

One-pot, selective synthesis of orthorhombic and rhombohedral NaNbO₃ by hydrothermal method

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Abstract

The pure orthorhombic- and rhombohedral-structure NaNbO₃ microcrystals were obtained selectively by a facile, additive-free hydrothermal procedure using commercialized Nb₂O₅, NaOH, KOH as starting materials. The obtained samples were characterized by X-ray powder diffraction, field-emission scanning electron microscopy, energy dispersive spectrometry, Raman spectroscopy. The results showed that the required hydrothermal temperatures to synthesize single crystalline phase of rhombohedral and orthorhombic NaNbO₃ are as low as 180 and 200 °C for 24 h, respectively. The phase composition of the hydrothermal product was found to be strongly dependent on (K⁺ + Na⁺)/Nb⁵⁺ molar ratio. Interestingly, by using the (K⁺ + Na⁺)/Nb⁵⁺ molar ratio of 9.0, the pure metastable phase of NaNbO₃ with rhombohedral structure was readily synthesized in the hydrothermal temperature range of 180-200 °C. However, as this molar ratio crossed over 12.0, the polymorphic type of NaNbO₃ was received at 180 °C only and the orthorhombic type existed purely when the reaction temperature reached 200 °C.

Keywords. NaNbO₃, surfactant-free, polymorphism, hydrothermal method.

1. INTRODUCTION

Multifunctional sodium niobate (NaNbO₃)-based materials have been studied intensively due to their interesting diversified properties with potential applications like piezoelectricity, ferroelectricity, water splitting, photocatalysis ... [1-7]. It was indicated that many properties of these materials, namely, piezoelectricity, photocatalysis can be improved via engineering their surface crystallographic texture [8, 9]. However, it was difficult to apply this effective method, especially by chemical synthesis routes, to orthorhombic NaNbO₃ (NN), the most studied polymorphic type of this compound. Recently, by using rhombohedral NaNbO₃ powders prepared by the hydrothermal method as a precursor for sintering process, Y. Lu *et al.* synthesized high crystallographic oriented NN ceramics [10]. By using sodium dodecylbenzene sulfonate as a surfactant, these rhombohedral NN powders were hydrothermally synthesized at 200 °C for 10 h from Nb₂O₅, KOH and NaOH. For other reported surfactant-free hydrothermal procedures using Nb₂O₅ and alkaline hydroxide, the rhombohedral NN powders were purely provided only when the temperature approached to 240 °C [11, 12].

In this paper, we present a one-pot, surfactant-

free hydrothermal procedure to synthesize rhombohedral and orthorhombic NaNbO₃ powders selectively at temperatures from 180 to 200 °C using KOH, NaOH and commercialized Nb₂O₅ as starting materials.

2. EXPERIMENTAL

2.1. Chemicals and Methods

For the synthesis of NaNbO₃ powders, all Nb₂O₅, KOH and NaOH were used as received from Sigma-Aldrich.

The obtained samples were characterized by X-ray diffraction (XRD) (Bruker D8 Avance diffractometer with CuK_α radiation ($\lambda = 1.5406 \text{ \AA}$), Field-Emission Scanning Electron Microscopy (FESEM) (Hitachi S-4800 equipped with an energy-dispersive spectroscopy (EDS) unit), and Raman spectroscopy (Labram-1B, Horiba).

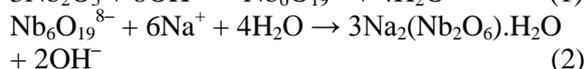
2.2. Synthesis of NaNbO₃ powders

In a typical experiment, 0.665 g Nb₂O₅ was added into a certain amount of equimolar mixture of 6M NaOH and 6M KOH during continuous stirring for 30 min. The obtained mixture was then transferred into a 30-ml Telfon-line stainless steel autoclave,

filled with distilled water up to 70 %. The autoclave was finally sealed and heated at certain temperatures ranged from 160-200 °C for 24 h under autogenous pressure.

