Microstructural Evolution During Crystallization of $\text{Ba}_5\text{Nb}_4\text{O}_{15}$ from Ba–Nb Ethoxide

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Ba–Nb エトキシドから $\text{Ba}_5\text{Nb}_4\text{O}_{15}$ の結晶化過程の微構造的考察

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$\text{Ba}_5\text{Nb}_4\text{O}_{15}$ was successfully crystallized from Ba–Nb ethoxide by heating. Microstructural characterization of specimens annealed at various temperatures was performed by using a transmission electron microscope (TEM). Below 673 K, the ethoxide was decomposed to an amorphous matrix. At 773 K, small crystals with a size of 2–3 nm formed in the amorphous phase. The crystal was grown by heating, and then $\text{Ba}_5\text{Nb}_4\text{O}_{15}$ crystals 70–150 nm in size formed at 1173 K. The crystallization process was successfully observed *in situ* by TEM using a thermal specimen stage. The grain growth process from polycrystal to five single crystals could be recorded. We propose a formation mechanism of $\text{Ba}_5\text{Nb}_4\text{O}_{15}$ from Ba–Nb ethoxide.

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1. Introduction

Dielectric resonators (DRs) play an important role in the miniaturization of microwave components. In order to reduce the size of DRs, it is necessary to increase the dielectric constant value of the material.¹⁾ $\text{Ba}_5\text{Nb}_4\text{O}_{15}$ has a five-layer perovskite-related structure.²⁾ The compound has been reported to have dielectric and luminescence properties, and it has been a useful material in microwave communication applications.^{3),4)} Ratheesh et al.⁵⁾ reported good values of the dielectric properties of $\text{Ba}_5\text{Nb}_4\text{O}_{15}$: the value of quality factor ($Q \times f$) was 53000 GHz at 16 GHz and that of dielectric constant (ϵ_r) was 40.

For fabrication of advanced electronic components, high-quality powders are required; these must provide homogeneous quality, fine grains, and uniform grain sizes. In general, $\text{Ba}_5\text{Nb}_4\text{O}_{15}$ is produced by solid-state reactions at the higher temperature of 1473 K. Recently, Suyama et al. reported a new preparation route of the compounds BaTiO_3 ⁶⁾ and $\text{Ba}_5\text{Nb}_4\text{O}_{15}$,⁷⁾ in which this compound could be successfully synthesized from double-metal alkoxides. This method could achieve synthesis at low temperature and obtain fine particles.

In the present work, the specimens obtained from Ba–Nb ethoxide annealed at various temperatures were observed with a high-resolution transmission electron microscope (HRTEM). Next, we tried to prepare a $\text{Ba}_5\text{Nb}_4\text{O}_{15}$ crystal from Ba–Nb ethoxide on the thermal stage of a TEM device and observe *in situ* the crystallization process of the $\text{Ba}_5\text{Nb}_4\text{O}_{15}$ crystal. We discuss the formation mechanism of the $\text{Ba}_5\text{Nb}_4\text{O}_{15}$ crystal by a new preparation method.

2. Experimental procedure

$\text{Nb}(\text{OEt})_5$ and $\text{Ba}(\text{OEt})_2$ were synthesized in ethanol from Nb_2O_5 and Ba metal, respectively. A crystal of Ba–Nb ethoxide was obtained from the $\text{Nb}(\text{OEt})_5$ and $\text{Ba}(\text{OEt})_2$. The procedure has been reported in detail elsewhere.⁷⁾

The crystal was annealed at 373–1273 K in air for 1.5 h.

Those specimens were structurally analyzed by powder X-ray diffraction (XRD) (Rigaku RINT–2000, Cu K α , Tokyo) and a high-resolution transmission electron microscope (HRTEM) (JEM–3000F, JEOL) equipped with energy-dispersed spectroscopy (EDS).

The crystallization process was observed *in situ* by TEM (JEM–2000EX) using a thermal stage (EM–SHH4). The Ba–Nb ethoxide was annealed at 873 K in air for 1.5 h and was used as a starting material for *in situ* TEM observation. The temperature on the stage was controlled by hand from room temperature to 1173 K. The heating rate was about 800 K/0.5 h. The observed temperature used was 973 K, 1133 K, and 1173 K. The temperature was kept at 1133 K for 75 minutes for *in situ* observation. TEM images were recorded in real time using a video device.

