



# Preparation of nanocrystalline perovskite $\text{KNbO}_3$ by peroxo-precursor decomposition method

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## ABSTRACT

Nanocrystalline perovskite  $\text{KNbO}_3$  is prepared by a peroxo-precursor decomposition method at moderate temperatures of 650–900 °C. Peroxo-heteropoly-niobic acid is prepared by direct reaction between NbC powder and  $\text{H}_2\text{O}_2$  aq, and mixing the peroxo-heteropoly-niobic acid with KOH aq yields an amorphous precursor salt. Perovskite  $\text{KNbO}_3$  is obtained by heating the precursor in air for 1 h at 650–900 °C. The X-ray diffraction patterns were well fitted with the space group  $Pm\bar{3}m$  in the Rietveld analysis. The X-ray diffraction peak profiles and field emission scanning electron microscope images indicate the crystallite size is in the range of 25–35 nm.

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## 1. Introduction

Potassium niobate ( $\text{KNbO}_3$ ) is an important ferroelectric material for acousto-optic, electro-optic, nonlinear optical, and photorefractive applications in frequency doublers, optical waveguides, and holographic storage devices [1]. It is also of interest for replacing the piezoelectric lead zirconate titanate (PZT) materials because of the toxicity of lead [2]. Potassium niobate is conventionally prepared by solid state reactions between potassium carbonate and niobium oxide [3]. However, the heterogeneous mixing of the starting materials and the evaporation of potassium oxide make it difficult to obtain a homogeneous product in a single phase. Many investigations have been reported on soft-chemical processes such as the hydrothermal method [4–13], the sol-gel method [14–18], and the precursor decomposition method [19,20] to overcome the disadvantages in preparation of  $\text{KNbO}_3$ . In the hydrothermal method,  $\text{KNbO}_3$  was synthesized by reacting  $\text{Nb}_2\text{O}_5$  with KOH at elevated temperatures 150–250 °C, and the difference in KOH concentrations was reported to bring about large variations in the amount of the product [10]. Kim and Matijevic prepared  $\text{KNbO}_3$  by calcination of amorphous potassium niobate precipitated from the solution of potassium salt and polymeric niobium oxo-hydroxide ion, and discussed the chemical mechanism for the formation and transformation [20]. Self-assembly technique using

layered perovskite  $\text{K}_2\text{NbO}_3\text{F}$  was also reported for preparation of  $\text{KNbO}_3$  thin film [21].

We have developed soft-chemical synthetic routes for preparing metal oxides from peroxo-polymetallic acid obtained by direct reaction of metallic or metallic carbide powder with hydrogen peroxide solution. Our synthetic methods have advantages in preparation of homogeneous and fine powders, because nucleation and subsequent crystalline growth in amorphous solid matrix proceed at lower temperatures. Generally, it is essential to mix raw materials equally at microscopic scale to ensure the quality of the products. In our synthetic routes, raw materials are mixed equally at nanometer scale, and they are appropriate for the preparation of ordinary particles as well as nano-sized particles. For example, peroxo-polytungstic acid is obtained by vigorous reaction between metallic tungsten powder and hydrogen peroxide solution, and an amorphous precursor is precipitated by mixing an alkali solution with the peroxo-polytungstic acid [22–25]. Heating the precursor at 500–700 °C yields alkali tungstates or tungsten bronzes. Similarly, molybdenum, niobium, vanadium, titanium and their carbide powders react with hydrogen peroxide, and yield the corresponding peroxo-polymetallic acids [26–32]. Such peroxo-polyacids based on tungsten and niobium were investigated as negative inorganic resist materials for microlithography and as lithium intercalation materials [23,28]. Preparation of nano-sized tetragonal  $\text{BaTiO}_3$  was achieved by heating the barium salt of peroxo-polytitanic acid at 650 °C [33]. In the present paper, we describe the synthetic details of nanocrystalline  $\text{KNbO}_3$  powders through a new route and its characterizations using the Rietveld refinement of X-ray diffraction (XRD).

