Preparation of needle-like NaNbO$_3$ by molten NaOH method

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Needle-like NaNbO$_3$ has been prepared in two steps by a molten NaOH method. First, Na$_7$(H$_3$O)Nb$_6$O$_{19}$·14H$_2$O precursor was synthesized by the reaction of Nb$_2$O$_5$ with a molten NaOH at 450°C for 50 h in air. The Na$_7$(H$_3$O)Nb$_6$O$_{19}$·14H$_2$O precursor was a needle-like single crystal 0.25–1.5 µm wide and >3 µm long. Then, the Na$_7$(H$_3$O)Nb$_6$O$_{19}$·14H$_2$O precursor crystal transformed to NaNbO$_3$ through an intermediate Na$_7$(H$_3$O)Nb$_6$O$_{19}$ by a heating above 500°C. The NaNbO$_3$ was a needle-like polycrystal with a perovskite-type structure.

1. Introduction

Pb(Zr,Ti)O$_3$ (PZT) has been widely used in several applications due to its excellent piezoelectric properties. However, PZT contains a large concentration of harmful lead. Therefore, developing lead-free piezoelectric materials is desired. Among lead-free piezoelectric materials, alkali niobate families, such as (K$_{0.5}$Na$_{0.5}$)NbO$_3$ (KNN) and (Na$_{0.52}$K$_{0.44}$Li$_{0.04}$)(Nb$_{0.84}$Ta$_{0.10}$Sb$_{0.06}$)O$_3$ (LF4), exhibit large piezoelectric properties comparable to PZT.[1)–4)]

We have previously reported that KNbO$_3$ (KN), KNN, and LF4 materials could be synthesized at 500–600°C through a modified solid-state solution method using metal oxide, alkali oxalate, and urea.[5)–7)] However, toxic NH$_3$ gas is evolved in this process. Zhu et al. reported that NaNbO$_3$ was synthesized from Nb$_2$O$_5$ and NaOH aqueous solution by a hydrothermal process.[8)] In this process, a high-pressure condition is required. Recently, some oxide superconductors were synthesized by a molten hydroxide route at low temperatures.[9)] The molten hydroxide process does not require high temperature, high pressure, or emission of toxic gases.

NN is a promising lead-free piezoelectric material and exhibits interesting behavior under an electric field.[1),10)] However, there is no report on synthesis of NN by a molten hydroxide process. In this study, we synthesized NN by the molten NaOH route.

2. Experimental

The NaNbO$_3$ was synthesized in two steps, preparation and then heating of the precursor compound. Nb$_2$O$_5$ (99.9%) and NaOH (>98%) starting powders were weighed with a molar ratio of Nb$_2$O$_5$:NaOH = 1:10. Weighed Nb$_2$O$_5$ and NaOH (m.p. = 318°C) powders were put into an Al$_2$O$_3$ crucible and heated at 450°C for 5 h and 50 h in air, respectively. The sample in the crucible was washed with distilled water to remove the excess NaOH. Washed powder was filtrated and dried at 150°C for 15 min. Then, the obtained white precursor powder was heated at 500°C for 4 h in air.

The samples were analyzed by powder X-ray diffraction (XRD; Rigaku RINT 2500V X-ray diffractometer using Cu Kα

radiation). The morphologies of the obtained powders were observed in a scanning electron microscope (SEM; KEYENCE VE-9800) and a transmission electron microscope (TEM; JEOL JEM-2100 operated at 200 kV). A transmission electron diffraction (TED) pattern was obtained by TEM. Thermogravimetry (TG) and differential temperature analysis (DTA) of the precursor powder were performed on a TG-DTA2000SA (Bruker). The sample was put on a platinum vessel and 20%O$_2$ gas diluted by N$_2$ gas was flowed at 50 ml/min. The sample was heated at a rate of 200°C/h. α-Al$_2$O$_3$ was used as a reference sample.