3. Results and discussions

3.1 Structures of the Ba–Nb ethoxide annealed at various temperatures

A crystal of Ba–Nb ethoxide, whose sizes were 1–5 mm with rectangular shapes, was heated at various temperatures in the range of 373–1273 K.

Figure 1 shows powder XRD patterns of specimens annealed at various temperatures. The crystal of Ba–Nb ethoxide was decomposed to an amorphous state by heating. At >973 K, small peaks appeared, which indicated existence of $\text{Ba}_5\text{Nb}_4\text{O}_{15}$ crystals with a trigonal phase ($a=0.5798$ nm, $c=1.1746$ nm, $\gamma=120^\circ$ calculated as a hexagonal axis at 1073 K). Those peak intensities increased by increasing temperature. A small amount of BaNb_2O_6 crystals with monoclinic phase was involved, as indicated by the white circles. ($a=0.3952$, $b=0.6049$, $c=1.0434$ nm, $\beta=90.35^\circ$ [Inorganic Crystal Structure Database ICSD #39272]).

We observed TEM images to examine the exact temperature at which the crystals begin to form in the amorphous matrix. **Figure 2** shows TEM images of specimens annealed at 473 K in

Fig. 1. Powder XRD patterns of specimens annealed at various temperatures.

Fig. 2. HRTEM images and SAD patterns of specimens annealed at various temperatures for 1.5 h in air. (a) at 473 K, (b) at 673 K, (c) at 773 K and (d) at 873 K.

(a), 673 K in (b), 773 K in (c), and 873 K in (d). Below 673 K, the specimen was an amorphous state, as seen in the halo patterns. At 773 K, small crystalline phases formed in the amorphous matrix with sizes of 2–5 nm in Fig. 2(c). The crystalline phases grown to an average of 10 nm at 873 K, and the selected area diffraction (SAD) pattern showed a polycrystalline ring, as seen in Fig. 2(d). At 973 K, the crystalline region extended to the hole of the specimen and the crystalline sizes grew to 20–30 nm as shown in Fig. 3 (a). In the enlarged image enclosed by the rectangle in Fig. 3(a), a lattice image with a repeat distance of 0.24 nm was observed along the c -direction as a $\text{Ba}_5\text{Nb}_4\text{O}_{15}$ crystal with a trigonal structure, as shown in Fig. 3(b). The inset image is a Fourier transform pattern from the TEM image. The periodicity, however, did not correspond to that of $\text{Ba}_5\text{Nb}_4\text{O}_{15}$. The periodicity of $\text{Ba}_5\text{Nb}_4\text{O}_{15}$ is 5 times that of perovskite-like blocks along the c -axis in the unit cell. The stacking was caused by the mixture of cubic closed-packed (ccp) and hexagonal closed-packed

Fig. 3. (a) TEM image and SAD pattern of specimen annealed at 973 K for 1.5 h in air. (b) Enlarged image enclosed by the rectangle in (a), and inset is a Fourier transform pattern.

Fig. 4. HRTEM image taken from the $[0001]$ zone axis. For a specimen annealed at 973 K for 1.5 h in air. Inset is a Fourier transform pattern.

(hcp) sequences, as hhc (5H).

Figure 4 shows a TEM image of the specimen annealed at 973 K taken from the $[0001]$ zone axis. The inset image is a Fourier transform pattern from the TEM image. Small crystals embedded in the amorphous matrix and the orientation of each crystal comes to match each other, and the crystalline size becomes larger. In the simulated diffraction image, strong reflection appeared with rhombohedral symmetry ($-h+k+l=3n$), but few weak reflections were observed as a trigonal cell. These results showed that the structure of the specimen annealed at 973 K was not as complete as the $\text{Ba}_5\text{Nb}_4\text{O}_{15}$ crystal.

