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Wire Structure and Morphology Transformation of Niobium Oxide and Niobates by Molten Salt Synthesis

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Perovskite alkaline niobates, especially of one-dimensional morphology, have many important industrial applications. Wirelike Nb_2O_5 and $ANbO_3$ (A = K, Na, (Na,K)) were fabricated by a topochemical method based on the molten salt synthesis. First, the precursor KNb_3O_8 with wire structure was prepared under the condition of molten salt KCl environment at 800 °C for 3 h. Then, rodlike $H_3ONb_3O_8$ and Nb_2O_5 were obtained from the wirelike KNb_3O_8 precursor. Finally, the rodlike $ANbO_3$ (A = K, Na, (Na,K)) were achieved with the intermediate oxide Nb_2O_5. The wirelike structure of the final product can be achieved when using wirelike Nb_2O_5 precursor only. The structural evolution was investigated among protonic niobate, niobium oxide, and niobates. The mechanism of these shape transitions was elucidated in the view of structure recombining and atomic diffusing. The (Na,K)NbO_3 ceramic sintered from the as-prepared rodlike particles under pressureless condition in the air performed with high piezoelectricity (d_{33} = 140 pC/N), which is much better than that of ceramics obtained from cubic or spheric particles.

Introduction

One-dimensional (1D) morphology of oxides, including tubes[1−3] and rods and wires,[4−17] have received much attention, because of their novel shape-dependent properties, such as ferroelectric,[8] piezoelectric,[4,12] and optical properties.[5] Normally, the shape of crystalline particles depends on their internal structure, which means that materials with a cubic structure will normally form isotropic particles.[17] Therefore, it is intresting to apply special methods to form highly anisotropic particles with a cubic structure.

Perovskite alkaline niobates represent a particularly interesting class of materials that exhibit a variety of considerable nonlinear optical, ferroelectric, piezoelectric, electro-optic, ionic conductive, pyroelectric, photorefractive, and photocatalytic properties.[18] Particularly, alkaline niobates with high anisotropy exhibit unique shape-dependent piezoelectric[19] and nonlinear optical properties.[5] For instance, platelet seeds of $NaNbO_3$ were used to form texture ceramics of niobate, which possessed high performance piezoelectric properties and were potential substitutes for the traditional lead zirconium titanate (PZT), by the reactive template grain growth (RTGG) method.[19] Wirelike $KNbO_3$ was used to compose a kind of tunable nanometric light source compatible with physiological environments, which could be imposed to implement a novel form of subwavelength microscopy.[5] Therefore, high anisotropic alkaline niobates, especially 1D ones, have aroused great interest in various synthetic approaches. A sol−gel method was reported for the synthesis of needlelike $KNbO_3$ by using niobium chloride precursors complexed with organic compounds.[17] Hydrothermal reactions were used to form $KNbO_3$ wires[13,20] and $Na_2Nb_2O_6 \cdot {}^2/_3H_2O$ fibers.[14] Wirelike $K_2Nb_8O_{21}$ was obtained by the molten-salt synthesis (MSS).[9] The advantages of MSS are its rapid and large-scale fabrication of materials and the control of powder morphology.[21] Moreover, rodlike $NaNbO_3$

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and $CaNb_2O_6$ were synthesized by a topochemical method based on MSS.[10] The topochemical method is one of strategic approaches aimed at controllable synthesis, which is associated with using localized solid-state compound transformations via the exchange, deletion, or insertion of individual atoms.[19,22−24] This type of topochemical method based on MSS has been carried out to prepare various alkaline niobates with two dimensions (2D), such as platelike $NaNbO_3$ using the template of $Bi_{2.5}Na_{3.5}Nb_5O_{18}$,[19] $KNbO_3$ using $K_4Nb_6O_{17}$,[22] and $(Na,K)NbO_3$ using $K_4Nb_6O_{17}$.[23] Although rodlike $NaNbO_3$ and $CaNb_2O_6$ were fabricated by the topochemical method, only a limited amount of work was available to synthesize 1D morphology complex niobates, especially for more than two types of cations, because it was difficult to control the composition or/and the crystal structure. $K_2Nb_8O_{21}$, which was used as template, had high synthesized temperature (1000 °C).[10] Therefore, it is still a challenge to synthesize more complex oxides with 1D morphology at lower temperature. Furthermore, the structure evolution of alkaline niobates with 1D morphology from the template to the intermediate and final product during the reaction remains unexplored.

