Hydrothermal synthesis of perovskite-type BiFeO$_3$

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Single crystals of BiFeO$_3$ were prepared by hydrothermal synthesis using hydrate sodium bismuth oxide (NaBiO$_3$nH$_2$O) and iron nitrates (Fe(NO$_3$)$_3$·9H$_2$O) in the potassium hydroxide solutions. The size of BiFeO$_3$ single crystals increased with the reaction temperature and duration. Single crystals of sillenite-type Bi$_{12.5}$Fe$_{0.5}$O$_{19.5}$ and Bi$_2$Fe$_3$O$_8$ were also obtained depending on the conditions. From the chemical analysis, the chemical composition of the crystals was deduced to be Bi$_{96}$K$_{0.5}$FeO$_3$. Although the crystals contained a small amount of potassium, the lattice parameters of the crystals agreed well with the pure BiFeO$_3$ and the Curie temperature was not affected by this replacement.

Key-words : Perovskite, Crystal growth, Hydrothermal, Bismuth ferrite

1. Introduction

Bismuth ferrite, BiFeO$_3$ (BFO) was synthesized for the first time in 1957$^1$ and it has a rhombohedrally distorted perovskite-type structure with the space group $R3c$$^2$. Several studies have been done on this compound for years especially as ceramics body$^{3,4}$ because BFO is one of the leading candidates of multiferroic materials. Multiferroic materials exhibit ferroelectricity and magnetic ordering at the same time, however numbers of studies are limited. Such materials are expected to be the basis of a novel memory device by combination of dielectric and magnetic ordering. BFO shows antiferromagnetic behavior with a relatively high Néel temperature (~370°C) and a ferroelectric behavior with high Tc (~830°C)$^3$.

It is difficult to synthesize BFO single phase because of the narrow temperature stability range of this compound. If the temperature is not controlled accurately, the other phases were obtained. Up to date, there are primarily two kinds of successful methods in synthesizing pure BFO powder. One is the conventional solid state method, for example, bismuth oxide and iron oxide as starting materials were mixed and sintered at the temperature range of 800–880°C. In this case the unreacted phase Bi$_2$O$_3$ and impurity phases such as Bi$_2$Fe$_3$O$_8$ appeared at the same time and these were eliminated by nitric acid leaching.$^6$ The other method is a soft chemical route using bismuth nitrate and iron nitrate solution.$^7$ On the other hand BFO thin films were successfully prepared by pulsed-laser depositions method,$^9,10$ and recently sol–gel method$^{11}$ were used in preparing BFO thin films. BFO powder is also prepared by hydrothermal synthesis recently,$^{12,13}$ while the particle of BFO powder is the nanometer size. Single crystals of BFO were also grown in a Bi$_2$O$_3$/Bi$_2$O$_3$/Fe$_3$O$_4$ flux at 620°C.$^{15}$ It is important to obtain a high quality single crystal of BFO in order to evaluate its physical properties. There are still few works done on BFO large single crystals at lower synthetic temperature, though many studies have been focused on the synthesis of BFO powders and thin film.

In this work large single crystals of BFO were prepared by hydrothermal reaction, and the phases and morphology of the products obtained under hydrothermal conditions were discussed.

2. Experimental

Hydrothermal reaction was carried out in a Teflon-lined autoclave (70mL) using NaBiO$_3$nH$_2$O and Fe(NO$_3$)$_3$·9H$_2$O as starting materials. The equimolar mixture of the two starting materials and KOH were put into the autoclave and dissolved in 40 ml of distilled water. The molar ratio of Bi:Fe:K was 1:1:15–300. The reaction temperature ranged from 180 to 260°C and the reaction duration were from 2 to 42 d. The solid products were filtered, washed with distilled water for several times and dried at 50°C in air. The powder sample and millimeter size crystals were separated by decantation with distilled water and ethanol. At last the crystals and powders were dried at 100°C.

The products were identified by the X-ray powder diffraction using monochromated Cu Kα radiation. The thermal stability was investigated by TG–DTA with a heating rate of 10°C/min. The samples were completely dissolved in the mixture of HCl + HNO$_3$ at room temperature. And the amounts of bismuth, iron and potassium were determined by induced coupled plasma and atomic absorption spectroscopy. The morphology of the single crystals was observed by optical microscopy.