When the specimen was annealed at 1173 K, the crystal grew to 70–150 nm in size. Figure 5 shows a TEM image and EDS spectra of the crystals annealed at 1173 K. The inset image is an HRTEM image of one crystal taken from the $[2\bar{1}10]$ zone

axis. The periodicity of the crystal was 5 times along the *c*-direction, as shown in the HRTEM image and diffraction pattern. The SAD pattern included weak streaks along the *c**-direction, indicating that stacking faults occur on the (000*l*) plane. Each small crystal in the crystalline block was analyzed by EDS. As the result, two types of phases were produced from the Ba₅Nb₄O₁₅ ethoxide, and numbers 1 and 2 corresponded to Ba₅Nb₄O₁₅ and BaNb₂O₆, respectively. The crystal block involved a small amount of BaNb₂O₆ crystal.

3.2 *In situ* observation of crystallization process of Ba₅Nb₄O₁₅ by heating in TEM

The crystallization process was observed *in situ* in a TEM device using a hot stage. The starting material was used a specimen annealed at 873 K in air for 1.5 h., which has small crystals in the amorphous matrix. **Figure 6** shows the changes in the microstructure of the crystalline phase during TEM observation from ambient temperature to 1173 K on the hot stage. Small crystals grew on the hot stage, and at 1133 K, dark contrast regions as a crystal phase increased in the matrix, as seen in Fig. 6(c). The temperature was kept at 1133 K for about 85 min. During observation at that temperature, the polycrystal containing an amorphous phase became dense crystals (Fig. 6(e)). At 1173 K, the bulk consisted of

five crystals, as shown in Fig. 6(f). The area enclosed by the rectangle was focused on and recorded on video tape. **Figure 7** shows the structural changes at 1133 K for 50 minutes. The crystal region extended into the hole of the matrix during time of 10 : 20–10 : 40. In the next step, the boundaries moved by merging the small grains. At 11 : 00, crystal 1 moved toward the large crystal. From 11 : 06 to 11 : 08, the boundary between the crystal 1 and 2 moved quickly, and small crystal 2 moved toward crystal 1. Eventually, crystals 1 and 2 disappeared. These movements occurred with decreasing the boundary's energy, as seen in ZrO₂.⁸⁾ However, crystal 3 remained at 11 : 10. This finding indicated that crystal 3 was not the same as crystals 1, 2 and the large crystal, and, therefore, crystal 3 did not diffuse in the large crystal. These findings showed that each crystal of Ba₅Nb₄O₁₅ and BaNb₂O₆ grew separately by merging small crystals with the same structure.

The product in the TEM device was characterized by HRTEM equipped with EDS. Two types of structures were observed in the product, as shown in **Fig. 8**: Ba₅Nb₄O₁₅ crystal and BaNb₂O₆ crystal. Figure 8(b) is an HRTEM image of a

Fig. 5. TEM image of specimen annealed at 1173 K for 1.5 h in air. Inset is a HRTEM image of one crystal and SAD pattern. EDS spectra are obtained from crystal 1 and crystal 2, respectively.

Fig. 7. Enlarged TEM images enclosed by the rectangle in Fig. 5, from 10 : 20 to 11 : 10 A.M.

Fig. 6. Structural changes in the specimens by heating in TEM. Starting material is used a specimen annealed at 873 K for 1.5 h in air.

BaNb_2O_6 crystal taken from the $[2\bar{2}1]$ zone axis, and the inset is the corresponding SAD pattern. In Fig. 8(a), HRTEM image of $\text{Ba}_5\text{Nb}_4\text{O}_{15}$ crystal showed the 5 times of stacking sequence along the c -direction, although stacking disorders were included in the structure. However, oxygen content was lower than that of $\text{Ba}_5\text{Nb}_4\text{O}_{15}$ produced in air. As a result, the product was an oxygen-deficient $\text{Ba}_5\text{Nb}_4\text{O}_{15-x}$ crystal due to the vacuum condition in TEM device. The oxygen-deficient structure of the $\text{Ba}_5\text{Nb}_4\text{O}_{15-x}$ crystal has been reported by Pa-gola et al.⁹⁾

