

Synthesis of KNbO_3 nanostructures by a microwave assisted hydrothermal method

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Abstract

One-dimensional nanostructures of KNbO_3 have attracted a great interest in the scientific community, mainly because of their promising application as nanoelectromechanical systems (NEMS). However, the synthesis of KNbO_3 structures becomes complex due to the natural tendency to form non-stoichiometric potassium niobates. In this context, we report on the crystallization of one-dimensional KNbO_3 nanostructures through the reaction between Nb_2O_5 and KOH under microwave-assisted hydrothermal synthesis (M-H). The use of this synthesis method made possible a very fast synthesis of singlecrystalline powders. Based on SEM, TEM and XRD characterizations, the influence of the synthesis time and the reactants concentration in the structure and morphology of the resultant KNbO_3 was established. The conditions that favor the crystallization of nanofingers were determined to be small amounts of Nb_2O_5 and short reaction times.

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1. Introduction

Due to its many applications in several technological fields, potassium niobate (KNbO_3) has recently attracted much attention from the scientific community. It finds applications in electro-optic and non-linear optic devices, acting as optical waveguides, as a frequency doubling material and as a holographic storage medium [1–5]. The material also possesses a highly promising use in surface acoustic wave devices, since its electromechanical coupling coefficient is higher than that of LiNbO_3 , which is the most manufactured material for this application [6].

KNbO_3 is a perovskite-structured material that shows ferroelectricity below 435 °C and also has a great similarity with BaTiO_3 phase transitions. The synthesis of this material faces some complications when carried out via normal solid-state reactions, mainly because of a natural tendency to form non-stoichiometric stable products with K/Nb ratios different from 1 [7]. Nevertheless, over the last years, hydrothermal

synthesis has proven to be an efficient method for the production of pure and homogeneous KNbO_3 powders at significantly low temperatures [8–12]. In this method, changes in the processing parameters such as temperature, time and

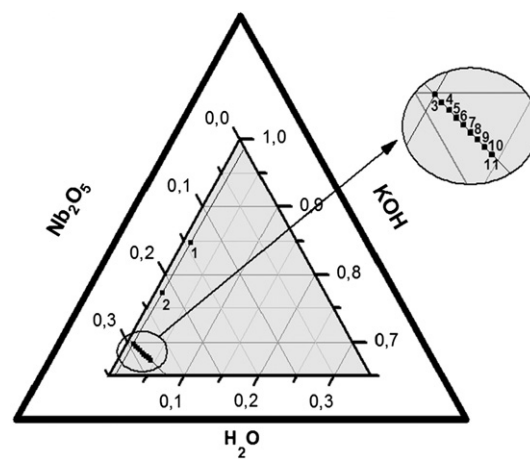


Fig. 1. $\text{Nb}_2\text{O}_5/\text{H}_2\text{O}/\text{KOH}$ ternary phase diagram indicating the ratios used for the synthesis of KNbO_3 .

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Table 1
 $\text{Nb}_2\text{O}_5/\text{H}_2\text{O}/\text{KOH}$ ratios in %-weight

Reactants	Samples										
	1	2	3	4	5	6	7	8	9	10	11
Nb_2O_5	1.12	1.03	0.93	1.38	1.84	2.28	2.73	3.17	3.60	4.00	4.40
H_2O	84.68	77.27	69.77	69.42	69.16	68.82	68.47	68.13	67.9	67.6	67.3
KOH	14.2	21.7	29.3	29.2	29.0	28.9	28.8	28.7	28.5	28.4	28.3

reactants concentration are responsible for the production of singlecrystalline KNbO_3 powders with different morphologies. The synthesis of one-dimensional (1D) KNbO_3 nanostructures has been recently reported in the literature [13]. Since then, a great interest involving this peculiar structure (also known as nanofinger) arose due to possible applications in novel nano-electromechanical systems (NEMS) [14].

