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Hydrothermal synthesis of potassium niobate powders

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Abstract

Potassium niobate ($KNbO_3$) powders with the orthorhombic structure were successfully synthesized through the hydrothermal reaction of Nb_2O_5 and KOH at 200 °C. The concentration of KOH had a great effect on the morphology and particle size of $KNbO_3$ powders. The morphology of $KNbO_3$ powders changed from rod-like to cubic particles when the potassium hydroxide (KOH) concentrations was in the range of 6.25–15 M. Particularly, when the KOH concentration was 7.5 M and the amount of Nb_2O_5 was 0.02 mol, dodecahedral crystalline was found in the precipitations.
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Keywords: Potassium niobate; Hydrothermal synthesis; Morphology; Crystal growth

1. Introduction

Potassium niobate ($KNbO_3$) is a well known ferroelectric material for applications such as optical wave-guiding, frequency doubling, holographic storage and surface acoustic wave devices [1–6]. The material, including its solid solutions, has attracted considerable interest among material scientists because of its high-temperature ferroelectricity and piezoelectricity. Recently, Saito et al. [7] synthesized high performance lead-free ceramics based on the (K, Na)NbO_3 system. However, $KNbO_3$-based ceramics are very difficult to synthesize by conventional solid-state reaction because the high temperature sintering often leads to stochiometric deviation in the composition of the final product. Various chemical methods have been developed for producing $KNbO_3$ powders such as homogeneous precipitation method [8], polymerized complex (PC) method [9] and hydrothermal synthesis method [10–14]. Compared with solid-state preparation, the hydrothermal process has been confirmed to be a more efficient method in controlling the morphology and chemical composition of powders [15,16].

The starting materials for hydrothermal synthesis of $KNbO_3$ are usually niobium pentoxide (Nb_2O_5) and the aqueous solution of potassium hydroxide (KOH) [10–12]. It was reported that $KNbO_3$ crystals could be obtained only when the alkaline concentration was above 6 M [10]. Hydrothermal reactions of Nb_2O_5 with KOH may provide $KNbO_3$, KNb_3O_8, $K_4Nb_{16}O_{17}{\cdot}3H_2O$ or potassium hexaniobates like $K_6H_2[Nb_6O_{19}]{\cdot}13H_2O$ [12,17]. The concentration of KOH played an important role in the reaction.

We report here the hydrothermal synthesis of microcrystalline $KNbO_3$ using Nb_2O_5 and KOH as reactants. Different concentrations of KOH and different amounts of Nb_2O_5 were examined. The powders obtained in the hydrothermal reaction at different conditions displayed four different crystal shapes: rod-like, brick-like, dodecahedral and cubic shapes. The effects of the amount of raw materials added for the reaction on the morphology and particles size of $KNbO_3$ powders was investigated.

2. Experimental

Analytical grade potassium hydroxide (KOH) and niobium oxide (Nb_2O_5, 99.5%) were used as raw materials. KOH was dissolved in deionized water and mixed with various amounts of Nb_2O_5. Then the mixed slurries were placed in a Teflon-lined cylindrical autoclave apparatus (100 cm^{-3} capacity), and

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Table 1
Products obtained in the hydrothermal reaction between KOH and Nb_2O_5 at various conditions

Sample no.	Concentration of KOH (M)	Amount of Nb_2O_5 (mol)	Reaction temperature (°C)	Reaction time (h)	Particle morphology
1	6.25	0.01	200	12	No precipitates
2	7.5	0.02	200	12	Dodecahedronal
3	10	0.01	200	12	Brick-like
4	12.5	0.01	200	12	Rod-like
5	15	0.02	200	6	Cubic

introduced in an oven pre-heated to 200 °C for 6–12 h. After the hydrothermal reaction, the obtained powders were washed with deionized water and absolute ethanol for several times. After drying in desiccator at 80 °C for 5 h, the powders were collected for characterizations.

Phase identification of the samples was determined by X-ray diffraction (XRD, Rigaku D/MAX 2200). The size and morphology of powders was examined with a field emission scanning electron microscope (FESEM, JSM 6700F). Transmission electron microscopy (TEM) and electron diffraction (ED) pattern were taken on Shimadzu model JEM-2100F. The Fourier transform infrared (FTIR) spectra were recorded on a NEXUS FTIR spectrometer, using KBr pellets. Raman spectra (RS) were performed in a NEXUS FT-Raman spectrometer. The element compositions were analyzed by an electron probe X-ray microanalysis (EPMA-8705QH2).

