Synthesis of Single-crystalline KNbO_3 Nanowires with a Sacrificial Template Method and Their Second Harmonic Generation Response

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Abstract: High yield orthorhombic single-crystalline KNbO_3 nanowires with widths of 60~150 nm and lengths up to a few microns were synthesized, using Nb_2O_5 nanobelts as reactants as well as templates via the hydrothermal process. The products were determined by XRD, and the morphology and the structure were characterized by SEM, TEM, HRTEM, and SAED techniques. The growth direction of KNbO_3 was determined to be the [001] crystallographic direction. Results show that synthesized nanowires exhibit a second harmonic generation (SHG) response, an efficient nanoscale second harmonic light source. The excellent nonlinear optical properties of KNbO_3 have potential applications in nano-optical devices.

Key words: KNbO_3 ; nanowires; hydrothermal reaction; SHG (second harmonic generation)

Template-directed synthesis represents a straightforward approach to generating one-dimensional (1D) nanostructures. In this approach, the template serves as a scaffold against which other materials are assembled with morphology complementary to that of the template. Both “hard” templates (such as carbon nanotubes or anodic aluminum oxide nanostructures) and “soft” templates (such as surfactant-directed micelles, reverse micelles, or block copolymers) have been developed^[1]. The sacrificial template method has been proven to be a facile and efficient route for the synthesis of nanowires^[2-4]. Few such templates have been identified and this approach has seldom been used to fabricate nanowires. The development of effective sacrificial templates for nanowire production could be of great significance.

KNbO_3 is one of the most promising materials for nonlinear optical and electro-optical devices because of its large nonlinear susceptibility and high photorefractive coefficient^[5,6]. One-dimensional nanostructures have novel

characteristics, differing from bulk structures. They provide new opportunities for research and technological development. Wire like KNbO_3 has been used to make a tunable nanometric light source which is compatible with physiological environments. It could be used to construct a novel form of subwavelength microscopy. The synthesis of KNbO_3 nanowires is a topic of great interest^[7,8].

The hydrothermal method is widely used in the synthesis of nanowires. The synthesis of nanowires by this method can be directed by anisotropic crystal structures or using surfactant as a soft template. The hydrothermal method can be used to control morphology during the synthesis of KNbO_3 ^[9-19]. The effects of concentration, fill factor, reactive time, temperature, pressure, surfactant and structure directing agents in the hydrothermal synthesis of KNbO_3 have been evaluated, but the synthesis of KNbO_3 nanowires is still inadequate. There are problems with the structure and morphology that result in poor reproducibility and low yield. Huang and co-workers^[9] developed a

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hydrothermal method to synthesize KNbO_3 nanoneedles on a polycrystalline Al_2O_3 substrate using a 5 day reactive time. Wang et al.^[12] reported the formation of KNbO_3 nanorods using hydrothermal synthesis and a 24 h reaction time. The sizes of the particles were more than 100 nm, and rods were formed, not nanowires. Although much progress has been made in the synthesis of KNbO_3 nanowires, a sacrificial template method to generate single-crystalline KNbO_3 nanowires using a hydrothermal process has not been reported.

We describe a novel solution-phase template approach to synthesize single-crystalline KNbO_3 nanowires. High yields of nanowires were obtained using Nb_2O_5 nanobelts as both template and reactant in a KOH based hydrothermal process. The evolution of the crystal shape and a possible mechanism of formation of KNbO_3 nanowires were proposed. The nanowires were an efficient nanoscale second harmonic light source.

1 Experiment

The reactant Nb_2O_5 nanobelts used as a sacrificing template in the present study were synthesized as previously described^[20]. In brief, KNb_3O_8 nanowires were produced using a molten-salt process. 1g Nb_2O_5 powder was mixed with 3.3 g KCl and 3.9 g K_2SO_4 and ground for 20~30 min. The mixture was placed in a combustion boat, annealed at 800 °C for 4 h in a tube furnace, and naturally cooled to room temperature. The products were washed and dried. The KNb_3O_8 nanowires were added to a 2 mol/L HNO_3 solution and stirred for 36 h. The products were filtered, washed with distilled water, and dried to form wire like $\text{H}_3\text{ONb}_3\text{O}_8$. The $\text{H}_3\text{ONb}_3\text{O}_8$ was heated at 650 °C for 1h to form Nb_2O_5 nanobelts.