In the current work, the wirelike KNb_3O_8 was prepared by the MSS method. Rodlike $H_3ONb_3O_8$, Nb_2O_5, and $ANbO_3$ (A = K, Na, (Na,K)) were obtained from KNb_3O_8 template by the topochemical method. The structure and morphology of the as-prepared particles were characterized by X-ray diffraction patterns (XRD) and scanning electron microscopy (SEM), and the thermal behavior of the protonic niobate powder was examined by thermogravimetry and differential scanning calorimetry (TG−DSC) methods. The elemental analyses were conducted by energy dispersive X-ray (EDX). The piezoelectric property of $(Na,K)NbO_3$ ceramic obtained from rodlike $(Na,K)NbO_3$ particles was determined. The structural evolution was investigated among KNb_3O_8, $H_3ONb_3O_8$, Nb_2O_5, and $KNbO_3$.

Experimental Section

Analytical reagent grade Nb_2O_5 (>99.9%), K_2CO_3 (>99.0%), Na_2CO_3 (>99.8%), NaCl (>99.9%), KCl (>99.5%), and ethanol (>99.7%) were used as raw materials. In order to prepare 1D wirelike alkaline niobates, KNb_3O_8 was first prepared by MSS. Nb_2O_5 and KCl were mixed in ethanol according to a molar ratio of 1:10. After the mixture was dried at 80 °C, it was transferred to a crucible, loaded into an alumina furnace, and then heated at 800 °C for 3 h. The product was washed several times with hot deionized water to remove KCl salt. Second, 1 g of as-synthesized wirelike KNb_3O_8 was added to a 400 mL HNO_3 (2 M) solution and stirred for 48 h at room temperature. The rodlike $H_3ONb_3O_8$ was obtained, after the products were filtered, rinsed with distilled water, and dried in the oven. Third, the as-prepared $H_3ONb_3O_8$ was heated at 550 °C for 1 h to transform it into rodlike Nb_2O_5 powder. Finally, rodlike alkaline niobates, such as $KNbO_3$, $NaNbO_3$, and $(Na,K)NbO_3$, were synthesized from the previously prepared precursors of wirelike KNb_3O_8, $H_3ONb_3O_8$, and Nb_2O_5 by MSS, respectively. As for the synthesis of rodlike $KNbO_3$, all these three kinds of 1D precursors were tried. The molar ratios of KNb_3O_8:K_2CO_3, $H_3ONb_3O_8$:K_2CO_3, and Nb_2O_5:K_2CO_3 were 1:1, 1:1.5, and 1:1, respectively. The mixtures were heated at 850 °C for 10 min in an equal weight of molten salt KCl. As for the synthesis of $NaNbO_3$, rodlike Nb_2O_5 and Na_2CO_3 were mixed with equal mole ratio and then were heated at 850 °C for 10 min in an equal weight of molten salt NaCl. Complex alkaline niobates of $(Na,K)NbO_3$ was also prepared with the rodlike reactants Nb_2O_5, K_2CO_3, and Na_2CO_3 in an equal weight of molten salt KCl carried out at 850 °C for 10 min. The molar ratio of the reactants was 1:0.45:0.55. The remnant molten salts were removed from the products by washing with hot deionized water several times. The as-synthesized powders were finally dried at 120 °C. Without any special treatment, the as-prepared rodlike $(Na,K)NbO_3$ powders were pressed into disks and then were sintered at 1100 °C for 2 h. The ceramic pellets were polished and coated with silver paste on both sides. Polarization was carried out in a silicon oil bath at 100 °C under applied fields of $E_p = 3.5$ kV/mm for 20 min. The specimens were cooled to room temperature in the silicon oil bath and then aged for 24 h in air before measuring the piezoelectric property.

The structure of samples was characterized by X-ray powder diffraction (XRD) patterns, which were obtained on a 21 kW extra power X-ray diffractometer (model M21XVHF22, MAC Science Co., Ltd.) using Cu Kα radiation. The microstructure of the samples was observed using scanning electron microscopy (SEM, model LEO1530, LEO Electron Microscopy Ltd.). The composition of powders was determined by energy dispersive X-ray (EDX) analysis with the field-emission scanning electron microscope. Transmission electron microscopy (TEM) observation and the corresponding selected area electron diffraction (SAED) patterns were determined with a Hitachi H-800 TEM, and the samples were prepared by placing a drop of dilute alcohol dispersion of crystals on the surface of a copper grid. The thermal behaviors of the precursor powders were studied by differential scanning calorimetry (DSC, model Q600 SDT-DSC, TA Instruments, New Castle, DE) in air, at a heating rate of 20 °C/min. The piezoelectric coefficient d_{33} of the samples was measured using a quasi-static d_{33}/d_{31} meter (model ZJ-6A, Institute of Acoustics, Beijing, China).

