

Hydrothermal synthesis of submicron NaNbO_3 powders

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Abstract

Nano-crystals of ferroelectric NaNbO_3 phase were prepared by hydrothermal method in one step. The influence of temperature, concentration of Nb_2O_5 and NaOH , and reaction duration on structure and morphology was analyzed. Temperature has a marked effect on phase formation, while concentration of Nb_2O_5 and NaOH can affect both structure and morphology. Lower ratio of $\text{NaOH}/\text{Nb}_2\text{O}_5$ facilitates formation of orthorhombic NaNbO_3 . Reaction duration only plays an important role in the formation process at lower temperatures. The intermediate phases of sodium niobates may transform into NaNbO_3 by prolonging reaction duration or annealing at certain temperature.

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1. Introduction

NaNbO_3 has been attracting increasing interests for its applications in lead-free piezoelectric ceramics [1,2]. It has a variety of structures. It is generally accepted that NaNbO_3 transforms from cubic phase to tetragonal phase at 640 °C, then to orthorhombic phase at 370 °C, and finally to rhombohedral phase at −103 °C [3]. Here, the orthorhombic phase involves the transition among four different orthorhombic structures.

Ferroelectric and piezoelectric ceramics made from NaNbO_3 based solid solutions have great potential applications in electromechanical and nonlinear optical devices [4–7]. One striking example showed that NaNbO_3 was one of the important components of the environment-friendly, lead-free piezoelectric ceramics that could most likely replace the widely used lead zirconium titanate (PZT) [8].

Hydrothermal synthesis has been widely used to prepare various nano-materials [9–13] and thin films [14] due to the advantages including low cost, morphology-controllability, etc. Kinomura et al. [15] hydrothermally synthesized ilmenite-type NaNbO_3 using polyniobate as the starting material; Goh et al. [16] synthesized NaNbO_3 with 8.4 M

NaOH ; Zhu et al. [17] prepared NaNbO_3 with 10 M NaOH ; Wu et al. [18,19] synthesized NaNbO_3 with 0.6–4 M NaOH and discussed formation mechanism of sodium niobate at lower concentration of NaOH , and the influence of reaction duration and $[\text{OH}^-]$ concentration on the structure and morphology of the products.

In the above-mentioned reports, the effect of hydrothermal parameters such as temperature and concentration of alkali metal hydroxide on the synthesis of sodium niobate was investigated, and the structure evolution and reaction mechanism under certain circumstances were discussed. However, so far, the influence of hydrothermal parameters on the final products with NaOH concentration above 10 M has not been systematically studied. Further analysis is needed in order to optimize the hydrothermal parameters and attain nanorods, nanoplates, fibers, and various hydrates. In this paper, we analyzed the influence of these parameters involved in the synthesis of sodium niobates and the effect of annealing. In consideration of contrast, previous results are also given to wholly comprehend the reaction mechanism.

2. Experimental

Analytical grade solid NaOH (>96%) and 99.99% purity Nb_2O_5 were used as raw materials in hydrothermal preparation of various samples with given hydrothermal parameters. Firstly,

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Nb_2O_5 was well dispersed in aqueous sodium hydroxide solution (25 mL) with magnetic stirring for 40 min, the mixture was then transferred to a Teflon-lined autoclave (50 mL). After several hours of reaction at selected temperatures, the reaction product was separated and washed neutrally by de-ionized water, then dried at 60 °C for 24 h.

All the samples were characterized by using a JSM-6360LA scanning electron microscope (SEM) and a Bruker D8 X-ray Diffractometer. $\text{CuK}\alpha 1$ radiation was used as the source for X-ray diffraction (XRD). XRD was carried out at an interval of 0.02° with 2θ ranging from 5° to 80°.

3. Results and discussion

Fig. 1(a) shows XRD patterns of samples synthesized at 180 °C for 8 h with 0.1 M Nb_2O_5 and different concentrations of NaOH and the literature pattern for ferroelectric phase NaNbO_3 (JCPDS No. 82-0606 [20]), the enlarged patterns for Fig. 1(a) at different two-theta ranges are shown in Fig. 1(b) and (c). Since both peak position and intensity of the patterns for samples are well consistent with the standard pattern for ferroelectric phase NaNbO_3 , it's most likely that ferroelectric phase NaNbO_3 can be easily hydrothermally prepared with proper synthesis conditions. The peak separation ranging from 20° to 35° and from 45° to 60° in Fig. 1(b) and (c) becomes weaker as the concentration of NaOH increases. This is consistent with earlier results made by Wu et al. [18] at lower concentration of NaOH. Moreover, in our results the morphology changes from nanorods and nanoplates to large cubes as we reduce the concentration of NaOH (Fig. 2).

