

## Synthesis of Sodium Tantalate Nanorods by Alkalide Reduction

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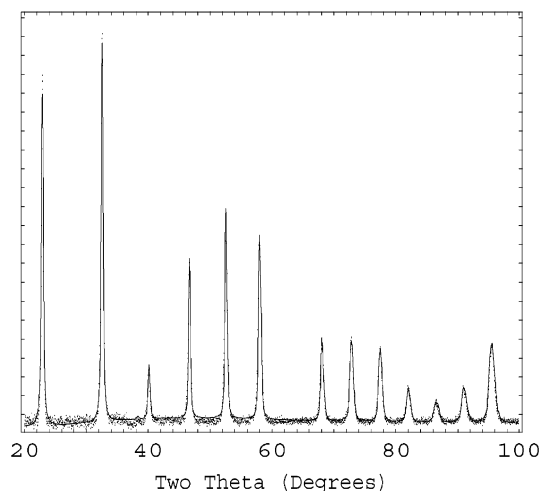
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The synthesis of nanomaterials appropriate for a wide variety of advanced technologies has been of great interest for more than a decade. As the field has matured, synthetic techniques have advanced, allowing the production of more and more complex materials, moving from single elements to binary, and more recently, ternary and higher-order phases. In parallel with this effort, the factors which affect the size, size distribution, and shape of the products has received considerable attention, due to the size and shape dependence of material properties as physical dimensions are reduced to the nanoscale.<sup>1–5</sup> It is generally recognized that, depending on the application, some degree of size and shape control will be necessary. With respect to nanoelectronic and optical devices, one-dimensional structures, exemplified by nanotubes and nanorods, will be required both as interconnects and active components.<sup>1,6,7</sup>

Nanoparticulate electroceramics have been of interest for some time, due to their strongly size-dependent properties and potential applications in nanoelectronics, including in low loss, high permittivity capacitors, electroceramic memories, ferroelectric transistors, sensors, and actuators.<sup>8,9</sup> Nanocrystalline electroceramics with a perovskite-type structure have received particular attention of late.<sup>8,10–14</sup> However, only very recently was a route to nanorods of this class of materials reported, a solution-based decomposition of bimetallic alkoxides shown capable of producing BaTiO<sub>3</sub> and SrTiO<sub>3</sub>.<sup>15</sup> Here we report a second route to perovskite nanorods, with the synthesis of nanorods of another member of the ABO<sub>3</sub> family, NaTaO<sub>3</sub>, by alkalide reduction.

Alkalides are crystalline ionic salts consisting of crown ether or cryptand complexed alkali metal cations charged balanced by a stoichiometric number of alkali metal anions.<sup>16,17</sup> Alkalides produce alkali metal anions when dissolved in nonreducible solvents. The alkali metal anion is nearly as thermodynamically powerful a reductant as a solvated electron, the most powerful reductant possible in any given solvent, and is capable of simultaneous two-electron transfers. Alkalide reduction of metal salts results in the formation of a colloid of nanoscale (~2–15 nm diameter) particles. Colloid stability varies from minutes to hours, depending on the metal reduced and the reaction conditions. Following aggregation and removal of the solvent, the byproducts can be washed away, recovering the crown ether and leaving bare metal nanoparticles. The method is general across the periodic table,<sup>18–21</sup> including the lanthanides.<sup>22</sup> Furthermore, it has been shown to be a route to nanocrystalline carbides,<sup>23</sup> nitrides,<sup>24</sup> alloys,<sup>18–20</sup> and oxides.<sup>25</sup>

NaTaO<sub>3</sub> nanorods were synthesized as follows. TaCl<sub>5</sub> (Aldrich, anhydrous 99.99%) was dissolved in ~20 mL of tetrahydrofuran (THF) and then reduced with a 5% excess of the alkalide K<sup>+</sup>(15-crown-5)<sub>2</sub>Na<sup>-</sup> dissolved in an equal volume of THF at -20 °C. THF (99.9+% HPLC grade, inhibitor free) was purified by stirring over KNa alloy until a persistent blue solution was obtained and 15-crown-5 (Alfa-AESAR) by vacuum distillation. The K<sup>+</sup>(15-crown-5)<sub>2</sub>Na<sup>-</sup> was formed in situ.<sup>24</sup> Generally, following the reduction, the next step in nanoparticle synthesis is to remove the

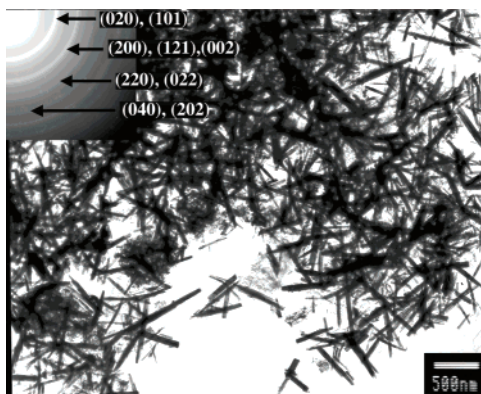


**Figure 1.** Powder X-ray diffraction pattern of NaTaO<sub>3</sub> nanorods (dots), and fit to orthorhombic structure (solid line).