3. RESULTS AND DISCUSSION

XRD diagrams of the as-prepared NaNbO₃ synthesized with different (K⁺ + Na⁺)/Nb⁵⁺ molar ratios at 180 °C for 24 h were presented in Fig 1. For samples synthesized with the (K⁺ + Na⁺)/Nb⁵⁺ molar ratio of 4.5, the rhombohedral NaNbO₃ phase (PDF card No. 37-1076) was formed together with Na₂(Nb₂O₆).H₂O phase (PDF card No. 73-7869) as an impurity phase. Based on the existence of the later phase, the growth mechanism of NN during the hydrothermal processing, in which Na₂(Nb₂O₆).H₂O phase served as an intermediate compound, can be suggested as follows [12]:



It was necessary to note that, with this growth mechanism, KOH played a role as a mineralizer only and produced no K-containing compounds.

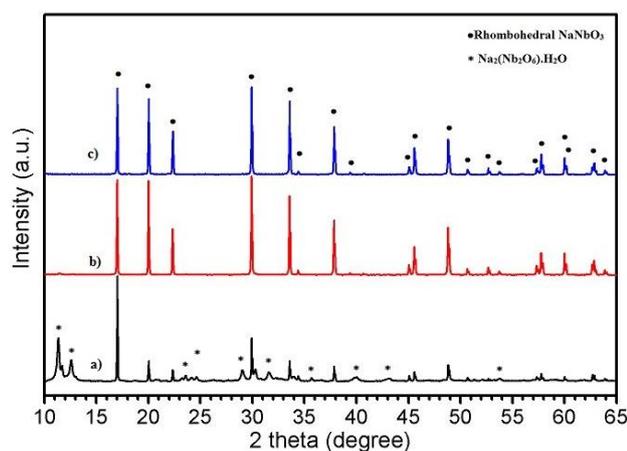


Figure 1: XRD patterns of samples synthesized at 180 °C for 24 h with the (K⁺ + Na⁺)/Nb⁵⁺ molar ratio of: (a) 4.5; (b) 9.0; and (c) 12.0

Further increasing the (K⁺ + Na⁺)/Nb⁵⁺ molar ratio to 9.0 and 12.0 led to the unique formation of rhombohedral NN. It is clear that, with this molar ratio, the pure metastable phase of NaNbO₃ with rhombohedral structure was formed at 180 °C, significantly lower than that of surfactant-free hydrothermal procedures [11, 12]. This can be understood that the rate of phase formation of the rhombohedral NN strongly depended on the

(K⁺ + Na⁺)/Nb⁵⁺ molar ratio. In our study, the suitable range of this molar ratio was selected to be investigated. As a result, the rhombohedral NaNbO₃ phase was stabilized and can be collected at low hydrothermal temperatures.

To determine the temperature range that provides the rhombohedral NN powders, samples were synthesized with the (K⁺ + Na⁺)/Nb⁵⁺ molar ratio of 9.0 at different hydrothermal temperatures in the range of 160-220 °C for 24 h (Fig. 2a). One can realize that the rhombohedral polymorphic type of NN can be synthesized without any other impurities with hydrothermal temperature ranged from 180 to 200 °C. The unreacted Nb₂O₅ was still detected for the reaction at 160 °C, while the orthorhombic NN phase began to form when the hydrothermal temperature valued at 220 °C. However, by using the

