Hydrothermal Synthesis of Perovskite Bismuth Ferrite Crystallites with the Help of NH$_4$Cl

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Bismuth ferrite nanopowders were hydrothermally synthesized with and without NH$_4$Cl for comparison. The effects of NaOH concentration, reaction temperature and reaction time on the product phases and morphologies were studied in detail. Pure BiFeO$_3$ was synthesized in a wide hydrothermal condition with the help of NH$_4$Cl. Especially, it can be synthesized at low temperature of 140 °C. X-ray diffraction and Fourier transform infrared spectra revealed the BiFeO$_3$ products had a perovskite structure. Scanning electron microscopy images showed that different BiFeO$_3$ morphologies were formed under different hydrothermal conditions. NH$_4$Cl played a key role in the BiFeO$_3$ formation and BiFeO$_3$ morphologies. Part BiFeO$_3$ samples exhibited weak magnetic properties.

Keywords: Bismuth Ferric Oxide, Hydrothermal Method, X-ray Diffraction, SEM.

1. INTRODUCTION

Multiferroic materials, which possess a coexistence of ferroelectric and magnetic order parameters, have attracted considerable attention recently because of their fascinating physical behaviors and potential applications in data storage, sensors and spintronic devices. BiFeO$_3$ is one of the well-known multiferroic compounds displaying coexistence of ferroelectricity ($T_C = 830$ °C) and antiferromagnetism ($T_N = 370$ °C). Different properties about BiFeO$_3$ have been studied, such as ferroelectricity, magnetism, magnetoelectricism, photocatalytic activity, and thermodynamic stability, where the properties in nanosize were especially helpful for understanding the foundational ferroelectric and magnetic mechanism. Various techniques have been developed to synthesize BiFeO$_3$ nanoparticles, for instance, conventional solid-state reaction, sol–gel process, chemical spray pyrolysis method, co-precipitation and hydrothermal method. Though many efforts have devoted to prepare BiFeO$_3$, only a few approaches by the hydrothermal method were reported about the pure BiFeO$_3$ with irregular shapes, spindle shapes, and cubic crystallites. The bismuth ferrite powders in these works were synthesized by using bismuth nitrate [Bi(NO$_3$)$_3$·5H$_2$O] and iron nitrate [Fe(NO$_3$)$_3$·9H$_2$O] as start materials, which reacted to produce pure BiFeO$_3$ phase in a limited experimental range. In this paper, pure BiFeO$_3$ crystallites were synthesized by using FeCl$_3$·6H$_2$O and BiCl$_3$ as start materials and NH$_4$Cl as an addition in wide hydrothermal conditions. We compared the bismuth ferrite powders synthesized with NH$_4$Cl and without NH$_4$Cl.

2. EXPERIMENTAL DETAILS

Bismuth ferrite powders were prepared via a hydrothermal process using a stoichiometric mixture of FeCl$_3$·6H$_2$O and BiCl$_3$ as metal precursors and NaOH as a mineralizer. All chemicals were used without further purifications. The processes to prepare the precursors involved the following steps: firstly, 1.44 mmol FeCl$_3$·6H$_2$O and BiCl$_3$, keeping the reactants and resultant concentration 0.05 M, were dissolved in distilled water under mechanical stirring; then, NaOH solution was slowly added into the above solution to coprecipitate Fe$^{3+}$ and Bi$^{3+}$ ions and adjust different alkali concentrations, followed by adding 1.29 g (1 M) NH$_4$Cl to part samples; finally, the brown suspension was transferred into a 29 mL Teflon vessel filled at 4/5 of its volume. The hydrothermal treatment was performed with different reaction temperatures and reaction times.

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After cooling down to room temperature naturally, the products were washed several times with distilled water and then dried in an oven at 70 °C.

X-ray diffraction (XRD) analysis was performed by using a D/max2550 V diffractometer system with a Cu Kα source to determine the powder phases. Scanning electron microscopy (SEM Quan200) was employed to investigate the product morphologies. Fourier transform infrared (FTIR) spectra of bismuth ferrite powders were performed on an AVATAR 370 infrared spectrophotometer. The magnetic properties of part samples were measured with an LDJ9600 type of vibrating sample magnetometer (VSM).