Results and Discussion

KNb_3O_8 was prepared in a KCl melt (melting point, 761 °C) at 800 °C for 3 h. To identify the largest developed planes of as-synthesized particles, the XRD patterns are obtained from the particles that are dispersed in ethanol and then cast on glass substrates, which is called the oriented particulate layer X-ray diffraction measurement technique.[25] By using this casting method, the largest developed plane of the particles are easily aligned with the glass plane.[22] Figure 1 shows the XRD patterns of cast and noncast KNb_3O_8 particles. The terms cast and noncast are used to differentiate the powder deposited on a substrate by coating with a suspension and the loose powder without any special treatment. From the XRD pattern of the cast particles, the predominant diffraction intensity of (020), (040), and (080) peaks are clearly seen, which indicates that the surface plane of the precursor are parallel to (0*k*0). All of the XRD peaks of the noncast particles (Figure 1b) can be assigned to the orthorhombic phase of KNb_3O_8 (JCPDS 75-2182) with lattice

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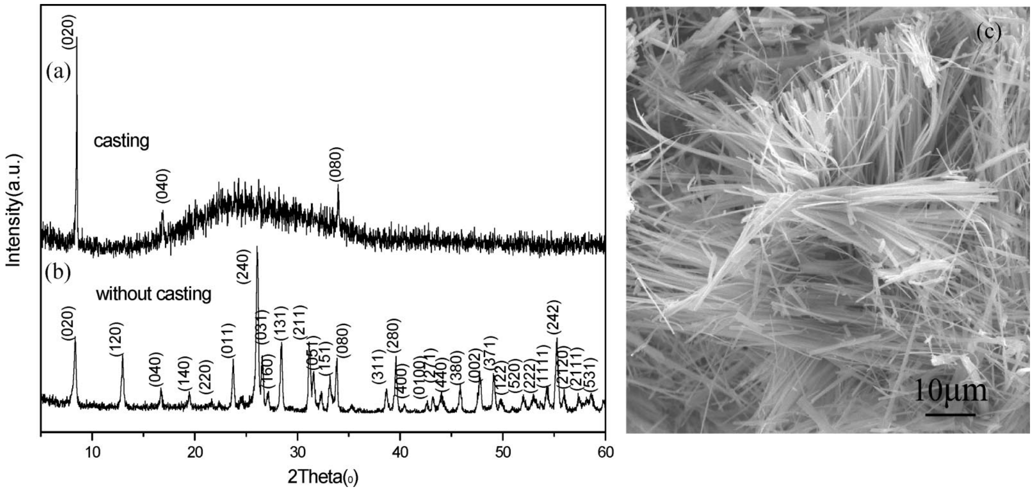

Figure 1. XRD pattern of KNb_3O_8 particles prepared by molten salt synthesized at 800 °C for 3 h (a) cast on a glass substrate and (b) without casting. (c) SEM micrograph of the KNb_3O_8 particles.

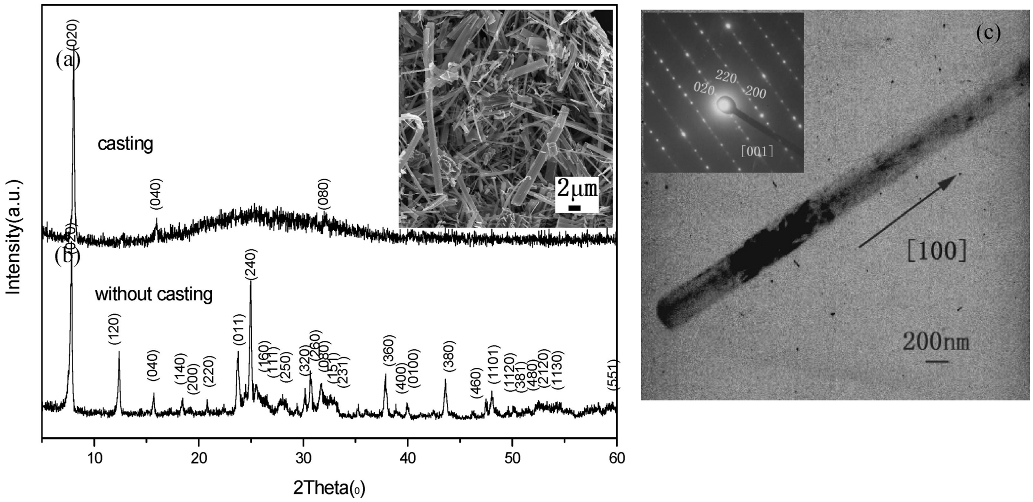

Figure 2. XRD pattern of $H_3ONb_3O_8$ particles obtained from wirelike KNb_3O_8 particles (a) cast on a glass substrate and (b) without casting. The inset is a SEM micrograph of the $H_3ONb_3O_8$ particles. (c) TEM image of an isolated $H_3ONb_3O_8$ rod with (inset) a typical SEAD pattern obtained from the same rod.

parameters of $a = 8.920$ Å, $b = 21.18$ Å, and $c = 3.805$ Å. The morphology of the synthesized KNb_3O_8 particles is shown in the Figure 1c. A large amount of wires with diameters of several hundred nanometers and the length of tens of micrometers was achieved.

