Hydrothermal Synthesis of BiFeO₃ Fine Particles

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Fine particles of BiFeO₃ were prepared from bismuth nitrate and iron nitrate in KOH solution by hydrothermal reaction. A single phase of BiFeO₃ was prepared under hydrothermal condition of K/Bi ≥ 120 and above 180 ºC. The TG curves of single phase of BiFeO₃ indicated that the products included a small amount of OH group or water in spite of no detection of potassium atom by EDX. The particle size of BiFeO₃ was ~ 10 µm and 10 ~ 20 µm for the products at 180 and 220 ºC, respectively. The particle prepared at 220 ºC was formed by aggregation of ~ 10 nm size particles with a cubic shape. From the pH dependence of ζ-potential the isoelectric point was about three.

Key words: BiFeO₃, Hydrothermal, ζ-potential, Particle size

1. INTRODUCTION
A bismuth ferrite, BiFeO₃ (hereafter, BFO) which is one of the very few multiferroic materials with coexistence of ferroelectricity and magnetism has the perovskite-type structure [1-2]. BFO has been studied extensively for preparation and multiferroic properties [3-4]. In 2007 it was reported that BFO had photocatalytic activity under visible light irradiation [5]. Although great achievements have been made for BFO thin films prepared by the pulsed-laser deposition (PLD) method [6-7], it was hard to avoid generating impurity phases by the conventional solid-state reaction. BFO perovskite could only stabilize within a narrow ranged temperature. Hydrothermal reaction and sol-gel method are useful to obtain a pure powder sample with uniform particle size [8-12]. So far there have been many papers for hydrothermal synthesis of BFO. We also reported preparation of BFO crystals with mm size by hydrothermal reaction [13]. Under this investigation a single phase of BFO fine particles could be prepared and their particle size distribution and ζ-potential were measured. To our knowledge there has been no report for ζ-potential of BFO fine particles by hydrothermal reaction. In this paper hydrothermal synthesis of BFO fine particles and its ζ-potential will be described.

2. EXPERIMENTALS
Hydrothermal reaction was carried out in an autoclave (70 mL) using Bi(NO₃)₃·5H₂O (1.00g) and Fe(NO₃)₃·9H₂O (0.833g) 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. After stirring the solution at room molar ratio of K/Bi was 5-160 and the reaction duration was 48 hours. When the molar ratio of K/Bi was 5, the amount of KOH was 0.578g and the value of pH was about 13 before and after the hydrothermal reaction. In the case of higher concentration of KOH the value of pH was over 13 before and after the reaction. The products were filtrated and washed with distilled water, and then dried in air at 70 °C. X-ray powder diffraction (XRD) was performed on an X-ray powder diffractometer (Rigaku RINT-2000) with graphite-monochromated CuKα radiation. Scanning electron microscopy (SEM) images were taken with a field emission scanning electron microscope (JEOL JEM-6500F). The particle size distribution was measured by a laser diffraction particle analyzer (Malvern Zetasizer Nano Z).

3. RESULT and DISCUSSION
3.1 Hydrothermal synthesis
At 140 ºC no pure phase of BFO was obtained for any K/Bi ratio and a single phase of BFO was prepared under hydrothermal condition of K/Bi ≥ 120 and above 180 ºC. Under the condition of K/Bi = 5 and 180 ºC a mixture of transparent plate-like crystals and brown powder was obtained. Figure 1 shows X-ray powder diffraction patterns of the products at 180 ºC. The X-ray powder pattern of the product under the condition of K/Bi = 5 and 180 ºC a mixture of transparent plate-like crystals and brown powder was obtained. Figure 1 shows X-ray powder diffraction patterns of the products at 180 ºC. The X-ray powder pattern of the product under the condition of K/Bi = 5 and 180 ºC was very similar to that of the product prepared by hydrothermal reaction of NaBiO₃·nH₂O and Fe(NO₃)₃·9H₂O. This compound has not been identified yet, and included transparent plate-like crystals. It can therefore be presumed that the...
220 °C a single phase of BFO also appeared in high value of K/Bi ratio. In this work pure phase of BFO was obtained in higher concentration of KOH solution, however, Chen et al. reported that in higher concentration of KOH solution Bi$_2$Fe$_4$O$_9$ and Bi$_{25}$FeO$_{40}$ were coexisted as well as BFO. This difference may come from the reaction duration; our hydrothermal reactions were carried out for long time (48h.) and Chen et al. adopted short time (6h.). When iron oxides are prepared in FeSO$_4$ or FeCl$_2$ solution, in low pH solution iron oxyhydroxides are precipitated and in higher pH solution iron oxides can be crystallized. In this work an oxyhydroxide or oxynitrate including bismuth and iron atoms may be crystallized in lower concentration of KOH solution and BFO can be prepared by increasing concentration of KOH.

The X-ray powder diffraction pattern of the single phase of BFO prepared at 180 and 220 °C was indexed with the hexagonal cell and the lattice parameters were $a=5.584(9)$ Å, $c=13.867(1)$ Å and $a=5.584(1)$ Å for BFO prepared at 180 and 220 °C, respectively and these values agreed well with the published ones ($a=5.5787(16)$ Å and $c=13.8688(3)$ Å).

A small amount of mass loss (0.78 mass%) was observed in TG curve of the single phase of BFO prepared at 220 °C as shown in Fig. 2. The mass loss for BFO prepared at 180 °C was 0.80 mass%. These results indicated that the products included a small amount of OH group or water. The value of $n$ in BiFeO$_3$·$n$H$_2$O was calculated to be 0.14. Similar incorporation of protons or water molecules into the perovskite-type structure was found in KNbO$_3$ and BaTiO$_3$ prepared by hydrothermal reaction. No potassium atom in the single phase of BFO was detected by EDX analysis though single crystals of BFO prepared by hydrothermal reaction contained a small amount of potassium atom. In the DTA curve an endothermic peak at 840 °C is observed and this temperature corresponds to the ferroelectric phase transition reported to occur at 810 ~ 830 °C.

3.2 Particle size distribution and ζ-potential

Figure 3 shows particle size distribution of BFO prepared at 180 and 220 °C. The mean particle size of BFO prepared at 180 °C was smaller than that of BFO at 220 °C.

Fig. 3 Particle size distribution of BFO prepared at (a)180 and (b)220 °C.

Fig. 4 SEM photographs of BFO prepared at (a)180 and (b)220 °C.

Fig. 5 SEM photograph of BFO prepared at (a)180 and (b)220 °C.
that in high pH region aggregation does not occur and is consistent with the particle size distribution. BFO prepared at 180 °C was formed by aggregation of ~ 1 µm size particles with a rectangular shape. On the other hand BFO prepared at 220 ºC was formed not by surface charge of particles but by aggregation of ~ 10 nm size particles with a cubic shape.

Figure 4 shows SEM photographs of BFO prepared at 180 ºC. Fine particles of BiFeO$_3$ were prepared from bismuth ferrite (7.7) and magnetite (6.5)21). This result suggests that in high pH region aggregation does not occur and is consistent with the particle size distribution of BFO.

4. CONCLUSION

Fine particles of BiFeO$_3$ were prepared from bismuth nitrate and iron nitrate in KOH solution by hydrothermal reaction. A single phase of BiFeO$_3$ was prepared under hydrothermal condition of K/Bi ≥ 120 and above 180 °C. BFO prepared at 180 ºC was ~ 10 µm size particles formed by aggregation of ~ 1 µm size particles with a rectangular shape. BFO prepared at 220 ºC was 10 ~ 20 µm size particles by aggregation of by ~ 10 nm size particles with a cubic shape.

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