Solvothermal synthesis of KNbO₃ nanocubes using various organic solvents

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Potassium niobate (KNbO₃) nanocubes were synthesized via a solvothermal method using various organic solvents as the reaction medium. The solvothermal synthesis was conducted in different alcohols and ether-type solvents, and in mixtures of alcohol and ether-type solvents. The starting materials for the solvothermal synthesis were niobium oxide and potassium hydroxide. X-ray diffraction confirmed the presence of perovskite-structured KNbO₃. The morphology of KNbO₃ was investigated using scanning electron microscopy, transmission electron microscopy, and scanning transmission electron microscopy (STEM). Energy-dispersive X-ray (EDX) spectrometry was used to determine the elements present in the KNbO₃. The KNbO₃ nanocubes were the same length as the alkyl chain in the solvent that was used. The STEM and EDX analyses indicated that three elements, potassium, niobium, and oxygen, were present in the KNbO₃ nanocubes, and that these elements were distributed homogeneously throughout the nanocubes.

Key-words: KNbO₃, Nanocube, Solvothermal method, Perovskite oxide

1. Introduction

The synthesis of inorganic nanocubes has attracted a lot of attention in recent years.¹,² Perovskite-structured nanocubes have great potential for use in electroceramics and other functional materials. A few studies were published in the early 21st century in which syntheses of perovskite oxide nanocubes were described.

There are two key points that need to be considered when synthesizing nanocubes. The first is that the sizes of the particles need to be controlled. In general, nanoparticles of inorganic compounds are prepared using wet chemical reactions. There have also been many reports of nanocrystals being prepared using a dispersant or a surfactant, and fatty acids, such as oleic acid and linoleic acid, have been found to be useful in nanocrystal syntheses.³,⁴ The second is that the shapes of the particles need to be controlled. Many studies have been published in which nanocube syntheses have been described, and the usual targets of nanocube syntheses are metals.¹,²,⁵ There have only been a few studies published on nanocube synthesis of a ternary oxide with a perovskite structure.

We have focused on the surfaces of nanocubes, with the aim of developing enhanced electroceramic materials. The surface of a particle is a very important factor in developing such materials. The surfaces of nanocubes need to be bare, so that we do not induced the presence of perovskite-structured KNbO₃. The morphology of KNbO₃ was investigated using scanning electron microscopy, transmission electron microscopy, and scanning transmission electron microscopy (STEM). Energy-dispersive X-ray (EDX) spectrometry was used to determine the elements present in the KNbO₃. The KNbO₃ nanocubes were the same length as the alkyl chain in the solvent that was used. The STEM and EDX analyses indicated that three elements, potassium, niobium, and oxygen, were present in the KNbO₃ nanocubes, and that these elements were distributed homogeneously throughout the nanocubes.

SrTiO₃ nanocubes. That study was novel because we controlled the formation of the SrTiO₃ nuclei and the growth of the crystals using a mixture of raw materials, where titanium dioxide (TiO₂) and titanium tetraisopropoxide [(C₃H₇O)₄Ti] were the titanium sources. [(CH₃)₄CHO]Ti and TiO₂ contributed to rapid nucleation and crystal growth, respectively, in the system. A composite-hydroxide-mediated approach was used to synthesize BaZrO₃ and SrZrO₃ nanocubes.¹⁰ This method was based on the chemical reactions of materials in a eutectic hydroxide, melted at around 200°C, and at ambient pressure and in the absence of organic dispersants or capping reagents. The eutectic point for a mixture of NaOH and KOH with a molar ratio of 51.5:48.5 is about 165°C. ZrO₂ was dissolved in the eutectic hydroxide and BaZrO₃ and SrZrO₃ nanocubes were synthesized within the NaOH and KOH mixture.⁷,⁹ The synthesis of potassium niobate (KNbO₃) nanocubes has been attempted via a solvothermal method, which was recently reported to be successful.¹¹ In this method, KNbO₃ nanocubes were prepared at low temperatures using Nb₂O₅ and KOH as starting materials and ethanol as the reaction medium. The effect of the amount of KOH present in the system was also investigated.¹¹ In the present study, we investigated the synthesis of KNbO₃ nanocubes using a solvothermal reaction. In particular, we examined the effect of the solvent on the products. We presumed that the particle sizes would change due to the different polarities of the different kinds of solvent. We also tried to decrease the particle sizes of the KNbO₃ nanocubes using different reaction conditions.

