Effects of raw materials on NaNbO₃ nanocube synthesis via the solvothermal method

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1. Introduction

Perovskite sodium niobate (NaNbO₃), which has an orthorhombic structure [1], is widely recognized and used as an antiferroelectric material. Previous studies identified the local NaNbO₃ structure using high-energy X-ray diffraction, along with the structures of potassium niobate (KNbO₃) and silver niobate (AgNbO₃) [2,3]. In this study, an examination of the morphology of NaNbO₃ was conducted in addition to an analysis of its crystal structure.

Liquid reaction processes such as the coprecipitation, sol-gel, and solvothermal methods are effective techniques for synthesizing nanoparticles. Among these methods, the solvothermal method is particularly effective at controlling the particles’ size and shape. Based solely on particle morphology, nanocubes, which are nanoscale single crystals, are considered advantageous for the development of small, high-performance electronic devices, laminated ceramic capacitors, and next-generation memory due to the nanocube’s suitability as a capacitor [4–15]. Nanocubes not only allow manufacturers to use fewer capacitors, but also to develop smaller capacitors. In our previous studies, we have investigated the properties and morphologies of particles for nanocube synthesis, such as barium titanate (BaTiO₃) [5,6], strontium titanate (SrTiO₃) [6–9], potassium niobate (KNbO₃) [10–12], barium zirconate (BaZrO₃) [13,14], and strontium zirconate (SrZrO₃) [15]. These nanocubes were synthesized using the solvothermal, hydrothermal, or composite-hydroxide-mediated approaches.

The raw material morphology affects the morphology of newly formed NaNbO₃. NaNbO₃ microparticles were obtained via hydrothermal synthesis when niobium (Nb) or niobium oxide (Nb₂O₅) powders were used as the raw-material sources for Nb [16,17]. Previous studies have focused on the particle sizes of the raw materials, especially during the synthesis of Nb₂O₅ nanoparticles from peroxo niobic compounds [18,19]. For crystalline Nb₂O₅, the crystal system differs depending on the temperature used during heat treatment [19,20]. According to the abovementioned previous studies, there is a variety of niobium compounds with various particle sizes, crystal systems, and solubilities in solvents. When conducting a synthesis process, the choice of suitable raw materials is an important factor in controlling the NaNbO₃ morphology. When it is a liquid reaction process, solvothermal methods have the advantage of enabling control of the morphology [10–12]. The key factors in controlling the morphology while applying the solvothermal method are the reactant concentrations, reactant solubility, reaction temperature, reaction time, choice of the solvent, and pressure.
In this study, we examined NaNbO$_3$ nanocube synthesis using the solvothermal method to yield nanocubes suitable for electroceramic applications. Since the particle surface affects the electroceramic properties, neither dispersants nor surfactants were advantageous for the development of small, high-performance electronic devices, laminated ceramic capacitors, and next-generation memory. We therefore used no dispersants or surfactants during the nanocube synthesis experiments in this study. In addition, this study employed some novel methods to enable the use of a raw Nb material as a source for synthesizing NaNbO$_3$ nanocubes. Finally, we analyzed the effects of these raw materials on NaNbO$_3$ nanocube synthesis using the solvothermal method.

2. Experimental procedures

2.1. Synthesis of Nb raw material

The raw material was obtained by metallic Nb hydrolysis for preparation of the precursor, followed by heat treatment of the obtained precursor (Figure 1). 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.) and 15 ml of ammonia solution (NH$_3$, purity: 28.0–30.0%, Kanto Chemical Co., Inc.) in an ice-cooled bath. The metallic Nb was dissolved, and the solution was heated on a hot plate to 60°C and then transferred into a Teflon reactor and dried at 80°C. This process yielded the precursor, which was then heated in the range of 300–1000°C to produce the Nb raw material.

2.2. NaNbO$_3$ nanocube synthesis

NaNbO$_3$ was synthesized from the raw material via the solvothermal method (Figure 2). Reaction media (40 ml) comprising methanol (CH$_3$OH, 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 compounds were placed in a stainless-steel autoclave Teflon reactor with an internal volume of 100 ml. The autoclave was then sealed and maintained at 200°C for 24 h. After completion of the reaction, the autoclave was allowed to cool to room temperature. The product was then collected with a centrifugal separator operating at 15,000 rpm. Methanol was used again to rinse 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 X-ray diffraction (XRD; UltimaIV, Rigaku Co., Japan) using a diffractometer with Cu Kα radiation (wavelength: 0.15418 nm) and operated at 40 kV/30 mA in the 2θ range of 10°–80° at room temperature. Thermal analysis was performed using thermogravimetry and differential thermal analysis (TG-DTA; Thermo plus EVO, Rigaku Co., Japan). We examined the particle morphology using scanning electron microscopy (SU-5000; Hitachi, Japan) operated at 10 kV or 15 kV, or scanning transmission electron microscopy (HD-2700; Hitachi, Japan) operated at a 200 kV acceleration voltage.

