c) and (d)). However, $Bi_2O_2CO_3$ still exists and the reaction is incomplete. Pure $BiFeO_3$ is formed when the temperature reaches 500 °C (Fig. 1(e)). All diffraction peaks of pure $BiFeO_3$ agree well with the powder data of JCPDS Card No. 86-1518 (space group $R3c$, $a = b = 5.577$ Å, $c = 13.86$ Å). The result indicates that the as-prepared $BiFeO_3$ has a rhombohedral structure. Compared to Ref. [16], pure $BiFeO_3$ can be synthesized in the molten KNO_3–$NaNO_3$ within a broader temperature range. No $Bi_2Fe_4O_9$ or $Bi_{25}FeO_{40}$ impurities occur when the temperature is up to 550 °C.

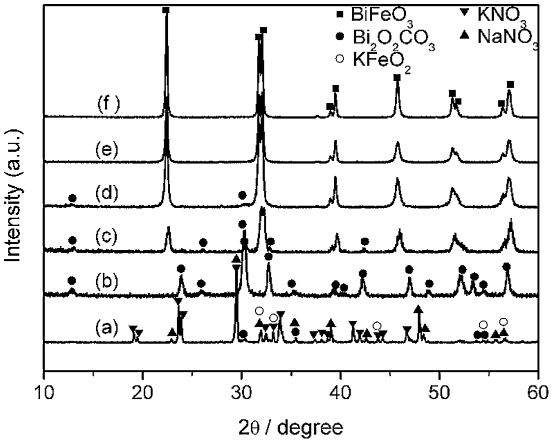

Fig. 1. XRD patterns of the unwashed solidified melts calcined at 250 °C (a) and the washed samples synthesized in molten KNO_3–$NaNO_3$ at temperature for 4 h: (b) 250 °C; (c) 350 °C; (d) 450 °C; (e) 500 °C; (f) 550 °C.

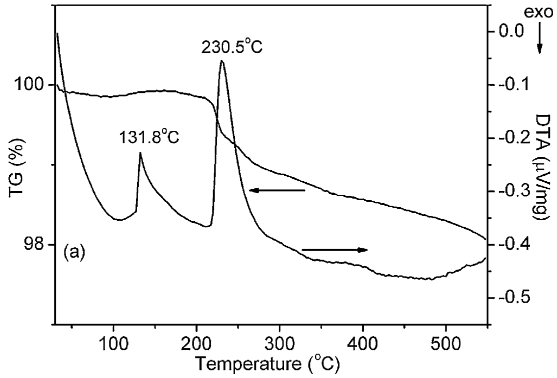

Fig. 2. Thermal analysis curves of the mixture of nitrates and the $BiFeO_3$ precursor in the weight ratio of 30:1.

The thermal behaviors of the mixture of $BiFeO_3$ precursor and nitrates have been studied by TG–DTA and the results are shown in Fig. 2. On the DTA curve, the sharp endothermic peak at around 230.5 °C with a major mass loss can be related to the decomposition of the metallic complexes and minor amounts of nitrates, which can correspond to the mass spectrometric curves presented in Fig. 3. The mass spectroscopy shows CO_2 to be continuously evolved till about 380 °C due to the decomposition of the metallic complexes, while the formation of NO_2 arises from the break of nitrates. Furthermore, because of no obvious mass loss and gas signal peaks, the endothermic peak at around 131.8 °C may be assigned to the melting of nitrates.

The mechanism of formation of $BiFeO_3$ can be proposed as follows. Molten nitrates are the basic and oxidizing media, in

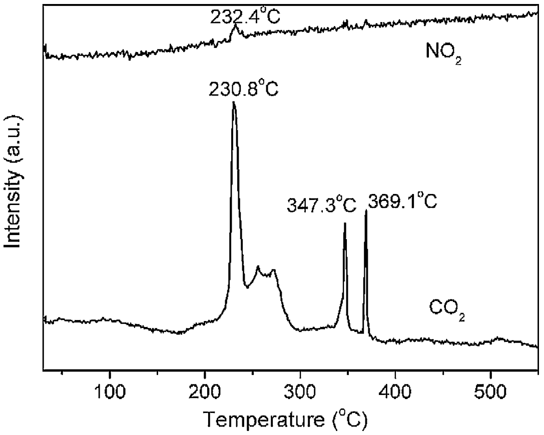

Fig. 3. Mass spectroscopy curves of the mixture of nitrates and the $BiFeO_3$ precursor in the weight ratio of 30:1.

