Inorg. Chem. **2004**, *43*, 1594–1596

Inorganic Chemistry
Communication

Hydrothermal Synthesis of Prismatic $NaHoF_4$ Microtubes and $NaSmF_4$ Nanotubes

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Received July 16, 2003

A new example of tubular materials based on sodium rare-earth tetrafluorides, $NaHoF_4$ and $NaSmF_4$, has been fabricated by a simple hydrothermal method. In addition, an unusual nanotube with a perfect couple of an outer prismatic shell with an inner concentric prismatic nanorod at the center is found. According to the architectures of various products, the general growth mechanism of these tubes is proposed.

The discovery of carbon nanotubes has initiated a worldwide interest in one-dimensional (1D) hollow nanostructures due to their unique architecture and unusual chemical, electrical, optical, and mechanical properties.[1,2] The formation of concentric carbon nanotubes is thought to be the result of the scrolling of graphitic sheet structures at an elevated temperature.[1] A number of tubular materials from analogous layered structures have been reported,[2] such as BN,[3] dichalcogenides,[4] Bi_2S_3,[5] and $NiCl_2$.[6]

Low temperature solution-phase synthesis provides a simple method to produce nanotubes based on layered structures, such as carbon,[7] InS,[8] Bi,[9] VO_x,[10] rare earth oxides (hydroxides),[11] titania,[12] and niobates.[13] The use of organic molecules with nitrogen or oxygen donors facilitates the generation of tubular structures.[10,11] These organic molecules are embedded into alternating inorganic layers (slices) to build up lamellar frameworks.

Other typical examples of inorganic nanotubes formed by a templating mechanism in aqueous solution are zinc oxide,[14] silica,[15] alumina,[16] and some transition metal sulfides.[17] Mayers and Xia proposed a helical model for the growth of hexagonal prismatic Te nanotubes in hot organic solvent.[18] Hollow and hexagonal 1D $Dy(OH)_3$ nanoprisms with outer diameter of about 50−400 nm were also reported.[19] However, there have been no reports concerning fluoride nanotubes, particularly synthesized by simple wet chemistry. In this report, we will describe the first example of tubular fluorides.

Rare-earth elements are of great importance in magnetic, electronic, and optical materials because of the number of

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(1) (a) Iijima, S. *Nature* **1991**, *354*, 56. (b) Hu, J. T.; Odom, T. W.; Lieber, C. M. *Acc. Chem. Res.* **1999**, *32*, 435. (c) Baughman, R. H.; Zakhidov, A. A.; de Heer, W. A. *Science* **2002**, *297*, 787.

(2) (a) Rao, C. N. R.; Nath, M. *Dalton Trans.* **2003**, *1*, 1. (b) Patzke, G. R.; Krumeich, F.; Nesper, R. *Angew. Chem., Int. Ed.* **2002**, *41*, 2446. (c) Tenne, R. *Chem. Eur. J.* **2002**, *8*, 5297. (d) Tremel, W. *Angew. Chem., Int. Ed.* **1999**, *38*, 2175.

(3) Chopra, N. G.; Luyken, R. J.; Cherrey, K.; Crespi, V. H.; Cohen, M. L.; Louie, S. G.; Zettl, A. *Science* **1995**, *269*, 966.

(4) (a) Tenne, R.; Margulis, L.; Genut, M.; Hodes, G. *Nature* **1992**, *360*, 444. (b) Feldman, Y.; Wasserman, E.; Srolovitz, D. J.; Tenne, R. *Science* **1995**, *267*, 222. (c) Nath, M.; Rao, C. N. R. *J. Am. Chem. Soc.* **2001**, *123*, 4841. (d) Nath, M.; Rao, C. N. R. *Angew. Chem., Int. Ed.* **2002**, *41*, 3451. (e) Brorson, M.; Hansen, T. W.; Jacobsen, C. J. H. *J. Am. Chem. Soc.* **2002**, *124*, 11582.

(5) Ye, C.-H.; Meng, G.-W.; Jiang, Z.; Wang, Y.-H.; Wang, G.-Z.; Zhang, L.-D. *J. Am. Chem. Soc.* **2002**, *124*, 15180.

(6) Hacohen, Y. R.; Grunbaum, E.; Tenne, R.; Sloan, J.; Hutchison, J. L. *Nature* **1998**, *395*, 336.

