Microwave synthesis of KNbO₃ nanocubes

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Potassium niobate (KNbO₃) nanocubes were obtained by microwave synthesis. The synthesis was performed using niobium oxide (Nb₂O₅) and potassium hydroxide (KOH) as starting materials. Water was used as the reaction medium. KNbO₃ particles with perovskite structure were confirmed from X-ray diffraction (XRD). The morphology of the KNbO₃ was investigated using transmission electron microscopy (TEM). KNbO₃ nanocubes were synthesized by microwave synthesis at low temperature.

Key-words : KNbO₃, Nanocube, Microwave synthesis, Perovskite oxide

1. Introduction

Nanocubes are nanocrystals with great potential for use in the creation of high-quality materials. We have been studying the preparation of nanocubes with the perovskite structure, such as barium titanate (BaTiO₃), strontium titanate (SrTiO₃), barium zirconate (BaZrO₃), strontium zirconate (SrZrO₃), sodium niobate (NaNbO₃), and potassium niobate (KNbO₃). These nanocubes were synthesized by a wet chemical reaction. BaTiO₃ and SrTiO₃ were prepared by a solvothermal method with an organic solvent using a composite-hydroxide-mediated (CHM) approach. Regarding the synthesis of nanocubes with the perovskite structure, there are two key points that need to be considered. First, the size of the particles needs to be controlled to give nano-sized particles. Generally, nanoparticles of inorganic compounds are prepared using wet chemical reactions. Second, the shape of the particles needs to be controlled to produce cubic particles. Many studies have been published in which nanocube syntheses have been described, and the usual targets are metals. However, there have only been a few studies published on nanocube synthesis of ternary oxides with a perovskite structure.

Wet chemical reaction is an excellent technique to synthesize the nanoparticles. These particles are known to agglomerate as the particle size decreases, such that many researchers employ surfactants in their syntheses. Morphology control of nanoparticles is an additional characteristic that has been studied for a long time to aid the development of enhanced materials. Reports suggest that nanocrystals are synthesized using wet chemical reactions with a dispersant or a surfactant, and fatty acids, such as oleic acid and linoleic acid, are useful in nanocrystal syntheses. The surface is a critical factor in advanced materials, but this is damaged when surfactants are used. Therefore, we have investigated the syntheses of highly dispersed and homogeneous nanoparticles without the use of a surfactant. Microwave synthesis is a good technique to form nuclei rapidly, because the heating speed and temperature of the reaction medium can be controlled while changing the microwave power. We used 40 ml water as the solvent, while 20 mmol Nb₂O₅ (Rare Metallic Co., Ltd.) and 800 mmol KOH (Kanto Chemical Co., Inc.) were used as raw materials. The compounds were placed into a Teflon reactor with 100 ml internal volume. Thereafter, the autoclave was sealed and kept at 200°C for 60 min. Stirring speed is 400 rpm. After the reaction, the autoclave was cooled to room temperature. The product was then collected using a centrifugal separator at 10000 rpm. Water and ethanol was used to rinse the centrifugal separator three times. Subsequently, the product was dried overnight in a dryer at 80°C.

The crystallinity and phase purity of the prepared samples were analyzed by X-ray diffraction (XRD) using an Ultima IV diffractometer (Rigaku Co., Japan), which used Cu Kα radiation (with a wavelength of 0.15418 nm) and was operated at 40 kV and 30 mA in the 2θ range from 10 to 80° at room temperature. The powder samples were analyzed by transmission electron microscopy (TEM) using a Tecnai Osiris instrument (FEI Co.). A sample was prepared for TEM analysis by dispersing it in ethanol in an ultrasonic bath (operated at 45 kHz) for 10 min, transferring a drop of the colloidal solution to a Cu microgrid with a holey carbon film and leaving it under ambient conditions until the ethanol had evaporated.

2. Experimental procedure

KNbO₃ was prepared using a microwave synthesis. The temperature was measured by optical fiber thermometer equipped with the StartSYNTH. The maximum power of the microwave was 500 W. The temperature was controlled while changing the microwave power. We used 40 ml water as the solvent, while 20 mmol Nb₂O₅ and 800 mmol KOH (Kanto Chemical Co., Inc.) were used as raw materials. The compounds were placed into a Teflon reactor with 100 ml internal volume. Thereafter, the autoclave was sealed and kept at 200°C for 60 min. Stirring speed is 400 rpm. After the reaction, the autoclave was cooled to room temperature. The product was then collected using a centrifugal separator at 10000 rpm. Water and ethanol was used to rinse the centrifugal separator three times. Subsequently, the product was dried overnight in a dryer at 80°C.