3. Results and discussion

Figure 1(a) shows an SEM micrograph of the precursor powder obtained by the reaction of Nb$_2$O$_5$ with the molten NaOH for 50 h. The precursor powder had a needle-like shape that was 0.25–1.5 µm wide and >3 µm long. **Figure 2**(a) shows the X-ray diffraction (XRD) pattern of the precursor powder. Figure 2(b) and (c) show XRD patterns of the starting material, Nb$_2$O$_5$, and a simulated XRD pattern of NaNbO$_3$ (ICSD#97669) for reference. The XRD pattern of the precursor powder was obviously different from those of Nb$_2$O$_5$ and NaNbO$_3$.

Recently, Ke et al. prepared needle-like Na$_2$Nb$_2$O$_6$·H$_2$O crystal by the reaction of Nb$_2$O$_5$ with 10 M NaOH solution by a hydrothermal synthesis method.[11)] We considered that our precursor powder was a kind of sodium niobate hydrate. However, the XRD pattern of our powder was different from that of Na$_2$Nb$_2$O$_6$·H$_2$O.[8),11)] In the hydrothermal process, Na$_{8−x}$(H$_3$O)$_x$Nb$_6$O$_{19}$·nH$_2$O was formed as an intermediate compound.[8)] The simulated XRD pattern of Na$_7$(H$_3$O)Nb$_6$O$_{19}$·14H$_2$O (ICSD#200967) is shown in Fig. 2(d). Na$_7$(H$_3$O)Nb$_6$O$_{19}$·14H$_2$O corresponds to Na$_{8−x}$(H$_3$O)$_x$Nb$_6$O$_{19}$·nH$_2$O with $x = 1.0$ and $n = 14$. The XRD pattern of Na$_7$(H$_3$O)Nb$_6$O$_{19}$·14H$_2$O is similar to that of the precursor powder obtained by the reaction of Nb$_2$O$_5$ with a molten NaOH. Therefore, we understood that Na$_7$(H$_3$O)Nb$_6$O$_{19}$·14H$_2$O was synthesized by the reaction of Nb$_2$O$_5$ with molten NaOH. Zhu et al. reported that Na$_2$Nb$_2$O$_6$·H$_2$O was prepared through the intermediate compound of Na$_7$(H$_3$O)Nb$_6$O$_{19}$·14H$_2$O by a hydrothermal synthesis method.[8)] Na$_2$Nb$_2$O$_6$·H$_2$O was converted to NaNbO$_3$ by heating. However, Na$_2$Nb$_2$O$_6$·H$_2$O was not observed in the present molten NaOH process. We thought that a high-pressure condition would be required for the formation of Na$_2$Nb$_2$O$_6$·H$_2$O. Figure 1(b) shows