3. Results and discussion

Three types of single crystals, BiFeO$_3$ (BFO), Bi$_{12.5}$Fe$_{0.5}$O$_{19.5}$ and Bi$_2$Fe$_3$O$_8$ were synthesized through the hydrothermal reactions for 48 h with the K/Bi molar ratios ranging from 15 to 300 and the reaction temperatures ranging from 180 to 260°C. When the K/Bi molar ratio was 120–240 and the temperature was 180°C, large crystals of BFO and powder sample of mixture of Bi$_{12.5}$Fe$_{0.5}$O$_{19.5}$ and Bi$_2$Fe$_3$O$_8$ were obtained. Large crystals of BFO were easily separated from the powder sample by decantation. The size of cubic shape BFO large crystals was approxi-
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mately 0.1 × 0.1 × 0.1 mm. The size of the BFO large crystals increased with the reaction duration as shown in Fig. 1. The size of the BFO crystals obtained from the 7 d reaction was approximately 0.5 × 0.5 × 0.5 mm. When the reaction temperature was increased to 220 or 260°C at the same K/Bi molar ratio, only the powder sample of the mixture of Bi₁₂.₅Fe₀.₅O₁₉.₅ and Bi₂Fe₄O₉ was obtained.

Under the condition of K/Bi molar ratio of 15 or 30 at the temperature of 220 or 260°C, large crystals of sillenite-type Bi₁₂.₅Fe₀.₅O₁₉.₅ were synthesized together with the powder sample of the mixture of Bi₁₂.₅Fe₀.₅O₁₉.₅ and Bi₂Fe₄O₉. When the K/Bi molar ratio was 300 at the temperature of 260°C, the synthesized samples turned to large crystals of Bi₂Fe₄O₉ and powders of the mixture of Bi₁₂.₅Fe₀.₅O₁₉.₅ and Bi₂Fe₄O₉.

X-ray powder diffraction pattern of BFO large crystals synthesized under the condition of K/Bi molar ratio of 180 at 180°C showed a single phase of the perovskite-type compound as shown in Fig. 2. The lattice parameters of the BFO crystals were a = 5.583(2) and c = 13.870(4) Å, and these values agreed well with the published ones (a = 5.57874(16) and c = 13.8688(3) Å).²

From the chemical analysis, the ratio of Bi: K: Fe in the BFO crystals prepared with the K/Bi molar ratio of 180 at 180°C for 7 d was found to be 0.96:0.03:1.00 and a small amount of potassium were detected. The ratio of Bi: K: Fe of the smaller BFO crystals prepared with the K/Bi molar ratio of 180 at 180°C for 2 d was almost the same as that of the large crystals prepared for 7 d. No mass loss was observed in the TG-curve as shown in Fig. 3. From these results, the chemical composition of BFO large crystals could be deduced to be Bi₀.₉₆K₀.₀₃FeO₃. Taking into account the starting compound with Bi⁵⁺, the charge neutrality of this compound may be held by the mixed valence of Bi atom as presented by Bi³⁺₀.₉₁⁵Bi⁵⁺₀.₀₄₅K⁺₀.₀₃Fe³⁺O₃. Some of perovskite-type compounds prepared by hydrothermal reaction contained OH⁻ group as found in KNbO₃,¹⁶,¹⁷ and BaTiO₃,¹⁸–²⁰ however, no OH⁻ group was observed in the BFO crystals. In the DTA curve an endothermic peak appeared at 829°C as shown in Fig. 3. This temperature corresponds to the ferroelectric phase transition which was reported to occur at 810–830°C.²¹ Although the BFO large crystals contained a small amount of potassium, the Curie temperature was not affected by this replacement.

References
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Fig. 1. Micrographs of BFO crystals prepared by hydrothermal synthesis at 180°C with the K/Bi molar ratio of 180 for 2 d (A) and 7 d (B).

Fig. 2. XRD pattern of BFO crystals prepared with the K/Bi molar ratio of 180 at 180°C for 7 d.

Fig. 3. TG-DTA curve of BFO crystals prepared with the K/Bi molar ratio of 180 at 180°C for 7 d.