Protonic niobate was obtained via an ion-exchange reaction between KNb_3O_8 wires and HNO_3 (2 M) solution. The XRD patterns of cast and noncast protonic niobate particles were displayed and compared in part a and b of Figure 2. From the cast XRD pattern, the predominant diffraction intensities of (020), (040), and (080) peaks are observed, and the surfaces of protonic niobate can be determined to be parallel to (0*k*0). The phase of the obtained protonic niobate can be confirmed to be an orthorhombic $H_3ONb_3O_8$ (JCPDS 44-672) with lattice parameters of $a = 9.173$ Å, $b = 22.47$ Å, and $c = 3.743$ Å by the XRD pattern without casting.[27] A large quantity of rodlike protonic niobates is shown in the insert of Figure 2a. The diameter and length of the as-synthesized rodlike protonic niobates are several hundred nanometers and several micrometers, respectively. The EDX pattern shows that no K^+ ions exist, which indicates the complete conversion from KNb_3O_8 to $H_3ONb_3O_8$ (see Figure S1, Supporting Information). The SAED pattern (inset of Figure 2c and Figure S2b, Supporting Information) taken from the individual rod shown in Figure 2c and Figure S2a (Supporting Information) describes the nature of a single crystal of $H_3ONb_3O_8$ with the growth direction along direction [100], which is parallel to the surface of protonic niobates (0*k*0) detected by the XRD pattern.

The rodlike Nb_2O_5 can be obtained by heat treatment of as-prepared precursor $H_3ONb_3O_8$. The TG−DSC of $H_3ONb_3O_8$ shows that Nb_2O_5 could be formed above 400 °C (Figure S3, Supporting Information). Therefore, via heat treatment of $H_3ONb_3O_8$ at 550 °C, a large scale of niobium oxide rods was obtained (see the inset of Figure 3a and Figure S4, Supporting Information). The as-prepared niobium oxide rods, which become shorter and have a diameter of a few hundred nanometers and a length from a few hundred nanometers to several micrometers, retain the shape of the precursors $H_3ONb_3O_8$ and KNb_3O_8. The phase of obtained niobium oxide was determined to be monoclinic Nb_2O_5

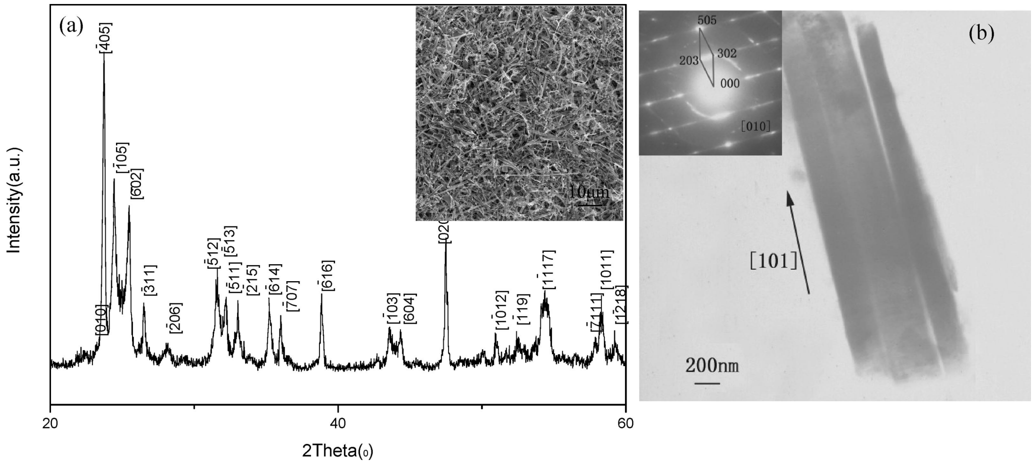

Figure 3. (a) XRD pattern of Nb_2O_5 particles obtained from rodlike $H_3ONb_3O_8$ particles. The inset is a SEM micrograph of the Nb_2O_5 particles. (b) TEM image of Nb_2O_5 rods with (inset) a typical SEAD pattern obtained from the rods.

