Available online at www.sciencedirect.com
ScienceDirect
Ceramics International 34 (2008) 435–437
CERAMICS INTERNATIONAL
www.elsevier.com/locate/ceramint

Short communication

A facile molten salt route to $K_2Nb_8O_{21}$ nanoribbons

Cheng-Yan Xu [a], Liang Zhen [a,*], Li Yang [a], Kai He [a], Wen-Zhu Shao [a], Lu-Chang Qin [b,c]

[a] School of Materials Science and Engineering, Harbin Institute of Technology, Harbin 150001, China
[b] Department of Physics and Astronomy, University of North Carolina at Chapel Hill, Chapel Hill, NC 27599-3255, USA
[c] Curriculum in Applied and Materials Sciences, University of North Carolina at Chapel Hill, Chapel Hill, NC 27599-3255, USA

Received 14 June 2006; received in revised form 28 September 2006; accepted 4 October 2006
Available online 8 December 2006

Abstract

Single-crystalline $K_2Nb_8O_{21}$ nanoribbons with width of 100–500 nm and thickness of *ca*. 30 nm, and length up to tens of micron, have been successfully synthesized by simply calcining Nb_2O_5 powders in molten KCl, and characterized with XRD, SEM, SEM, HRTEM and selected-area electron diffraction technique. The growth direction of the obtained $K_2Nb_8O_{21}$ nanoribbons was determined to be the ⟨1 0 0⟩ crystallography direction.

Keywords: $K_2Nb_8O_{21}$ nanoribbons; Crystal growth; Molten salt synthesis

1. Introduction

One-dimensional (1D) nanostructures of ternary metal oxides have become the focus of study since they might exhibit novel size-dependent properties on nanoscale, *i.e.*, ferroelectric and multiferroic properties, compared with 1D nanostructures of elements and binary compounds. Urban et al. [1] first reported the successful synthesis of single-crystalline $BaTiO_3$ and $SrTiO_3$ nanorods by solution-phase decomposition of bimetallic alkoxide precursors in the presence of coordinating ligands. They have also measured the ferroelectric properties of individual $BaTiO_3$ nanowire using scanning probe microscopy (SPM) [2]. $BaTiO_3$ nanowires and nanotubes have been fabricated via a solid-state reaction method or a hydrothermal route [3]. The family of chromates, including $PbCrO_4$, $SrCrO_4$, or other ternary metal oxides with ABO_4-type structure, such as tungstate, has been well explored, using mostly hydrothermal routes [4]. The hydrothermal method has been also used to the synthesis of other families of ternary metal oxides, including $Na_2Ti_4O_9$ [5], $K_2Ti_6O_{13}$ [6], $K_2Ti_8O_{17}$ [5,7], $Na_2V_6O_{13}$ [8], etc.

In a recent communication, we reported a successful synthesis of sodium hexatitanate and potassium hollandite nanowires from the reaction of TiO_2 and molten salt with the presence of a nonionic surfactant NP-9 [9]. The molten salts serve also as reaction precursor for the synthesis of alkali titanates except as reaction media. Herein we choose potassium niobate as the studied system since alkali or alkali metal niobates might exhibit excellent nonlinear optical properties or dielectric properties, etc. [10]. Conventionally, potassium niobates could be obtained by high-temperature calcination using K_2CO_3 and Nb_2O_5 as starting materials [11]. $K_2Nb_8O_{21}$ was first reported by Guerchais [12], and they also obtained the powder X-ray diffraction patterns. However, the crystal structure and lattice parameters of $K_2Nb_8O_{21}$ were not well documented until Teng's work on $K_2Nb_8O_{21}$ single crystal using electron diffraction and lattice imaging technique [13], since it is not so easy to obtain phase-pure $K_2Nb_8O_{21}$. The crystal structure of $K_2Nb_8O_{21}$ was determined to be orthorhombic with lattice parameters $a = 3.75$ nm, $b = 1.25$ nm, and $c = 0.396$ nm. In this Communication, we present the successful synthesis of single-crystalline $K_2Nb_8O_{21}$ nanoribbons, using a simple solid-state method without employing particular atmosphere or any surfactants. The synthesized nanoribbons were characterized with X-ray diffraction (XRD), electron diffraction, scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

* Corresponding author. Tel.: +86 451 86412133; fax: +86 451 86413922.
E-mail address: zhenl@hit.edu.cn (L. Zhen).