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## 2. Experimental

### 2.1. Synthesis

Niobium carbide powder (NbC, 1.9 g, 1–3  $\mu\text{m}$  particle size, as received from Rare Metallic Co., Ltd., Tokyo, Japan) was dissolved in 100 mL of 30 wt%  $\text{H}_2\text{O}_2$  solution (Wako Pure Chemical Industries, Ltd., Osaka, Japan) at 40  $^\circ\text{C}$ . A severe reaction involving gas generation occurred and yielded a yellow transparent aqueous solution of peroxo-heteropoly-niobic acid (denoted by NbC-HPA). The heteroatom is carbon, and the solute is a kind of peroxo-oxalate complex of niobium. The solution was filtered using 0.45  $\mu\text{m}$  filter to remove insoluble after reaction completion. The insoluble mostly consisted of carbon derived from NbC. Reduced-pressure distillation of the solution using rotary evaporator yielded 4.8 g of yellow amorphous solid. Because this yellow solid was insoluble in water, we used the as-prepared NbC-HPA solution for the synthesis.

A white gelatinous precipitate was formed by mixing the NbC-HPA solution with KOH aq, and it was washed and separated by centrifugation. Mixing molar ratio (K/Nb) was changed in the range of 0.2–3.0. After drying the precipitate at 115  $^\circ\text{C}$  for 24 h, 1.0 g of amorphous potassium salt of NbC-HPA was obtained. Potassium niobium oxides were obtained by heating the salts as precursors in air at 650–900  $^\circ\text{C}$ .

### 2.2. Characterization

The ultraviolet–visible (UV–vis) absorption spectrum of the NbC-HPA solution was taken using a spectrophotometer (V570, JASCO, Tokyo, Japan). The absorbance at 370 nm was monitored during the reaction between NbC and  $\text{H}_2\text{O}_2$  to estimate the time required to complete the reaction. The thermal behavior of the precursor salt was investigated by thermogravimetry and differential thermal analysis (TG/DTA, DTG-50, Shimadzu, Tokyo, Japan) at a heating rate of 20  $^\circ\text{C}/\text{min}$ . The X-ray diffraction patterns were measured with a diffractometer (Ultima IV, Rigaku, Tokyo, Japan) using graphite-monochromatized  $\text{Cu K}\alpha$  radiation ( $\lambda = 0.15406 \text{ nm}$ ) at 40 kV and 30 mA. The crystalline parameters of the obtained  $\text{KNbO}_3$  were refined by the Rietveld method using the RIETAN-2000 program [34]. The crystallite sizes of  $\text{KNbO}_3$  were determined by

$$p = \frac{180K\lambda}{\pi X} \quad (1)$$

where  $p$  is the crystallite size,  $K$  is the Scherrer constant (0.9),  $\lambda$  is the wavelength of X-ray, and  $X$  is a peak profile parameter, the Lorentzian Scherrer broadening obtained in the Rietveld refinement. The K/Nb molar ratios of the specimens were determined by X-ray fluorescence spectrometry (XRF-1700, Shimadzu, Tokyo, Japan) using the fundamental parameter (FP) method. The morphology of the potassium niobium oxides after heating was observed by a field-emission scanning electron microscope (FE-SEM, S-4800, Hitachi, Tokyo, Japan) with an accelerating voltage of 2 kV.

## 3. Results and discussion

The UV–vis absorption spectrum of NbC-HPA aqueous solution (0.20 mol/L as to Nb) is shown in Fig. 1. A broad absorption band ranging from 250 to 500 nm was observed, and the molar extinction coefficient ( $\epsilon$ ) of the NbC-HPA solution at 370 nm was estimated as  $1.84 \times 10^4 \text{ cm}^2 \text{ mol}^{-1}$ . The absorption in the range of 250–500 nm is considered to be due to electronic transitions in niobium complex ion with peroxo and oxalate groups as ligands. Time-courses of the absorbance at 370 nm after