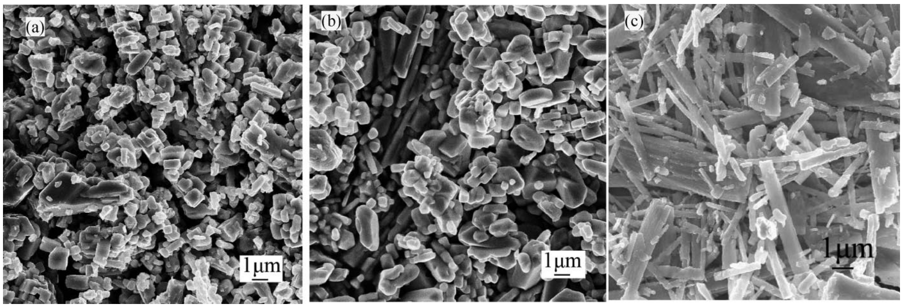

Figure 4. SEM images of $KNbO_3$ particles obtained from different precursors: (a) KNb_3O_8 particles, (b) $H_3ONb_3O_8$ particles, and (c) Nb_2O_5 particles.

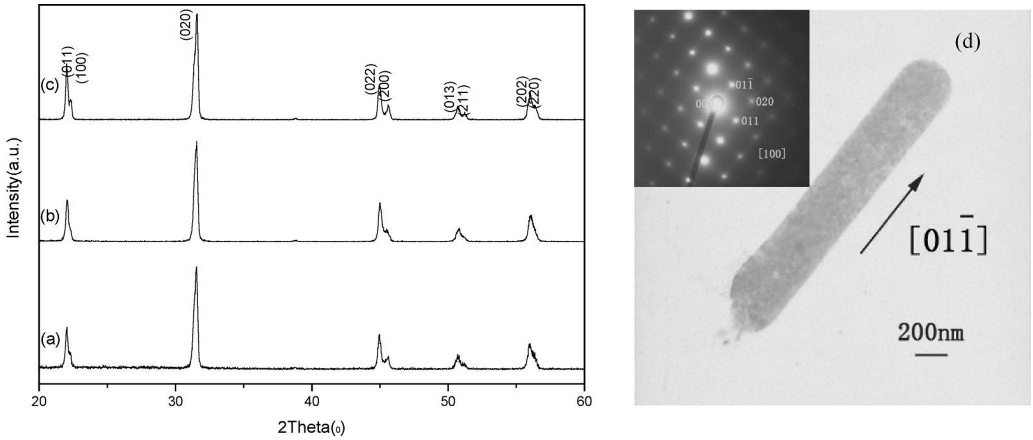

Figure 5. XRD patterns of $KNbO_3$ particles obtained from different precursors: (a) KNb_3O_8 particles, (b) $H_3ONb_3O_8$ particles, and (c) Nb_2O_5 particles. (d) TEM image of an isolated $KNbO_3$ rod obtained from the precursors Nb_2O_5 particles with (inset) its corresponding SEAD pattern.

(JCPDS 71-5, Figure 3a) with lattice parameters of $a = 21.17$ Å, $b = 3.822$ Å, $c = 19.38$ Å and $\beta = 119.8°$, which was along the [101] growth direction (Figure 3b).

The $KNbO_3$ particles were synthesized at 850 °C for 10 min by using different 1D precursors KNb_3O_8, $H_3ONb_3O_8$, and Nb_2O_5, respectively. Even though the pure $KNbO_3$ can be obtained by these three different precursors, the shapes of the product are much different. There were lots of small cubic $KNbO_3$ particles (Figure 4a,b) that did not follow the shape of the precursors KNb_3O_8 and $H_3ONb_3O_8$; however, the rods of $KNbO_3$ (Figure 4c) inherited the Nb_2O_5 precursor's shape. The synthesis of $KNbO_3$ with different shape is supposed to be a kind of self-sacrificing templated process. The XRD patterns (Figure 5a−c) confirm that all of the synthesized $KNbO_3$ products are orthorhombic system (JCPDS 71-946). The XRD patterns of cast and noncast $KNbO_3$ particles with lattice parameters of $a = 3.972$ Å, $b = 5.664$ Å, and $c = 5.690$ Å transformed from rodlike Nb_2O_5 are displayed and compared in Figure S5a,b (Supporting Information). The XRD pattern with casting was reindexed in a pseudocubic perovskite notation. The larger peaks of (011), (100), (022), and (200) were accordingly reindexed

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as {100} plane in the pseudocubic, which indicated that $KNbO_3$ rods grew along the ⟨100⟩ axis in a pseudocubic notation. The SAED pattern taken from an individual rod (see Figure 5d) shows that the as-prepared $KNbO_3$ particle has single-crystalline nature. The growth direction of $KNbO_3$ wires is also found to be matched with the pseudocubic perovskite structure along the [010] direction, which coincided with ⟨100⟩ axis in a pseudocubic notation (see Figure S6, Supporting Information).