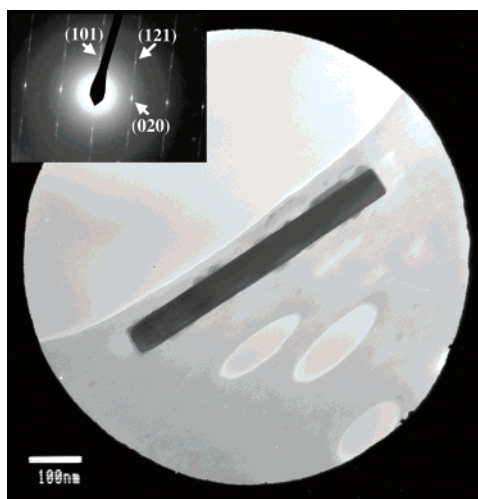
byproducts and excess reductant by washing and decanting, in which case one could recover Ta nanoparticles.<sup>24</sup> However, this was not done here; only the solvent was removed by vacuum distillation. The product, which includes K<sup>+</sup>(15-crown-5)<sub>2</sub>Cl<sup>-</sup>, NaCl, and Ta nanoparticles, was then collected in a N<sub>2</sub>-filled glovebox, put in a fused-silica tube, and heated under dynamic vacuum (10<sup>-3</sup> Torr) at 250 °C for 3 h, and subsequently at 600 °C for 4 h. The product was then washed with deionized H<sub>2</sub>O (18 MΩ), removing the byproducts, NaCl, KCl, and crown ether decomposition products that were not fully removed by the heating process.

The final product is a black, free-flowing powder. Powder X-ray diffraction is consistent with orthorhombic (*Pcmn*) NaTaO<sub>3</sub> (Figure 1). The cell parameters are in good agreement with those found for bulk material,  $a = 5.526 \text{ \AA}$ ,  $b = 7.810 \text{ \AA}$ , and  $c = 5.487 \text{ \AA}$ .<sup>26,27</sup> This correspond to a 0.5% increase in the cell volume, primarily due to a 0.3% expansion along the *b*-axis. Elemental analysis (flame emission, Perkin-Elmer AAnalyst 100) is consistent with the formula NaTaO<sub>3</sub> (metals basis), with less than 0.6 at % K, presumably in byproducts not removed by the washing procedure.

Examination by transmission electron microscopy (TEM, 60 keV) found that the product is primarily (>90%) composed of nanorods strewn out like matches in a pile (Figure 2). The rods tend to bundle: many are seen in groups of three or more rods joined along their unique axis. Selected area electron diffraction (SAD) is consistent with orthorhombic NaTaO<sub>3</sub>, with no discernible evidence of other phases in the ring patterns. Some of the nanorods exceed 1 μm; a large number of them exceed 500 nm. The width of the rods varies between ~10 and 100 nm, the majority being between 30 and 60 nm, and the aspect ratios, generally between 10 and 20:1. In addition to the nanorods, some NaTaO<sub>3</sub> nanocrystals (~10 nm diameter) can be seen, as well as what appears to be a very small percentage of organic residue that clings to some of the nanorods. The single rod (~530 × 50 nm) shown in Figure 3 has



**Figure 2.** Rod-shaped nanocrystals of  $\text{NaTaO}_3$ . Upper left inset is selected area electron diffraction pattern of the rods, Miller indices are shown for the first four diffraction rings.



**Figure 3.** Single  $\text{NaTaO}_3$  crystalline nanorod. Upper left is selected area electron diffraction pattern of this rod, with three of the Miller indices indicated.

a particularly large percentage of this residue present; generally, little to none is observed. SAD patterns of the rods are consistent with the rods being single crystals, their long axis corresponding to the  $[010]$  direction.

It is unclear why our synthetic method results in nanorods rather than nanoparticulate materials. However, it seems reasonable that the growth mechanism is related to that which produces  $\text{BaTiO}_3$  and  $\text{SrTiO}_3$  nanorods in decomposing alkoxides, in which case it was suggested that the precursors and oleic acid may form micelle structures that direct the rod growth.<sup>15</sup> The decomposition of

alkalides is known to involve the reductive cleavage of the complexants to primarily form ethene and alkali metal glycolate products.<sup>28,29</sup> It is possible that the alkali metal glycolates could accommodate the nanorod growth and serve as a source of oxygen for the reaction with Ta nanocrystals and NaCl. In any case, it is clear that the complexed cation is shielded from the reaction even after crown decomposition as evidenced by the formation of  $\text{NaTaO}_3$  rather than  $\text{KTaO}_3$  or a mixture of the two. Furthermore, preliminary results show that  $\text{KTaO}_3$  is formed when  $\text{K}^+(15\text{C}5)2\text{K}^-$  rather than the sodide is used as the reductant. Thus, it may be possible to control which alkali metal is incorporated into the  $\text{ABO}_3$  structure by altering the alkali metal anion used as the reductant.

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