



Synthesis of homogeneous $(\text{Na}_{1-x}\text{K}_x)\text{NbO}_3$ nanorods using hydrothermal and post-heat treatment processes

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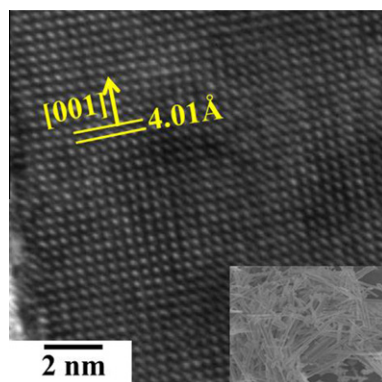
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HIGHLIGHTS

- ▶ NKN nanorods have been produced using hydrothermal method for the first time.
- ▶ The growth direction of the NKN nanorod is [001].
- ▶ $(\text{Na}_{8x}\text{K}_{8-8x})\text{Nb}_6\text{O}_{19} \cdot n\text{H}_2\text{O}$ produced at 160 °C and transformed into NKN nanorods at 500 °C.
- ▶ The NKN nanorods can be used for the piezoelectric energy harvester.

GRAPHICAL ABSTRACT



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ABSTRACT

To synthesize $(\text{Na}_{1-x}\text{K}_x)\text{NbO}_3$ nanorods, the Nb_2O_5 -added $(1-y)\text{NaOH}-y\text{KOH}$ specimens with $0.0 \leq y \leq 0.9$ were heated at 160 °C and subsequently annealed at 500 °C. Homogeneous Na-rich $(\text{Na}_{1-x}\text{K}_x)\text{NbO}_3$ nanorods were only synthesized for the specimen with $y = 0.15$. However, NaNbO_3 nanorods were formed for specimens with $y < 0.15$, and K-rich $(\text{Na}_{1-x}\text{K}_x)\text{NbO}_3$ nanoplates were obtained for specimens with $y > 0.2$. The $(\text{Na}_{8x}\text{K}_{8-8x})\text{Nb}_6\text{O}_{19} \cdot n\text{H}_2\text{O}$ transient phase was formed in the specimen with $y = 0.15$ heated at 160 °C for 8.0–12.0 h, and this phase transformed into the Na-rich $(\text{Na}_{1-x}\text{K}_x)\text{NbO}_3$ nanorods after annealing at 500 °C. Therefore, the formation of a homogeneous $(\text{Na}_{8x}\text{K}_{8-8x})\text{Nb}_6\text{O}_{19} \cdot n\text{H}_2\text{O}$ phase at a low temperature is very important for the synthesis of the $(\text{Na}_{1-x}\text{K}_x)\text{NbO}_3$ nanorods. The $(\text{Na}_{8x}\text{K}_{8-8x})\text{Nb}_6\text{O}_{19} \cdot n\text{H}_2\text{O}$ phase was considerably influenced by the heating temperature, and the processing time. The Na-rich $(\text{Na}_{1-x}\text{K}_x)\text{NbO}_3$ nanorods have rectangular shape with various sizes, and the growth direction of these nanorods is [001].

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1. Introduction

Wasted mechanical energy in the environment can be converted into electrical energy using piezoelectric nanogenerators. Recently, there has been increasing interest in piezoelectric nanogenerators,

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because they can be used to power wireless sensors and implantable biosensors without the need for a battery [1–6]. The output energy density (u) produced by a piezoelectric nanogenerator is given as $u = 1/2(d_{ij}^2/\epsilon_{ij})(F/A)^2$, where d_{ij} is the piezoelectric strain constant, ϵ_{ij} is the dielectric constant, F is the applied force, and A is the area [7]. Therefore, piezoelectric materials for the nanogenerator should have a large d_{ij} value to produce a large output energy. ZnO nanowires have been investigated for applications as piezoelectric nanogenerators, but the d_{ij} value of ZnO nanowires is

relatively small, 14.3–26.7 pm/V [8]. $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$ (PZT) nanowires have been also investigated because of their large d_{ij} value of 400 pm/V [9], but they contain more than 60.0 wt% of PbO, which leads to environmental problems [10–12]. Therefore, it is necessary to develop Pb-free piezoelectric nanowires that have good piezoelectric properties.