3. Results and discussion

Hydrothermal reactions of Nb_2O_5 with aqueous KOH were performed at 200 °C under autogenic pressure in an autoclave with KOH concentrations ranging from 6.25 to 15 M. The reaction time and molar ratio of KOH:Nb_2O_5 were varied. The experimental conditions and the particle morphology of the products are listed in Table 1. It is found that Nb_2O_5 was all dissolved in the solution after 12 h reaction with the KOH concentration of 6.25 M (sample 1). When the KOH concentration was more than 7.5 M, crystallized powders were formed.

Typical XRD patterns of the as-synthesized products are shown in Fig. 1 with the main peaks readily indexed. The main diffraction peaks of samples 3–5 with KOH concentrations of 10–15 M were assigned to the orthorhombic $KNbO_3$ phase, with lattice constants $a = 5.697$ Å, $b = 3.971$ Å and $c = 5.721$ Å (JCPDS 71-2171). When the concentration of KOH equals to 7.5 M (sample 2), orthorhombic $KNbO_3$ powders were formed with some impurity presented in products. The peaks of the impurity are close to those of $K_6H_2[Nb_6O_{19}]\cdot 13H_2O$, as reported by Santos et al. [17]. However, there is no correspondent powder X-ray diffraction patterns of $K_6H_2[Nb_6O_{19}]\cdot 13H_2O$ published. We also studied the infrared spectrum of sample 2 (Fig. 2). The peaks were assigned to Nb=O and Nb–O–Nb stretching vibrations which are the characteristic pattern of the hexaniobate anions ($H_xNb_6O_{19}^{(8-x)-}$). The general formula of potassium hexaniobates is $K_{8-x}H_x[Nb_6O_{19}]\cdot nH_2O$, $x = 0$–3 [17]. We are currently determining the stoichiometry of the unknown potassium hexaniobates crystal structure.

The FESEM images of the powders obtained from the reactions performed with different KOH concentrations are shown in Fig. 3. When the KOH concentration was 7.5 M, scattered dodecahedronal crystals (potassium hexaniobates) and aggregated $KNbO_3$ particles with cubic shape were observed (Fig. 3(a and b)). The particle size of dodecahedronal

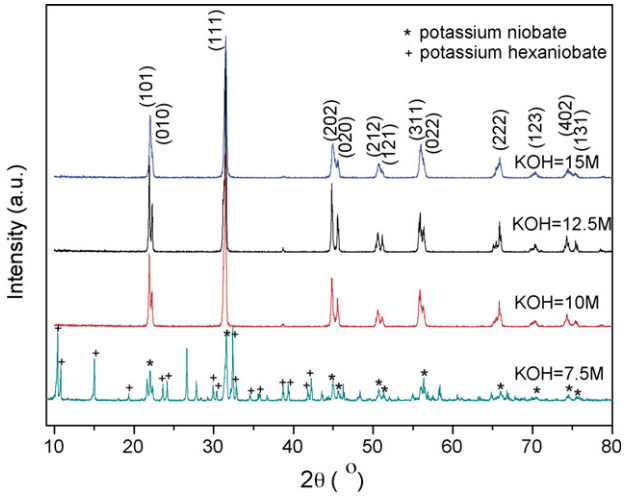

Fig. 1. X-ray diffraction patterns of the powders obtained after 6–12 h hydrothermal reaction, with different KOH concentrations ranging from 7.5 to 15 M. The main peaks corresponding to $KNbO_3$ are indexed.

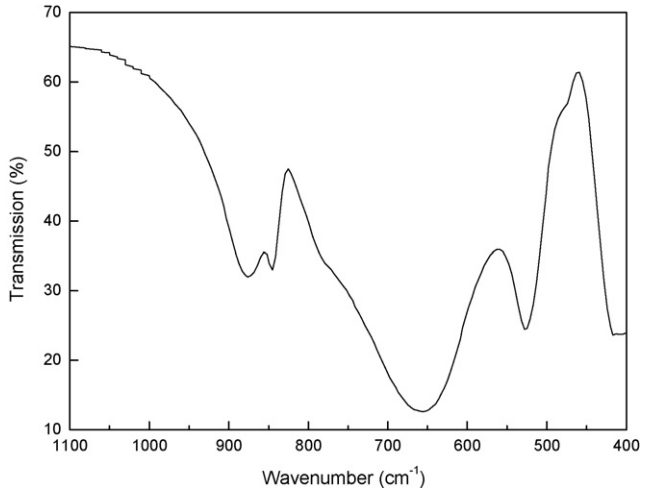

Fig. 2. FTIR spectrum of the powders obtained after 12 h reaction time using 7.5 M KOH solution.

