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Short communication

Low-temperature synthesis of single-crystalline $BiFeO_3$ using molten KCl–KBr salt

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Abstract

Single-crystalline $BiFeO_3$ powder was successfully synthesized by using molten KCl–KBr salt at 750 °C. The as-prepared powder was characterized by X-ray diffraction, FT-IR–Raman spectrometry and high-resolution transmission electron microscopy. It was suggested that the molten salt would result in the formation of rhombohedral $BiFeO_3$ at a low synthesizing temperature. The magnetic behavior was characterized by a superconducting quantum interference device. The single-crystalline $BiFeO_3$ powder showed weak ferrimagnetic nature at low magneitc field.

Keywords: C. Magnetic properties; $BiFeO_3$; Molten salt synthesis; Single-crystalline

1. Introduction

Multiferroic materials, showing the coexistence of magnetic and ferroelectric orders in a certain range of temperature, have attracted much attention recently because of the fundamental aspects of the novel mechanism that gives rise to magnetic–ferroelectric coupling [1,2], and their potential applications for new types of electronic devices, such as multiple-state memories, spintronic devices and sensors [3,4]. As a typical single-phase multiferroic material, perovskite-type $BiFeO_3$ (BFO) is one of the well-known multiferroic compounds having relatively high Neel temperature (T_N=397 °C) and Curie temperature (T_C=836 °C). It has attracted increasing research interest during the past several years, because it could be widely used in micro-electronic devices such as multiple-state memory devices, performer, executor, and optical devices, etc. [5,6].

Usually, multiferroic material BFO with a rhombohedrally distorted perovskite structure was prepared using a variety of synthetic methods, such as solid-state reaction [7], hydrothermal synthesis [8,9] and sol–gel technique [10,11] etc. During the solid-state reaction synthesis of BFO, the kinetics of phase formation in the Bi_2O_3–Fe_2O_3 system can easily lead to the appearance of second phases ($Bi_{25}FeO_{40}$, $Bi_2Fe_4O_9$), which need to be removed by using diluted nitric acid [3]. Although the single phase BFO could also be obtained by conventional solid-state reaction followed by an immediate quenching process, its quenching rate was up to ~100 °C/min. Compared with the solid-state reaction methods, the highly pure BFO with fine particle size could be obtained by the wet-chemical synthesis method, whereas its disadvantages were relatively complicated processing steps, higher cost and lower level of yield, and it was not suitable for industrial production. Therefore, it is important to develop a simple, economical and large-scale production synthesis method for multiferroic material BFO. Molten salt synthesis is a promising technology. Its merits include enhanced reaction selectivity, lower processing temperature and time [12,13]. Recently, Chen et al. [14] reported that BFO nanostructures were successfully prepared by the molten NaCl–Na_2SO_4 salt. The pure BFO could be synthesized at 800 °C for 20 min, whereas it was only formed within a very narrow temperature range (800 ± 10 °C). In the present work, the single-crystalline BFO was synthesized by molten KCl–KBr salt at

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a low temperature, and their microstructure and magnetic properties were investigated.

2. Experimental

In a typical reaction, analytical grade reactants Fe_2O_3 (SCRC, ≥99.0%), Bi_2O_3 (SCRC, ≥99.0%), KCl (SCRC, ≥99.0%) and KBr (SCRC, ≥99.0%) were used as raw materials. To obtain the BFO precursor, the reactants Fe_2O_3 and Bi_2O_3 were weighted in stoichiometric proportion, and were mixed in ethanol by ball milling for 5 h. Then, the dried reactants were mixed with molten KCl–KBr salt (a molar ratio of 1:1) in the weight ratio of 1:1. The mixture of reactants and salt was calcined in an alumina crucible covered with an alumina plate at different temperatures for 2 h. Finally, the pure BFO were obtained from the solidified mass by repeated washing with deionized water until no white precipitate was detected by the $AgNO_3$ solution.

The crystalline structure of samples was examined by an X-ray diffraction spectrometer (XRD, Shimadzu LabX XRD-6000) using Cu-Kα radiation. Their microstructure were observed through a field-emission scanning electron microscopy (Hitachi, S-4800) and high-resolution transmission electron microscopy (HRTEM, JEOL JEM-2010). Raman-scattering data were collected by a FT-IR–Raman Spectrometer (Nexus 870). The magnetic properties of BFO were measured by a Quantum Design superconducting quantum interference device (SQUID) magnetometer (MPMS XL5) at room temperature.