Fig. 3 displays the XRD patterns of samples prepared at 180 °C for 8 h with 14 M NaOH and various concentrations of Nb_2O_5 . Although all those four samples are orthorhombic phase NaNbO_3 , yet enough attention should be paid to the peak separation ranging from two theta 45° to two theta 60°. The inset (enlarged patterns) clearly shows that the peaks separate sharply as the concentration of Nb_2O_5 increases. Comparing Figs. 1 and 3 it seems that the peak separation in the XRD patterns for orthorhombic NaNbO_3 weakens as the ratio of NaOH/ Nb_2O_5 increases.

As the concentration of Nb_2O_5 decreased, morphology of NaNbO_3 changed from cubes to nanorods or nanoplates (Fig. 4). It is clearly indicated that lower concentration of Nb_2O_5 facilitates the formation of sodium niobate nanocrystals. Since nanowires of NaNbO_3 were mostly synthesized by annealing their fiber-like intermediates [21–23], our results indicate that it is possible to obtain nanocrystals of NaNbO_3 in one-step process by hydrothermal synthesis.

Formation of NaNbO_3 in the hydrothermal process is highly dependent on temperature. According to our result, the lowest temperature to get pure NaNbO_3 is approximately 150 °C. Fig. 5 displays the XRD patterns of samples prepared at different temperatures with 0.05 M Nb_2O_5 and 14 M NaOH for 8 h. It is most likely that the sample synthesized at 130 °C is $\text{Na}_8\text{Nb}_6\text{O}_{19} \cdot 13\text{H}_2\text{O}$ [24] and the sample synthesized at 180 °C is orthorhombic NaNbO_3 , while the sample synthesized at 160 °C contained two phases. One of them is orthorhombic