With microwave energy as the heating source of the aqueous solution, positive gains could be achieved during the hydrothermal synthesis. The volumetric heating is responsible for a more homogeneous crystallization, and the fast kinetic process lowers the synthesis costs. Furthermore, it is also possible to produce powders with morphologies that differ from those obtained by conventional hydrothermal methods [8,15]. However, even if these facts have been already recognized, as far as the authors' knowledge, there are no studies describing the KNbO_3 production by this method. In this way, the synthesis of KNbO_3 by a microwave-assisted hydrothermal method through the reaction between niobium pentoxide (Nb_2O_5) and potassium hydroxide (KOH) was performed and is described in this work.

2. Experimental

The reaction between KOH (Mallinckrodt, 99%) and Nb_2O_5 (Alfa-Aesar, 99.5%) was carried out in a Teflon vessel model XP-1500 (CEM Corp.), in a MARS-5 microwave digestion system operating at 2.45 GHz (CEM Corp.), with an output power of 300 W. In order to prepare the suspensions, 0.696 g of Nb_2O_5 were added to 50 mL of a 7.5 M KOH solution. This resultant dispersion was transferred into Teflon vessels and placed inside the microwave furnace. Under hydrothermal conditions, the Nb_2O_5 is dissolved as hexaniobate ($\text{Nb}_6\text{O}_{19}^{8-}$) ion. The synthesis was carried out at 200 °C for different periods, after a heating time of 40 min necessary to reach this desired temperature. The pressure inside the vessel increased to 150 PSI after 50 min and remained constant thereafter. The products were thoroughly washed with water by centrifugation, and finally dried. The samples were identified as follows, with the reaction times between parenthesis: P1(1 h), P2(2 h), P4 (4 h), P8(8 h) and P12(12 h).

The effects of variations in the Nb^{5+} and KOH concentrations in the reaction medium were also studied. The samples were prepared using solutions of 50 mL with different ratios of $\text{Nb}_2\text{O}_5/\text{H}_2\text{O}/\text{KOH}$ (in %-weight). These syntheses were also carried out at 200 °C following the same procedure described above and with the difference that the treatment lasted 4 h for all combinations tested. The combinations used between $\text{Nb}_2\text{O}_5/\text{H}_2\text{O}/\text{KOH}$ are shown in the ternary diagram of Fig. 1, and the respective weight ratios are given in Table 1. Products

were labeled as P4-X, where X corresponds to the combinations 1 to 11.

X-ray powder diffraction patterns were acquired using a Rigaku Rink 2000 instrument, equipped with a rotating anode, operating at 50 KV and 100 mA, with $\text{Cu K}\alpha$ radiation. The morphology of the resultant products was analyzed by means of scanning (Zeiss, Supra 35) and transmission electron microscopies (Philips, CM-200).

3. Results and discussion

As seen in the XRD patterns shown in Fig. 2, independently of the synthesis time, KNbO_3 was the unique phase formed. Among the obtained powders, the P1(1 h) product could be indexed to a rhombohedral phase (R3m space group) with cell parameters $a=4.016$ Å and $\alpha=89.817^\circ$ (ICSD 09534). However, its structure appears to be a solid solution between this phase and the orthorhombic phase recognized in the P4(4 h) product and subsequent ones. This orthorhombic structure, of space group Amm2 (ICSD 9533), possesses the following cell parameters: $a=3.9710$ Å, $b=5.6920$ Å and $c=5.7190$ Å. According to Fig. 2, the occurrence of a transition from the rhombohedral to the orthorhombic phase with increasing synthesis time could be inferred, being the latter completely formed after 4 h.

The morphology of the powders obtained after 1, 4, 8 and 12 h (P1, P4, P8 and P12) of synthesis was evaluated through scanning electron microscopy (Fig. 3a, b, c and d). KNbO_3 nanofingers were only obtained after 1, 2 and 4 h of reaction (Fig. 3a and b). For greater times (8 and 12 h), the increase of the particle size is accompanied by the loss of this peculiar morphology (Fig. 3c and d). This later-growth phenomenon is a consequence of a coarsening process or Ostwald ripening. This process can be briefly described as the growth of a determined particle through the dissolution of smaller ones, and their subsequent deposition over the surface of the greater particles. The process happens spontaneously, in an attempt to decrease the total

