Solvolothermal synthesis and morphology control of NaNbO$_3$ nanocubes using a reaction medium of water and/or methanol

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ABSTRACT

NaNbO$_3$ particles were prepared by solvothermal synthesis at 230°C in a reaction medium of either water or methanol. Morphological control of the particles was achieved by varying the synthesis conditions, such as the starting material and the reaction medium. The starting material was prepared by a process involving heat treatment of an Nb precursor at 400°C and 800°C. The crystal structure of the starting material depended on the heat treatment temperature, with the preferred orthorhombic Nb$_2$O$_5$ obtained at 800°C. Large particles were obtained when water was used as the reaction medium, whereas fine particles were obtained using methanol. Under appropriate conditions, NaNbO$_3$ nanocubes can be synthesized using orthorhombic Nb$_2$O$_5$ as the starting material and methanol as the reaction medium.

1. Introduction

Perovskite oxides are an important class of ceramic materials with numerous technological applications. Among the various perovskite oxides, sodium niobate (NaNbO$_3$) has been identified for use in a variety of functions, including piezoelectric devices [1], photocatalysts [2], and photoelectrochemical applications [3]. The effective piezoelectric coefficient of NaNbO$_3$ nanowires was measured by piezoresponse force microscopy [1]. Photocatalytic activity for hydrogen (H$_2$) or oxygen (O$_2$) evolution in the presence of sacrificial regents and overall water splitting under UV-light irradiation was observed in NaNbO$_3$ nanowires [2]. NaNbO$_3$ was used as the core of the heterostructure for photoelectrochemical water splitting [3].

Particle morphology is often a critical factor influencing the performance of ceramic materials. Morphology control of various perovskite oxides during synthesis has consequently attracted a great deal of interest over the past several decades [4–9]. As regards the NaNbO$_3$, the synthesis of cubic [10] or nanowire [11] NaNbO$_3$ was studied using a hydrothermal reaction or calcination, respectively. The effect of the starting material on NaNbO$_3$ nanocube synthesis via the solvothermal method has also been reported recently [12]; in that case, however, the NaNbO$_3$ nanocubes were synthesized using a two-step solvothermal process and only one reaction medium (i.e., methanol).

The focus of the present work was on both the Nb-containing starting material and the reaction medium. We considered that both these factors may affect the morphology of the obtained NaNbO$_3$ particles. For the reaction medium, water (which has a large dielectric constant and is categorized as a polar solvent) and/or methanol (which has a smaller dielectric constant) was chosen. These properties were expected to influence the solubility of the starting material, the particle growth mechanism during solvothermal synthesis, and, ultimately, the size and shape of the obtained NaNbO$_3$ particles.

As regards the starting material, particles with low solubility that initially adopt a perovskite structure tend to become nanocubes during solvothermal synthesis [8,12]. We examined morphology control of NaNbO$_3$ via the solvothermal method based on this knowledge. The Nb precursor was prepared by metallic Nb hydrolysis followed by heat treatment at 400°C and 800°C. Thereafter, solvothermal synthesis was performed using the prepared Nb starting material. The obtained powders were characterized using X-ray diffraction (XRD) measurements and electron microscopy observations.

2. Experimental procedures

2.1. Synthesis of the Nb starting material

The starting material was obtained by hydrolysis of metallic Nb to form a precursor solution, followed by heat treatment of the obtained precursor solution [12–14]. Metallic Nb (5 mmol) was dissolved in 60 ml of hydrogen peroxide (H$_2$O$_2$, purity: 30.0–35.5%; Kanto Chemical Co., Inc., Tokyo, Japan) and 15 ml of ammonia solution (NH$_3$, purity: 30.0–35.5%; Kanto Chemical Co., Inc., Tokyo, Japan)
purity: 28.0–30.0%; Kanto Chemical Co., Inc.) in an ice bath. The resultant aqueous solution was heated on a hot plate at 60°C, and the product was then collected using a centrifugal separator operating at 10,000 rpm. Water and ethanol were used to rinse the product in the centrifugal separator, and the product was subsequently dried overnight at 80°C. This process yielded the Nb precursor, which was then heated at 400°C or 800°C to produce the Nb starting material.