The synthesized process of the as-prepared $KNbO_3$ particles with different shape, which are transformed from different precursors (Figure 4), was deduced. First, Nb_2O_5 and KCl were reacted to produce KNb_3O_8. Then an ion-exchange of the K^+ ion by the hydronium ion was observed according to the reaction

$$KNb_3O_8 \underset{K^+}{\overset{H_3O^+}{\rightleftharpoons}} H_3ONb_3O_8$$

It was also reported that the exchange reaction was reversible: the action of $H_3ONb_3O_8$ in a potassium salt solution led to the KNb_3O_8.[27] Afterward, $H_3ONb_3O_8$ was heated to lose H_2O, and the reactions derived from DSC (Figure S3, Supporting Information) are depicted as follow:

$$H_3ONb_3O_8 \rightarrow HNb_3O_8 + H_2O\uparrow$$

$$HNb_3O_8 \rightarrow \frac{3}{2}Nb_2O_5 + \frac{1}{2}H_2O\uparrow$$

Finally, wirelike KNb_3O_8 and rodlike $H_3ONb_3O_8$ and Nb_2O_5 were heated with K_2CO_3 in KCl melt. The $KNbO_3$ grains in Figure 4a,b might be ascribed to a "breaking up" of the wirelike KNb_3O_8 and $H_3ONb_3O_8$ particles, respectively. During these two reactions, both of the wirelike KNb_3O_8 and $H_3ONb_3O_8$ were broken up into small Nb_2O_5 particles and then reacted with K_2O dissolved in KCl molten salt by a topochemical reaction. This phenomenon was also observed for the rod-shaped $K_2Ti_4O_9$.[16] The reactions are as follows:

$$KNb_3O_8 + K_2CO_3 \rightarrow \frac{3}{2}Nb_2O_5 + \frac{3}{2}K_2O + CO_2\uparrow \rightarrow 3KNbO_3 + CO_2\uparrow$$

$$H_3ONb_3O_8 + \frac{3}{2}K_2CO_3 \rightarrow \frac{3}{2}Nb_2O_5 + \frac{3}{2}K_2O + \frac{3}{2}CO_2\uparrow \rightarrow 3KNbO_3 + \frac{3}{2}CO_2\uparrow + \frac{3}{2}H_2O\uparrow$$

The formation of the rods $KNbO_3$ from the rodlike Nb_2O_5 particles can be explained by a "dissolution−precipitation" mechanism[28] and "template formation" mechanism.[29] The reaction is

$$Nb_2O_5 + K_2CO_3 \rightarrow Nb_2O_5 + K_2O + CO_2\uparrow \rightarrow 2KNbO_3 + CO_2\uparrow$$

Among various niobium oxides, niobium pentoxide (Nb_2O_5) is the thermodynamically stable phase.[30] In this case, K_2O is much more soluble than Nb_2O_5, which almost does not dissolve[31] in KCl. K_2O primarily dissolves into the salt and diffuses onto the surfaces of the much less soluble Nb_2O_5. Simultaneously, some of the Nb_2O_5 particles with the same tropism are assemble, which can be explained by the so-called "contact epitaxy" mechanism previously observed from silver clusters supported on a Cu (001) surface.[32] Finally, K^+ defused into Nb_2O_5 and $KNbO_3$ is synthesized by topochemical reaction. Therefore, the as-synthesized $KNbO_3$ grains, to a large extent, inherit the morphology of rodlike Nb_2O_5 and some of the $KNbO_3$ rods appear to be merged together. A schematic representation of the size- and shape-dependence of the morphological transformation of KNb_3O_8, $H_3ONb_3O_8$, Nb_2O_5, and $KNbO_3$ is shown in Figure 6.

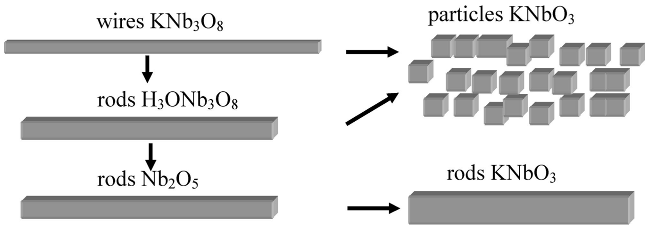

Figure 6. The schematic representation of the size- and shape-dependence of the morphological transformation of KNb_3O_8, $H_3ONb_3O_8$, Nb_2O_5, and $KNbO_3$.

