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Synthesis of potassium sodium niobate nanostructures by hydrothermal combining with the sol-gel method

Xianghe Meng, Wen Wang*, Hua Ke, Jiancun Rao, Yu Zhou

Institute for Advanced Ceramics, School of Materials Science and Engineering, Harbin Institute of Technology, Harbin 150001, PR China

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ABSTRACT

In this paper the $K_{1-x}Na_xNbO_3$(KNN) nanostructures were synthesized by hydrothermal method using KNN gel powders as precursors. $KNbO_3$-type orthorhombic KNN nanowires and perovskite KNN microfingers with a morphotropic phase boundary (MPB) between rhombohedral and tetragonal characterized by X-ray diffraction and Raman spectroscopy were obtained at 190 °C and 220 °C, respectively. $KNbO_3$-type orthorhombic KNN nanowires had rectangular shape and the growth direction of these nanowires was [001]. The rhombohedral-tetragonal KNN microfingers were metastable, and changed the rhombohedral-tetragonal phase into the orthorhombic phase via thermal treatment at 600 °C then cooled down to room temperature. Sodium dodecyl sulfate (SDS) as surfactant was added to the hydrothermal reaction. It was found that SDS could improve the crystallinity of the rhombohedral-tetragonal $K_{0.52}Na_{0.48}NbO_3$ and reduce the impurity effectively. The tetragonal-cubic phase transition temperature (*Tc*) of the rhombohedral-tetragonal powders appeared at 555 °C.

1. Introduction

The synthesis of nanoscale perovskite crystals is attracting increasing attentions because of their novel and interesting properties [1–3]. In particular, ferroelectric and piezoelectric nanostructures have been extensively studied due to the size effect, which can change the magnitude and direction of spontaneous electric polarization, the crystal structure and the Curie temperature comparing with their ferroelectric bulk counterparts [3–5]. Potassium sodium niobate (KNN), as a kind of lead-free piezoelectric, is one of the most potentially useful candidates to replace the lead-based ferroelectrics because of its non-toxic high piezoelectric constant and high Curie temperature [6].

In 1976, the phase diagram for KNN was originally reported by Ahtee and Glazer [7]. In the phase diagram, the rhombohedral polymorph is not mentioned as it only appears at very low temperatures (~115 °C) [8]. And a morphotropic phase boundary (MPB) was observed at $x = 0.5$, where the symmetry changes abruptly from an orthorhombic unit cell (phase M) to a monoclinic one (phase L) [9]. But the XRD patterns of both M and L phases could be indexed as the orthorhombic form [10]. It was reported that $K_{0.5}Na_{0.5}NbO_3$ ceramics have the highest d_{33} in KNN system owe to the MPB [11]. So it is very significant to synthesize the $K_{0.5}Na_{0.5}NbO_3$ nanostructure.

So far, hydrothermal method [12–18] and molten salt method [19,20] are used for the synthesis of $KNbO_3$(KN) and KNN based nanostructures. Between them, the hydrothermal method is cost-effective, controllable, and reacts at low temperature [3]. Homogeneous orthorhombic KN nanowires were synthesized by hydrothermal method, and this process requires a reaction time of ~1 week [21]. Tetragonal KN nanowires were formed via decreasing the reaction time to 48 h by Mi-Ri Joung et al. [22]. The existence of OH^- and H_2O was responsible for the formation of tetragonal KN nanowires. For the KNN nanostructures, it is difficult to keep the mole ratio of K/Na of products around 1:1 because the ionic radius of Na is smaller than K that Na^+ occupies the interval of oxygen octahedra easily leading to forming Na-rich KNN. In recent years, the synthesis of $K_{1-x}Na_xNbO_3$ 1D nanostructure has been demonstrated, the rectangular shapes with various sizes of Na-rich $K_{1-x}Na_xNbO_3$ nanorods were fabricated by Xu et al. [13]. For some cases the $K_{0.5}Na_{0.5}NbO_3$ nanorods were obtained by controlling the ratio of K^+/Na^+ in starting solution, the formation mechanism was also achieved, and the band gap of the nanorods is 3.09 eV [12]. However, the $K_{0.5}Na_{0.5}NbO_3$ powders have two phases, and the $K_{0.5}Na_{0.5}NbO_3$ nanorods are only $NaNbO_3$-type monoclinic phase belonging to crystal structure of $K_{0.02}Na_{0.98}NbO_3$ (JCPDS Card No. 74-2449), and the $KNbO_3$-type orthorhombic KNN nanorods or nanowires weren't observed. The plate-like $K_{1-x}Na_xNbO_3$ were prepared by adding the surfactants and heat treatment, but the accurate compositions of the powders weren't obtained [17]. In these literatures, the niobic oxide is used as precursor. There are

* Corresponding author.
E-mail address: wangwen@hit.edu.cn (W. Wang).