2.2. NaNbO₃ nanocube synthesis

NaNbO₃ was synthesized from the starting material via the solvothermal method. A reaction medium (40 ml) comprising water and/or methanol (CH₃OH; Kanto Chemical Co., Inc.) was used during the solvothermal process. Sodium hydroxide (10 mmol NaOH; Kanto Chemical Co., Inc.) was used as the Na source. The reactants were placed in a Teflon-lined stainless-steel autoclave reactor with an internal volume of 100 ml. The autoclave was then sealed and maintained at 230°C for 24 h. After the reaction was completed, the autoclave was allowed to cool down to room temperature. The product was then collected with a centrifugal separator operating at 10,000 rpm. Water, methanol, or ethanol was used to rinse the product in the centrifugal separator, after which the product was dried overnight at 80°C.

2.3. Characterization

The crystallinity and phase purity of the prepared samples were analyzed by XRD (Ultima IV; Rigaku Co., Tokyo, Japan) using a diffractometer with Cu Ka radiation (wavelength: 0.15418 nm), operated at 40 kV/30 mA in the 2θ range of 10–80° at room temperature. Crystal structure analysis was performed by the Rietveld method using a Jana2006 [15]. The peak profiles were corrected for asymmetry by the axial divergence method according to Finger-Cox-Jephcoat and fitted with the Thompson-Cox-Hastings pseudo-Voigt function [16]. We examined the particle morphology using scanning electron microscopy (SEM) (SU5000; Hitachi, Tokyo, Japan; accelerating voltage: 3 kV); transmission electron microscopy (TEM) (Technai Osiris; FEI Co., Hillsboro, OR, USA; accelerating voltage: 200 kV); and scanning transmission electron microscopy (STEM) using an instrument equipped with an energy-dispersive X-ray (EDX) spectrometer.

3. Results and discussion

The XRD patterns of the Nb-containing starting materials are shown in Figure 1, and the XRD pattern of the Nb precursor with no heat treatment, also shown in Figure 1(a), indicates that the obtained powder was amorphous. No XRD peaks were observed after heat treatment of the Nb precursor at 400°C, indicating that the obtained compound remained amorphous (Figure 1(b)). Conversely, XRD peaks were observed after heat treatment at 800°C (Figure 1(c)). These XRD peaks were assigned to a single phase of orthorhombic Nb₂O₅ (JCPDS file: 30–0873). Secondary electron (SE) images of the starting materials are shown in Figure 2. Before heat treatment, the Nb precursor comprised many fine particles (Figure 2(a)). Heat treatment at 400°C (Figure 2(b)) and 800°C (Figure 2(c)) led to corresponding increases in the particle size, with the particles treated at 800°C becoming larger than those treated at 400°C.

Solvothermal synthesis was first performed using the Nb-containing starting material prepared by heat treatment of the Nb precursor at 400°C. As mentioned above, the starting material prepared at this temperature was amorphous. Figure 3 shows the XRD patterns of NaNbO₃ produced via the solvothermal method using the starting material treated at 400°C and either water (Figure 3(a)) or methanol (Figure 3(b)) as the reaction medium. Both the XRD patterns in Figure 3(a,b) were assigned to a single phase of orthorhombic NaNbO₃ (JCPDS file: 33–1270). However, the orientation and maximum peak intensity of the XRD patterns in Figure 3(a,b) are different. Figure 4 shows SE images of NaNbO₃ produced via the
Solvothermal method using the starting material treated at 400°C. Large cubic particles were obtained using water as the reaction medium (Figure 4(a)). The corners and edges of the NaNbO$_3$ particles produced by this hydrothermal method were not sharp. On the other hand, fine cubic particles with sharp corners and edges were obtained by the solvothermal method employing methanol (Figure 4(b)). Solvothermal synthesis was then performed using the Nb-containing starting material that was prepared by heat treatment at 800°C. As mentioned above, the starting material comprised orthorhombic Nb$_2$O$_5$. Figure 5 shows XRD patterns of NaNbO$_3$ produced via the solvothermal method using the starting material treated at 800°C. The XRD pattern of the sample prepared using only water as the medium is shown in Figure 5(a), and the XRD pattern of the sample using only methanol is shown in Figure 5(g). XRD patterns of samples prepared using reaction media comprising mixtures of water and methanol in various ratios are shown in Figure 5(b–f). All the XRD patterns were assigned to orthorhombic NaNbO$_3$ (JCPDS file: 33–1270). The maximum peak intensities and orientations derived from the XRD patterns are almost the same for all the XRD patterns in Figure 5. Figure 6 shows SE images of NaNbO$_3$ produced via the solvothermal method using the starting material treated at 800°C. Square particles can be observed in all the SE images in Figure 6. Large particles were obtained using pure water as the reaction medium (Figure 6(a)), and the particle size decreased as the concentration of methanol increased (Figure 6(b–f)). NaNbO$_3$ nanocubes were obtained using pure methanol as the reaction medium (Figure 6(g)). Detailed analyzes of Rietveld refinement and electron microscopy observations of the obtained NaNbO$_3$ nanocubes were performed on the same samples as those used in Figure 6(g).

