

# Morphology control and phase transition of hexagonal sodium niobate particles

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## ABSTRACT

Hexagonal  $\text{NaNbO}_3$  particles with an ilmenite structure and plate-like morphology were synthesized by a hydrothermal method. The morphological evolution of the solid products with the increasing mineralizer concentration was monitored via SEM during the hydrothermal reaction. By carefully controlling the mineralizer concentration, particles with a diameter of 10–60  $\mu\text{m}$  and a thickness of 1–10  $\mu\text{m}$  were obtained. The particles were transformed from the ilmenite structure into the perovskite structure during the thermal treatment at 600 °C. Their plate-like morphology was maintained with some cracking on the surface. The surface orientation of the perovskite particles was micro- and macroscopically characterized by EBSD and XRD analysis, respectively. The results indicate that thinner particles tend to be more oriented in the (001) crystal planes.

## 1. Introduction

Alkaline niobates are receiving increasing attention due to their excellent nonlinear optical, ferroelectric, piezoelectric, electro-optic, and photocatalytic properties [1–6]. They are widely used in acoustic transducers, delay lines and filters, optical modulators, second harmonic generators, beam deflectors, dielectric waveguides, and holographic data storage [7–9]. For example, sodium niobate is currently of significant interest due to its exceptional piezoelectric response in  $\text{NaNbO}_3$ -derived ceramics such as the solid solution  $\text{K}_x\text{Na}_{1-x}\text{NbO}_3$  (KNN) [10,11]. Its high performance has the potential to make KNN-based ceramics a viable lead-free alternative to the most widely used piezoelectric material,  $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$  (PZT).

Among the many methods to further improve the performance of KNN-based piezoelectric ceramics, engineering their surface texture [12] is recognized as an effective method. High-aspect-ratio plate-like or fibrous perovskite  $\text{NaNbO}_3$  template particles are crucial for engineering surface textures. However, perovskite  $\text{NaNbO}_3$  belongs to the cubic crystal system, which is highly symmetric. According to Gibbs-Wulff theorem, a droplet or crystal will arrange itself to minimize its surface Gibbs free energy by assuming a shape that maintains a low surface energy, thus making directly synthesizing high-aspect-ratio perovskite powders difficult. The most successful ap-

proaches rely on topochemical micro-crystal conversion (TMC) of two-dimensional perovskite structures. However, the complexity of the TMC process limits its application. In the present study, plate-like hexagonal  $\text{NaNbO}_3$  particles with the ilmenite structure were synthesized using a simple hydrothermal method. Then, plate-like perovskite particles were obtained by heating them to 600 °C. Controlling the particle morphology during the hydrothermal synthesis and the surface orientation after thermal treatment were investigated.

## 2. Experimental procedure

Hexagonal  $\text{NaNbO}_3$  particles were prepared by a hydrothermal method. In a typical procedure, 0.5 g of  $\text{Nb}_2\text{O}_5$  and 1 wt% sodium dodecylbenzenesulfonate (SDBS) were dispersed in 40 mL of an aqueous mineralizer solution, namely, KOH and NaOH at a  $\text{K}^+:\text{Na}^+$  ratio of 2:1 and concentrations ranging from 0.5 M to 2 M. The mixture was transferred into a teflon-lined stainless steel autoclave (50 mL capacity), which was heated at 200 °C for 10 h. After cooling, the white precipitates were repeatedly washed with de-ionized water before drying at 80 °C in air.