3. RESULTS AND DISCUSSION

Figure 1(A) shows the XRD patterns of samples synthesized at 200 °C for 6 hours with different initial NaOH concentrations of 1, 2, 3 and 3.5 M. The XRD patterns (a)∼(c) can be indexed as pure BiFeO₃ according to the powder data of JCPDF card (No. 86-1518). It reveals that the pure BiFeO₃ can be synthesized at 1∼3 M NaOH. However, the second phase Bi₂Fe₄O₉ appears when the NaOH concentration reaches up to 3.5 M. Figure 1(B) shows the XRD patterns of samples synthesized under the similar experimental conditions with 1 M NH₄Cl. The diffraction patterns (b)∼(e) reveal that pure BiFeO₃ was synthesized in the NaOH concentration range of 2∼5 M with the help of 1 M NH₄Cl. The second phase Bi₂Fe₄O₉ is not detected until the NaOH concentration rises to 6 M. The pure BiFeO₃ phase can be synthesized at an appropriate experimental range of NaOH concentration and this range can be broadened with the help of NH₄Cl. These may attribute that NH₄Cl as a nonaqueous solvent can enhance the precursor dissolvability in the water.23 And then the precursors have more chances to react to BiFeO₃. It is noticeable that the intensity of the diffraction peaks keeps consistent with the card No. 86-1518 for the sample prepared at 1 M, but the (012) intensity enhances with the increase in NaOH concentration in Figure 1(A), and the intensity of the peak (012) at 5 M NaOH is higher than that at low NaOH concentration in Figure 1(B). At low NaOH concentration, NaOH can not change the surface energy of the particles, so the BiFeO₃ grows along different crystal plane equivalently. At high NaOH concentration, NaOH could change the surface energy of the crystal plane, resulting in an orientational growth, which leads to the diffraction intensity enhance at some crystal directions.

Figures 2(a∼c) show the SEM images of the samples synthesized at 200 °C for 6 hours with the NaOH concentrations of 1, 2 and 3 M without NH₄Cl, respectively. The BiFeO₃ particles become more regular and homogenous with increasing NaOH concentration. This phenomenon can be explained by the electric charge effect on the surfaces of BiFeO₃ particles. In hydrothermal environment, the surfaces of produced particles are negatively charged.24 With increasing OH⁻ in the reaction medium, BiFeO₃ particles tend to be more insular due to the repulsion force between the negatively charged particles in the alkaline environment. The dispersive particles hampered the agglomeration, providing a change for growing homogeneous particles. Figures 2(d∼g) show the SEM images of the samples synthesized at 200 °C for 6 hours with 1 M NH₄Cl at the NaOH concentrations of 2, 3, 4 and 5 M, respectively. The sample synthesized at 2 M exhibits spherical particles about 17 μm in size. The inset of Figure 2(d) shows the spherical particles comprises some slices about 0.3 μm in thickness. The particles synthesized at 3 M are spherical about 20 μm in size. The inset of Figure 2(e) shows that the particles are agglomerated by a great number of small and irregular grains. At low NaOH concentration, precursors can react to form small BiFeO₃ crystal slices with the help of NH₄Cl. Then these slices aggregate together to big particles due to the random aggregation.23 When the NaOH concentration is 4 M, the particles are regular cube about 10 μm in size as shown in Figure 2(f). The sample synthesized at 5 M shares the similar experimental conditions with 1MN H⁴Cl. The second phase Bi₂Fe₄O₉ shows the XRD patterns (b) without NH₄Cl and (B) with 1 M NH₄Cl.

Fig. 1. X-ray diffraction patterns of the samples obtained at 200 °C for 6 hours under the different NaOH concentrations (A) without NH₄Cl and (B) with 1 M NH₄Cl.
Hydrothermal Synthesis of Perovskite Bismuth Ferrite Crystallites with the Help of NH4Cl

Qiu et al.

Fig. 2. Typical SEM images of the samples obtained at 200 °C for 6 hours without NH4Cl under the NaOH concentrations of (a) 1 M, (b) 2 M and (c) 3 M and with 1 M NH4Cl under the NaOH concentrations of (d) 2 M, (e) 3 M, (f) 4 M and (g) 5 M.

Fig. 3. X-ray diffraction patterns of the samples synthesized at 3 M and various temperatures for 6 hours (A) without and (B) with 1 M NH4Cl.

similar morphology with the last one but with big particles about 19 μm in size. With the NaOH concentration rising, the small grains are attacked to dissolve and the big grains continue to grow. So the slices and grains have chances to grow and become large cube particles. More morphologies were obtained, which were controlled by the NaOH concentration with the help of NH4Cl.