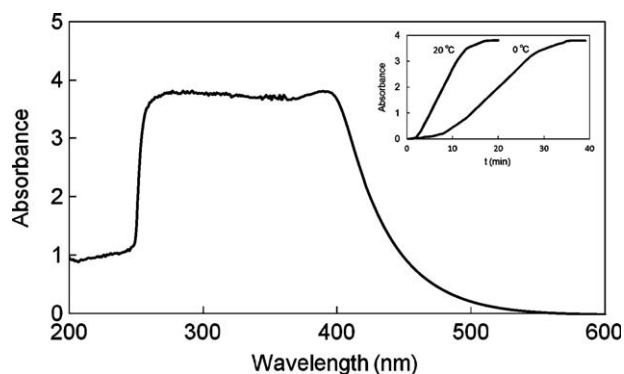


Fig. 1. UV–vis absorption spectrum of NbC-HPA aqueous solution containing 0.20 mol/L of Nb. Inset shows the time-courses of the absorbance at 370 nm after mixing NbC with  $\text{H}_2\text{O}_2$  solution at the initial temperature of 0  $^\circ\text{C}$  and 20  $^\circ\text{C}$ .

mixing NbC with  $\text{H}_2\text{O}_2$  solution indicated that the reaction was completed in 18 min at the initial temperatures of 20–40  $^\circ\text{C}$  and in 35 min at the initial temperature of 0  $^\circ\text{C}$ . The dependence on the initial temperatures was relatively low because of the heat release in the reaction.

The relationship between the K/Nb molar ratio in the precipitated salt and the mixing molar ratio K/Nb of the solutions is shown in Fig. 2. The K/Nb ratio in the salt increased with increasing the mixing molar ratio up to 2.0 and stayed almost constant at 1.0 above the mixing molar ratio of 2.0. It is interesting to note that the excess concentration of KOH over 0.40 mol/L (the K/Nb ratio = 2) did not affect the content in the precipitate. In the hydrothermal methods the large excess KOH has been reported to be essential for dissolving niobium oxide into the aqueous solution, and the high K/Nb molar ratio of raw materials in the range of 50–800 is a critical requisite for the hydrothermal formation of  $\text{KNbO}_3$  [4,11]. These earlier studies support our experimental fact that the excess amount of KOH over the K/Nb ratio of 2 did not affect the composition in the precipitate. In our precursor decomposition method, the large excess KOH was not essential because the niobium was dissolved by the reaction with  $\text{H}_2\text{O}_2$  and the role of KOH was simply to provide counter ion for the formation of salt.

The mixing molar ratio K/Nb was set to 2 hereafter because it gave a precipitate having the K/Nb ratio of 1.03 close to that of  $\text{KNbO}_3$ . Fig. 3 shows the DTA/TG curves of an amorphous precursor salt precipitated by mixing 100 mL of 0.20 mol/L NbC-HPA aq with 100 mL of 0.40 mol/L KOH aq. After a broad endothermic peak due to water desorption ranging from room temperature to 200  $^\circ\text{C}$ , an

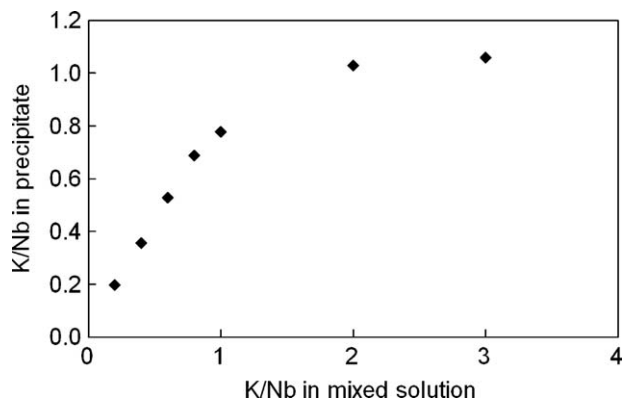
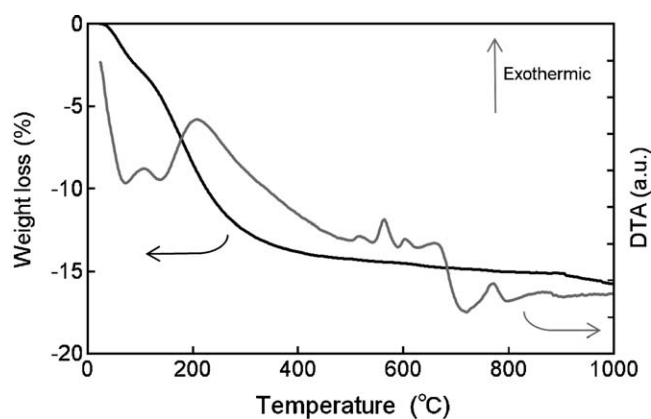


