Pr_6O_{11} Single-Crystal Nanotubes from a Molten-Salt Synthetic Method

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Pr_6O_{11} single-crystal nanotubes with a typical 3-D crystal structure in the bulk have been successfully obtained through a template-free molten-salt synthetic method, the formation of which has been attributed to the periodical defect cluster distribution in the Pr_6O_{11} species. It is believed that the synthesis of this new type of 3-D nanotubes will be helpful to explore more rational synthetic methods to nanotubes of 3-D compounds.

Introduction

Nanotube materials have drawn continuous research attention because of their distinctive structural features combined with novel chemical and physical properties, which are of great research and application interest in electronic, energy and catalyst fields etc.[1−12] Various substances have been processed into nanotubes driven simply by one motivation: what if they are nanotubes?

It is generally believed that nanotubes are only thermodynamically stable when they have a similar layer structure to graphite.[1] Therefore, for many technologically and scientifically important compounds which do not possess layer structures, such as silicon,[5] GaN,[6] and metals,[7] templates are usually needed to confine and stabilize the growth of their nanotubes, including porous membranes,[8] carbon nanotubes,[9] nanorod arrays[5,6] and nanowires.[7] Some syntheses of nanotubes from 3-D compounds, such as ZnO and Te, have been achieved by melting Zn cores[10] or using Te[11] colloidal seeds as self templates, respectively. Meanwhile, stimulated by the possible rolling process in the formation of nanotubes, the thin-solid-film rolling method has been successfully developed by controlled release of polycrystalline layers from substrates.[12] These 3-D compounds, although restricted by large-scale preparation or crystalline quality, have undoubtedly enriched the nanotube categories and given us more inspiration on the exploration of new synthetic methods. Here, we demonstrate that single-crystal Pr_6O_{11} nanotubes, which have a typical 3-D crystal structure in the bulk, can be obtained through a template-free synthetic method. The formation of this nanotube is believed to be related to the periodical defect-cluster distribution in the Pr_6O_{11} species.

Results and Discussion

Our method was based on a molten-salt synthetic process, which has been widely adopted to prepare oxide nanowires by Wang et al.[13,14] and was recently expanded to the preparation of ZnO microtube arrays by us.[15]

The phase purity of the samples has been characterized on a Bruker D8-advance X-ray powder diffractometer with Cu-K_α radiation ($\lambda = 1.5418$ Å). As shown in Figure 1, all the reflections of the XRD patterns can be readily indexed to a pure face-centered cubic face of the Pr_6O_{11} crystal with lattice constants $a = 5.4678$ Å (JC,PDS 42−1121). The 2θ peaks at values of 28.26, 32.81, 47.04, 55.72, 58.46 and 68.64° correspond to the crystal planes of [111], [200], [220], [311], [222] and [400] of the crystalline Pr_6O_{11} species, respectively. The d values at 28.26° are calculated to be approximately 0.318 nm, corresponding to the [111] plane

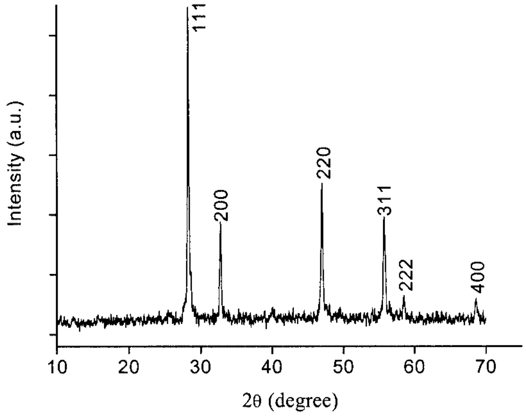

Figure 1. XRD patterns of the Pr_6O_{11} crystal after molten salt thermal treatment

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spacing of the Pr_6O_{11} species. All the information from this XRD pattern indicates that the crystal structure of the Pr_6O_{11} species has been maintained after thermal treatment under current experimental conditions.

Thorough TEM analysis (Figure 2, a and b) has indicated that about 30 % of the raw Pr_6O_{11} microparticles have been converted into nanotubes. TEM analysis have shown that these nanotubes usually have diameters of approximately 10−20 nm and lengths of 100−500 nm; all of them have open ends. It is interesting to find that these nanotubes tend to aggregate together around the microparticles, which may serve as evidence for a possible exfoliation process for the formation of these nanotubes from the starting microparticles of the Pr_6O_{11} species.