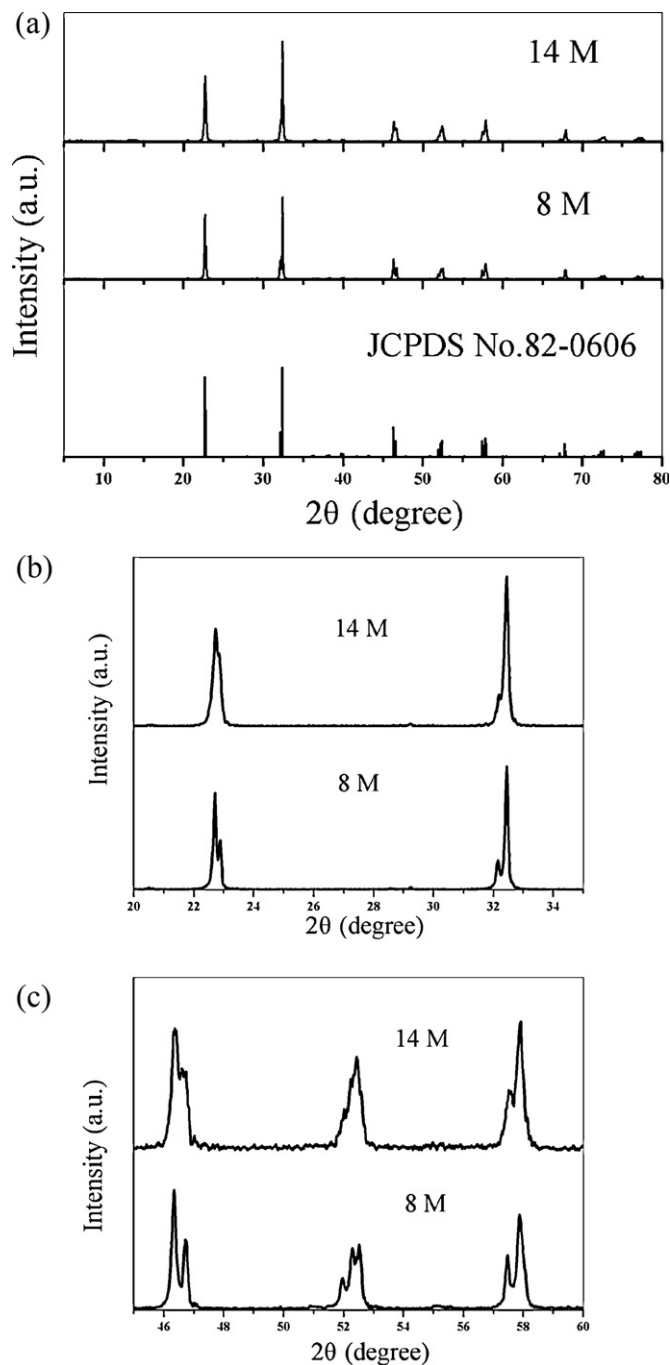


Fig. 1. (a) XRD patterns of samples prepared at 180 °C for 8 h with 0.1 M Nb_2O_5 and different concentrations of NaOH and the literature pattern for ferroelectric phase NaNbO_3 (JCPDS No. 82-0606); (b) The enlarged patterns for the above ones at two theta ranging from 20° to 35°; (c): The enlarged patterns for the above ones at two theta ranging from 45° to 60°.

phase NaNbO_3 , the other is probably the so-called Sandia Octahedral Molecular Sieve (SOMS) as reported by Xu et al. [25]. According to their results, this SOMS has a monoclinic structure (space group C2/c , $a = 17.0511(9)$ Å; $b = 5.0293(2)$ Å; $c = 16.4921(9)$ Å; $\beta = 113.942(9)^\circ$). Fig. 6 shows the corresponding SEM images. Micro-tubed hexanio-bate (a) and fiber-like SOMS (b) were transformed into plate-like NaNbO_3 (c) at higher reaction temperature. This transition

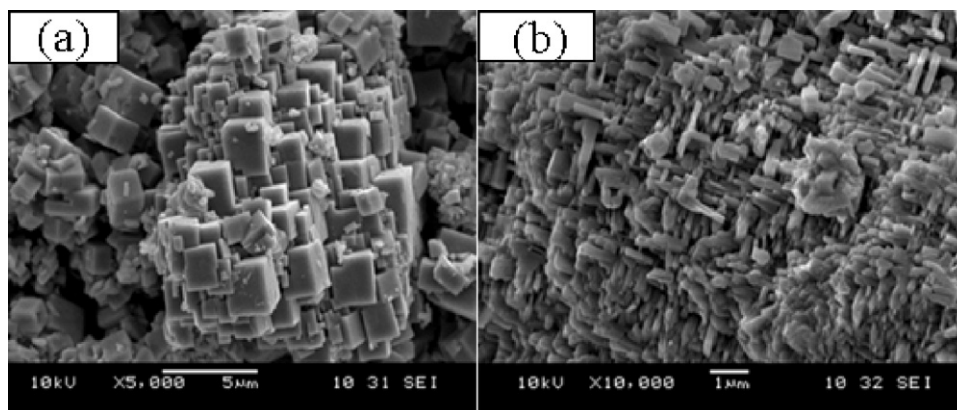


Fig. 2. SEM images of samples prepared at 180 °C for 8 h with 0.1 M Nb_2O_5 and different concentrations of NaOH (a: 8 M, b: 14 M).

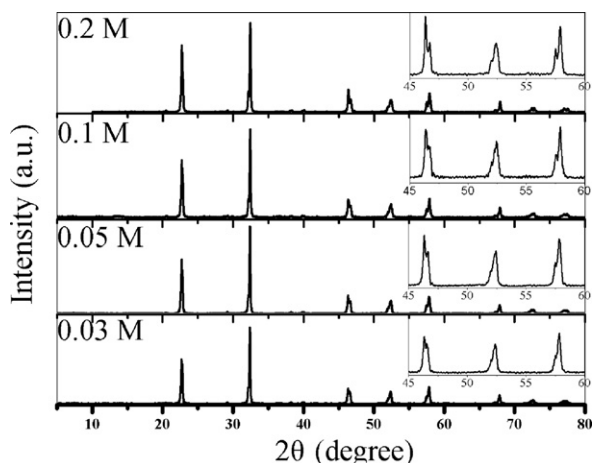


Fig. 3. XRD patterns of samples prepared at 180 °C for 8 h with 14 M NaOH and different concentrations of Nb_2O_5 , the inset is their local enlarged patterns.