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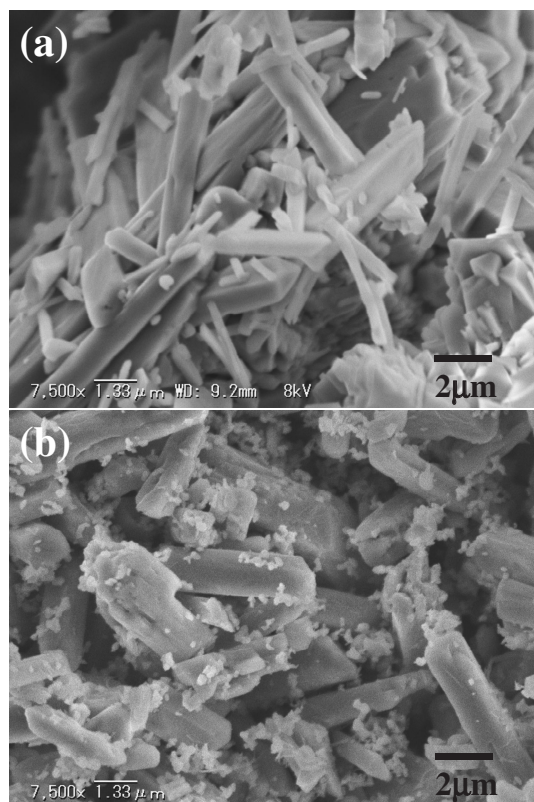
Fig. 1.   SEM micrograph of Na$_7$(H$_3$O)Nb$_6$O$_{19}$·14H$_2$O synthesized by the reaction of Nb$_2$O$_5$ with molten NaOH for (a) 50 h and (b) 5 h.
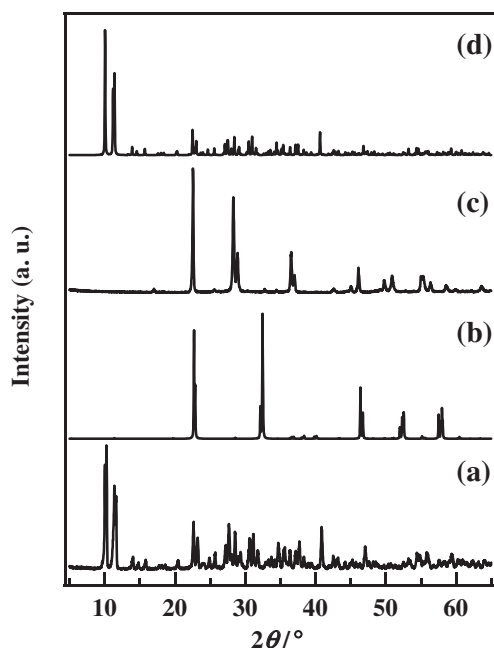
Fig. 2.   X-ray diffraction patterns of (a) Na$_7$(H$_3$O)Nb$_6$O$_{19}$·14H$_2$O synthesized by the reaction of Nb$_2$O$_5$ with a molten NaOH, (b) starting powder of Nb$_2$O$_5$, and simulations of (c) NaNbO$_3$ (ICSD#97669) and (d) Na$_7$(H$_3$O)Nb$_6$O$_{19}$·14H$_2$O (ICSD#200967).

an SEM micrograph of the precursor powder obtained by the reaction of Nb$_2$O$_5$ with the molten NaOH for 5 h. The obtained powder was Na$_7$(H$_3$O)Nb$_6$O$_{19}$·14H$_2$O as confirmed by XRD. We found that Na$_7$(H$_3$O)Nb$_6$O$_{19}$·14H$_2$O was synthesized after 5 h by
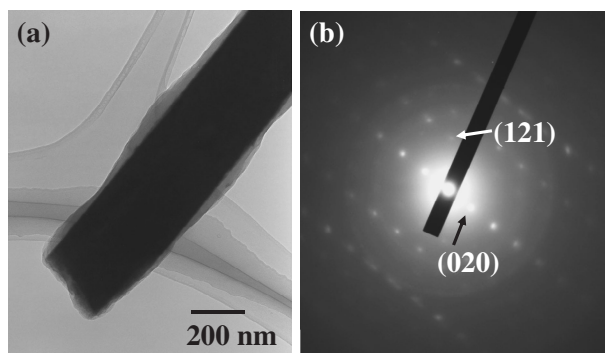
Fig. 3.   (a) TEM micrograph and (b) TED pattern of Na$_7$(H$_3$O)Nb$_6$O$_{19}$·14H$_2$O synthesized by the reaction of Nb$_2$O$_5$ with a molten NaOH.
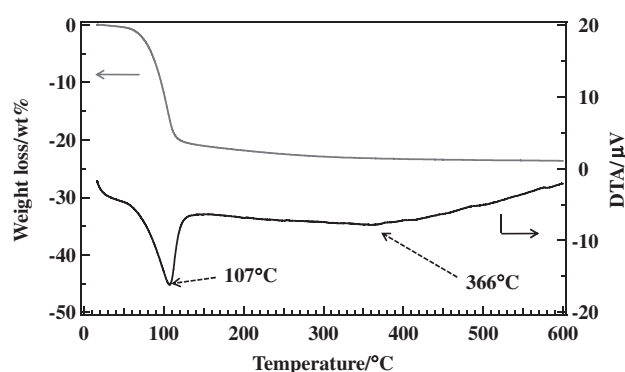
Fig. 4.   TG–DTA curves of Na$_7$(H$_3$O)Nb$_6$O$_{19}$·14H$_2$O synthesized by the reaction of Nb$_2$O$_5$ with a molten NaOH.