Toward this goal, Pb-free KNbO_3 nanowires have been investigated. They have been synthesized using the hydrothermal method [13–19] and also via templated crystallization of a precursor sol [20,21]. However, the processing time for KNbO_3 nanowires synthesized using the hydrothermal method is very long (6–7 days), and the templated crystallization of a precursor sol uses two-step processes that involve high processing temperatures. Many investigations have also been conducted on NaNbO_3 nanowires because of their piezoelectric properties and photocatalytic properties [22–24]. However, the NaNbO_3 oxides are known to be antiferroelectric [25]. The phase diagram of NaNbO_3 and KNbO_3 phases indicates that they form a complete solid solution of $(\text{Na}_{1-x}\text{K}_x)\text{NbO}_3$ for all composition ranges [26]. In particular, the $(\text{Na}_{0.5}\text{K}_{0.5})\text{NbO}_3$ oxides have been extensively investigated because of their large d_{33} value of approximately 120 pm/V and high Curie temperatures [10,27]. Moreover, the $(\text{Na}_{0.5}\text{K}_{0.5})\text{NbO}_3\text{--Li}(\text{Nb},\text{Ta},\text{Sb})\text{O}_3$ oxides produced using a reactive-templated grain growth method have been reported to exhibit a large d_{33} value of 300 pm/V that is similar to that of the PZT-based piezoelectric oxides [11,28,29]. Therefore, $(\text{Na}_{1-x}\text{K}_x)\text{NbO}_3$ nanowires are expected to have a large d_{33} value and thus may be promising piezoelectric nanogenerators. $(\text{Na}_{0.5}\text{K}_{0.5})\text{NbO}_3$ nanopowders have been investigated to a considerable extent for applications in bulk piezoelectric devices [30]. However, $(\text{Na}_{1-x}\text{K}_x)\text{NbO}_3$ -based nanowires and nanorods have not been investigated. Therefore, in this work, the synthesis of $(\text{Na}_{1-x}\text{K}_x)\text{NbO}_3$ nanorods has been investigated systematically, and $(\text{Na}_{1-x}\text{K}_x)\text{NbO}_3$ nanorods have been produced for the first time. Furthermore, the variations in the morphology and compositions of the phases with respect to the process conditions have been also studied.

2. Experimental procedures

Analytical-grade solid potassium hydroxide (KOH, >99%, High Purity Chemicals, Osaka, Japan), sodium hydroxide (NaOH, >99%, High Purity Chemicals, Osaka, Japan), and niobium oxide (Nb_2O_5 , 99.9%, High Purity Chemicals, Osaka, Japan) were used as the starting materials. A typical synthesis of $(\text{Na}_{1-x}\text{K}_x)\text{NbO}_3$ nanorods is as follows. Nb_2O_5 (0.002 mol) was added to a solution of $(1-y)\text{NaOH--yKOH}$ (14.0 mol) with $0.0 \leq y \leq 0.9$ in distilled water (40 mL). Then, the mixture was stirred for 2 h, poured into a Teflon vessel, and placed in an autoclave. The autoclave was heated to a temperature range of 140–180 °C for 8–20 h, and the sample was subsequently annealed at 500 °C for 6 h. The product was filtered, washed with distilled water, and dried at 80 °C for 12 h. The structural properties of the specimens were examined using X-ray diffraction (XRD; Rigaku D/max-RC, Tokyo, Japan). The shape and growth direction of the $(\text{Na}_{1-x}\text{K}_x)\text{NbO}_3$ nanorods were determined using scanning electron microscopy (SEM; Hitachi S-4300, Osaka, Japan) and field-emission transmission electron microscopy (FE-TEM; Tecnai F20, FEI, Netherlands).

3. Results and discussion

Fig. 1a–f shows the XRD patterns of the Nb_2O_5 -added $(1-y)\text{NaOH--yKOH}$ specimens with $0.0 \leq y \leq 0.9$ heated at 160 °C for 8 h. For the specimen with $y = 0.0$, peaks for the $\text{Na}_2\text{Nb}_2\text{O}_6\cdot\text{H}_2\text{O}$ (SOMS) [31], $\text{Na}_8\text{Nb}_6\text{O}_{19}\cdot 13\text{H}_2\text{O}$ (JCPDS No. 14-0370), and NaNbO_3 (JCPDS No. 82-0606) phases, indicated by stars, filled circles, and filled squares, respectively, were observed, as shown in Fig. 1a.

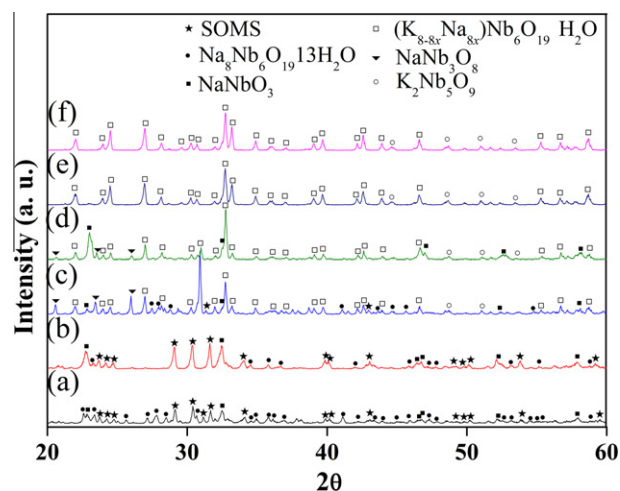


Fig. 1. XRD patterns of the Nb_2O_5 -added $(1-y)\text{NaOH--yKOH}$ specimens with $0.0 \leq y \leq 0.9$ heated at 160 °C for 8 h: (a) $y = 0.0$, (b) $y = 0.1$, (c) $y = 0.15$, (d) $y = 0.2$, (e) $y = 0.35$, and (f) $y = 0.9$.