Then we studied the effects of reaction temperature at 3 M for its pure BiFeO3 phase in the products. Figure 3(A) shows the XRD patterns of samples synthesized at various temperatures for 6 hours without NH4Cl. Pure BiFeO3 can be synthesized only at 200 °C. The XRD patterns of samples synthesized under the similar conditions with 1 M NH4Cl are shown in Figure 3(B), which reveals that pure BiFeO3 were synthesized in the temperature range of 140–230 °C. Thus, NH4Cl can broaden the temperature range of synthesizing pure BiFeO3, which is wider than the previous works.2,11,21,22 Pure BiFeO3 can be synthesized at the temperature as low as 140 °C, which is lower in comparison with the previous reports by the hydrothermal method.21,22 NH4Cl as a nonaqueous solvent enhances the precursor dissolvability in the water23 and accelerates the precursor reaction to produce BiFeO3.

Then we investigated the morphologies of part samples with SEM. Figure 4(a) shows the pure BiFeO3 synthesized at 200 °C without NH4Cl, exhibiting some regular cubic particles about 20 μm in size. Figures 4(b–e) show the pure BiFeO3 synthesized at different temperatures with 1 M NH4Cl corresponding to the XRD patterns shown in Figure 3(B). The sample synthesized at 140 °C exhibits spherical particles about 28 μm in size, which are agglomerated by a great number of small and irregular slices. When the temperature is 170 °C, the particles are compact about 18 μm in size with smooth surfaces. The powders synthesized at 200 °C still exhibit spherical particles about 20 μm in size but with unsmooth surfaces, which comprise a great number of small and irregular slices about 1 μm in size as shown in the inset of Figure 4(d). Then these slices aggregate together as different particles.
for the different reaction temperature due to the random aggregation. When the temperature is up to 230 °C, the particles disperse to a lot of slices about 0.33 μm in thickness. The BiFeO₃ morphologies are greatly affected by the reaction temperature. With the temperature increases, the spherical particles are broken to form a great number of slices due to their high energy. It means the agglomerate degree of products is weak at high reaction temperature.

In order to investigate the BiFeO₃ formation mechanism, the experiments with different reaction times were carried out. Figure 5(A) displays the XRD patterns of samples synthesized at 200 °C for different reaction times without NH₄Cl addition. The powders after hydrothermal treatment for 1 hour or 3 hours are BiFeO₃ mixed with foreign phases Bi₂Fe₄O₉ and Bi₂O₃. The pure BiFeO₃ crystallites are obtained with the reaction time longer than 6 hours. The XRD patterns of samples synthesized with 1 M NH₄Cl for different reaction times are shown in Figure 5(B). The sample obtained after reacting 1 hour is BiFeO₃ mixed with Bi₂O₃. When the reaction time is longer than 3 hours, the pure BiFeO₃ crystallites are obtained, which means that the pure BiFeO₃ can be obtained at short reaction time with the help of NH₄Cl. The XRD patterns obtained at different times provide important information to probe the reaction mechanism although it may be complicated in the hydrothermal process. We propose that the BiFeO₃ formation in the hydrothermal treatment involves three stages:

1. The chlorides first transform into hydroxide precipitations after adding NaOH;
2. Bi(OH)₃ and Fe(OH)₃ react to form unstable Bi₂O₃ and Bi₂Fe₄O₉ under the appropriate hydrothermal conditions. Bi₂O₃ and Bi₂Fe₄O₉ crystallines are completed in cooling process and detected by XRD;
3. But in the hydrothermal environment with high temperature and pressure, the mixture reacts to form the final BiFeO₃ products under limited experimental conditions.