In a typical experimental procedure for the synthesis of KNbO_3 nanowires, 0.26 g Nb_2O_5 nanobelts, 25.5 g KOH and 2.0 g KCl were stirred in 30 mL H_2O . The mixture was transferred into a 50 mL Teflon-lined autoclave, and the autoclave was kept in an oven at 150 °C for 3d. The composites were cooled to room temperature, washed with distilled water and ethanol, and dried at 100 °C for 12 h. The samples were collected for characterization. The yield of KNbO_3 nanowires was approximately 91%, referred to reactant Nb_2O_5 nanobelts.

The morphology, the structure and the composition of the products were characterized by scanning electron microscopy (SEM, S-4177, Japan), transmission electron microscopy (TEM, JEM 2100HR, Japan), high resolution electron microscopy (HRTEM, JEM 2100HR, Japan), X-ray diffractometry (XRD, Rigaku D/max, Japan) with a Cu $\text{K}\alpha$ radiation source ($\lambda=0.15406$ nm), and selected area electron diffraction (SAED, JEM 2100HR Japan). A standard scanning confocal microscope (Leica TCS SP2) was used to characterize the nonlinear optical properties of the

synthesized material.

2 Results and Discussion

2.1 Morphology and structural properties

Phase identification and crystalline product analysis were performed using powder X-ray diffraction (XRD). Fig.1 shows the XRD patterns of the intermediate products. All of the XRD peaks from Fig.1a can be assigned to the orthorhombic phase of KNb_3O_8 (JCPDS 75-2182) with lattice parameters of $a=0.8903$ nm, $b=2.116$ nm, and $c=0.3799$ nm. The crystal is a highly crystallized pure phase without any impurity. The phase of the intermediate product could be confirmed to be an orthorhombic $\text{H}_3\text{ONb}_3\text{O}_8$ (JCPDS 44-0672) (Fig.1b) with lattice parameters of $a=0.91987$ nm, $b=2.24733$ nm, and $c=0.38237$ nm. The phase of the niobium oxide is monoclinic Nb_2O_5 (JCPDS 43-1042) with lattice parameters of $a=0.39887$ nm, $b=0.38506$ nm, and $c=1.27645$ nm. Fig.1d shows the XRD pattern of the final product. The diffraction peaks are in agreement with the Joint Committee on Power Diffraction Standard No. 32-0822, indicating that the product is highly crystallized pure phase KNbO_3 without any impurities. The crystal structure of KNbO_3 is orthorhombic phase with lattice parameters $a=0.56823$ nm, $b=0.57169$ nm, and $c=0.39882$ nm.

Fig.2a shows the SEM image of KNb_3O_8 product with diameters of 200~500 nm and the lengths ranged from several micrometers to tens of micrometers. The morphology of the wires does not change obviously after HNO_3 treatment (Fig.2b). A large number of Nb_2O_5 nanobelts are observed after calcination. Their diameters are 300~700 nm (Fig.2c). Fig.2d shows the SEM image of the final product. A large number of KNbO_3 nanowires are observed after the template-directed hydrothermal process. Their diameters are 50~150 nm. The composition of single-crystal nanowires was calculated using the EDX spectrum (Fig.2e). The ratio of K:Nb:O is very close to 1:1:3, which is consistent with the stoichiometry of KNbO_3 .

TEM analysis provides an insight into the structural features of the KNbO_3 nanowires. Fig.3a shows the TEM

Fig.1 XRD patterns of the intermediate products

Fig.2 SEM images of synthesized KNb_3O_8 (a), $\text{H}_3\text{ONb}_3\text{O}_8$ (b), Nb_2O_5 (c), and KNbO_3 (d); EDX spectrum for Fig.2d (e)

image of an individual KNbO_3 nanowire. The diameter is 80 nm. The surfaces of the nanowires are smooth and regular. The HRTEM image demonstrates a well-defined lattice fringe on the nanowire. As shown in Fig.3b, the lattice fringe spacings along the growth and lateral directions are 0.397 and 0.404 nm, respectively. This is indexed as (001) and (110) planes of an orthorhombic KNbO_3 crystal. This is in agreement with the selected area electron diffraction (SAED) results shown in Fig.3c. The sharp diffraction spots in the SAED pattern are consistent with single-crystalline nanowires that grow in the [001] crystallographic direction.