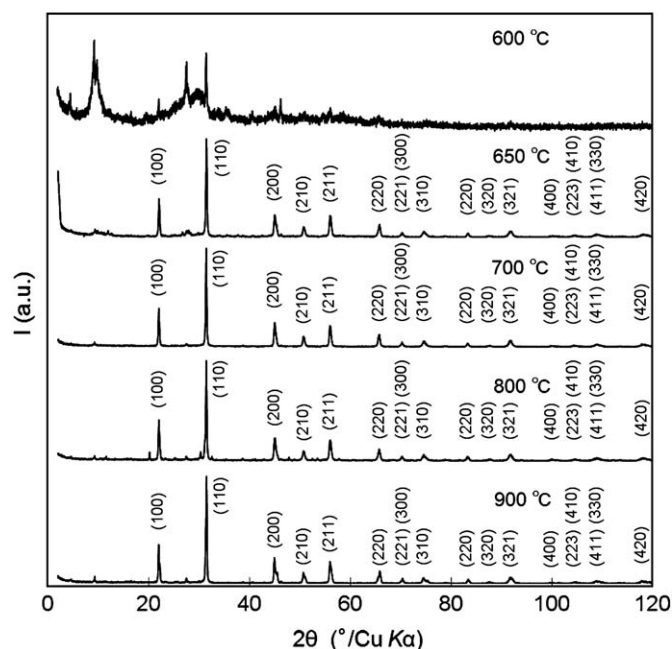
Fig. 2. Relationship between the K/Nb molar ratio in the precipitated salt and the K/Nb molar ratio of the mixed solutions.



**Fig. 3.** TG and DTA curves of the amorphous precursor at heating rate 20 °C/min in air. The potassium salt of NbC-HPA was obtained by mixing molar ratio at K/Nb = 2.

exothermic peak due to crystallization appeared around 570 °C. This suggests that a crystalline product can be obtained by heating the precursor above 570 °C. Additionally, a broad endothermic peak ranging from 670 to 850 °C was also observed. This is considered to be due to fusion of crystallites, because endothermic reactions at elevated temperatures thermodynamically accompany entropy increase.

The XRD patterns for the samples heated in air for 1 h. at 600, 650, 700, 800 and 900 °C are shown in Fig. 4. The amorphous precursor partly remained in the product obtained at 600 °C because two broad peaks were observed around 9.4° and 30.6°. The precursor entirely changed into crystal phase over 650 °C, and the XRD patterns for the samples obtained by heating over 650 °C were coincident with those of the cubic KNbO<sub>3</sub> (PDF-080212). The crystallinity of the KNbO<sub>3</sub> was almost the same from 650 to 900 °C in spite of the increase in heating temperature. The structural parameters for KNbO<sub>3</sub> obtained from the Rietveld refinement are summarized in Table 1. All the data were well fitted with the space group *Pm3m*, and the crystallite size of KNbO<sub>3</sub> determined from the peak profile parameters was in the range of 25–35 nm indepen-



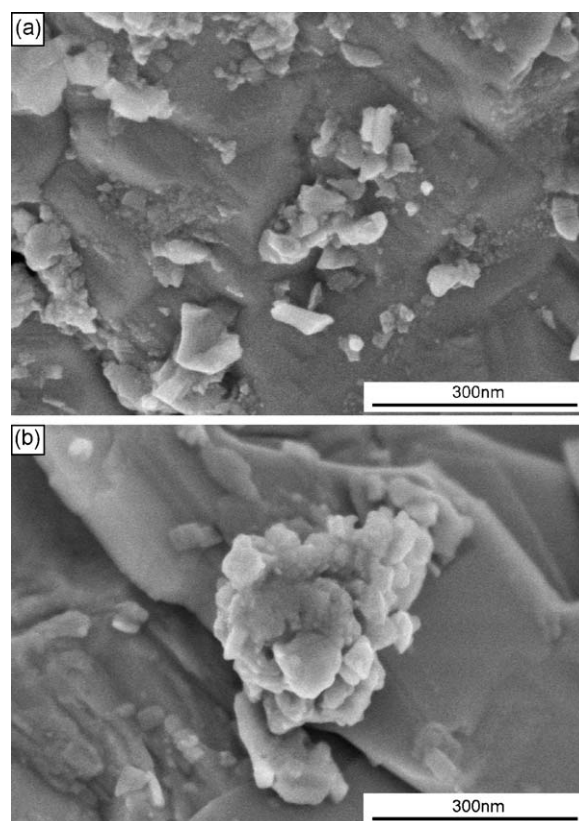
**Fig. 4.** XRD patterns of KNbO<sub>3</sub> samples obtained by heating the amorphous precursor in air for 1 h at 650–900 °C.