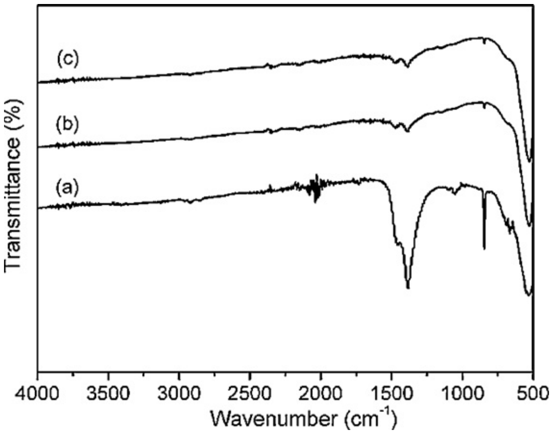

Fig. 4. FTIR spectra of $BiFeO_3$ synthesized in molten KNO_3–$NaNO_3$ at different temperatures: (a) 350 °C; (b) 450 °C; (c) 550 °C.

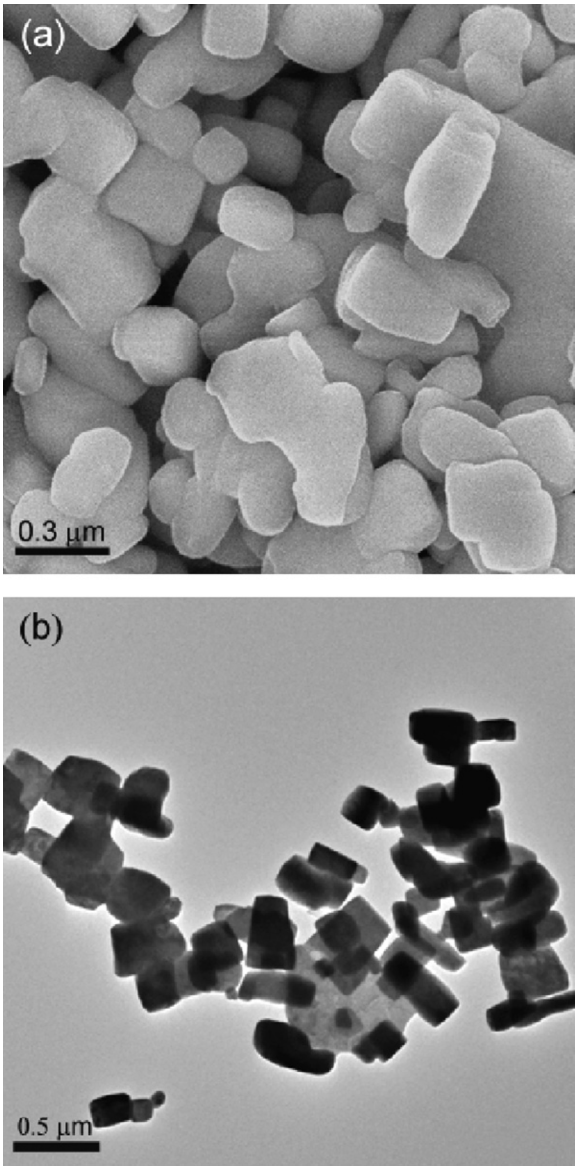

Fig. 5. SEM (a) and TEM (b) micrographs of as-prepared $BiFeO_3$ powders at 550 °C.

which nitrate anions act as oxygen anions donors or oxygen atoms donors. The so-called Lux–Flood (L–F) acid–base reactions between molten nitrates and other raw materials exist [18]. The reaction equations could be given as follows [18,19]:

$$2NO_3^- \rightarrow 2NO_2 + (1/2)O_2 + O^{2-} \quad (1)$$

$$M^{n+} + (n/2)O^{2-} \rightarrow MO_{n/2} \quad (2)$$

where M^{n+} represents the metal cation with n positive charges.

According to the above experiment results and L–F acid–base reaction equations, the reactions for synthesis of $BiFeO_3$ are suggested as

$$Fe(NO_3)_3 + KNO_3 \rightarrow KFeO_2 + 4NO_2 + O_2 \quad (3)$$

$$Bi_2O_2CO_3 + 2KFeO_2 \rightarrow 2BiFeO_3 + CO_2 + K_2O \quad (4)$$

The FTIR spectra of $BiFeO_3$ synthesized in molten nitrates at different temperatures are shown in Fig. 4. The bands at 800–860 and 1350–1410 cm^{-1} are due to the existence of the trapped nitrates [17]. The bands in the range of 1410–1500 cm^{-1} may correspond to the vibration of carbonates which could arise from the $Bi_2O_2CO_3$. With the increase of reaction temperature, the intensity of these peaks becomes weaker probably due to reactions (3) and (4). Furthermore, the peak at 560 cm^{-1} attributes to the Fe–O bonding.

Fig. 5 shows the SEM and TEM images of pure $BiFeO_3$ powders. The as-prepared $BiFeO_3$ powders exhibit plate-like morphology with average length and width of 400 and 200 nm, respectively. The anisotropic growth of $BiFeO_3$ could be due to the crystal structure with the different lattice parameters of a_0 (5.577 Å) and c_0 (13.86 Å) [20].