2.2 Proposed formation mechanism

The structural evolution of KNbO_3 was described as the following reactions.

The synthesis of KNbO_3 occurs in a KOH solution via

dissolution precipitation, described as the following three reactions:

The hydrothermal synthesis has no catalyst serving as the energetically favorable site for the absorption of reactant molecules and no template to guide the directional growth of nanowires. The driving force for the anisotropic growth is mainly derived from the inherent crystal structure of the materials. In our process, the Nb_2O_5 nanobelts are converted to soluble $\text{Nb}_6\text{O}_{19}^{8-}$. A minimal reorganization of the parent solid structure is the key to the formation of the single-crystalline KNbO_3 nanowires. The atomic arrangement in the template is unaffected during the course of this reaction, so KNbO_3 inherits the shape of the Nb_2O_5 precursor. The formed particles become anisotropic. These anisotropic clusters serve as seeds for subsequent growth along the smallest surface energy direction, resulting

Fig.3 TEM image of the KNbO_3 nanowire (a), HRTEM image from the side of the nanowire (white square in Fig.3.a) (b) and SAED pattern from the same area of the nanowire (c)

in the formation of nanowires^[21]. Our experiments prove the viewpoint. Using a reaction time of 12 h, a large number of cluster KNbO_3 nanowires are formed (Fig.4a). The nanowires are a highly crystallized pure phase without any impurity identified by XRD. The length of the nanowires is short. With the extending of reactive time, the cluster gradually disappear, as shown in Fig.4b. Longer nanowires are formed when the reaction time is prolonged.

At the same time, there is a strong dependence of KNbO_3 shape and reaction rate on composition of the starting mixture. KOH is essential for wire-shaped growth. Without KOH in the reaction system, the particles are isotropic and grow in a radial direction. Nanowires are not formed. Reaction (5) is fast and reaction (6) is very slow at 150 °C. The higher the KOH concentration, the larger the solubility of Nb_2O_5 , which benefit the formation of KNbO_3 . However, if the KOH concentration is too high, reaction (7) is inhibited. The proper concentration of KOH is needed. The reaction consumes KOH and produces H_2O . This lowering of KOH concentration reduces the reaction rate, increasing the time required to form KNbO_3 nanowires. A small amount of KCl introduced into the solution increases the K^+ concentration, which increases the formation of KNbO_3 . The KNbO_3 nanowires are synthesized with a high yield in short time. The exact transformation mechanism from Nb_2O_5 nanobelts to KNbO_3 single-crystalline nanowires is not completely understood. Further investigation of the detailed reaction process is underway.

Fig.4 SEM images of synthesized KNbO_3 at 12 h (a) and 24 h (b)

2.3 Nonlinear optical properties

After producing KNbO_3 nanowires, we decided to examine their second-harmonic generation response, a second-order nonlinear optical phenomenon. We first used a standard scanning confocal microscope (Leica TCS SP2) to test whether our synthesized nanowires generated any SHG signals. This approach permits a fast characterization of many nanowires. Unlike fluorescence, the SHG process occurs without nonradiative energy loss and involves only virtual electron energy transition. Therefore, SHG structures do not bleach over time and emit a stable, nonblinking signal that does not saturate with increasing of excitation power. Prior to imaging, the KNbO_3 precipitate was diluted with deionized water, deposited on a glass slide, and examined with a confocal microscope. The laser beam from a Ti: sapphire oscillator, operated at a 860 nm wavelength with 150 fs pulse and 80 MHz repetition rate, was focused to a 20 μm diameter on the sample. The average power was 250 mW. The SHG signal at 430 nm was then collected with an oil immersion microscope objective and recorded on a photomultiplier that filtered out the pump wavelength. The polarization of the pump beam was rotated with a half-wave plate to obtain a polarization-dependent SHG response. During the measurement, the incident laser polarization was varied by 10°, and at each angle the SHG signal was recorded by acquiring an image (Fig.5 inset). All images were analyzed using a program which detected the highest intensity spot on each image and extrapolated the intensity. A polar plot of the SHG maximum value for each incident polarization angle was created by plotting the maximum normalized intensity values versus the polarization angle. Fig.5 shows the polarization-dependent response of the SHG emission for a single KNbO_3 nanowire.