3. Results and discussion

3.1. Synthesis of the Nb raw material

The Nb raw material precursor was prepared via metallic Nb hydrolysis. The TG-DTA curve of the precursor was measured across a temperature range extending from room temperature to 1000°C (Figure 3). The

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**Figure 1.** Flow chart of Nb raw material precursor synthesis.

**Figure 2.** Flow chart showing NaNbO$_3$ synthesis via the solvothermal method.
amount of precursor used for the TG-DTA measurement was 18.7 mg. For the TG curve, weight reductions were measured from room temperature to 580°C. We observed a first-order weight reduction in the range from room temperature to 290°C, which corresponded to a 22% weight reduction. This weight reduction was considered to result from removal of the precursor’s water content. A second-order weight reduction was observed from 428°C to 580°C. This weight reduction was related to an exothermic peak observed in the DTA curve. The DTA curve was characterized by several exothermic peaks across a broad temperature range. The crystalline Nb$_2$O$_5$ was analyzed based on the XRD data (Figure 2), which is presented below and in previous studies [19,20]. The exothermic peak at 163°C is a consequence of the precursor’s water content. The exothermic peak at 466°C correlates with Nb$_2$O$_5$ formation in the hexagonal system. The exothermic peak near 555°C correlates with the phase transition from a hexagonal to an orthorhombic system. The exothermic peak at 965°C correlates with the phase transition from the orthorhombic to a monoclinic system.

The Nb raw material precursor underwent heat treatment. Sample XRD patterns are shown in Figure 4. Figure 4(a) displays XRD patterns for the Nb raw material precursor. The Nb raw material precursor comprised an amorphous compound and did not crystallize at 300°C (Figure 4(b)). XRD peaks were observed at 500°C and 600°C (Figure 4(c,d)), which were assigned to a single Nb$_2$O$_5$ phase with a hexagonal system (JCPDS file 7-0061). According to the DTA precursor curve, crystallization of the Nb$_2$O$_5$ with a hexagonal system occurred at 466°C (Figure 3). As shown in Figure 4(e), the XRD peaks also changed at 800°C and were assigned to a single Nb$_2$O$_5$ phase with an orthorhombic system (JCPDS file 30-873). According to the TG curve for the Nb raw material precursor, weight reduction was not observed above 580°C (Figure 3). Thus, the phase transition occurred only from the hexagonal to the orthorhombic Nb$_2$O$_5$ system. The Nb$_2$O$_5$ transition occurred at 1000°C and XRD peaks were assigned to the monoclinic Nb$_2$O$_5$ system (Figure 4(f)) (JCPDS file 37-1468). Based on the DTA curve for the Nb raw material precursor, Nb$_2$O$_5$ crystallization with a monoclinic system occurred at 965°C (Figure 3).

The morphology of the Nb raw material was analyzed using secondary electron (SE) images (Figure 5). The precursor, which comprised an amorphous compound, displayed particle aggregation after its heat treatment at 300°C (Figure 5(a,b)) as shown in Figure 5(c); however, the shape of the particles changed at 500°C compared with the precursor and the results of heat treatment at 300°C (Figure 5(a,b)). At above 600°C, the particle surface melted (Figure 5(d–f)). Fine particles were obtained at 600°C and 800°C (Figure 5(d,e)), and particle grain growth was observed at 1000°C (Figure 5(f)).

### 3.2. NaNbO$_3$ nanocube synthesis

The purpose of this study was to synthesize and examine NaNbO$_3$ nanocubes using various Nb raw material sources. Figure 6 shows the XRD patterns of the Nb$_2$O$_5$ obtained when applying the solvothermal method. As shown in Figure 6(a), a single phase of NaNbO$_3$ was obtained from the XRD data when solvothermal
synthesis was performed using the Nb raw material precursor. We also observed a single NaNbO$_3$ phase using raw materials obtained through heat treatment from 300°C to 800°C (Figure 6(b–e)). These XRD peaks were assigned to a single NaNbO$_3$ phase with an orthorhombic system (JCPDS file 33-1270). The unreacted raw material of Nb$_2$O$_5$ with a monoclinic system was confirmed, moreover, even with the NaNbO$_3$ formation (Figure 6(f)).

We observed the morphology of NaNbO$_3$ with an orthorhombic system as revealed by SE images (Figure 7). A large particle with a cube-like shape was observed when using the Nb raw material precursor without heat treatment (Figure 7(a)). The particle morphology also displayed a step-like cubic shape. The large size and step-like cubic shape developed due to the raw material’s solubility in the solvent, which has a significant influence on particle morphology. The precursor and fine particles dissolved rapidly in the solvent with progressive crystal growth. With heat treatment of the raw material to 300°C, the particles became large and acquired a cube-like shape (Figure 7(b)). This raw material had a similar morphology to that of the materials used in Figure 7(a). Heat treatment of the raw materials to varying temperatures to incite Nb$_2$O$_5$ crystallization led to fine particles on the nanoscale (Figure 7(c–e)), which were cubic in shape. We observed, in particular, that the NaNbO$_3$ nanocubes were formed when we used Nb$_2$O$_5$ raw materials with an orthorhombic system (Figure 7(e)). We propose that nanocube formation is related to the solubility of the raw materials in the solvent [7,10–12,15]. Nanocubes were formed at around 200°C during solvothermal synthesis. Nuclei formation and NaNbO$_3$ crystal growth occurred after the raw materials had dissolved in the solvent at around 200°C during solvothermal synthesis. When we used Nb$_2$O$_5$ raw materials with