Figure 7 shows the Rietveld refinement of the $Pbcm$ model of NaNbO$_3$ with the orthorhombic system carried out using Jana2006 software [15,16]. Table 1 summarizes the Rietveld refinement parameters. The numbers assigned to the Na, Nb, and O positions were 2, 1, and 4, respectively. The U factor indicated the isotropic atomic displacement parameter. The occupancy of all the elements was 1. Taken together with the values of all the atoms in the $x$, $y$, and $z$ axes, this confirmed that the system was orthorhombic. The obtained powders were the single phase of NaNbO$_3$, as shown by the result of the Rietveld analysis. The lattice parameters of NaNbO$_3$ were $a = 5.51018(11)$ Å, $b = 5.5640(10)$ Å, $c = 15.5433(2)$ Å and $\alpha = \beta = \gamma = 90^\circ$. The unit cell volume was 476.656(15) Å$^3$.

A bright-field (BF) TEM image and the corresponding selected area electron diffraction (SAED) pattern, a high-angle annular dark-field (HAADF) STEM image, and a corresponding elemental analysis EDX of a single
The NaNbO$_3$ nanocube has sharp edges and corners (Figure 8(a–d)), and the SAED pattern (Figure 8(b)) reveals that the nanocube is a single crystal. The EDX investigation reveals that the nanoscale elemental composition of the NaNbO$_3$ nanocube is spatially uniform. Furthermore, only Na, Nb, and O peaks were detected in the EDX spectrum (Figure 8(c)). The two-dimensional elemental mapping of the Na, Nb, and O demonstrates that all three elements are distributed homogeneously across the NaNbO$_3$ nanocube. These results confirm that the nanocubes were composed of pure NaNbO$_3$.

During solvothermal synthesis, the particle size became fine when methanol was used as the reaction medium, whereas the particle size became large when water was used as the reaction medium. This difference between methanol and water was due to their dielectric constant and polarity. The dielectric constant has a close relationship with polarity, and it affects the solubility during particle formation in solvothermal synthesis. The solubility influences the crystal growth of the particles. The dielectric constant of methanol is lower than that of water. The solubility is low when the dielectric constant is low; thus, a low dielectric constant retards the crystal growth of the particles, and the particle size becomes fine as a result. In this study, the particle size of the obtained powders can be explained using the dielectric constant.

As regards the shape of the obtained powders, cubic particles are formed by crystal growth in facets. The particles become cubic when all the facets of the crystal grow at the same speed. In this study, the shape of the particles became cubic when methanol was used as the reaction medium for solvothermal synthesis, and this shape was caused by a crystalline system. NaNbO$_3$ has an orthorhombic system. Additionally, methanol as the reaction medium led to formation of NaNbO$_3$ nanocube are shown in Figure 8. The BF-TEM and HAADF-STEM observations clearly show that the NaNbO$_3$ nanocube has sharp edges and corners (Figure 8(a–d)), and the SAED pattern (Figure 8(b)) reveals that the nanocube is a single crystal. The EDX investigation reveals that the nanoscale elemental composition of the NaNbO$_3$ nanocube is spatially uniform. Furthermore, only Na, Nb, and O peaks were detected in the EDX spectrum (Figure 8(c)). The two-dimensional elemental mapping of the Na, Nb, and O demonstrates that all three elements are distributed homogeneously across the NaNbO$_3$ nanocube. These results confirm that the nanocubes were composed of pure NaNbO$_3$.