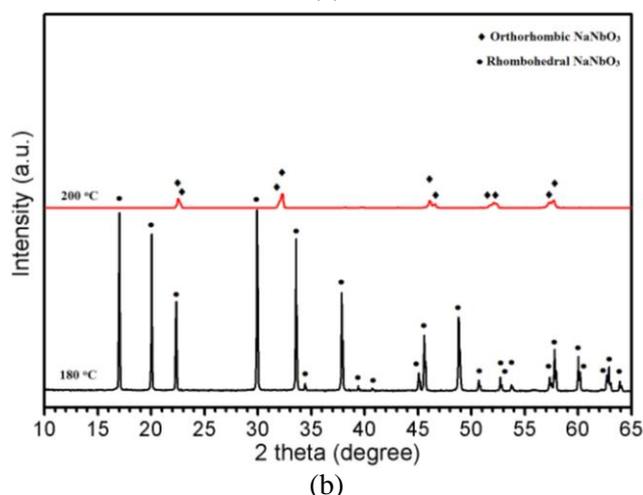
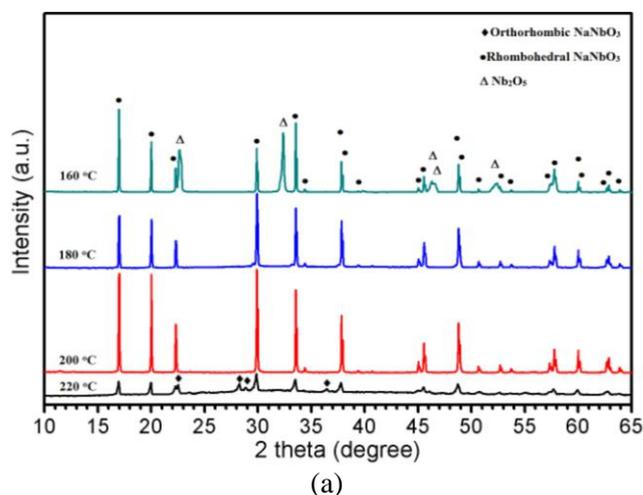
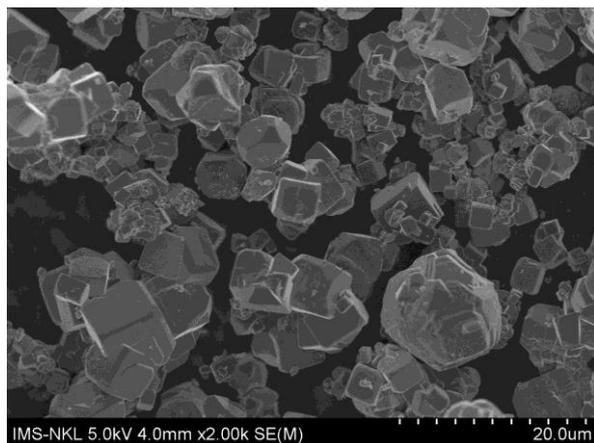


Figure 2: XRD patterns of the as-prepared NaNbO₃ samples synthesized for 24 h with the (K⁺ + Na⁺)/Nb⁵⁺ molar ratio of: (a) 9.0 at: 160, 180, 200 and 220 °C and (b) 12.0 at 180 and 200 °C

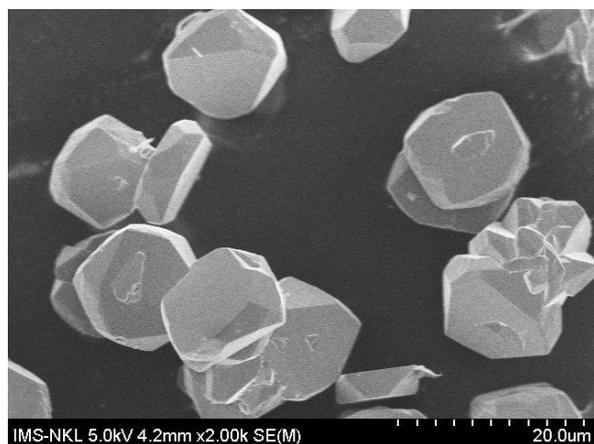
(K⁺+Na⁺)/Nb⁵⁺ molar ratio of 12.0, the complete phase change from rhombohedral to orthorhombic

polymorphism was observed when increasing temperature from 180 to 200 °C (Fig. 2b).

Morphology of the pure orthorhombic and rhombohedral NN samples can be observed via FESEM images (Fig. 3). While cubic grains with an average size of 4.0 μm were found in the orthorhombic sample that of rhombohedral NN was comprised of plate-like microcrystals with the diameter of 12.0 μm and the thickness of 4.0 μm in average.