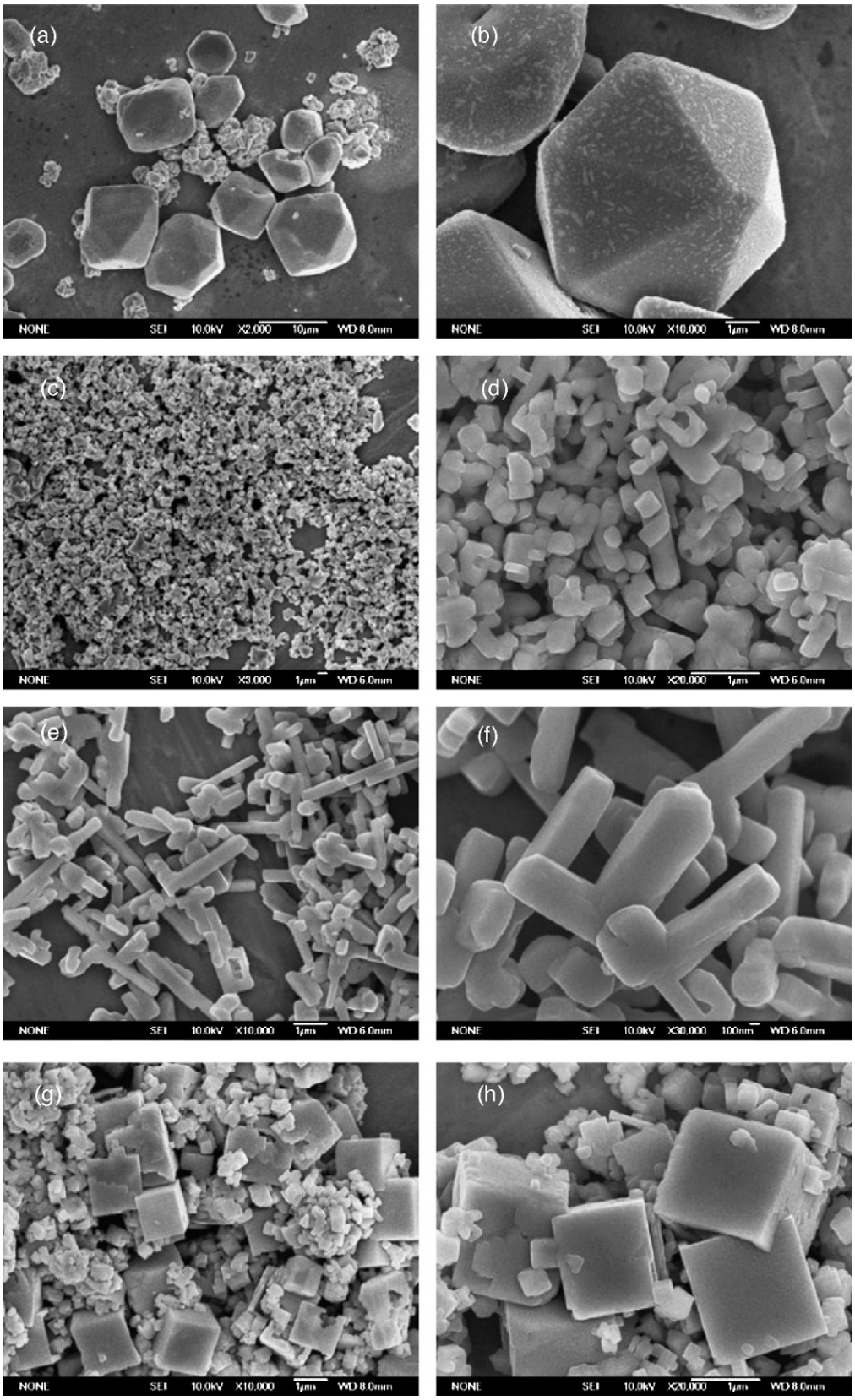

Fig. 3. FESEM photographs of the powders obtained with different KOH concentrations for 6–12 h: (a and b) 7.5 M; (c and d) 10 M; (e and f) 12.5 M; (g and h) 15 M.