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3. Results and discussion

The heating rate is a very important factor when morphology control is conducted. Microwave radiation enables the rapidly increasing temperature. For example, the temperature of water reaches 200°C within a few minutes when a microwave is used. First, the microwave synthesis was performed at 200°C with various reaction times using Nb₂O₅ and KOH as raw materials. Figure 1 shows the XRD patterns of the samples obtained via using a microwave synthesis. In particular, we focused on the heating speed and temperature of the reaction medium. We assumed that the particles become nanocubes because of the rapidly increasing temperature caused by microwave radiation.

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the microwave synthesis using the above reaction conditions. KNbO₃ was not obtained for 6 min and the XRD peaks of an unknown phase were observed [Fig. 1(a)]. However, KNbO₃ was formed after 20 min, although a single phase was not obtained [Fig. 1(b)]. The XRD peaks of the unknown phase decreased as the time increased. Accordingly, we conducted the experiment with increasing reaction times. A single phase of KNbO₃ was formed after 30 and 60 min, from the XRD measurements [Figs. 1(c) and 1(d)]. Compared with the previous reports, the synthesis time in the present study is very short.⁶,⁷ The TEM images of the products obtained by the microwave synthesis conducted at 200°C for 20–60 min are shown in Fig. 2. Nanocubes were not produced after 20 min [Fig. 2(a)]. When the reaction times were 30 and 60 min, the shape of the particles became nanocubes [Figs. 2(b) and 2(c)].

Figure 3 shows the XRD patterns of the samples obtained via the microwave synthesis at various temperatures. Radiation of microwave was stopped when the temperature reached at 230 or 250°C. That is to say, there is no keeping time. The main XRD peaks were assigned to KNbO₃, but there were some peaks corresponding to a second phase [Fig. 3(a)]. On the other hand, a single phase of KNbO₃ was obtained at 250°C [Fig. 3(b)]. The TEM images of the products obtained by the microwave synthesis conducted at 230 and 250°C are shown in Fig. 4. Fine particles were observed at 230°C [Fig. 4(a)]. However, the particles became cubic at 250°C [Fig. 4(b)].

Figure 5 shows the XRD patterns of the samples obtained via the microwave synthesis at various temperatures and times. A single phase of KNbO₃ was indicated by the XRD peaks at 230 and 250°C [Figs. 5(a) and 5(b)]. The TEM images of the products obtained by the microwave synthesis conducted at 230 and 250°C are shown in Fig. 6. Nanocubes were observed at 230 and 250°C [Figs. 6(a) and 6(b)]. It seems that the nanocubes were accumulated during the TEM observation but more experimental data on this is necessary.

The formation mechanism of KNbO₃ nanocubes was related with the dissolving speed of raw materials in the reaction medium. We have considered that nanocubes are obtained if the nuclei were formed at high temperature. That is to say, the nanocubes are not obtained when the nuclei are formed at an early stage. In this study, the raw materials were dissolved and nuclei were formed rapidly because the temperature increased at 200–250°C due to the microwave radiation. Subsequently, the crystal growth of KNbO₃ nanocubes occurred.

4. Conclusions

In this study, KNbO₃ nanocubes were obtained by microwave synthesis at a low temperature using Nb₂O₅ and KOH as starting materials and water as the reaction medium. The XRD measurement confirmed that the KNbO₃ particles have the perovskite structure. The TEM observations revealed that the particles...
Fig. 3. XRD patterns for samples produced via the microwave synthesis at various temperatures. Nb$_2$O$_5$: 20 mmol, KOH: 800 mmol, Water: 40 ml, Time: 0 min. Temperature: (a) 230°C, (b) 250°C. ○: KNbO$_3$

Fig. 4. TEM images of samples produced via the microwave synthesis at various temperatures. Nb$_2$O$_5$: 20 mmol, KOH: 800 mmol, Water: 40 ml, Time: 0 min. Temperature: (a) 230°C, (b) 250°C.

Fig. 5. XRD patterns for samples produced via the microwave synthesis at various temperatures and times. Nb$_2$O$_5$: 20 mmol, KOH: 800 mmol, Water: 40 ml, Temperature: (a) 230°C, (b) 250°C. Time: (a) 30 min, (b) 14 min 40 s. ○: KNbO$_3$

Fig. 6. TEM images of samples produced via the microwave synthesis at various temperatures and times. Nb$_2$O$_5$: 20 mmol, KOH: 800 mmol, Water: 40 ml, Temperature: 200°C. Time(min): (a) 20, (b) 30, (c) 60.
had a cubic shape with sharp-edged corners. KNbO₃ nanocubes were synthesized by microwave synthesis at a relatively low temperature.

References