(a)



(b)

Figure 3: FESEM images of (a) orthorhombic and (b) rhombohedral NaNbO_3 samples synthesized at 180 °C for 24 h

From elemental analysis results by EDS method given in table 1, one can see that both pure orthorhombic and rhombohedral NN samples contained Na, Nb and O elements without any trace of K^+ cations. This confirmed the above-mentioned suggested growth mechanism for NaNbO_3 by our hydrothermal synthesis procedure, in which KOH played a role solely as a mineralizer.

The Raman spectra of pure rhombohedral and orthorhombic NN samples were demonstrated in Fig. 3. For a rhombohedral NN sample, similarly to

Ref. [12], only characteristic bands at 254, 287, 489 and 723 cm^{-1} of the rhombohedral polymorphic type were observed (Fig. 4a). On the other hand, for pure orthorhombic NN sample, there were typical Raman bands corresponding to the orthorhombic NaNbO_3 phase (257, 281, 574, 613 and 873 cm^{-1}) (Fig. 4b) [13, 14]. Two bands locating at 257 and 281 cm^{-1} can be assigned to symmetric O–Nb–O bending vibrations (ν_5 modes), whereas other bands at 574 and 613 cm^{-1} can be attributed to symmetric O–Nb–O stretching vibrations (ν_1 modes) of the NbO_6 octahedron. The band of ($\nu_1 + \nu_5$) combination mode was observed at 873 cm^{-1} . Obviously, no peaks of other impurities were detected at spectroscopic level for these two samples.

Table 1: EDS analysis of the pure orthorhombic and rhombohedral NaNbO_3 samples

Sample	Na/Nb molar ratio		K content (at. %)
	Theoretical	Practical	
Orthorhombic NN	1	1.077	0
Rhombohedral NN	1	1.003	0

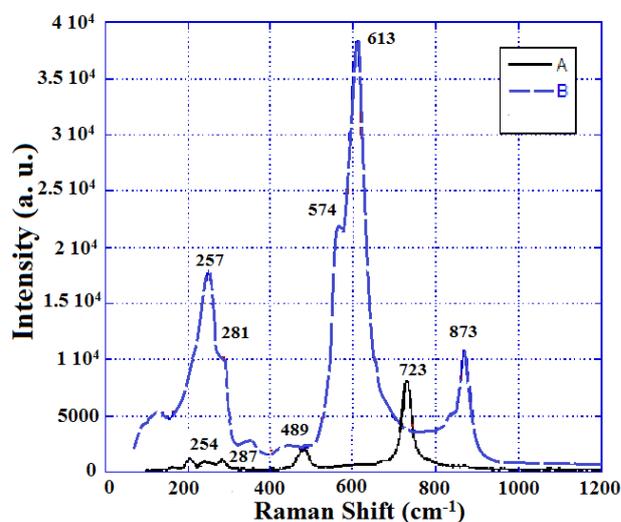


Figure 4: Raman spectra of: (a) rhombohedral- and (b) orthorhombic-structure NaNbO_3 samples synthesized at 180 °C for 24 h

4. CONCLUSION

By simply tuning the $(\text{K}^+ + \text{Na}^+)/\text{Nb}^{5+}$ molar ratio from 9.0 to 12.0, the pure rhombohedral and orthorhombic NaNbO_3 microcrystals were selectively synthesized by an additive-free hydrothermal procedure using commercialized Nb_2O_5 , NaOH, KOH as starting materials at 180 and 200 °C, respectively, for 24 h. The results showed

that the phase composition of hydrothermal product was found to be strongly dependent on the $(K^+Na^+)/Nb^{5+}$ molar ratio. In addition, the hydrothermal temperature range of 180-200 °C for obtaining the single crystalline phase of the rhombohedral $NaNbO_3$ was determined. The growth mechanism of $NaNbO_3$ with the aid of KOH as a mineralizer was also identified.

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