Figure 5. SE images of the raw materials comprising the Nb raw material. Heat-treatment temperatures: (a) precursor, (b) 300°C, (c) 500°C, (d) 600°C, (e) 800°C, and (f) 1000°C. Time of heat treatment: 2 h. Acceleration voltages of the SE images: (a, b) 200 kV, (c–f) 15 kV.

Figure 6. XRD patterns of NaNbO$_3$ produced via the solvothermal method. Heat-treatment temperatures applied to the raw material: (a) no heat treatment, (b) 300°C, (c) 500°C, (d) 600°C, (e) 800°C, and (f) 1000°C. Time of heat treatment: 2 h.
〇: NaNbO$_3$, ▲: Nb$_2$O$_5$ (monoclinic system).
a monoclinic system, the raw materials remained due to their low solubility in solvent (Figure 7(f)). These results indicate and confirm the clear effect that raw materials have on NaNbO$_3$ nanocube synthesis when using the solvothermal method. As regards the sample in Figure 7(e), detailed observations of the BF and HAADF images in addition, the SE image were carried out (Figure 8). NaNbO$_3$ nanocubes with sharp edges and corners were confirmed in all the SE (Figure 8(a)), BF (Figure 8(b)), and HAADF (Figure 8(c)) images. BF and HAADF observation can confirm internal particles due to transmission imaging. BF and HAADF images indicate that there is no void within the nanocubes.

3.3. Discussion for NaNbO$_3$ nanocube synthesis

We have determined the effect of raw materials on NaNbO$_3$ nanocube synthesis via the solvothermal method. The main factor for the synthesis of NaNbO$_3$ nanocubes is raw material solubility. The particle sizes of the Nb$_2$O$_5$ raw material increase in accordance with the heat treatment temperature as shown in Figure 5. Large particles such as particles of Nb$_2$O$_5$ with monoclinic systems (Figure 5(f)) did not dissolve completely in the solvent during solvothermal synthesis; residual Nb$_2$O$_5$ particles with monoclinic systems were observed from the XRD data after the solvothermal reaction (Figure 4(f)). In other words, there is an ideal particle size for Nb raw materials employed in NaNbO$_3$ nanocube synthesis. NaNbO$_3$ nanocubes are confirmed in Figure 7(d,e). There are three similarities among the two Nb raw materials in these solvothermal syntheses. First, the particle size of the Nb raw materials was on the order of tens of nanometers. Second, the particles were spherical in shape. And third, the crystal systems were orthorhombic. These three factors lead to NaNbO$_3$ nanocube formation via the solvothermal method. In this study, the obtained NaNbO$_3$ nanocubes had neither a uniform particle size nor many

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Figure 7. SE images of NaNbO$_3$ produced via the solvothermal method. Heat-treatment temperatures applied to the raw material: (a) precursor, (b) 300°C, (c) 500°C, (d) 600°C, (e) 800°C, and (f) 1000°C. Time of heat treatment: 2 h. Acceleration voltages of the SE images: (a, b) 200 kV, (c-f) 10 kV.

Figure 8. STEM observations of NaNbO$_3$ produced via the solvothermal method. Heat-treatment temperature applied to the raw material: 800°C. Time of heat treatment: 2 h. Acceleration voltage of the SE image: 200 kV. (a) SE image, (b) BF image, (c) HAADF image.
dispersion particles. Therefore, this study shows that irregular particle sizes and a lack of dispersion particles in the Nb raw material lead to the irregular particle sizes in the obtained NaNbO₃ nanocubes. Thus, uniform NaNbO₃ nanocubes can be obtained if the Nb raw material’s particle size and dispersion are uniform.

4. Conclusions

In conclusion, we were able to successfully control the NaNbO₃ morphology during nanocube formation. The NaNbO₃ particle size was in the range of tens of nanometers. In this study, we observed that raw materials and reaction mediums are important factors to consider when conducting NaNbO₃ nanocube synthesis. A two-step process enables the formation of NaNbO₃ nanocubes: the first step is synthesis of the raw material, and the second is solvothermal synthesis of NaNbO₃ nanocubes. We used orthorhombic \( \text{N}_2\text{O}_5 \) as a raw material to yield NaNbO₃ nanocubes. Methanol was used as a reaction medium during the solvothermal method. The raw material's solubility affects the morphology of the obtained powder. Solubility can be controlled and determined via certain combinations of raw materials and reaction mediums. A combination of orthorhombic \( \text{N}_2\text{O}_5 \) and methanol enables the formation of NaNbO₃ nanocubes via the solvothermal method.

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Disclosure statement

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