the molten NaOH method. Although needle-like Na$_7$(H$_3$O)-Nb$_6$O$_{19}$·14H$_2$O could be observed, a lot of small particles were formed. Therefore, a long reaction time would be required to obtain needle-like Na$_7$(H$_3$O)Nb$_6$O$_{19}$·14H$_2$O without small particles.

A TEM micrograph of the Na$_7$(H$_3$O)Nb$_6$O$_{19}$·14H$_2$O precursor compound is shown in **Fig. 3**(a). Na$_7$(H$_3$O)Nb$_6$O$_{19}$·14H$_2$O is a homogeneous needle-like crystal without any grain boundaries. Figure 3(b) shows the TED pattern of Na$_7$(H$_3$O)Nb$_6$O$_{19}$·14H$_2$O. Clear diffraction spots could be observed and the indices of the diffraction spots could be indexed on the basis of orthorhombic Na$_7$(H$_3$O)Nb$_6$O$_{19}$·14H$_2$O structure (space group: *Pmnn*, lattice parameters: $a = 10.072$ Å, $b = 12.148$ Å, $c = 12.722$ Å). Therefore, we understood that the needle-like Na$_7$(H$_3$O)Nb$_6$O$_{19}$·14H$_2$O crystal was a single crystal. The growth direction of needle-like Na$_7$(H$_3$O)Nb$_6$O$_{19}$·14H$_2$O crystal was determined to be along the $\langle 101 \rangle$ axis.

To obtain perovskite-type NaNbO$_3$ from the Na$_7$(H$_3$O)-Nb$_6$O$_{19}$·14H$_2$O precursor crystal, we investigated the dehydration behavior of Na$_7$(H$_3$O)Nb$_6$O$_{19}$·14H$_2$O by TG–DTA. **Figure 4** shows TG–DTA curves of Na$_7$(H$_3$O)Nb$_6$O$_{19}$·14H$_2$O heated at 200°C/h in a mixed gas of 20% O$_2$ and 80% N$_2$. About 20% weight loss was observed at 55–110°C in the TG curve, and the corresponding endothermic peak appeared at about 107°C in the DTA curve. We thought that the weight loss resulted from the elimination of crystallization water or hydration water in Na$_7$(H$_3$O)Nb$_6$O$_{19}$·14H$_2$O. The 20% weight loss of Na$_7$(H$_3$O)-Nb$_6$O$_{19}$·14H$_2$O corresponds to the mass of 14.4H$_2$O. Therefore, we understood that the hydration water of ca. 14H$_2$O was eliminated in the temperature range of 55–110°C. The small
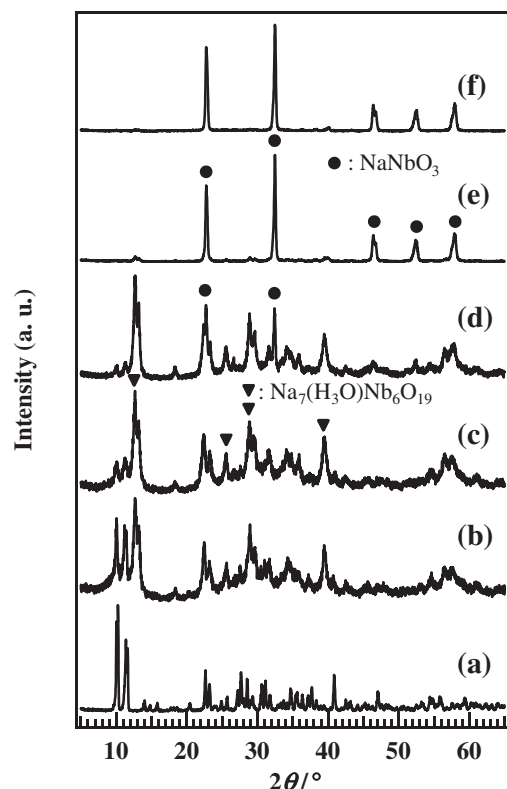
Fig. 5.   XRD patterns of (a) $Na_7(H_3O)Nb_6O_{19}\cdot14H_2O$ synthesized by the reaction of Nb_2O_5 with a molten NaOH and the $Na_7(H_3O)Nb_6O_{19}\cdot$ $14H_2O$ calcined at (b) 200°C, (c) 300°C, (d) 400°C, (e) 500°C, and (f) 600°C.