4. Discussions

We successfully crystallized *in situ* a $\text{Ba}_5\text{Nb}_4\text{O}_{15}$ by heating and observed using the hot stage in TEM. However, it had an oxygen-deficient structure because of the lack of oxygen pressure in TEM device. Therefore, preparation of a stoichiometric compound of $\text{Ba}_5\text{Nb}_4\text{O}_{15}$ is needed in an oxygen atmosphere. On the other hand, BaNb_2O_6 could be formed from the matrix without external oxygen. The lattice parameters of the compound annealed above 1073 K in air were calculated,

and the parameter of the c -axis increased with increasing temperature from 1073 K to 1273 K.⁷⁾ From the result, we assumed that oxygen was taken into the compound around those temperatures, and the structure with a stoichiometric composition was formed. This assumption was supported by the TG-DTA results for $\text{Ba}_5\text{Nb}_4\text{O}_{15}$ reported by Suyama et al., in which an exothermic reaction peak appeared at 973 K and around 1073 K,⁷⁾ and no exothermic reaction peak appeared in the case of BaTiO_3 .⁶⁾ The exothermic reaction peak was caused by the reaction with oxygen to crystallize the $\text{Ba}_5\text{Nb}_4\text{O}_{15}$.

We summarize the microstructural evidence in the schematic illustration of Fig. 9. Figure 9 shows the crystallization process of $\text{Ba}_5\text{Nb}_4\text{O}_{15}$ from Ba5-Nb4 ethoxide. In this process, the major reaction is assumed to occur by the following equation:

The weight loss between room temperature and 473 K in the TG curve⁷⁾ was caused by the generation of ethylene, ethanol and benzene from the ethoxide, as reported in BaTiO_3 .⁶⁾ Above 1173 K, single grains were made by the merging of small crystals around the large crystal and, accordingly, denser and larger grains were formed. The process was dominated by the crystal structure. In this experimental stage, a small amount of BaNb_2O_6 crystal formed. The reason for this might have been the formation of Ba1-Nb2 ethoxide as an impurity phase. The dielectric property of a $\text{Ba}_5\text{Nb}_4\text{O}_{15}$ - BaNb_2O_6 mixture was investigated as a microwave application by Kim et al.¹⁰⁾ In the future, preparation of a pure grain of $\text{Ba}_5\text{Nb}_4\text{O}_{15}$ will be possible through a pure Ba5-Nb4 ethoxide prepared by heating.

5. Conclusions

We succeeded in obtaining a $\text{Ba}_5\text{Nb}_4\text{O}_{15}$ grain with a grain size of the order of nanometers from a Ba5-Nb4 ethoxide by heating.

The structures of specimens annealed at various temperatures in air were characterized carefully by high-resolution

Fig. 8. HRTEM images and EDS spectra of product annealed at 1173 K in TEM; (a) and (c) $\text{Ba}_5\text{Nb}_4\text{O}_{15-x}$, (b) and (d) BaNb_2O_6 .

Fig. 9. Illustration of the formation mechanism of $\text{Ba}_5\text{Nb}_4\text{O}_{15}$ from Ba5-Nb4 ethoxide by heating.

TEM equipped with EDS. Furthermore, *in situ* observation of the crystal growth was performed using a hot stage in a TEM device from ambient temperature through 1173 K. Structural change in the $\text{Ba}_5\text{Nb}_4\text{O}_{15}$ crystal by heating was successfully occurred and recorded, in which the polycrystals with an average size of 10 nm became five single crystals of 70 nm in the TEM device. The product in the TEM device was, however, an oxygen-deficient compound of $\text{Ba}_5\text{Nb}_4\text{O}_{15-x}$ under a vacuum condition.

We propose a formation process of the $\text{Ba}_5\text{Nb}_4\text{O}_{15}$ crystal from the $\text{Ba}_5\text{-Nb}_4$ ethoxide as follows. Below 673 K, a crystal of $\text{Ba}_5\text{-Nb}_4$ ethoxide was decomposed to the amorphous phase by heating, and organic gases were generated with weight loss. At 773 K, small crystals appeared in the amorphous matrix. With increasing temperature, those crystals became larger and denser by merging the small crystals. At 1173 K, $\text{Ba}_5\text{Nb}_4\text{O}_{15}$ crystals 70–150 nm in size formed successfully in which the crystals formed by taking in oxygen in air.

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