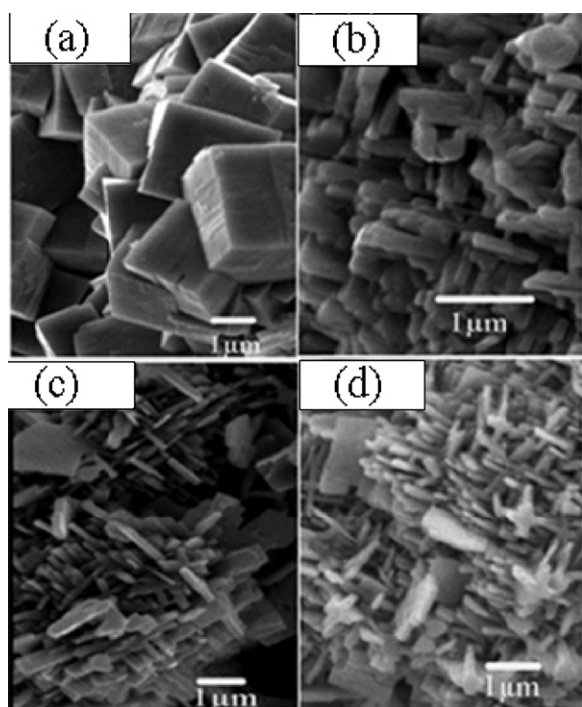


Fig. 4. SEM images of samples prepared at 180 °C for 8 h with 14 M NaOH and various concentrations of Nb_2O_5 (a: 0.2 M, b: 0.1 M, c: 0.05 M, d: 0.03 M).

process is consistent with earlier results that Nb_2O_5 was firstly converted to $\text{Nb}_6\text{O}_{19}^{8-}$, then these Lindqvist ions changed into SOMS ($\text{Na}_2\text{Nb}_2\text{O}_6 \cdot n\text{H}_2\text{O}$, $0 \leq n \leq 1$), and finally NaNbO_3 was gotten from those SOMS materials as reported by Zhu et al. [17].

Fig. 7 shows the XRD patterns of samples synthesized at 160 °C with 0.03 M Nb_2O_5 and 14 M NaOH for different reaction duration. For 4 h, SOMS, $\text{Na}_8\text{Nb}_6\text{O}_{19} \cdot 13\text{H}_2\text{O}$ and NaNbO_3 all emerged. For 8 h, the sample only contains NaNbO_3 and a small amount of SOMS. For 24 h, both SOMS and $\text{Na}_8\text{Nb}_6\text{O}_{19} \cdot 13\text{H}_2\text{O}$ vanished.

Based on the earlier results [17,26], structure of Nb_2O_5 is comprised of corner-sharing Nb–O polyhedra ($[\text{NbO}_6]$ and $[\text{NbO}_7]$), while NaNbO_3 is a network of $[\text{NbO}_6]$ and $[\text{NaO}_6]$. Although both intermediates $\text{Na}_8\text{Nb}_6\text{O}_{19} \cdot 13\text{H}_2\text{O}$ and SOMS contain edge-sharing $[\text{NbO}_6]$, yet Na^+ is freely distributed in the intervals of Nb_6O_{19} units for $\text{Na}_8\text{Nb}_6\text{O}_{19} \cdot 13\text{H}_2\text{O}$, while $[\text{NaO}_6]$ alternate with $[\text{NbO}_6]$ for SOMS. In order to realize the conversion of Nb_2O_5 to NaNbO_3 , $[\text{NbO}_7]$ must be ruptured in company with the implantation of Na^+ and the formation of $[\text{NaO}_6]$. According to the structural features, it is most likely