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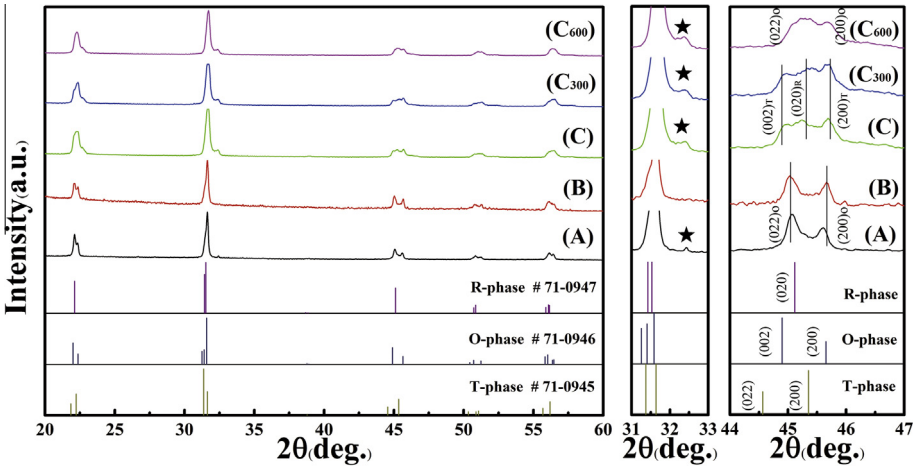

Fig. 1. XRD patterns of KNN powders via hydrothermal at 180 °C for 12 h (sample A), 190 °C for 12 h (sample B) or 220 °C for 12 h (sample C); XRD patterns of sample C by heat treated at 300 °C (sample C_{300}) or 600 °C (sample C_{600}).

seldom studies about using other Nb sources in the hydrothermal reaction. The single phase KNN nanostructures based on KN lattice weren't prepared by the hydrothermal method.

In this paper, we combine the sol-gel method with hydrothermal method, using the $K_{1-x}Na_xNbO_3$ gel powders as precursors, a MPB between the rhombohedral-tetragonal was found in KNN nanostructures synthetized at 220 °C. When hydrothermal temperature was 190 °C, the KNN phase is $KNbO_3$-type orthorhombic, and its morphology was nanowire. We found the gel powders to be more reactive than Nb_2O_5 in the hydrothermal reaction, the allowing orthorhombic and rhombohedral-tetragonal KNN nanostructures to be synthesized successfully only in 12 h. The surfactant SDS can improve the crystallinity of KNN powders. The ferroelectric-paraelectric phase transition of the rhombohedral-tetragonal KNN powders was achieved by measuring the dielectric properties using a precision impedance analyzer. Our study provides a new method to fabricate KNN nanostructures with MPB for researchers.

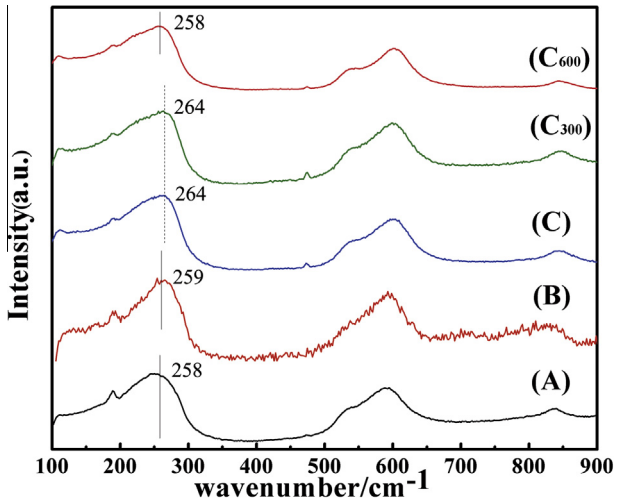

Fig. 2. Room-temperature Raman scattering spectra of KNN powders via hydrothermal at 180 °C for 12 h (sample A), 190 °C for 12 h (sample B) or 220 °C for 12 h (sample C); room-temperature Raman scattering spectra of sample C by heat treated at 300 °C (sample C_{300}) or 600 °C (sample C_{600}).

2. Experimental

2.1. Synthesis of KNN nanostructures

The KNN nanostructures were synthesized via a hydrothermal reaction using KNN precursor powders prepared by sol-gel method. Sodium acetate and potassium acetate were dissolved into ethylene glycol with the Na^+/K^+ = 2.4/7.6. Niobium ethoxide was added under constant stirring until the solution became transparent. A stable sol was obtained. The precursor solution was dried at 50–80 °C for about 1 week to obtain the K-Na-Nb dried gel powders. K-Na-Nb dried gel powders was added to a mixed solution of NaOH and KOH (Na^+/K^+ = 2.4/7.6), with stirring for 20 min. Then the slurry was introduced into a 10-mL Teflon-lined stainless steel autoclave (the filling factor was approximately 80 vol%) and heated in a furnace at the temperature range of 180–220 °C for 12 h. After gradually cooling down to room temperature, the creating precipitates were filtered and washed with distilled water and ethanol, then dried at 60 °C.

Table 1
The observed Raman band frequencies and assignments (in comparison with Ref. [12] $K_{0.74}Na_{0.26}NbO_3$ and Ref. [23] $KNbO_3$).

Assign.	Sample (A)	Sample (B)	Sample (C)	Sample (C_{300})	Sample (C_{600})	Freq./cm^{-1} (Ref. [12])	Freq./cm^{-1} (Ref. [23])
Mixed	187	187	191	191	191	192	196
B1(TO)						261	266
A1(TO)	258	259	264	264	258	272	280
A1(LO)+						289	298
B1(TO)							
A1(LO)						430	435
B1(TO)	540	537	541	541	541	537	535
A1(TO)	600	598	601	601	601	600	597
A1(LO)	838	x	844	844	844	839	836