0272-8842/$34.00
doi:10.1016/j.ceramint.2006.10.007

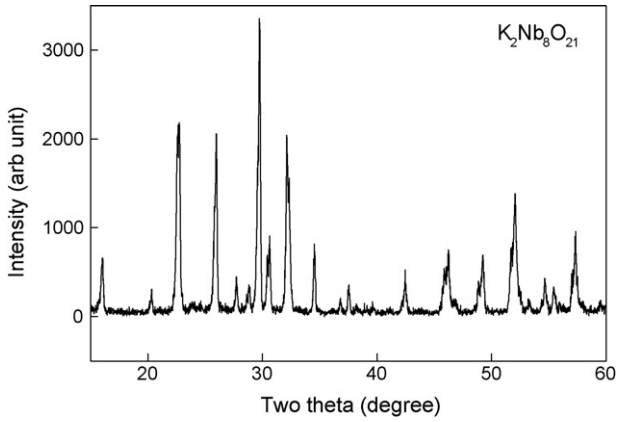

Fig. 1. XRD pattern of the as-synthesized $K_2Nb_8O_{21}$ nanoribbons.

2. Experimental

The chemical reaction for the synthesis of the potassium niobate ($K_2Nb_8O_{21}$) can be described as the following formula:

$$8Nb_2O_5(s) + 4KCl(s) + O_2(g) \rightarrow 2K_2Nb_8O_{21}(s) + 2Cl_2(g)$$

In a typical procedure, 0.3 g Nb_2O_5 powders were mixed with 1.6 g KCl and ground for 10 min. The mixture was first placed in a combustion boat and annealed in a tube furnace at 800 °C for 3 h and, subsequently, cooled naturally to room temperature. The pristine powders were washed with distilled water several times to remove the remnant KCl, and then dried at room temperature.

The morphology, structure and dimensions of the synthesized nanoribbons were characterized with XRD (Phillips

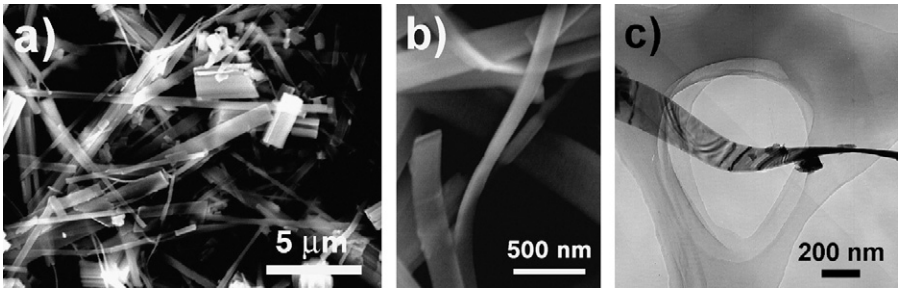

Fig. 2. (a) SEM image of $K_2Nb_8O_{21}$ nanoribbons showing general morphologies. (b) SEM image of several curled $K_2Nb_8O_{21}$ nanoribbons. (c) TEM image of a twisted $K_2Nb_8O_{21}$ nanoribbon.

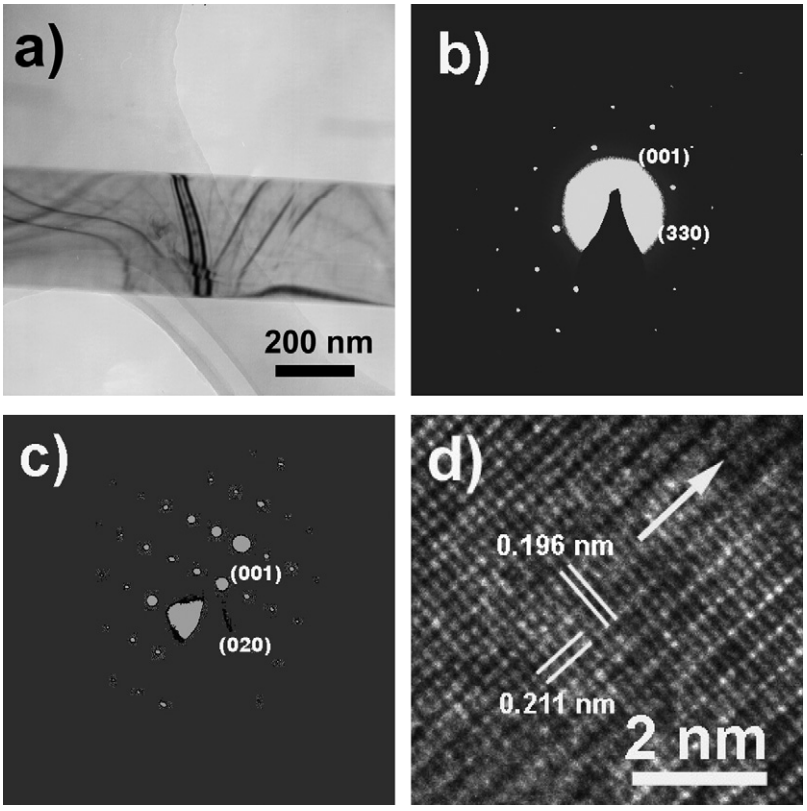

Fig. 3. (a) TEM image of an individual $K_2Nb_8O_{21}$ nanoribbon. (b–c) Electron diffraction patterns of the same $K_2Nb_8O_{21}$ nanoribbon tilted to zone axes of [−1, −1, 0] and [−1, 0, 0], respectively. (d) HREM image of $K_2Nb_8O_{21}$ nanoribbon.