HRTEM has provided further insight into the microstructure of these Pr_6O_{11} nanotubes. As shown in Figure 2 (c), the HRTEM image of an individual nanotube clearly demonstrates its multi-wall tubular structure with an outer diameter of approximately 20 nm and an inner diameter of about 6 nm; the interlayer spacing can be calculated to be about 0.320 nm, corresponding to the interlayer spacing of the [111] plane of the body-centered cubic Pr_6O_{11} species. The electron diffraction pattern of this nanotube (Figure 2, inset c) revealed its single-crystal nature and can be indexed as that of the [111] zone axis of the face-centered cubic Pr_6O_{11} species. EDS analysis (Figure 2, e) taken from an individual nanotube has indicated that only Pr and O atoms are present; no Na^+ or Cl^- ions were detected, indicating Pr_6O_{11} nanotubes.

In contrast to previously reported nanotubes obtained under unrestricted conditions, Pr_6O_{11} nanotubes have no layer structure. Why then are the nanotube structures thermodynamically stable? A further insight into the crystal structure of the Pr_6O_{11} species may help us to illustrate the structure principle of these nanotubes.

The Pr_6O_{11} species is the most thermodynamically stable form of the PrO_x series. X-ray powder diffraction experiments of Pr_6O_{11} nanotubes show that it is related to PrO_2,[16] which has the fluorite structure (Figure 3, a).

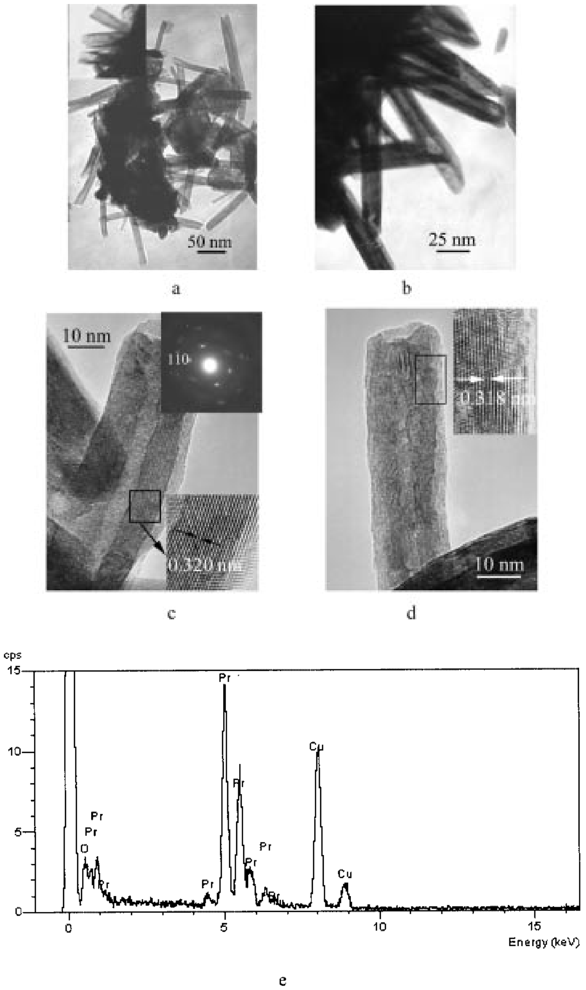

Figure 2. a) TEM images of Pr_6O_{11} nanotubes from NaCl melts; b) TEM images of Pr_6O_{11} nanotubes from KCl melts; c) HRTEM images of a single Pr_6O_{11} nanotube from NaCl melts; inset, electron-diffraction patterns of a single Pr_6O_{11} nanotube; d) HRTEM images of a single Pr_6O_{11} nanotube from KCl melts; e) EDS analysis of a single Pr_6O_{11} nanotube in Figure 2, c)

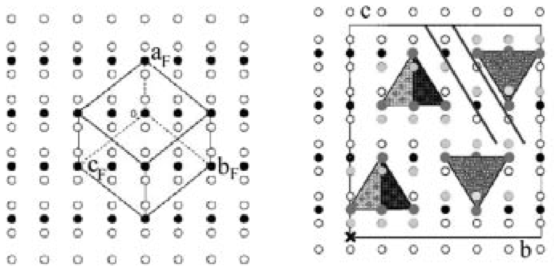

Figure 3. a) Model for the crystal structure of fluorite-type PrO_2; open circles, oxygen atoms; black circles, Pr atoms; b) model for the crystal structure of the Pr_6O_{11} sector viewed along [001] direction; open circles, oxygen atoms; black circles, Pr atoms with an oxidation state of +3; light gray circles, Pr atoms with an oxidation state of +4; dark gray circles, oxygen atoms in Pr_4O_6 vacancy cluster