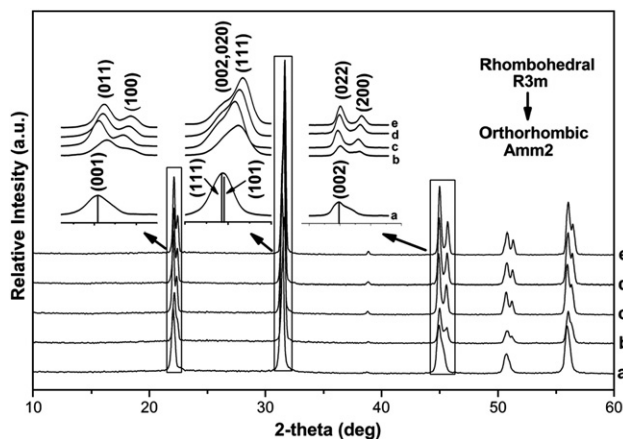


Fig. 2. XRD powder patterns of the products obtained after different synthesis times: (a) P1, (b) P2, (c) P4, (d) P8 and (e) P12. The major peaks of the KNbO_3 rhombohedral phase (P1) and the orthorhombic phase (P2, P4, P8 and P12) are indexed.

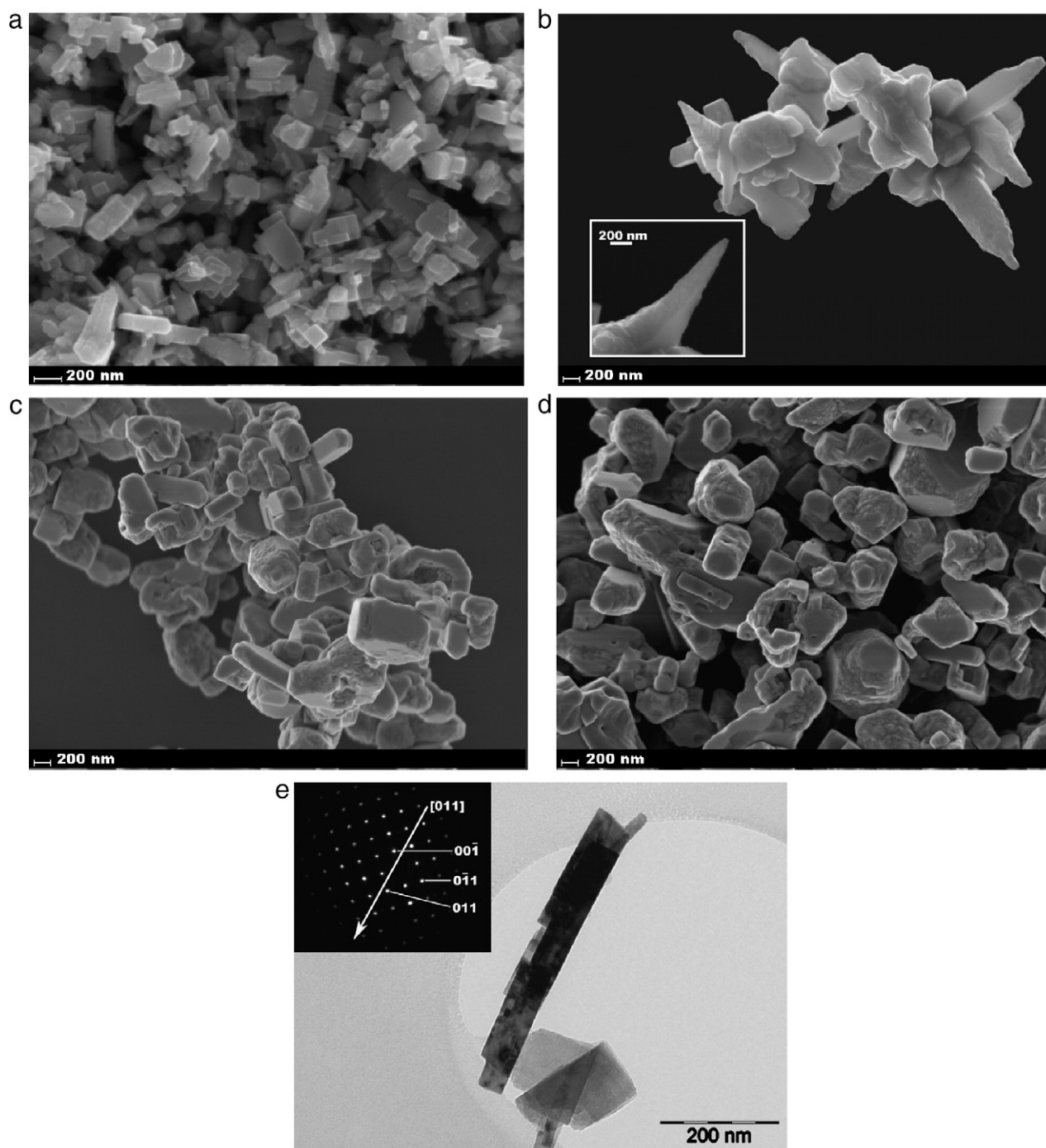


Fig. 3. SEM images of the reaction products for different times of synthesis: (a) P1, (b) P4, (c) P8 and (d) P12. (e) TEM image of KNbO_3 nanofingers obtained after 1 h of reaction (P1). The selected area electron diffraction pattern (SAED) is also shown.

surface energy. This phenomenon is independent of the crystal growth process occurred just after nucleation. Therefore, the one-dimensional crystallization occurs predominantly up to 4 h of synthesis (P4). For greater times, wherein possibly there is a non-supersaturated solution, Ostwald ripening is the predominant growth process. The structure of the nanofingers was also evaluated through selected area electron diffraction (SAED) in the transmission electron microscope. As observed in the indexed image (Fig. 3e), the one-dimensional growth of KNbO_3 after 1 h of reaction (P1) occurred along the [011] crystallographic axis, based on the rhombohedral unit cell assigned to this product. The zone axis was determined to be [100].

In order to evaluate the effects of the reactants concentration on the obtained products, the ratios between $\text{Nb}_2\text{O}_5/\text{H}_2\text{O}/\text{KOH}$ were modified. As can be observed in Fig. 1, a fixed ratio between H_2O and Nb_2O_5 was used for mixtures from (1) to (3), while there is an increase in the KOH concentration. From products (3) to (11), a fixed ratio between H_2O and KOH was used, and the amount of Nb_2O_5 was increased.

For combinations (1) and (2) (P4-1 and P4-2, respectively), no insoluble products could be collected, possibly because of the formation of soluble non-stoichiometric potassium niobates. Another possibility could be that the reaction between $\text{Nb}_6\text{O}_{19}^{8-}$ (hexaniobate) and K^+ was not possible to occur due to the low concentration of KOH.