Fig.5 Polarization response of the SHG from a single KNbO_3 nanowire in polar coordinates (inset: confocal image of the SHG signal from a single KNbO_3 nanowire)

3 Conclusions

1) High yield single-crystalline KNbO_3 nanowires can be synthesized using a sacrificial template process. The process does not require an organic additive.

2) Growth of the crystal occurs in the [001] crystallographic direction. The Nb_2O_5 nanobelt template plays an important role in the formation of KNbO_3 nanowires. Different morphology nanowires can be obtained by altering the reaction time. Our study provides a new method for the direct growth of single-crystalline nanowires and related materials.

3) The nanowires have a strong SHG response, which means they are an efficient nanoscale second harmonic light source.

References

- Gates B, Wu Y Y, Yin Y D et al. *Journal of the American Chemical Society*[J], 2001, 123: 11 500
- Wu C Y, Yu S H, Chen S F et al. *Journal of Materials Chemistry*[J], 2006, 16: 3326
- Li Z Q, Yang H, Ding Y et al. *Dalton Transactions*[J], 2006, 1: 149
- Yuan X S, Yang B J, Hao J W et al. *Crystal Research and Technology*[J], 2011, 46: 1296
- Grange R, Choi J W, Hsieh C L. *Applied Physics Letters*[J], 2009, 95: 143 105
- Dutto F, Raillon C, Schenk K et al. *Nano Letters*[J], 2011, 11: 2517
- Nakayama Y, Pauzauskie P J, Radenovic A et al. *Nature*[J], 2007, 447: 1098
- Pauzauskie P J, Radenovic A, Trepagnier E et al. *Nature Materials*[J], 2006, 5: 97
- Wang Y, Chen Z, Ye Z Z et al. *Journal of Crystal Growth*[J], 2012, 341: 42
- Magrez A, Vasco E, Seo J W et al. *Journal of Physical Chemistry B*[J], 2006, 110: 58
- Ding Q P, Yuan Y P, Xiong X et al. *The Journal of Physical Chemistry C*[J], 2008, 112: 18 846
- Wang G Z, Selbach S M, Yu Y D et al. *Cryst Eng Comm*[J], 2009, 11: 1958
- Liu J W, Chen G, Li Z H et al. *International Journal of Hydrogen Energy*[J], 2007, 32: 2269
- Wang Y, Yi Z G, Li Y X et al. *Ceramics International*[J], 2007, 33: 1611
- Santos I C M S, Loureiro L H, Silva M F P et al. *Polyhedron*[J], 2002, 21: 2009
- Wang C, Hou Y D, Ge H Y et al. *Rare Metal Materials and Engineering*[J], 2010, 39(2): 361 (in Chinese)
- Cao H Q, Wang F, Yu B et al. *Rare Metal Materials and Engineering*[J], 2010, 39(2): 487 (in Chinese)
- Li B, Hakuta Y, Hayashi H et al. *Journal of Supercritical fluids*[J], 2005, 35: 254
- Liu J F, Li X L, Li Y D. *Journal of Crystal Growth*[J], 2003, 247: 419
- Li L, Deng J, Chen J et al. *Chemistry of Materials*[J], 2009, 21: 1207
- Shi L, Xu Y M, Li Q. *The Journal of Chemical Physics C*[J], 2009, 113: 1795

牺牲模板法制备铌酸钾纳米棒单晶及其二次谐波产生

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摘 要: 首次使用五氧化二铌纳米棒作为原料通过水热反应合成出 60~150 nm 宽、几个微米长的高产率、斜方晶系铌酸钾纳米棒晶体。使用 X 射线衍射仪(XRD)、扫描电镜(SEM)、透射电镜(TEM)、高分辨透射电镜(HRTEM)、选区电子衍射技术(SAED)对铌酸钾纳米棒晶体的形貌和结构进行了表征。合成的铌酸钾纳米棒表现出二次谐波产生响应, 并发射出高效率的纳米二次谐波光线。铌酸钾纳米棒晶体沿着[001]方向生长。合成的铌酸钾纳米棒以其优异的非线性光学性能在纳米光学器件中的应用具有很好的发展前景。

关键词: 铌酸钾; 纳米线; 水热法; 二次谐波产生

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