

Solvothermal Synthesis of Sodium and Potassium Tantalate Perovskite Nanocubes

Yu He[†] and Yongfa Zhu^{*†,††}

[†]Department of Chemistry, Tsinghua University, Beijing 100084, P. R. China

^{††}Key Lab of Organic Optoelectronics & Molecular Engineering, Beijing 100084, P. R. China

(Received April 12, 2004; CL-040394)

A low-temperature solution-based synthetic method was developed for the synthesis of nanocubic structures of alkali tantalates. Two kinds of highly pure tantalate single crystalline nanocubes with the edge length of about 5 and 16 nm were synthesized successfully without introducing any templates or catalysts.

It is widely believed that the shape of nanocrystals influences their physical properties greatly.¹ Such changes in the physical properties produce a wide range of electrical, optical, or magnetic properties^{2,3} and open a new domain of both fundamental and technological interest. The nanostructures possess diverse morphologies, including nanosphere,⁴ nanorod,^{5,6} nanotube,⁷ nanobelt,⁸ and so on. Recently nanocubes, a new kind of nanoblock, have attracted extensive interest for their promising applications in building nanodevices, nanosensors, and functional nanomaterials.^{9–12} So far, many nanocubes, such as metal Au,⁹ Cu₂O,¹⁰ CaF₂,¹¹ Co₃O₄,¹² have been synthesized successfully via solution reaction. However, the exploration for the cube-like nanostructures and the application is still limited. Here we reported functional ternary transition-metal oxide nanocubes of NaTaO₃ and KTaO₃ newly synthesized with the simple solvothermal method.

Nanometer-scale NaTaO₃ and KTaO₃, as two kinds of important nanoparticulate electroceramics, have been of interest for a long time, because of their strongly size-dependent properties and potential applications in nanoelectronics, including in low loss, high permittivity capacitors, and electroceramic memories.¹³ Especially KTaO₃ is of a cubic-perovskite structure which represents a particularly interesting class of materials that exhibit a variety of unique electronic, magnetic, and optical properties, such as ferroelectricity,¹⁴ colossal magnetoresistivity,¹⁵ and large nonlinear optical coefficients.¹⁶ In the recent several years, NaTaO₃ and KTaO₃ also have been used as photocatalysts for overall water splitting and showed rather excellent photocatalytic activity.^{17,18} However, the conventional techniques for synthesizing these tantalates on the basis of the solid-state reaction, which requires long periods of heating above 1000 °C and the crystal size of the products was large of micrometer. Goh and his co-workers synthesized the perovskite and pyrochlore KTaO₃ powders via hydrothermal method,¹⁹ utilizing Ta₂O₅ and KOH as the starting materials, but the size of the products is still of several hundred nanometers. We developed the solvothermal method, using Ta(OC₄H₉)₅ as the starting material and ethanol as the solvent, and successfully prepared perovskites, NaTaO₃ and KTaO₃, with cubic morphology, whose edge lengths are about 5 and 16 nm, respectively.

In a typical synthesis procedure, 4 mL of Ta(OC₄H₉)₅ (99%, about 2 mmol) and 20 mmol hydroxide (0.80 g of NaOH (A. R.) or 1.12 g of KOH (A. R.) to obtain the corresponding NaTaO₃ or

KTaO₃) were dissolved into 30 mL of ethanol (A. R.) and added into a Teflon-lined autoclave with the capacity of 40 mL. The autoclave was sealed and maintained at 120 °C (for NaTaO₃) or 160 °C (for KTaO₃) for 24 h without staking or stirring and allowed to air cooled to room temperature. The powder product was filtered off, washed with deionized water and dried in air at 60 °C.

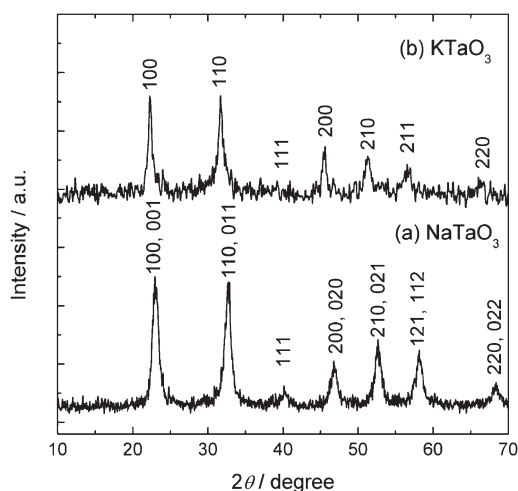


Figure 1. XRD patterns of the as-prepared (a) NaTaO₃ and (b) KTaO₃ powders.

The purity and crystallinity of the as-prepared samples were examined by powder X-ray diffraction (XRD) using a Bruker D8-advance X-ray diffractometer with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$). Figure 1a shows the XRD pattern of the as-prepared NaTaO₃ and all the reflections of the product can be readily indexed as a pure monoclinic phase [space group: 10] of NaTaO₃, identical to the reported data in the JCPDS cards (74-2478). Similarly, Figure 1b shows the XRD pattern of the as-prepared KTaO₃ whose reflections can be readily indexed as pure cubic-perovskite KTaO₃ [space group: 221], identical to the JCPDS cards (77-0918). The average crystal size was determined according to the Scherrer equation: $D_{\text{calcd}} = K\lambda/\beta \cos \theta$, in which β is the full-width at half-maximum and θ is the diffraction angle. The peak at 22.8° of NaTaO₃ or 22.3° of KTaO₃ was used for the calculation of the crystal sizes of the products. The average crystal size of the as-prepared NaTaO₃ and KTaO₃ were calculated to be about 6.4 and 14.8 nm, respectively.