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large nuclei and retarded the crystal growth of the particles. Therefore, NaNbO$_3$ nanocubes were formed during solvothermal synthesis using methanol as the reaction medium.

4. Conclusions

NaNbO$_3$ nanocubes were prepared by solvothermal synthesis. The effects of heat treatment of the Nb-containing starting material and the solvent used for the reaction medium on the final product were investigated. As regards the starting material, an amorphous Nb compound and orthorhombic Nb$_2$O$_5$ were obtained after heat treatment of Nb-containing precursor at 400°C and 800°C, respectively. Heat treatment of the Nb-containing precursor at 800°C resulted in orthorhombic Nb$_2$O$_5$ that was adequate for the synthesis of NaNbO$_3$ nanocubes. The reason for this is that the solubility of the starting material in the reaction medium affects the formation of NaNbO$_3$ nanocubes. Compared with the amorphous Nb compound resulting from 400°C heat treatment, the solubility of orthorhombic Nb$_2$O$_5$ is low. This low solubility was found to lead to the formation of more nearly ideal NaNbO$_3$ nanocubes in the present study. As regards the reaction medium, the morphology of the obtained powder depends on the reaction solvent. Large particles were formed when water was used as the reaction medium.
Table 1. Rietveld refinement structural parameters of the XRD pattern of NaNbO₃ produced using the solvothermal method. The temperature and duration of the heat treatment of the Nb-containing starting material were 800°C and 2 h, respectively. The temperature and duration of the solvothermal synthesis were 230°C and 24 h, respectively. The reaction medium used for the solvothermal synthesis was methanol.

NaNbO₃, \textit{Pbcm} model

| Atom | Site | x     | y     | z     | Occupancy | U    |
|------|------|-------|-------|-------|-----------|------|
| Na   | 4c   | 0.2560(29) | 1/4   | 0     | 1         | 0.016(10) |
| Na   | 4d   | 0.2530(28) | 0.2140(27) | 1/4   | 1         | 0.014(9)   |
| Nb   | 8e   | 0.2435(5)   | 0.7355(4) | 0.1247(15) | 1       | 0.0086(4) |
| O    | 8e   | 0.0340(20)  | 0.0260(27) | 0.1137(14) | 1       | 0.003(1)   |
| O    | 8e   | 0.4740(23)  | 0.0460(25) | 0.6429(13) | 1       | 0.003(1)   |
| O    | 4d   | 0.1690(41)  | 0.7220(37) | 3/4   | 1         | 0.003(1)   |
| O    | 4c   | 0.3040(42)  | 3/4   | 0     | 1         | 0.003(1)   |

\begin{align*}
\text{a} & = 5.51018(11)\text{Å} \\
\text{b} & = 5.56540(10)\text{Å} \\
\text{c} & = 15.5433(2)\text{Å} \\
\text{Volume of unit cell} & = 476.656(15)\text{Å}^3
\end{align*}

Figure 8. (a) The BF-TEM image, (b) corresponding SAED pattern, (c) EDX spectrum, and (d) HAADF-STEM image and the corresponding elemental analysis profiles of Na, Nb, and O obtained by EDX mapping (e–g) of a NaNbO₃ nanocube produced via the solvothermal method. The temperature and duration of the heat treatment of the Nb-containing starting material were 800°C and 2 h, respectively. The temperature and duration of the solvothermal synthesis were 230°C and 24 h, respectively. The reaction medium used for the solvothermal synthesis was methanol.
medium, whereas fine particles were formed when methanol was used as the reaction medium. The prepared NaNbO₃ tended to form finer nanocubes as the amount of methanol in the reaction medium was increased toward undiluted methanol. The obtained NaNbO₃ particles were single crystals, as shown by the SAED results, and only Na, Nb, and O were detected in the EDX spectrum.

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Disclosure statement
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