3. Results and discussion

Fig. 1 shows the XRD patterns of BFO calcined at different temperatures. The major diffraction peaks of the samples obtained at 700 °C are identified to be a rhombohedrally distorted perovskite structure (JCPDS 86-1518), while a small amount of impurity phase (*: $Bi_{25}FeO_{40}$, ^: Bi–O–Br) is detected. High purity BFO can be obtained at the temperature of 750 °C for 2 h. As the temperature rose up to 800 °C, a small amount of the new impurity phase can be indexed as $Bi_2Fe_4O_9$ (#).

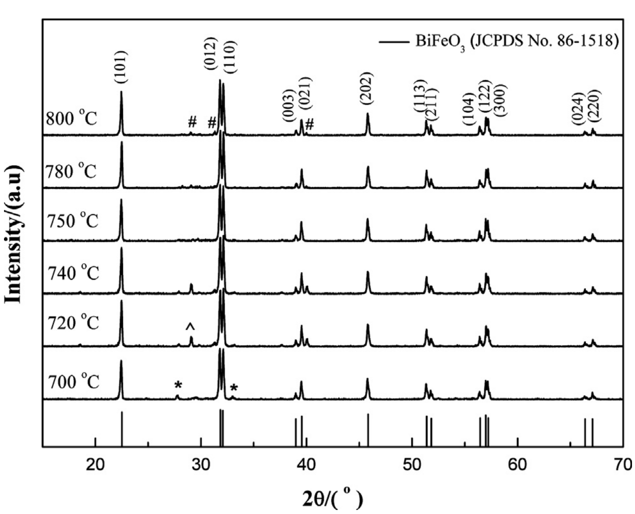

Fig. 1. XRD patterns of the samples calcined at different temperatures for 2 h.

Raman spectroscopy analysis as a supplementary method was chosen to identify the phase and purity of BFO. A representative Raman spectrum of BFO obtained at 750 °C is shown in Fig. 2. All the observed peaks can be indexed to a pure BFO phase according to the previous literatures [14,15]. The Raman spectrum of as-synthesized BFO shows LO–TO splitting of A1 symmetry in the lower-frequency region.

Fig. 3a and b shows the FESEM images of the BFO obtained at 750 °C. It can be seen that BFO mainly consists of cubic structures with an average size of ~0.6 μm. Fig. 3c shows a typical HRTEM image of Fig. 3b, displaying an intact and orderly single-crystalline structure. The corresponding selected area electron diffraction (SAED) pattern shows sharp diffraction spots (Fig. 3d), which further demonstrate that the single-crystalline structure BFO is formed.

Obviously, a large amount of molten KCl–KBr salt was used as the solvent to control powder characteristics (size, shape, etc), which contributed to lower the synthesizing temperature [16]. According to the phase diagram of Bi_2O_3–Fe_2O_3 binary system and mechanism of the molten salt synthesis, the BFO would be formed in the supersaturation solution of reactants and molten salt as the temperature was above 700 °C. Besides the major composition $BiFeO_3$, there were some $Bi_{25}FeO_{40}$ and unreacted Bi_2O_3 because of the low reaction temperature. Above 800 °C, the $BiFeO_3$ began to decompose to form $Bi_2Fe_4O_9$ and an amorphous phase [17].

Fig. 4 shows hysteresis loops of single-crystalline BFO at room temperature under a field from −50,000 to 50,000 Oe. The inset shows the enlarged magnetization–magnetic field (*M–H*) curve at low magnetic field. It is clear that magnetization moments are not collinear, which demonstrates the weak ferrimagnetic nature at room temperature.

4. Conclusion

In summary, a simple, low-temperature synthesizing method has been employed to prepare pure $BiFeO_3$ by molten KCl–KBr salt. FESEM, HRTEM and selected area electron diffraction analysis show the $BiFeO_3$ presents intact and

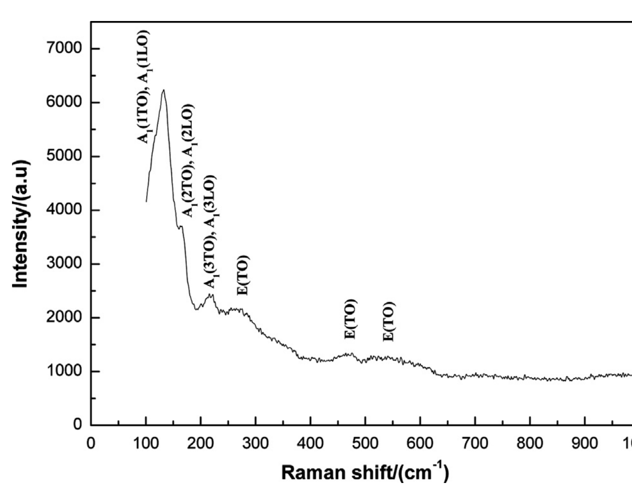

Fig. 2. Raman-scattering pattern of the sample obtained at 750 °C for 2 h.