4. Conclusions

Pure $BiFeO_3$ plate-like powders have been successfully synthesized using molten KNO_3–$NaNO_3$ at 500 °C. The mechanism of formation of $BiFeO_3$ has also been investigated. It is found that $KFeO_2$ and $Bi_2O_2CO_3$ intermediates exist during the synthesis of $BiFeO_3$ in molten nitrates.

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References

[1] M. Fiebig, Th. Lottermoser, D. Fröhlich, A.V. Goltsev, R.V. Pisarev, Observation of coupled magnetic and electric domains, Nature 419 (2002) 818–820.
[2] J.F. Scott, Applications of modern ferroelectrics, Science 315 (2007) 954–959.
[3] S.W. Cheong, M. Mostovoy, Multiferroics: a magnetic twist for ferroelectricity, Nature 6 (2007) 13–20.
[4] C. Blaauw, F.V.D. Woude, Magnetic and structural properties of $BiFeO_3$, J. Phys. C: Solid State Phys. 6 (1973) 1422–1431.

[5] P. Fischer, M. Polomska, I. Sosnowska, M. Szymański, Temperature dependence of the crystal and magnetic structure of $BiFeO_3$, J. Phys. C: Solid State Phys. 13 (1980) 1931–1940.

[6] M.M. Kumar, V.R. Palkar, K. Srinivas, S.V. Suryanarayana, Ferroelectricity in a pure $BiFeO_3$ ceramic, Appl. Phys. Lett. 76 (2000) 2764–2766.

[7] G.D. Achenbach, W.J. James, R. Gerson, Preparation of single-phase polycrystalline $BiFeO_3$, J. Am. Ceram. Soc. 50 (1967) 437–1437.

[8] C. Chen, J.R. Cheng, S.W. Yu, L.J. Che, Z.Y. Meng, Hydrothermal synthesis of perovskite bismuth ferrite crystallites, J. Cryst. Growth 291 (2006) 135–139.

[9] J.T. Han, Y.H. Huang, X.J. Wu, C.L. Wu, W. Wei, B. Peng, W. Huang, Tunable synthesis of bismuth ferrites with various morphologies, Adv. Mater. 18 (2006) 2145–2148.

[10] X.M. Lŭ, J.M. Xie, Y.Z. Song, J.M. Lin, Surfactant-assisted hydrothermal preparation of submicrometer-sized two-dimensional $BiFeO_3$ plates and their photocatalytic activity, J. Mater. Sci. 42 (2007) 6824–6827.

[11] T.J. Park, G.C. Papaefthymiou, A.J. Viescas, A.R. Moodenbaugh, S.S. Wong, Size-dependent magnetic properties of single-crystal multiferroic $BiFeO_3$ nanoparticles, Nano Lett. 7 (2007) 766–772.

[12] J.K. Kim, S.S. Kim, W.J. Kim, Sol–gel synthesis and properties of multiferroic $BiFeO_3$, Mater. Lett. 59 (2005) 4006–4009.

[13] N. Das, R. Majumdar, A. Sen, H.S. Maiti, Nanosized bismuth ferrite powder prepared through sonochemical and microemulsion techniques, Mater. Lett. 61 (2007) 2100–2104.

[14] L.Z. Guo, J.H. Dai, J.T. Tian, Z.B. Zhu, T. He, Molten salts synthesis of $ZnNb_2O_6$ powder, Mater. Res. Bull. 42 (2007) 2013–2016.

[15] P. Afanasiev, Ce–Zr mixed oxides prepared in molten nitrates, J. Alloys Compd. 340 (2002) 74–78.

[16] J. Chen, X.R. Xing, A. Watson, W. Wang, R.B. Yu, J.X. Deng, L. Yan, C. Sun, X.B. Chen, Rapid synthesis of multiferroic $BiFeO_3$ single-crystalline nanostructures, Chem. Mater. 19 (2007) 3598–3600.

[17] S. Ghosh, S. Dasgupta, A. Sen, H.S. Maiti, Low-temperature synthesis of nanosized bismuth ferrite by soft chemical route, J. Am. Ceram. Soc. 88 (2005) 1349–1352.

[18] P. Afanasiev, C. Geantet, Synthesis of solid materials in molten nitrates, Coord. Chem. Rev. 178–180 (1998) 1725–1752.

[19] P. Marote, C. Matei, C. Sigala, J.P. Deloume, Influence of spectator ions on the reactivity of divalent metal salts in molten alkali metal nitrates morphology of the resulting metal oxides, Mater. Res. Bull. 40 (2005) 1–11.

[20] S.L. Ran, L. Gao, Preparation of α-MnO_2 nanorods and Co_3O_4 submicrooctahedrons by molten salt route, Chem. Lett. 36 (2007) 688–689.