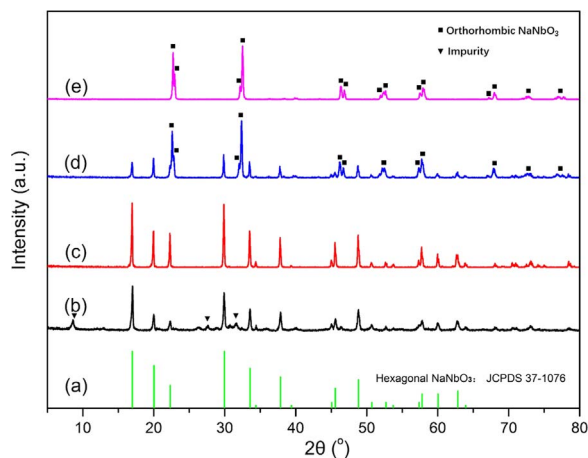
The morphology of the particles was characterized by scanning electron microscopy (SEM) (S-3000N, Hitachi Ltd., Tokyo, Japan). The crystal structure of the particles was identified by X-ray diffraction

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**Fig. 1.** (a) The standard diffraction data of hexagonal  $\text{NaNbO}_3$  (JCPDS Card No. 37-1076); XRD patterns of particles synthesized with different mineralizer concentrations: (b) 0.5 M; (c) 1.0 M; (d) 1.5 M; (e) 2.0 M.

(XRD) (Model RINT 2200, Rigaku Corporation, Japan) using  $\text{Cu K}\alpha$  radiation. Electron backscatter diffraction analysis (EBSD) was used to quantitatively analyze the microstructure on the nanometer scale. Lotgering factors,  $F$ , quantifying the degree of  $(001)_{\text{pc}}$  texture were calculated from the relative peak intensities of the particles using the data of the standard powder diffraction file (PDF) card as the reference.

### 3. Results and discussion

#### 3.1. Structure and morphology control

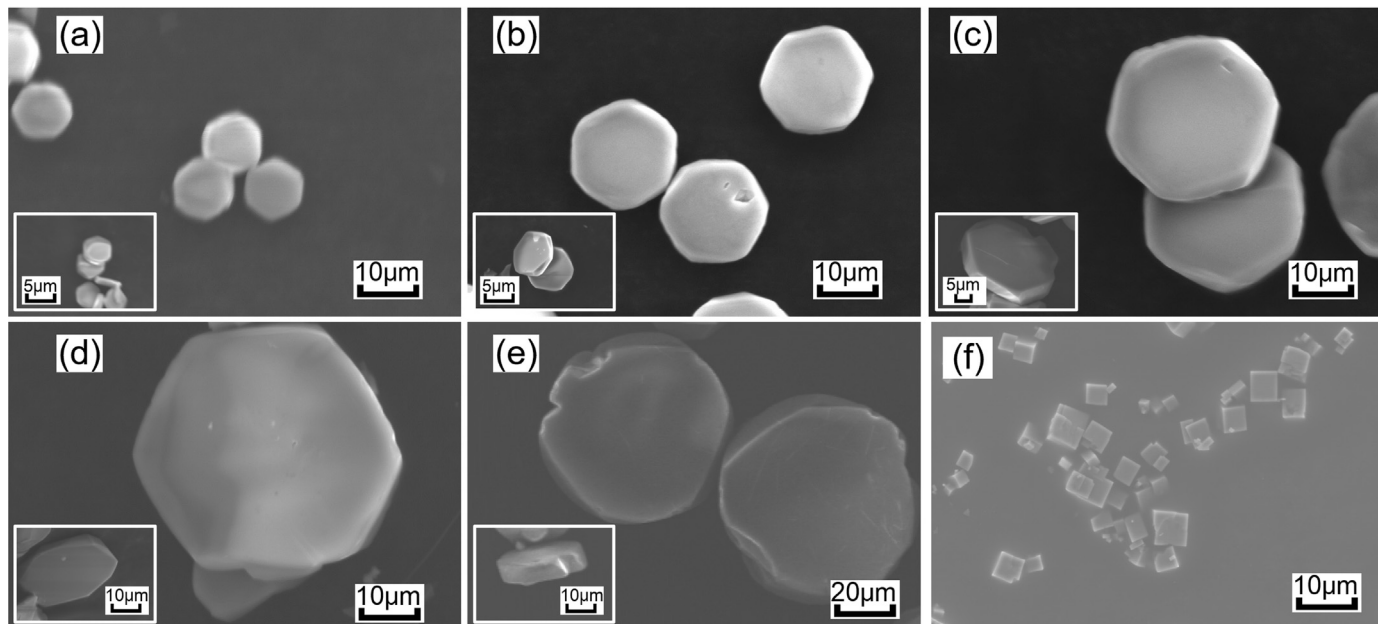
The XRD patterns in Fig. 1 demonstrate the evolution of the product with the increasing mineralizer concentration under the conditions of 200 °C, 10 h, and a  $\text{K}^+:\text{Na}^+$  ratio of 2:1. The mineralizer concentration played a key role in forming the hexagonal phase. A low mineralizer concentration, 0.5 M, yielded a mixture of particles with low crystallinity, as shown in Fig. 1(b), because the solubility of the raw materials was insufficient, and thus, crystallization was not effective in the solution. As the mineralizer concentration increased to 1 M (Fig. 1(c)), the diffraction peaks between 5 and 80° could be indexed to those of hexagonal  $\text{NaNbO}_3$  with reported lattice constants of  $a$