(7) (a) Viculis, L. M.; Mack, J. J.; Kaner, R. B. *Science* **2003**, *299*, 1361. (b) Wang, X.; Lu, J.; Xie, Y.; Du, G.; Guo, Q.; Zhang, S. *J. Phys. Chem. B* **2002**, *106*, 933.

(8) Hollingsworth, J. A.; Poojary, D. M.; Clearfield, A.; Buhro, W. E. *J. Am. Chem. Soc.* **2000**, *122*, 3562.

(9) Li, Y.-D.; Wang, J.-W.; Deng, Z.-X.; Wu, Y.-Y.; Sun, X.-M.; Yu, D.-P.; Yang, P.-D. *J. Am. Chem. Soc.* **2001**, *123*, 9904.

(10) (a) Krumeich, F.; Muhr, H. J.; Niederberger, M.; Bieri, F.; Schnyder, B.; Nesper, R. *J. Am. Chem. Soc.* **1999**, *121*, 8324. (b) Chen, X.; Sun, X.-M.; Li, X.-D. *Inorg. Chem.* **2002**, *41*, 4524.

(11) Yada, M.; Mihara, M.; Mouri, S.; Kuroki, M.; Kijima, T. *Adv. Mater.* **2002**, *14*, 309.

(12) Kasuga, T.; Hiramatsu, M.; Hoson, A.; Sekino, T.; Niihara, K. *Langmuir* **1998**, *14*, 3160.

(13) Saupe, G. B.; Waraksa, C. C.; Kim, H.-N.; Han, Y. J.; Kaschak, D. M.; Skinner, D. M.; Mallouk, T. E. *Chem. Mater.* **2000**, *12*, 1556.

(14) Zhang, J.; Sun, L.-D.; Liao, C.-S.; Yan, C.-H. *Chem. Commun.* **2002**, *3*, 262.

(15) Adachi, M.; Harada, T.; Harada, M. *Langmuir* **1999**, *15*, 7097.

(16) Lee, H. C.; Kim, H. J.; Chung, S. H.; Lee, K. H.; Lee, H. C.; Lee, J. S. *J. Am. Chem. Soc.* **2003**, *125*, 2882.

(17) (a) Lu, Q.-Y.; Gao, F.; Zhao, D.-Y. *Nano Lett.* **2002**, *2*, 725. (b) Xiong, Y.-J.; Xie, Y.; Yang, J.; Zhang, R.; Wu, C.-Z.; Du, G. *J. Mater. Chem.* **2002**, *12*, 3712.

(18) Mayers, B.; Xia, Y. N. *Adv. Mater.* **2002**, *14*, 279.

(19) Xu, A.-W.; Fang, Y.-P.; You, L.-P.; Liu, H.-Q. *J. Am. Chem. Soc.* **2003**, *125*, 1494.

10.1021/ic034833c CCC: $27.50

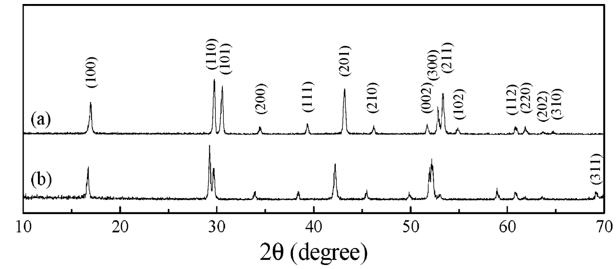

Figure 1. Powder XRD pattern (Cu Kα radiation $\lambda = 0.1541$ nm) of the hydrothermally synthesized (a) $NaHoF_4$ and (b) $NaSmF_4$.

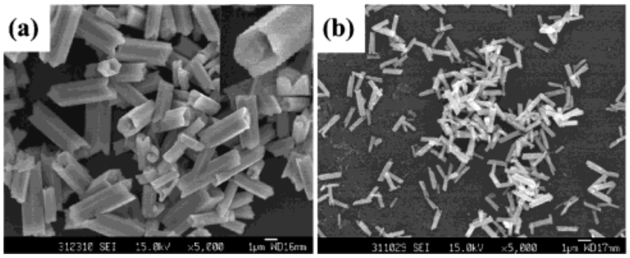

Figure 2. SEM images of the synthesized (a) $NaHoF_4$ microtubes and (b) $NaSmF_4$ nanotubes.