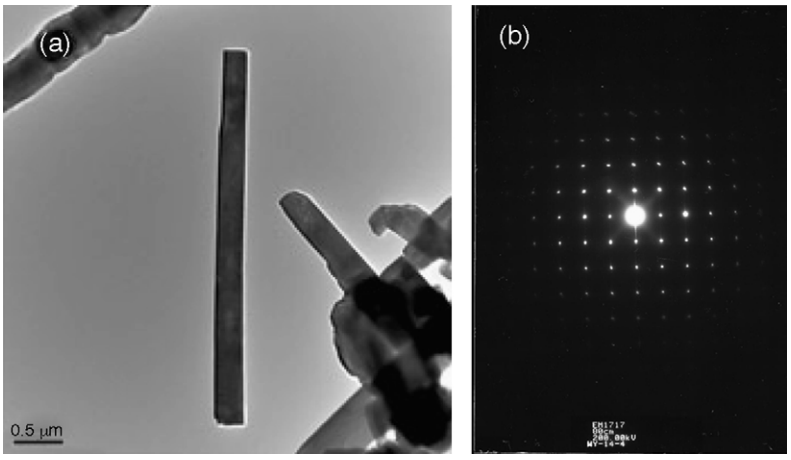

Fig. 4. TEM images (a) the $KNbO_3$ crystal obtained at the KOH concentration of 12.5 M and, (b) the electron diffraction pattern.

crystals reached about 10 μm and the size of $KNbO_3$ particles less than 1 μm. After increasing the KOH concentration to 10 M, it was observed that the potassium hexaniobates disappeared and brick-like $KNbO_3$ crystals with the particle size ranging from 100 nm to 1 μm were formed (Fig. 3(c and d)). Several rod-like crystals are presented. It is observed from Fig. 3(e and f), that the single crystal rod-like $KNbO_3$ are several micrometers in length and have diameters of about 500 nm. These nanorods showed a rectangular section. When the KOH concentration was as high as 15 M, well-crystallized cubic $KNbO_3$ crystals can be seen (Fig. 3(g and h)).

The above results reveal that the concentration of KOH is a critical factor for controlling the synthesis of $KNbO_3$ at a fixed temperature (200 °C). Raising the KOH concentration tends to increase the formation of $KNbO_3$.

Fig. 4 shows the TEM images and electron diffraction (ED) pattern of the $KNbO_3$ crystal obtained at a KOH concentration of 12.5 M. The ED pattern of the selected rod-like $KNbO_3$ crystal facet belongs to [1 0 1] zone axis ($[1\,0\,\bar{1}]$direction is parallel to long axis of the crystal while [0 1 0] direction is perpendicular). The ED pattern confirmed the epitaxial nature of the crystal growth.

4. Conclusions

Through the hydrothermal reaction of Nb_2O_5 with KOH, monophasic $KNbO_3$ powders with the orthorhombic structure were synthesized at 200 °C. The concentration of KOH had a great effect on the phase composition and morphology of the resultant powders and promoting the formation of orthorhombic $KNbO_3$. It is found that Nb_2O_5 was all dissolved in the solution after a 12 h reaction with the KOH at a concentration of 6.25 M. The crystal shapes of $KNbO_3$ powders changed from rod-like crystals to cubic particles with KOH concentrations in the range of 7.5–15 M. Most importantly, when the concentration of KOH was 7.5 M and the amount of Nb_2O_5 was 0.02 mol, dodecahedral crystals were found in the precipitations for the first time.

Compared with solid-state preparation, the hydrothermal process effectively reduced the synthesis temperature of $KNbO_3$, and has been confirmed to be a more efficient method in controlling the morphology and chemical composition of powders. The high reactive $KNbO_3$ fine powders with anisotropic shape can be used as seed templates for grain oriented piezoelectric ceramics. The work on piezoelectric properties of the $KNbO_3$-based ceramics sintered from the hydrothermal synthesized powders is being undertaken in our lab and it will be reported elsewhere.

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