$=5.335 \text{ \AA}$  and  $c = 15.611 \text{ \AA}$  (Fig. 1(a)) [13]. No diffraction peaks indicating impurities were observed, indicating the high purity of the final product. With the increasing mineralizer concentration, the phase of the obtained particles gradually changed from hexagonal to orthorhombic, and the crystal structure changed from ilmenite to perovskite (Fig. 1(d, e)). The optimal range for preparing the hexagonal  $\text{NaNbO}_3$  was confirmed to be 0.7–1.4 M.

The SEM images of the samples in Fig. 2 illustrate the controllable size of the particles hydrothermally synthesized at the optimized temperature of 200 °C. By carefully controlling the mineralizer concentration, particles with a diameter of 10–60  $\mu\text{m}$  and a thickness of 1–10  $\mu\text{m}$  were obtained. The mineralizer concentrations used to synthesize samples a–e shown in Fig. 2 were 0.7 M, 0.9 M, 1.0 M, 1.2 M and 1.4 M, respectively. The formation of plate-like topography was due to the crystal structure, because hexagonal  $\text{NaNbO}_3$  have anisotropic unit cell structures, which can induce anisotropic growth along crystallographically reactive directions, resulting in the formation of hexagonal structures. In addition, the reaction follows the two-dimensional nucleation growth mechanism. In the hexagonal system, the lowest surface energy of the (0001) faces leads to growth along the (0001) surface, resulting in plate-like morphology. The SEM results demonstrate that the particle size is particularly sensitive to the mineralizer concentration, perhaps because the solution supersaturation ( $\sigma$ ) increased with the increasing mineralizer concentration in this reaction. For two-dimensional nucleation and growth, the normal growth rate ( $R_n$ ) of particles is directly proportional to the solution supersaturation [14,15]. Therefore, the particle size increased rapidly, especially along (0001) plane. However, excessive mineralizer concentration resulted in excessive supersaturation, and thus, two-dimensional nucleation was replaced by three-dimensional nucleation, resulting in a cubic morphology (Fig. 2(f)).

#### 3.2. Phase transition

According to the XRD results, the thermal treatment at 600 °C for 2 h transformed the particles into the perovskite structure (Fig. 5(c, d)). Although the morphology of the particles remained intact, some cracks appeared on the surface, as shown in Fig. 3(a). During the thermal process, particles transformed from the hexagonal phase (H) at room temperature to the cubic phase (C) at high temperature and finally transformed into orthorhombic phase (O) after cooling down to



**Fig. 2.** SEM images of particles obtained in different mineralizer concentrations: (a) 0.7 M; (b) 0.9 M; (c) 1.0 M; (d) 1.2 M; (e) 1.4 M; (f) 2.0 M.

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