2. Experimental procedure

2.1 Synthesis of KNbO₃ nanocubes

KNbO₃ was synthesized via a solvothermal method using 40 ml solvent. Methanol (CH₃OH), ethanol (C₂H₅OH), 1-propanol (C₃H₇OH), 1-butanol (C₄H₉OH), 2-methoxyethanol (CH₃OC₂H₄OH), 2-ethoxyethanol (C₃H₅OC₂H₄OH), 2-propoxyethanol, (C₃H₇OC₂H₄OH), 2-isopropoxyethanol [(CH₃)₂CHOCH₂OH], [Received December 14, 2013; Accepted May 2, 2014]
and 2-n-butoxyethanol (C\textsubscript{4}H\textsubscript{9}OC\textsubscript{2}H\textsubscript{4}OH) were used as the solvent, and 1 mmol Nb\textsubscript{2}O\textsubscript{5} and 80 mmol KOH were used as the raw materials. The solvent and raw materials were placed in a Teflon reactor with an internal volume of 100 ml; the reactor was placed in a stainless steel autoclave. The autoclave was preheated to a selected temperature between 100 and 230°C. Thereafter, the autoclave was sealed and kept at the selected temperature for 18 h. The autoclave was then cooled to room temperature and the product was collected using a centrifugal separator set at 10,000 rpm. The centrifugal separator was rinsed three times with ethanol. The product was dried at 80°C overnight in a dryer.

2.2 Characterization

The crystallinity and phase purity of the samples that were prepared were analyzed by X-ray diffraction (XRD) using an Ultima IV diffractometer (Rigaku Co., Japan), which used Cu K\textalpha radiation (with a wavelength of 0.15418 nm) and was operated at 40 kV and 30 mA in the 2\theta range 10–80° at room temperature. Particle morphologies were examined by scanning electron microscopy (SEM) using an S-4500 microscope (Hitachi, Japan), which was operated at 15 kV. A sample powder was prepared for observation 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 silicon substrate, and leaving it under ambient conditions until the ethanol had evaporated. The powder samples were analyzed by transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM) using a Tecnai Osiris instrument (FEI Co.), which was operated at 200 kV and equipped with an energy-dispersive X-ray (EDX) spectrometer. EDX mapping was performed using the K-K\textalpha, Nb-K\textalpha, and O-K\textalpha lines. A sample was prepared for TEM/STEM 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.

3. Results and discussion

3.1 Synthesis of KNbO\textsubscript{3} nanocubes using various alcohols

Although difficult, it was very important that the correct technique is used to synthesize perovskite-structured nanocubes because the nanoparticles must each have an appropriate morphology for the desired application. We thought that solvothermal methods would control the morphology at an appropriate degree to allow the synthesis of perovskite-structured nanocubes. Any solvent can be used as the reaction medium in a solvothermal reaction. There are many factors to consider when carrying out a solvothermal reaction, such as the reactant concentrations, reactant solubilities, reaction temperature, reaction time, solvent choice, and pressure, each of which can be varied. We paid particular attention to the solvent used as the reaction medium. KNbO\textsubscript{3} particles are generally prepared via a hydrothermal method using water as the reaction medium.\textsuperscript{12-15} However, we have previously described the synthesis of KNbO\textsubscript{3} nanocubes via

Fig. 1. XRD patterns for samples produced via the solvothermal method in (a) methanol, (b) ethanol, (c) 1-propanol, and (d) 1-butanol. Temperature: 230°C; time: 18 h; Nb\textsubscript{2}O\textsubscript{5}: 1 mmol; KOH: 80 mmol; solvent: 40 ml.

Fig. 2. SEM images of samples produced via the solvothermal method in (a) methanol, (b) ethanol, (c) 1-propanol, and (d) 1-butanol. Temperature: 230°C; time: 18 h; Nb\textsubscript{2}O\textsubscript{5}: 1 mmol; KOH: 80 mmol; solvent: 40 ml.
a solvothermal method using ethanol as the reaction medium, and we have also determined the effect of using different amounts of the raw material KOH. However, we thought that solvents other than ethanol would offer the possibility of controlling the nanocube morphology, so we used a similar solvothermal method to synthesize KNbO3 nanocubes but used various solvents as the reaction medium.

The solvothermal reaction was performed using the following solvents: methanol, ethanol, 1-propanol, and 1-butanol. The reactions were performed at 230°C for 18 h using 1 mmol Nb2O5 and 80 mmol KOH (with a K:Nb atomic ratio of 40:1). Figure 1 shows the XRD patterns of the samples that were obtained. The synthesis using methanol as the reaction medium produced KNbO3 [Fig. 1(a)]. A single KNbO3 phase was also formed in the syntheses using ethanol, 1-propanol, and 1-butanol, and the KNbO3 diffraction peaks were assigned to the orthorhombic phase (JCPDS file 32-0822) [Figs. 1(b)–1(d)]. The SEM images of the samples are shown in Fig. 2. Cubic particles were obtained using all the test solvents [Figs. 2(a)–2(d)], but the particle sizes were dramatically different when different solvents were used. The particle size increased using the solvents in the following order: methanol, ethanol, 1-propanol, and 1-butanol. The particle size was very small when methanol was used as the reaction medium. The results illustrated in Figs. 2(a)–2(d) showed that KNbO3 nanocubes were obtained.