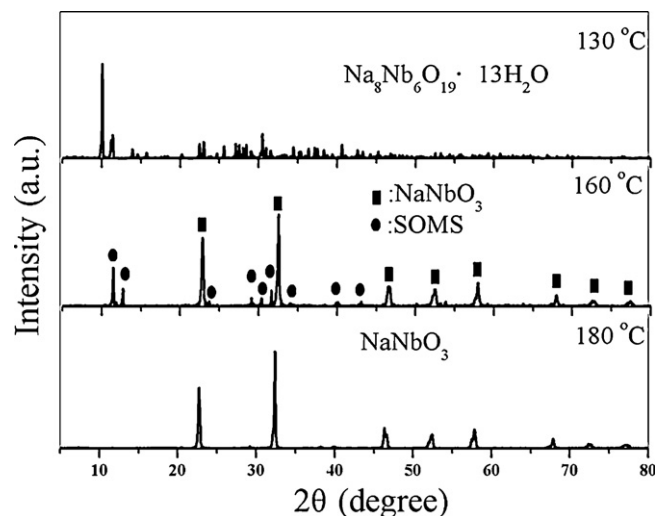


Fig. 5. XRD patterns of samples prepared at various temperatures with 14 M NaOH and 0.05 M Nb_2O_5 for 8 h.

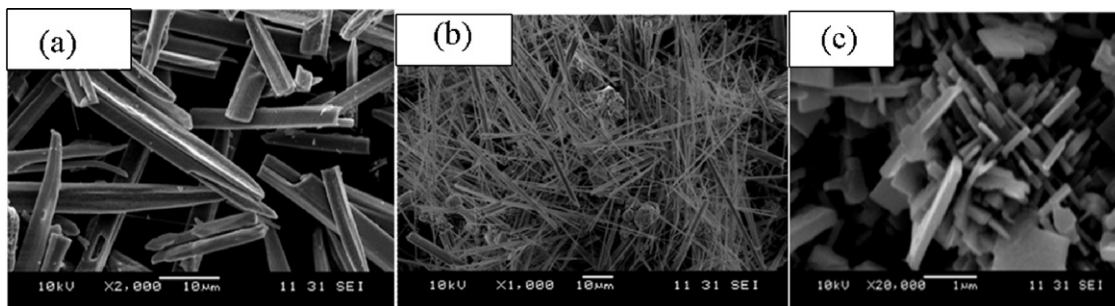


Fig. 6. SEM images of samples prepared at various temperatures with 14 M NaOH and 0.05 M Nb₂O₅ for 8 h (a: 130 °C, b: 160 °C, c: 180 °C).

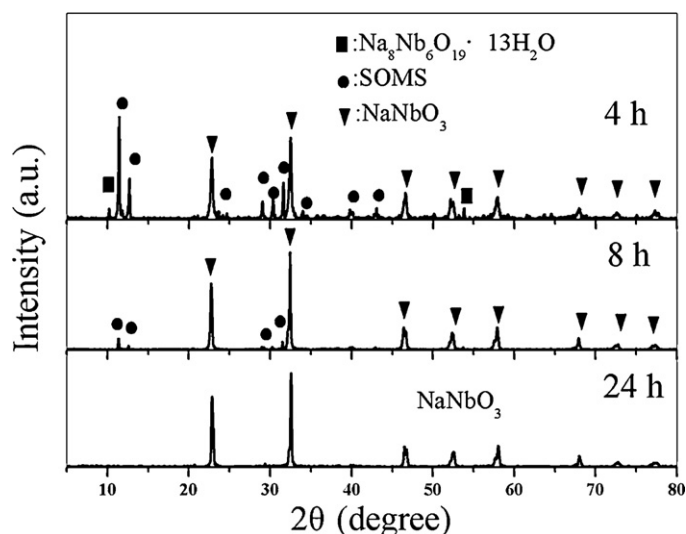


Fig. 7. XRD patterns of samples prepared at 160 °C for various reaction duration with 0.03 M Nb₂O₅ and 14 M NaOH.

that Na₈Nb₆O₁₉·13H₂O is synthesized first from Nb₂O₅, and then transformed into SOMS and NaNbO₃. The sample synthesized for 8 h is comprised of SOMS and NaNbO₃, rather than Na₈Nb₆O₁₉·13H₂O and NaNbO₃, which possibly give some evidence to the above-mentioned point. This transition process could also be proved by the change in morphology since our results show that fiber-like SOMS and Na₈Nb₆O₁₉·13H₂O (Fig. 8(a) and (b)) were gradually transformed into cubic NaNbO₃ (Fig. 8(c)).