From the point of view of the structure, the transformation shown in Figure 7 among KNb_3O_8,[33] $H_3ONb_3O_8$,[27,34] Nb_2O_5,[35] and $KNbO_3$[36] is further discussed. The structure of KNb_3O_8 could be characterized as a stacking of $-Nb_3O_8-$ sheets consisting of corner-sharing and edge-sharing NbO_6 octahedra, and K atoms are located between the $-Nb_3O_8-$ sheets. In each sheet, three NbO_6 octahedra connected with sharing corners and edges along the [001] direction. In the structure of $H_3ONb_3O_8$, H_3O^+ tended to take the place of K^+ between the $-Nb_3O_8-$ sheets, which were similar to that of KNb_3O_8. All three structures KNb_3O_8, $H_3ONb_3O_8$, and Nb_2O_5 could be described as being built up from identical units of three octahedra with corner- and edge-sharing shown in the oblong loop (Figure 7). This phenomenon explained that the transformation from $H_3ONb_3O_8$ to Nb_2O_5 was a soft reaction. H_3O^+ disengaged from $-Nb_3O_8-$ sheets and the sheets became closer and then connected by sharing the corner of NbO_6 octahedra.[27] So the shape of Nb_2O_5 did not change much from $H_3ONb_3O_8$, which corresponds to the morphology of Nb_2O_5. In the perovskite $KNbO_3$ crystal, NbO_6 octahedron units connected with sharing corners along the [001], [010], and [100] directions. When the topochemical reaction occurred in the molten salt KCl to produce $KNbO_3$ by using KNb_3O_8, $H_3ONb_3O_8$, or Nb_2O_5 crystals, K^+ needed to diffuse inside them, and this process involved the bond-breaking, rebonding, and new generation of bonds. Compared to the

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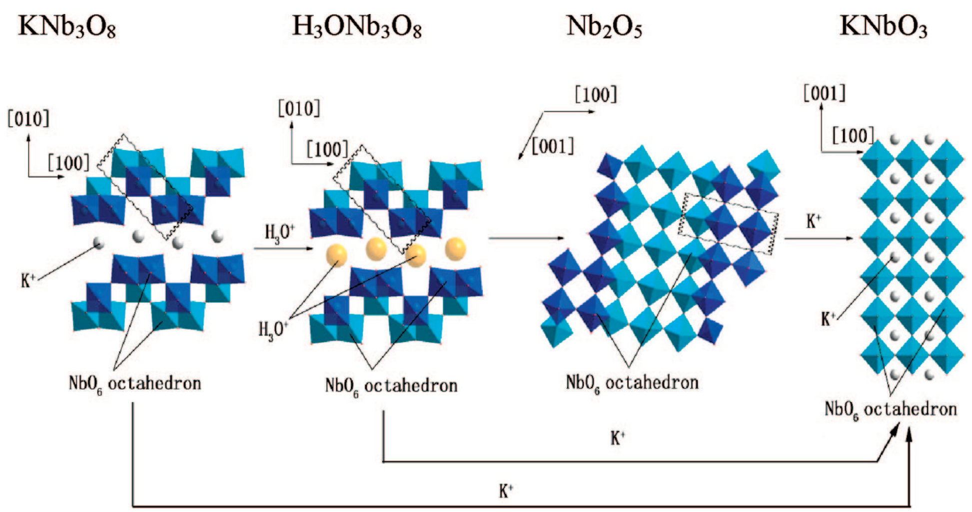

Figure 7. Schematic illustration of the structural transformations of Nb-containing species along with the mechanism of $KNbO_3$ synthesis by topochemical treatment.

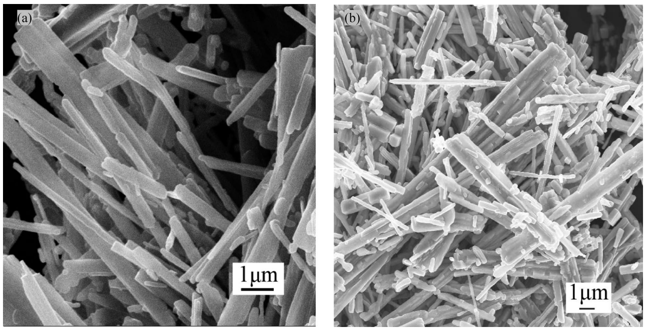

Figure 8. SEM micrographs of (a) the rodlike $NaNbO_3$ particles and (b) $(Na,K)NbO_3$ particles.

more compact and stable structure of Nb_2O_5, the layer structure, which belongs to KNb_3O_8 and $H_3ONb_3O_8$, might be easier to destroy by the transport of K^+ in the molten salt environment. This is why the small cubiclike, not rodlike, particles of $KNbO_3$ can be induced by using precursors KNb_3O_8 and $H_3ONb_3O_8$, and rodlike structure of $KNbO_3$ can well be inherited from the precursor Nb_2O_5.