The reaction temperature is an important factor in solvothermal synthesis. Figure 3 shows the XRD patterns of the samples obtained via the solvothermal method at various temperatures using methanol as the solvent. KNbO3 was formed at 100°C [Fig. 3(a)] but a single KNbO3 phase was not formed, and XRD peaks of an unknown phase were observed. Therefore, we performed the reaction at a series of high temperatures. The XRD peaks for the unknown phase decreased in size as the reaction temperature was increased [Figs. 3(b)–3(d)]. SEM images of the samples obtained using the solvothermal reaction at reaction temperatures of 100–230°C for 18 h, are shown in Fig. 4. Agglomeration particles were obtained at 100°C [Fig. 4(a)], and particles with cubic shapes were clearly observed as the reaction temperature was increased [Figs. 4(b)–4(d)]. Detailed TEM and STEM-EDX observations of the KNbO3 were made. A bright-field TEM image obtained when 80 mmol KOH was added (with a K:Nb atomic ratio of 40:1) is shown in Fig. 5. Figure 5(a) shows the KNbO3 nanocubes observed by TEM. STEM-EDX was used to investigate the nanoscale elemental composition and spatial uniformity of the element distribution in the particles. Two-dimensional elemental mapping of K, Nb, and O, and the EDX spectrum of the KNbO3 obtained using STEM-EDX are shown in Figs. 5(b)-1–5(b)-3, which demonstrated that all three elements were distributed homogeneously throughout the nanocubes. An EDX spectrum of a sample is shown in Fig. 5(c). Only K, Nb, peaks for K, Nb, and O were detected. These results confirm that the nanocube composition was KNbO3.
3.2 Synthesis of KNbO3 nanocubes using various ether-type solvents

Ether-type solvents are attractive reaction media. We performed the solvothermal synthesis using the following ether-type solvents: 2-methoxyethanol, 2-ethoxyethanol, 2-propoxyethanol, 2-isopropoxyethanol, and 2-n-butoxyethanol.

Figure 6 shows the XRD patterns and SEM images of the samples obtained via the solvothermal method using the ether-type solvents. The XRD patterns of all the samples that were produced indicated that KNbO3 was formed, and the KNbO3 diffraction peaks were assigned to the orthorhombic phase (JCPDS file 32-0822). However, a second phase was obtained using each of the solvents. The centrifugal separator was rinsed with ethanol after the solvothermal reaction had been completed. SEM observations revealed that nanoscale KNbO3 particles with cubic shapes and sharp-edged corners were formed. The KNbO3 nanocubes were the same length as the alkyl chain of the solvent that was used. Therefore, the smallest KNbO3 nanocubes were obtained when they were synthesized in 2-methoxyethanol.

3.3 Synthesis of KNbO3 nanocubes using mixtures of alcohol and ether-type solvents

As mentioned above, KNbO3 nanocubes were obtained when either an alcohol or an ether-type solvent was used as the reaction medium. We thought that KNbO3 nanocubes might have sharper corners when the solvothermal synthesis was performed using a mixture of an alcohol and an ether-type solvent. Figure 7 shows the XRD patterns of the samples produced using such mixtures. The XRD patterns showed that KNbO3 was the main product in all these samples. The main XRD peaks shown in Fig. 7(a) indicate that the KNbO3 samples that were produced had perovskite structures. The KNbO3 diffraction peaks shown in...
Figs. 7(b)–7(d) were assigned to the orthorhombic phase (JCPDS file 32-0822). SEM images of the samples obtained using various solvent mixtures are shown in Fig. 8. The SEM images showed that the KNbO₃ particles had nanoscale sizes, were cubic, and had sharp-edged corners. Again, the KNbO₃ nanocubes were the same length as the alkyl chain in the solvent that was used. The smallest KNbO₃ nanocubes were obtained from the synthesis using a mixture of methanol and 2-methoxyethanol.

4. Conclusions

KNbO₃ nanocubes were synthesized in solvothermal reactions at low temperatures using various organic solvents as reaction media. The synthesis was performed using Nb₂O₅ and KOH as starting materials. Three kinds of solvent (alcohols, ether-type solvents, and mixtures of these two types of solvent) were tested, and the morphology of the KNbO₃ nanocubes that were produced depended on the particular solvent that was used. XRD measurements confirmed that perovskite-structured KNbO₃ was formed under all the test conditions. The KNbO₃ morphology was investigated using SEM, which revealed that the KNbO₃ particles had nanoscale sizes, were cubic, and had sharp-edged corners. STEM-EDX demonstrated that K, Nb, and O were homogeneously distributed throughout each nanocube. Solvothermal syntheses using various ether-type solvents or mixtures of an alcohol and an ether-type solvent produced KNbO₃ nanocubes that were the same length as the alkyl chain in the solvent that was used.

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