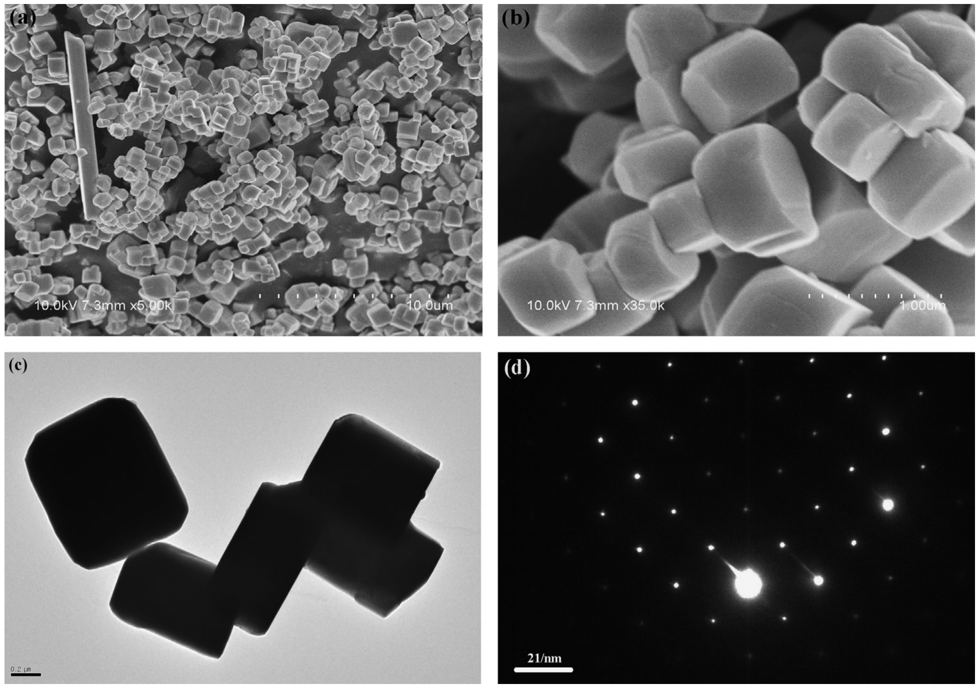

Fig. 3. (a) SEM image, (b) enlarged SEM image, (c) HRTEM image, and (d) SAED pattern of the BFO obtained at 750 °C for 2 h.

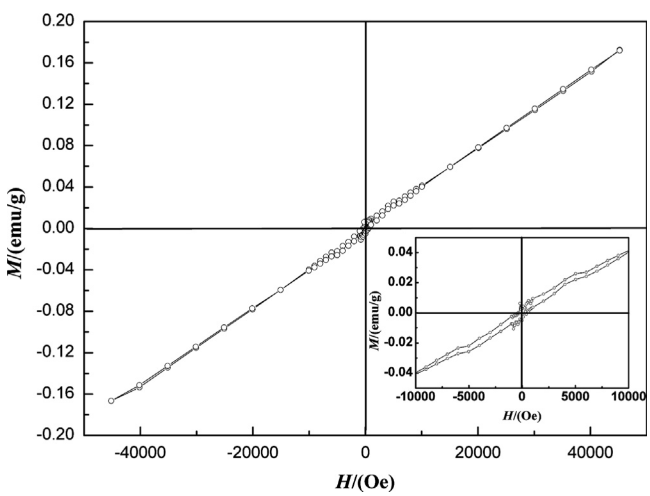

Fig. 4. Magnetic property of the BFO obtained at 750 °C.

single-crystalline structures. The characterization results of the hysteresis loops (*M–H*) at room temperature indicated that single-crystalline $BiFeO_3$ shows weak ferrimagnetic nature at low magneitc field.

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