Fig. 9(a) shows XRD patterns of samples synthesized at 160 °C for 4 h with 14 M NaOH and 0.03 M Nb₂O₅ and its corresponding annealed powder at different temperatures for

6 h. Fig. 9(b) gives the enlarged patterns at two theta ranging from 40° to 60° for all the above patterns. Obviously, the as-synthesized powder consisting of SOMS, Na₈Nb₆O₁₉·13H₂O and NaNbO₃ was completely converted to NaNbO₃ when annealing above 350 °C. Moreover, this tetragonal phase NaNbO₃ firstly changed into cubic phase, and then reverted to tetragonal phase at elevated annealing temperature.

Fig. 10 gives the corresponding SEM images. At lower annealing temperature, the fiber-like pre-annealing powder (a) was retained though suffering the phase transition from SOMS and Na₈Nb₆O₁₉·13H₂O to NaNbO₃ ((b) and (c)). Higher annealing temperature results in agglomeration (d). The point

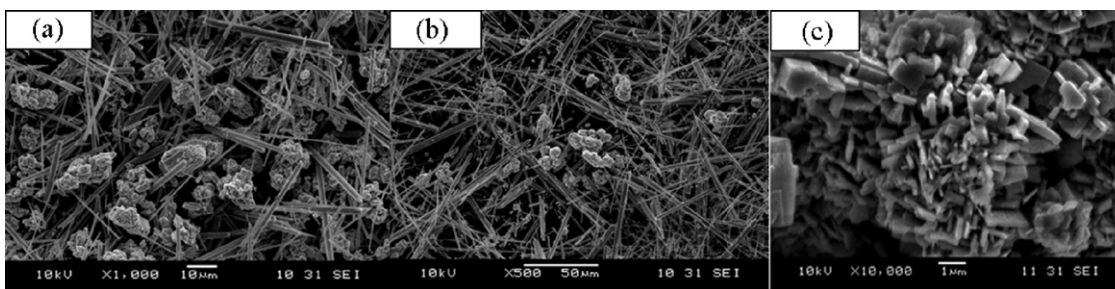


Fig. 8. SEM images of samples prepared at 160 °C for various reaction duration with 0.03 M Nb₂O₅ and 14 M NaOH (a: 4 h, b: 8 h, c: 24 h).