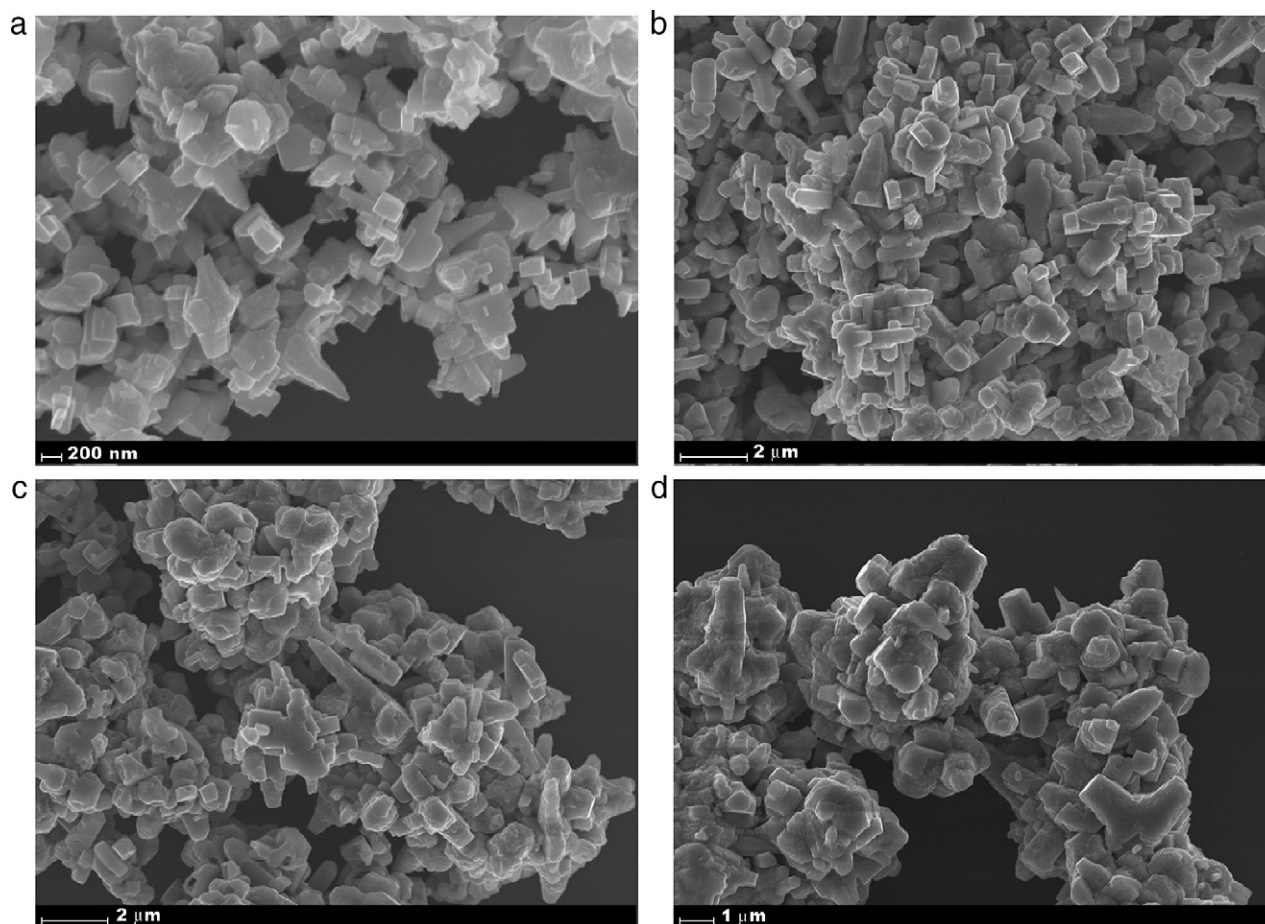


Fig. 4. SEM images of the products obtained for different ratios of $\text{Nb}_2\text{O}_5 / \text{H}_2\text{O} / \text{KOH}$: (a) P4-3, (b) P4-5, (c) P4-7 and (d) P4-9.

The XRD pattern for P4-3 revealed the presence of the rhombohedral-orthorhombic solid solution previously identified in this work. For the remaining products (from P4-4 to P4-11), the unique presence of the orthorhombic KNbO_3 phase was detected.

As seen in the SEM images of P4-3, P4-5, P4-7 and P4-9 (Fig. 4a, b, c and d), a pronounced particle growth took place. The increase of Nb_2O_5 quantity in the reaction medium (from P4-3 to P4-11) caused the degradation of the one-dimensional structures. Then, the presence of well-defined KNbO_3 nanofingers is limited for low concentrations of Nb^{5+} (Fig. 4a). As the concentration of this reactant is increased, the contribution of the coarsening process in the morphology of the resultant products becomes predominant over the nucleation and growth of the nanofingers.

4. Conclusions

Single-crystalline KNbO_3 particles were successfully synthesized through the reaction between Nb_2O_5 and KOH via a microwave-assisted hydrothermal method. The crystallization of nanofingers with well-defined shapes was achieved after 1, 2 and 4 h of reaction. For longer periods, the coarsening process (Ostwald ripening) causes the degradation of this peculiar morphology. It was also verified that for KOH concentrations lower than 7.5 M soluble products are formed. Increasing the concentration of Nb^{5+} in the reaction medium, a significant growth occurs at the same time that the one-dimensional structures are deteriorated.

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