The formation formula of BiFeO₃ can be written as follows:

\[\text{BiCl}_3 + \text{FeCl}_3 + 6\text{NaOH} \rightarrow \text{Bi(OH)}_3 + \text{Fe(OH)}_3 + 6\text{NaCl}_3\]  \hspace{1cm} (1)

\[4\text{Bi(OH)}_3 + 4\text{Fe(OH)}_3 \rightarrow \text{Bi}_2\text{O}_3 + \text{Bi}_2\text{Fe}_4\text{O}_9 + 12\text{H}_2\text{O}\]  \hspace{1cm} (2)

\[\text{Bi(OH)}_3 + \text{Fe(OH)}_3 \rightarrow \text{BiFeO}_3 + 3\text{H}_2\text{O}\]  \hspace{1cm} (3)

The pure BiFeO₃ can be synthesized in wider experimental conditions with the help of NH₄Cl and chlorides as precursors rather than nitrates. Cl⁻ with smaller ionic...
radius than NO\textsubscript{3} is more possible to enter the Bi and Fe hydrate gels, dissolving the hydrates, accelerating the precursors react to BiFeO\textsubscript{3}. Thus, the Cl\textsuperscript{−} ions accelerate the reaction, resulting in BiFeO\textsubscript{3} formation at low temperature and short time under wide NaOH concentrations.

The FTIR spectra of BiFeO\textsubscript{3} samples synthesized at 200 °C, 1 M NaOH with and without NH\textsubscript{4}Cl are shown in Figure 6. The strong absorptive peaks at 400–600 cm\textsuperscript{−1} are attributed to the Fe–O stretching and bending vibration, indicating that the octahedral FeO\textsubscript{6} groups exist and the products have a perovskite structure.\textsuperscript{2} The broad band at 3000–3600 cm\textsuperscript{−1} is attributed to the antisymmetric and symmetric stretching of bond H\textsubscript{2}O and OH\textsuperscript{−} groups, while the band at 1630 cm\textsuperscript{−1} corresponds to the bending vibrations of H\textsubscript{2}O.

We measured the magnetic properties of part BiFeO\textsubscript{3} samples synthesized with and without NH\textsubscript{4}Cl by VSM in order to investigate the magnetic order at room temperature. The hysteresis loops in Figure 7(a–d) correspond to the samples after hydrothermal treatment for 6 hours with 3 M NaOH and 1 M NH\textsubscript{4}Cl at various temperatures of 140, 170, 200 and 230 °C, respectively. The samples synthesized at 140 and 170 °C show weak magnetic loops and the samples synthesized at 200 and 230 °C show the linear relationship between magnetization and magnetic field. The magnetic response reaches maximum at 170 °C. The sample synthesized at 200 °C and 3 M for 6 hours without NH\textsubscript{4}Cl shows a weak hysteresis loop as Figure 7(e). Its magnetic property is similar to the samples synthesized at 230 °C with 1 M NH\textsubscript{4}Cl. It is well known that BiFeO\textsubscript{3} is an antiferromagnetic multiferroic material. The direction of the resulting small moment rotates, superimposing a spiral spin arrangement with a wavelength of 62 nm, resulting in a helimagnetic order and a vanishing magnetization in bulk.\textsuperscript{25} But when the BiFeO\textsubscript{3} particle size decreases to nanoscale, BiFeO\textsubscript{3} exhibits a magnetic characteristic due to the incomplete magnetic supercell that retain a net magnetic moment.\textsuperscript{9} The samples prepared at low temperature may have smaller crystals than that at high temperature. Thus, the BiFeO\textsubscript{3} powders prepared at low temperature enjoy high magnetic responses. NH\textsubscript{4}Cl and reaction temperature have important effects on the BiFeO\textsubscript{3} magnetic properties.

4. CONCLUSION

Bismuth ferrites have been hydrothermally synthesized with and without NH\textsubscript{4}Cl addition. Pure BiFeO\textsubscript{3} was obtained after hydrothermal reaction at 200 °C over 6 hours in the NaOH concentration range of 1–3 M without NH\textsubscript{4}Cl. The morphologies of these products change from agglomerate and irregular particles to regular and dispersive cubic particles. With the help of 1 M NH\textsubscript{4}Cl, pure BiFeO\textsubscript{3} with different morphologies can be synthesized in the reaction temperature range of 140–230 °C and NaOH range of 2–5 M over 3 hours. Pure BiFeO\textsubscript{3} was obtained in wider hydrothermal conditions and showed more morphologies with 1 M NH\textsubscript{4}Cl addition. The FTIR spectra revealed the BiFeO\textsubscript{3} had a perovskite structure. BiFeO\textsubscript{3} sample synthesized at 170 °C with 3 M NaOH and 1 M NH\textsubscript{4}Cl for 6 hours exhibits more compact particles and relative higher saturation magnetization.

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References and Notes

Qiu et al.

Hydrothermal Synthesis of Perovskite Bismuth Ferrite Crystallites with the Help of NH$_4$Cl


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