The morphologies and structures of the prepared products were further examined with transmission electron microscopy [TEM, Hitachi (Tokyo, Japan) H-800]. Figure 2 shows the TEM images of as-prepared NaTaO₃ and KTaO₃ products. It is evident that both the NaTaO₃ and KTaO₃ products consist exclusively of nanocubes with edges length of $5 \pm 1 \text{ nm}$ and $16 \pm 2 \text{ nm}$, respectively. The particle size is consistent with

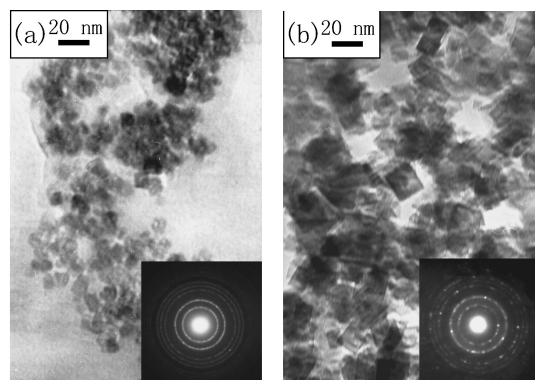


Figure 2. TEM image of as-prepared (a) NaTaO₃ and (b) KTaO₃. (Insets of (a) and (b) are selected area electron-diffraction patterns of the corresponding products.)

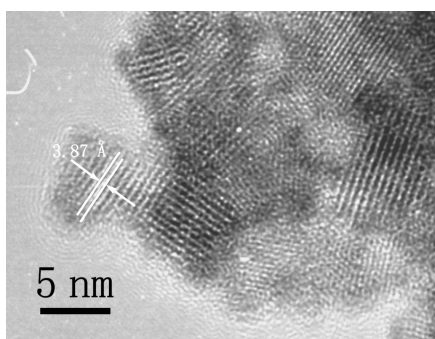
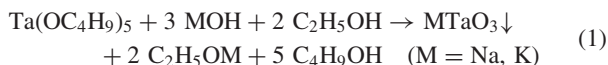


Figure 3. HRTEM image of as-prepared NaTaO₃.

the calculated XRD results. The insets of Figure 2 are the selected area electron-diffraction patterns of NaTaO₃ and KTaO₃ nanocubes. The patterns show polycrystalline rings' morphology, indicating that both the products are crystalline. Figure 2b shows that the KTaO₃ nanocube is effectively square in shape with sharp edges and corners, illustrating that the nanocubes are probably single crystals with no defects. Compared to the KTaO₃, NaTaO₃ nanocubes have the smaller size and can not be observed very clearly in TEM. So further investigation of NaTaO₃ was taken by high resolution TEM (HRTEM, JEOL-2010F), just as Figure 3 shows. The 2-D lattice fringes of the NaTaO₃ illustrate that the nanocubes are single crystals with no defects or dislocations. The interplanar spacings are 3.87 Å.

In the solvothermal process, Ta(OC₄H₉)₅ and MOH (M = Na, K) both can be dissolved in ethanol, forming some kind of homogeneous solution. The possible reaction could be formulated as:



According to the Ref. 19, Ta₂O₅ was utilized as the Ta source to synthesize KTaO₃ powder, instead of Ta(OC₄H₉)₅. However, Ta₂O₅ can barely dissolve in the solvent, even in the hydrothermal conditions. And the reaction follows the dissolution-precipitation process, so the rate of nucleation is rather low owing to the Ta₂O₅'s extremely low solubility, which leads to a much less number of particles. For a given amount of matter to precipitate, each particle reaches a larger size because fewer particles are growing at the same time.²⁰ That is why the KTaO₃ powders

can reach several hundreds nanometers in size.¹⁹ While in our case, Ta(OC₄H₉)₅ distributes in the solvent evenly and also contacts MOH sufficiently. In the solvothermal condition, the rate of heterogeneous nucleation could be rather high. A greater number of particles formed immediately, which led to the much smaller size of the products. In fact, metal alkoxides are widely used in the synthesis of superfine perovskite nanostructure, such as BaTiO₃,²¹ PbZr_xTi_{1-x}O₃,²² and so on. In those reactions, however, bimetallic alkoxide or several kinds of metal alkoxides should be used and cockamamie procedures and hard conditions are also demanded. In our case, metal alkoxide and inorganic hydroxide reacted directly in the solvothermal condition, demanding no shielding gas or complex calcination procedures. This way also could be applicable for preparing other important alkali/alkaline earth titanates or tantalates. This part of work is still in progress.

In summary, we have exploited a low-temperature solution-based method to synthesis of sodium and potassium tantalate perovskite single crystalline nanocubes, with the edge lengths of about 5 and 16 nm, respectively. We believe that this solution synthetic route, based on simple reactions with no participation of catalysts or templates, requiring no expensive equipment, and ensuring high purity and uniformity of the products, will greatly reduce the production cost and offer great opportunity for synthesis of such nanocube-structured materials.

This work was partly supported by Chinese National Science Foundation (20071021), the Excellent Young Teacher Program of MOE. P.R.C. and Visiting Scholar Foundation of Key Lab in Beijing University.

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