It was expected that other niobates and more complex oxides with 1D morphology, such as $NaNbO_3$ and $(Na,K)NbO_3$, could be obtained by the present topochemical method based on MSS. For synthesis of $NaNbO_3$, rodlike Nb_2O_5 and Na_2CO_3 mixed with NaCl were heated at 850 °C for 10 min. $NaNbO_3$ rods with a diameter of several hundred nanometers and a length of several micrometers were observed from Figure 7a. The phase of as-prepared $NaNbO_3$ was determined to be orthorhombic phase (JCPDS 82-606, Figure S7b, Supporting Information) with lattice parameters of $a = 5.564$ Å, $b = 7.767$ Å, and $c = 5.509$ Å. The XRD pattern of cast $NaNbO_3$ particles (Figure S7a, Supporting Information) showed that the strong peaks of (101) were accordingly indexed as {101} plane. This method was also used to synthesize $(Na,K)NbO_3$. Rodlike Nb_2O_5, K_2CO_3, and Na_2CO_3 mixed with KCl salts were heated at 850 °C for 10 min. $(Na,K)NbO_3$ rods had a diameter of several hundred nanometers and a length of several micrometers (Figure 8b). The phase of the obtained $(Na,K)NbO_3$ was determined to be orthorhombic (space group *Amm*2, Figure S8b, Supporting Information) with lattice parameters of $a = 3.964$ Å, $b = 5.661$ Å, and $c = 5.652$ Å, which was in agreement with the $(K,Na)NbO_3$ reported before.[23] The large peaks of (011) and (100) were accordingly reindexed as {100} plane of pseudocubic phase, which indicates that $(Na,K)NbO_3$ rods grew along the {100} plane in the pseudocubic phase, as determined from the casting XRD pattern (Figure S8a, Supporting Information). The ratio of Na:K of the product $(Na,K)NbO_3$ was about 0.55:0.45, as shown by EDX (Figure S8c, Supporting Information), which was close to that of reactants Na_2CO_3:K_2CO_3. Because of the short reaction time (10 min), the ratio of the Na:K of product $(Na,K)NbO_3$ is very close to the supposed nominal one by preventing the plentiful K^+ of KCl salt from reacting with products and further diffusing into the A-site of perovskite.[23] Therefore, the more complex oxides, especially those with more than two types of cations in the A-site, could be prepared by this method. Furthermore, Figure S9a (Supporting Information) shows the XRD pattern of the $(Na,K)NbO_3$ ceramic, which is sintered from as-prepared rodlike $(Na,K)NbO_3$ particles under pressureless condition in air. From the SEM image obtained from the surface of the ceramic (see Figure S9b, Supporting Information), it is found that the anitropic morphology of the particle is maintained. The piezoelectric constant d_{33} of the $(Na,K)NbO_3$ ceramic is 140 pC/N, which was much higher than that of $(Na_{0.5}K_{0.5})NbO_3$ ceramics reported before ($d_{33} = 97$ pC/N).[18] The reason for the high d_{33} of the present $(Na,K)NbO_3$ ceramic might be that the high anisotropic along pseudocubic {100} plane rods made the ceramic a little textured. Otherwise, it was reported that piezoelectric coefficients of textured piezoelectric ceramics were usually from 2 to 3 times higher than those of polycrystalline ones and as high as 90% of the single crystal values.[37] Therefore, if the ceramic was formed by textured methods with this kind of rods, such as reactive templated

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grain growth (RTGG) and templated grain growth (TGG) methods, the piezoelectric property could be largely improved.

Conclusions

Wirelike KNb_3O_8 particles were synthesized by MSS. Topochemical method based on molten salts had been demonstrated to synthesize single-crystalline niobates with 1D morphology. Rodlike $H_3ONb_3O_8$, Nb_2O_5, and $ANbO_3$ (A = K, Na, (Na,K)) were obtained step-by-step from wirelike KNb_3O_8 particles. The small cubiclike particles of $KNbO_3$ were induced by using precursors KNb_3O_8 and $H_3ONb_3O_8$. But the rodlike structure of $KNbO_3$, $NaNbO_3$, and $(Na,K)NbO_3$ can well inherit that of precursor Nb_2O_5. The structural evolution among protonic niobate, niobium oxide, and niobates was a kind of self-sacrificing templated process. Using normal sintering process, the $(Na,K)NbO_3$ ceramic derived from the rodlike powders produces a high piezoelectric constant $d_{33} = 140$ pC/N. This topochemical method may also be extended to fabricate other 1D morphology complex oxides.

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Supporting Information Available: EDX and TEM of $H_3ONb_3O_8$ particles obtained from wirelike KNb_3O_8 particles, TG−DSC of $H_3ONb_3O_8$ particles, SEM of Nb_2O_5 particles, XRD pattern and TEM of $KNbO_3$, XRD pattern of $NaNbO_3$ and $(Na,K)NbO_3$ particles, EDX of $(Na,K)NbO_3$ particles, and XRD pattern and SEM image of $(Na,K)NbO_3$ ceramic. This information is available free of charge via the Internet at http://pubs.acs.org.

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