X'pert), SEM (Hitachi S-4700 and S-570), TEM (Philips Tecnai 20 and JEOL 2010F). The nanoribbons were dispersed in ethanol aided by ultrasonic treatment. One drop of the suspension was added to a holey carbon film supported on a copper grid.

3. Results and discussion

The final products were phase-pure $K_2Nb_8O_{21}$, characterized by a X-ray diffractometer with Cu Kα radiation (λ = 1.5406 Å). The X-ray diffraction (XRD) pattern in Fig. 1 could be readily indexed to the orthorhombic $K_2Nb_8O_{21}$ (JCPDS 31-1060). Fig. 2a demonstrates the general morphology of the as-synthesized $K_2Nb_8O_{21}$ nanoribbons. Large quantity of nanoribbons with length up to tens of microns could be observed. The width of the synthesized nanoribbons ranges from 100 to 500 nm, while the thickness could be well defined from a curled nanoribbon shown in Fig. 2b, which is around 30 nm. The width of the shown nanoribbons is about 300 nm. Thus, the width–thickness ratio of this nanoribbon is around 10. The ribbon-like morphology could be also understood from the TEM image of a twisted nanoribbon, as shown in Fig. 2c.

To further confirm the crystal structure of the synthesized nanoribbons, we examined the electron diffraction patterns in several orientations by tilting an individual nanoribbon. Figs. 3b and 3c show two electron diffraction patterns taken from the same nanoribbon depicted in Fig. 3a. The two zone axes are determined as [−1, −1, 0] (Fig. 2b) and [−1, 0, 0] (Fig. 2c), respectively. The experimental rotating angle between the two zone axes is 18.4°, which is well consistent with the calculated value. The growth direction of the studied nanoribbon was thus determined to be the ⟨1 0 0⟩ crystallography direction according to the tilting experiment. Selective-area electron diffraction (SAED) patterns taken over a wealth of nanoribbons have also shown the synthesized nanoribbons are naturally single-crystalline. The two-dimensional lattice image (Fig. 3d), showing the lattice spacing of 1.96 and 2.11 Å, further demonstrates that the nanoribbon is single crystalline and is free of crystal defects. The white arrow in Fig. 3d indicates the crystal growth direction of ⟨1 0 0⟩ crystallography direction, which is consists with the SAED results.

4. Conclusions

In summary, we have demonstrated a facile, large-scale synthesis route to single-crystalline $K_2Nb_8O_{21}$ nanoribbons. The nanoribbons have widths of several hundred nanometers, a thickness of *ca*. 30 nm, and lengths up to several tens of microns. This method might also be extended to the fabrication of other ternary oxide nanostructures.

References

[1] J.J. Urban, W.S. Yun, Q. Gu, H.K. Park, J. Am. Chem. Soc. 124 (2002) 1186.
[2] W.S. Yun, J.J. Urban, Q. Gu, H.K. Park, Nano Lett. 2 (2002) 447.
[3] Y.B. Mao, S. Banerjee, S.S. Wong, J. Am. Chem. Soc. 125 (2003) 15718.
[4] J.H. Liang, Q. Peng, X. Wang, X. Zheng, R.J. Wang, X.P. Qiu, C.W. Nan, Y.D. Li, Inorg. Chem. 44 (2006) 9405.
[5] X.M. Sun, X. Chen, Y.D. Li, Inorg. Chem. 41 (2002) 4996.
[6] B.L. Wang, Q. Chen, R.H. Wang, L.M. Peng, Chem. Phys. Lett. 376 (2003) 726.
[7] Z.Y. Yuan, X.B. Zhang, B.L. Su, Appl. Phys. A 78 (2004) 1063.
[8] J.G. Yu, J.C. Yu, W.K. Ho, L. Wu, X.C. Wang, J. Am. Chem. Soc. 126 (2004) 3422.
[9] C.Y. Xu, Q. Zhang, H. Zhang, L. Zhen, J. Tang, L.-C. Qin, J. Am. Chem. Soc. 127 (2005) 11584.
[10] C.D. Whiston, A.J. Smith, Acta Cryst. 19 (1965) 169.
[11] A. Reisman, F. Holtzberg, J. Am. Chem. Soc. 77 (1955) 2115.
[12] J.E. Guerchais, Bull. Soc. Chim. France 1 (1962) 103.
[13] C.M. Teng, F.H. Li, D.Y. Yang, Q.Z. Wu, J. Chin. Ceram. Soc. 4 (1986) 484 (in Chinese).