It is believed that the structures of various intermediate praseodymium oxides are built from a simple basic defect cluster: Pr_4O_6. This defect cluster involves the vacant Pr_4 tetrahedron and its six edge-bridging oxygen atoms and is created when an oxygen atom is extracted from the parent fluorite structure PrO_2,[17,18] which results in two types of Pr cations in the Pr_6O_{11} species: Pr cations participating in the Pr_4O_6 vacancy cluster and those without an oxygen vacancy in their coordination sphere. The formal charge on these two types of Pr ions is +4 and +3, respectively. The result of the cation lattice relaxation is that the intracluster Pr−Pr distances have an average of 4.1 Å, while the intercluster Pr−Pr distances are about 0.4 Å shorter.[19] In other words, the Pr^{3+} ions are crowded into the region between the defect clusters. On the other hand, the dominant chemical force in the rare-earth oxides is ionic in nature, and the electrostatic repulsion between the defect clusters tends to separate them,[19] which may provide the possibility for the exfoliation process of Pr_6O_{11} single-molecule layers from the bulk. Among the different crystal planes of the Pr_6O_{11} structure, the [111] planes have the largest interlayer distance (0.318 nm) and thus the weakest interaction between layers, so the [111] plane would be the preferred exfoliation direction, and the obtained Pr_6O_{11} nanotubes would grow along $[1\bar{1}0]$ axis, which is consistent with our HRTEM and electron-diffraction analysis. Compared with the reported nanotubes of 2-D sheet structures, the interaction between layers is much stronger, so the crystal-lattice images are usually distorted to some extent (Figure 2, c and d).

The conditions of the exfoliation and the further tube-formation process would be critical considering that the following conditions must be met: 1) enough energy must be provided to overcome the strong electrostatic interaction between layers; 2) the provided energy should be moderate enough so that it cannot break all the layers to lead to the formation of irregular particles without a preferred direction; 3) once the layers have been exfoliated, appropriate hindrance should exist to avoid the recombination of the layers. Our experimental results show that NaCl and KCl melts meets these conditions.

Take NaCl as an example, at 840 °C (the melting point of NaCl is about 808 °C) NaCl will melt and ionize into Na^+ and Cl^- ions, which can attack the crowded $[Pr_x^{3+}O_y^{2-}]^{z-}$ anion and the positively charged $[Pr_4O_6]^{4+}$ vacancy cluster along all directions, so that combinations between layers can be loosened to some extent. Since the interaction between [111] layers is the weakest, exfoliation can occur first along the [111] planes, which can be then stabilized by the high viscosity of the NaCl flux and may lead to the formation of nanotubes.

Although the structural analysis is consistent with our experimental results, a thorough theoretical study is still needed to justify its reasonability. Nevertheless, for the first time, single-crystal nanotubes of Pr_6O_{11} with a typical 3-D crystal structure have been successfully obtained through this unrestricted molten-salt method, which we believe may be expanded to the synthesis of nanotubes with similar structures and will greatly encourage materials scientists to explore more rational synthetic methods for the formation of nanotubes from 3-D compounds.

Experimental Section

Synthesis of Pr_6O_{11} Nanotubes: In a typical synthesis procedure, analytical grade NaCl (1 g, or KCl) and Pr_6O_{11} (0.9 g, purity > 99.9 %) were mixed together, and ground in an agate mortar to form a homogeneous mixture, which was then transferred into a crucible, and calcined at 840 °C in air for 3 h. The system was allowed to cool to room temperature. The solidified NaCl-Pr_6O_{11} products obtained were immersed into fresh water for about ten hours to remove NaCl from the Pr_6O_{11} material, during which fresh water was constantly replaced. Aqueous solutions of $AgNO_3$ (0.1 mol/L) and HNO_3 (1 mol/L) were used to detect the remnant Cl^- ions present in the final products. The resultant black powders were filtered, and dried at 80 °C in air.

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