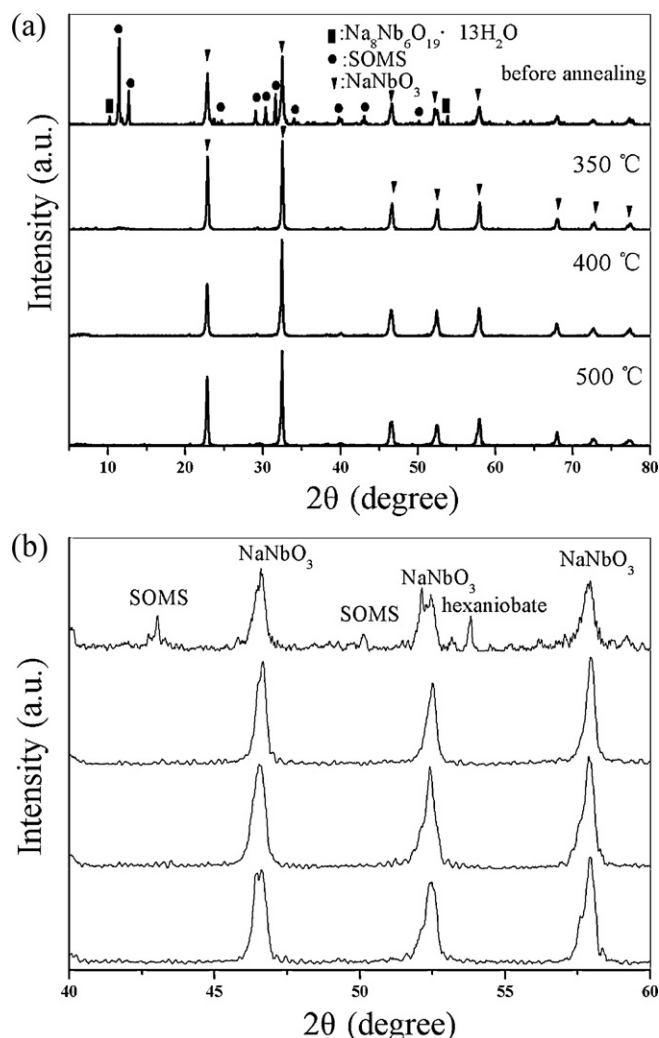


Fig. 9. (a) XRD patterns of samples prepared at 160 °C for 4 h with 14 M NaOH and 0.03 M Nb₂O₅ and its corresponding annealed powder at different temperatures for 6 h; (b) The enlarged patterns for all the above ones at two theta ranging from 40° to 60°.

that SOMS could be converted into NaNbO₃ by annealing was once confirmed by Xu et al. [25] using drop-solution calorimetric measurements. Moreover, Ke et al. [21] and Shi et al. [22] obtained nanowires of NaNbO₃ by annealing fiber-like SOMS. Here, our results indicate that these intermediates of sodium niobate can be converted into sodium niobate by elongating the reaction duration or annealing at certain proper temperature. Longer reaction duration changes the intermediate phase as well as its morphology, while the interesting morphology of intermediates can be maintained by annealing.

4. Conclusions

Orthorhombic NaNbO₃ of ferroelectric phase with different morphologies was synthesized by hydrothermal method. The influence of temperature, concentration of NaOH and Nb₂O₅, and reaction duration on structure and morphology of NaNbO₃ and the intermediates was analyzed.

NaOH and Nb₂O₅ concentrations have a remarkable influence on the sample morphology. Lower concentration of

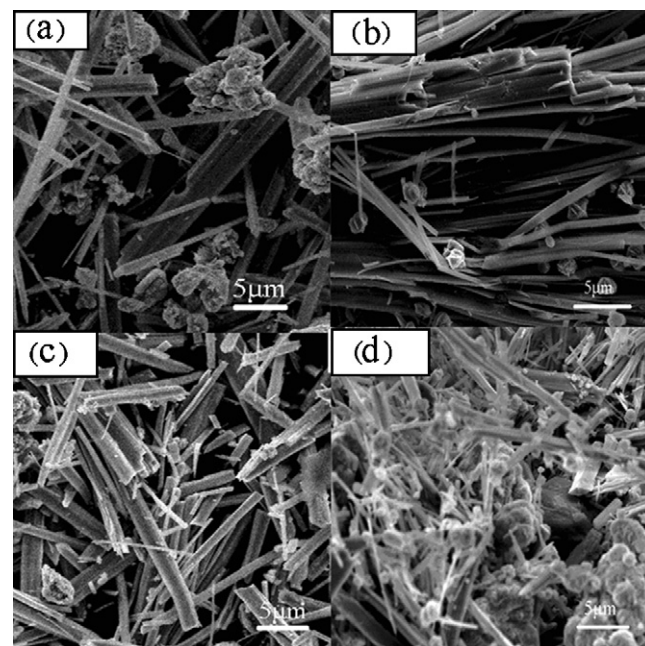


Fig. 10. SEM images of samples prepared at 160 °C for 4 h with 14 M NaOH and 0.03 M Nb₂O₅ and its corresponding annealed powder at different temperatures for 6 h (a: before annealing; b: 350 °C; c: 400 °C; d: 500 °C).

Nb₂O₅ is propitious to form NaNbO₃ nanorods and nanoplates, while lower concentration of NaOH facilitates the formation of NaNbO₃ cubes. They both have a little effect on the crystalline structure of NaNbO₃. Orthorhombic phase NaNbO₃ is more likely formed with lower ratio of NaOH/Nb₂O₅. In order to attain mono-phase NaNbO₃, a higher temperature is needed. Nb₂O₅ was converted into SOMS and Na₈Nb₆O₁₉ · 13H₂O, then NaNbO₃ was formed from these intermediates as reaction duration is increased. NaNbO₃ can be obtained by prolonging the reaction duration or annealing certain intermediates, while the morphology of these intermediates can be retained by annealing at certain temperature.

Acknowledgements

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