According to previous work, $\text{Na}_8\text{Nb}_6\text{O}_{19}\cdot 13\text{H}_2\text{O}$ and SOMS are transition phases that form during the formation of the NaNbO_3 phase. Moreover, it has been reported that the $\text{Na}_8\text{Nb}_6\text{O}_{19}\cdot 13\text{H}_2\text{O}$ phase forms first and then transforms into SOMS and NaNbO_3 phases. Finally, the SOMS phase is converted into the NaNbO_3 phase at elevated temperatures [32]. Three phases were also observed for the specimen with $y = 0.1$, but the amounts of the SOMS and NaNbO_3 phases increased while that of the $\text{Na}_8\text{Nb}_6\text{O}_{19}\cdot 13\text{H}_2\text{O}$ phase decreased, as shown in Fig. 1b. For the specimen with $y = 0.15$, the amounts of the NaNbO_3 , SOMS, and $\text{Na}_8\text{Nb}_6\text{O}_{19}\cdot 13\text{H}_2\text{O}$ phases considerably decreased. However, new peaks for the $(\text{Na}_4\text{K}_4)\text{Nb}_6\text{O}_{19}\cdot 9\text{H}_2\text{O}$ (JCPDS No. 14-0360) phase, indicated by open squares, appeared, and it became a major phase in this specimen. In addition, the NaNb_3O_8 (JCPDS No. 20-1143) and $\text{K}_2\text{Nb}_5\text{O}_9$ (JCPDS No. 47-0081) phases were also newly produced in this specimen. Previously, peaks for the $(\text{Na}_4\text{K}_4)\text{Nb}_6\text{O}_{19}\cdot 9\text{H}_2\text{O}$ phase, which formed during the formation of $(\text{Na}_{1-x}\text{K}_x)\text{NbO}_3$ powders, were indexed as the $(\text{Na}_{8x}\text{K}_{8-8x})\text{Nb}_6\text{O}_{19}\cdot n\text{H}_2\text{O}$ [33] phase based on the molar concentrations of K^+ and Na^+ . Furthermore, this phase was reported to be a transient phase that transforms into $(\text{Na}_{1-x}\text{K}_x)\text{NbO}_3$ nanopowders at 220–240 °C when sufficient processing time is allowed [33,34]. For the specimen with $y = 0.2$, the SOMS and $\text{Na}_8\text{Nb}_6\text{O}_{19}\cdot 13\text{H}_2\text{O}$ phases disappeared, but the amount of NaNbO_3 phase considerably increased, as shown in Fig. 1d. When the y value exceeded 0.2, the Na-related phases, such as the NaNbO_3 and NaNb_3O_8 phases, disappeared, but the $(\text{Na}_{8x}\text{K}_{8-8x})\text{Nb}_6\text{O}_{19}\cdot n\text{H}_2\text{O}$ phase and a small amount of $\text{K}_2\text{Nb}_5\text{O}_9$ phase were found, as shown in Fig. 1e and f.

Fig. 2a–f shows the XRD patterns of the Nb_2O_5 -added $(1-y)\text{NaOH--yKOH}$ specimens with $0.0 \leq y \leq 0.9$ specimens annealed at 500 °C for 6 h after being heated at 160 °C for 8 h. A homogeneous NaNbO_3 phase with an orthorhombic structure was observed from the specimens with $y \leq 0.1$, as shown in Fig. 2a and b. It is believed that the SOMS and $\text{Na}_8\text{Nb}_6\text{O}_{19}\cdot 13\text{H}_2\text{O}$ transient phases transformed into the orthorhombic NaNbO_3 phase during the annealing at 500 °C, and this transformation has been generally observed during the formation of NaNbO_3 nanowires [32]. For the specimen with $y = 0.15$, the homogeneous Na-rich $(\text{Na}_{1-x}\text{K}_x)\text{NbO}_3$ phase, which is discussed later, was observed, as shown in Fig. 2c. However, both the K-rich $(\text{Na}_{1-x}\text{K}_x)\text{NbO}_3$ and NaNbO_3 phases, which are shown later, were formed for the specimen with $y = 0.2$ (see Fig. 2d). Finally, when y exceeded 0.2, the homogeneous K-rich $(\text{Na}_{1-x}\text{K}_x)\text{NbO}_3$ phase developed, as shown in Fig. 2e and f. Therefore, the NaNbO_3 phase formed in the speci-

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