Fig. 6.   SEM image of $NaNbO_3$ obtained by heating of $Na_7(H_3O)$-$Nb_6O_{19}\cdot14H_2O$ at 500°C for 4 h.

Fig. 7.   (a) TEM micrograph and (b) TED pattern of $NaNbO_3$ synthesized by the heating of $Na_7(H_3O)Nb_6O_{19}\cdot14H_2O$ precursor compound.

weight loss continued until ca. 500°C. The total weight loss of 22% is equal to the mass of $15.8H_2O$ in $Na_7(H_3O)Nb_6O_{19}\cdot$ $14H_2O$. Therefore, the dehydration reaction would be completely finished at 500°C. Moreover, the slope of the DTA curve clearly changed at 366°C. We thought that the elimination rate of H_2O from precursor crystals almost changed at 366°C under the TG–DTA condition.

To confirm the results of TG–DTA, the $Na_7(H_3O)Nb_6O_{19}\cdot$ $14H_2O$ precursor was heated at several temperatures for 3 h in air and then the heated samples were analyzed by powder X-ray diffraction. **Figure 5**(a)–(f) show the XRD patterns of the $Na_7(H_3O)Nb_6O_{19}\cdot14H_2O$ precursor and the samples heated at 200, 300, 400, 500 and 600°C. The diffraction peaks at 12.6, 13.2, 25.5, and 39.4° are observed for the sample heated at 200°C as shown in Fig. 5(b). These peaks are attributed to $Na_7(H_3O)$-Nb_6O_{19}, which corresponds to $Na_{8-x}(H_3O)_xNb_6O_{19}\cdot nH_2O$ with $x = 1.0$ and $n = 0$.[8] The $Na_7(H_3O)Nb_6O_{19}$ remained for the sample heated at 400°C. Further, several diffraction peaks were observed at 22.7, 32.4, 46.3, 52.2, and 55.8° for the sample heated at 400°C, as shown in Fig. 5(d). These peaks are attributed to a perovskite-type $NaNbO_3$. When $Na_7(H_3O)Nb_6O_{19}\cdot$ $14H_2O$ was heated at 500°C for 3 h, most of it transformed to a perovskite-type $NaNbO_3$. Single phase $NaNbO_3$ could be obtained by heating at 600°C for 3 h. An SEM image of the obtained $NaNbO_3$ powder is shown in **Fig. 6**. The $NaNbO_3$ powders maintained the needle-like shape of the $Na_7(H_3O)$-$Nb_6O_{19}\cdot14H_2O$ single crystal. A TEM image and TED pattern of $NaNbO_3$ are shown in **Fig. 7**(a) and (b), respectively. These figures show that the needle-like $NaNbO_3$ is not a single crystal but a polycrystal.
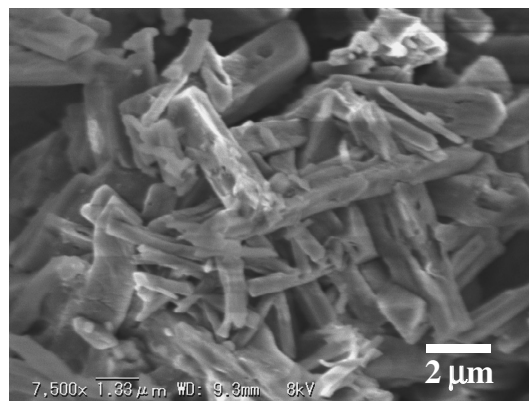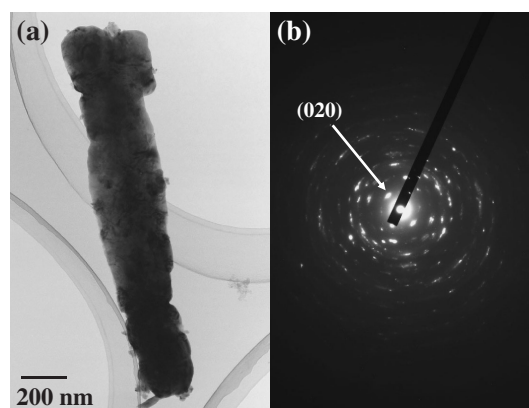
We discussed the formation mechanism of $NaNbO_3$ from the $Na_7(H_3O)Nb_6O_{19}\cdot14H_2O$ precursor based on the results of the TG–DTA and XRD. The TG–DTA profile showed that ca. $14H_2O$ was eliminated from $Na_7(H_3O)Nb_6O_{19}\cdot14H_2O$ in the temperature range of 55–110°C. On the other hand, XRD showed that $Na_7(H_3O)Nb_6O_{19}$ was formed after heating at 200°C. $Na_7(H_3O)$-Nb_6O_{19} corresponds to $Na_{8-x}(H_3O)_xNb_6O_{19}\cdot nH_2O$ with $x = 1.0$ and $n = 0$. $Na_7(H_3O)Nb_6O_{19}$ would be formed at low temperatures according to the following equation:

$$Na_7(H_3O)Nb_6O_{19}\cdot14H_2O$$
$$\rightarrow Na_7(H_3O)Nb_6O_{19} + 14H_2O\uparrow \qquad (1)$$
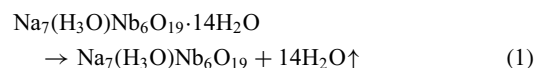
The decomposition of the formed $Na_7(H_3O)Nb_6O_{19}$ to $NaNbO_3$ starts at about 366°C by elimination of the crystal water because the slope of the DTA curve changed at 366°C and the formation of $NaNbO_3$ could be observed in the sample heated at 400°C. Although we did not have any information on excess Na, it might become NaOH as follows:

$$Na_7(H_3O)Nb_6O_{19} \rightarrow 6NaNbO_3 + NaOH + H_2O\uparrow \qquad (2)$$

In this way, $Na_7(H_3O)Nb_6O_{19}\cdot14H_2O$ decomposed to perovskite-type $NaNbO_3$ through intermediate $Na_7(H_3O)Nb_6O_{19}$ by heating above 400°C.

4.   Conclusion

Needle-like $NaNbO_3$ could be synthesized at 500°C by the molten NaOH method. The needle-like $Na_7(H_3O)Nb_6O_{19}\cdot14H_2O$

precursor single crystals were synthesized by the reaction of Nb_2O_5 with the molten NaOH at 450°C. The $Na_7(H_3O)Nb_6O_{19}\cdot14H_2O$ single crystal was 0.25–1.5 μm wide and >3 μm long. The growth of the orthorhombic needle-like $Na_7(H_3O)Nb_6O_{19}\cdot14H_2O$ crystal was in the ⟨101⟩ direction. Needle-like $NaNbO_3$ polycrystals were obtained by the dehydration of $Na_7(H_3O)Nb_6O_{19}\cdot14H_2O$ through an intermediate $Na_7(H_3O)Nb_6O_{19}$ under heating at 500°C.

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