**Table 1**

Refined crystallographic data for KNbO<sub>3</sub> obtained by heating the precursor at 650–900 °C.

Cubic; space group; <i>Pm3m</i> (221) <i>Z</i> = 1		
Atom	Site	Occupancy
K	1a (0, 0, 0)	1.0
Nb	1b (1/2, 1/2, 1/2)	1.0
O	2c (0, 1/2, 1/2)	1.0
650 °C	<i>a</i> = 4.0129(40)	Crystallite size: 35.0 nm
700 °C	<i>a</i> = 4.0122(28)	Crystallite size: 27.8 nm
800 °C	<i>a</i> = 4.0115(39)	Crystallite size: 25.0 nm
900 °C	<i>a</i> = 4.0136(53)	Crystallite size: 28.8 nm

dently of the heating temperature. This indicates that the precipitation of nano-sized crystallite from the amorphous matrix occurs at 650–900 °C and its crystal growth does not proceed at the temperature region. This is coincident with the fact that KNbO<sub>3</sub> was conventionally prepared by solid state reactions at 1000 °C or more [35]. Thus, the crystallite size was independent of the heating temperatures, because the heating temperatures were lower than those for the solid state reactions. Generally, heating amorphous precursors at temperature regions lower than those for solid state reactions is a recipe for the preparation of nano-sized particles. The space groups *P4mm* and *Amm2* were also considered in the fitting because the formation of tetragonal or orthorhombic phase of KNbO<sub>3</sub> was reported in earlier reports [4,36,37], but the fitting did not go well. The FE-SEM images of the KNbO<sub>3</sub> samples obtained by heating the precursor in air for 1 h at 700 and 900 °C are shown in Fig. 5a and b, respectively. The aggregates of nano-sized particles on an agglomerate are observed in both figures, and the agglomerate is thought to be fused crystallites. The crystallite sizes estimated from the XRD profiles were almost the same in the temperature region 650–900 °C, and the fusion of crystallites was



**Fig. 5.** FE-SEM images of KNbO<sub>3</sub> samples obtained by heating the amorphous precursor in air for 1 h at 700 °C (a) and 900 °C (b).

considered to take place from 670 to 850 °C. Therefore, it is appropriate to heat the precursor around 650 °C to prepare dispersed nano-sized particles without fusion. Additionally, the temperature region 670–950 °C is appropriate for the preparation of the agglomerates of nano-sized particles.

#### 4. Conclusions

NbC-HPA solution was prepared by direct reaction between NbC powder and H<sub>2</sub>O<sub>2</sub> aq. KNbO<sub>3</sub> was obtained by heating the amorphous precursor at 650–900 °C, which was precipitated by mixing NbC-HPA solution with KOH aq. All the X-ray diffraction data at 650–900 °C were well fitted with the space group *Pm3m* in the Rietveld analysis. The peak profiles in the X-ray diffraction patterns indicated that the crystallite size was in the range of 25–35 nm, and field emission scanning electron microscope images supported this result. This method can be applied to the preparation of the other niobium complex oxides such as LiNbO<sub>3</sub>, NaNbO<sub>3</sub>, AgNbO<sub>3</sub>. Peroxo-precursor decomposition methods offer attractive prospects for the preparation of nano-sized complex metal oxides, and the peroxo-precursor is expected to become a more commonly used precursor in soft chemical synthesis.

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