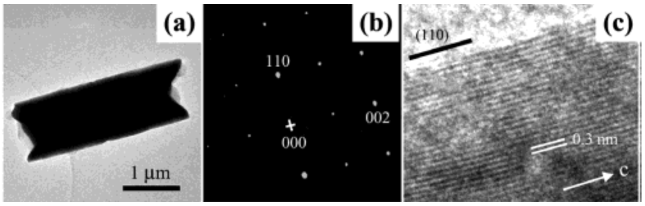

Figure 3. [1$\bar{1}$0] TEM images and a selected-area electron diffraction pattern of the $NaHoF_4$ microtubes: (a) Low magnification TEM, (b) [1$\bar{1}$0] zone-axis selected area diffraction pattern, and (c) HRTEM image.

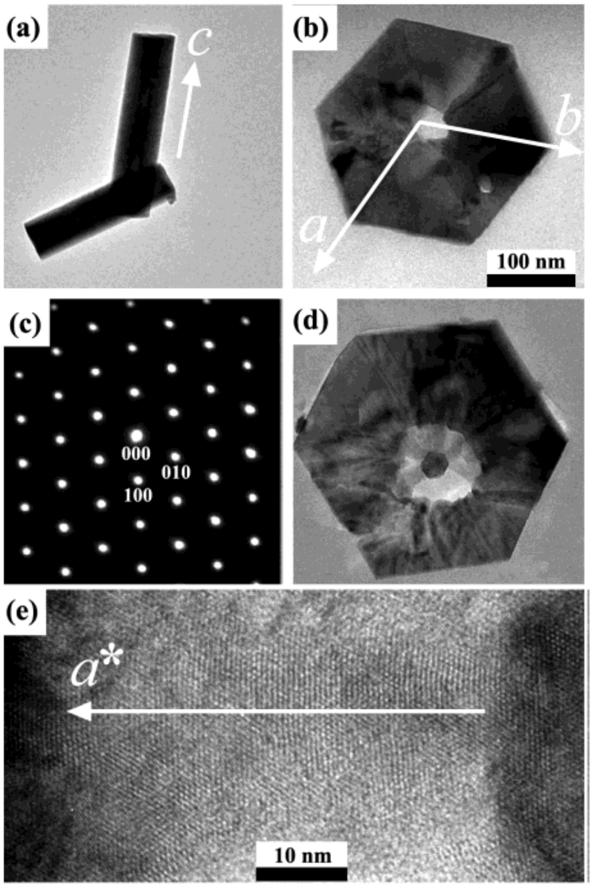

Figure 4. TEM images and an electron diffraction pattern of the $NaSmF_4$ nanotubes: (a) bright-field TEM image showing tubular structures; (b) a cross-section TEM image of a representative nanotube; (c) [001] SAED pattern; (d) cross-section TEM showing a-rod-inside-a-tube; (e) HRTEM image showing lattice fringes of one typical branch (center) connecting the central rod (right) and the inner wall (left).

spin electrons in their 4f shells. Sodium rare-earth fluorides with general formula $NaRF_4$ (R = rare-earth elements) possessing a high refractive index and low phonon energy are regarded as excellent host matrixes for performing luminescence and are used in solid-state lasers. As solid-state electrolytes, they have also been used in electrochemical devices. $NaRF_4$, such as $NaHoF_4$, can be prepared hydrothermally.[20] However, no reports have concerned the growth of tubular structures of rare earth fluorides, especially complex fluorides.

The synthesis of typical tubular structures of a ternary fluoride, $NaHoF_4$, involves a simple hydrothermal method. A pale pink product has been prepared from a mixture with molar composition of 3.00 NaF/1.00 $Ho(NO_3)_3$/6.00 NH_4HF_2/0.10 EDTA/800 H_2O (EDTA = ethylenediaminetetraacetic acid) at 140 °C for 14 h. The pH of the solution at room temperature is about 3.0. The powder X-ray diffraction (XRD) pattern (Figure 1a) confirms that the product is phase-pure hexagonal $NaHoF_4$. Comparing the powder diffraction pattern to the JCPDS card 18-1253, detailed diffraction peaks are labeled in Figure 1a. The calculated unit cell parameters are $a_0 = b_0 = 0.6007$ nm and $c_0 = 0.3540$ nm. The scanning electron microscopy (SEM) image obviously shows that these $NaHoF_4$ crystals are hollow hexagonal 1D prisms (Figure 2a). Bright-field transmission electron microscopy (TEM) images do not present the hollow interiors because of the thick walls as shown in Figure 3a. However, the growth direction along the *c*-axis can be confirmed by using either selected area electron diffraction (SAED) pattern (Figure 3b) or high-resolution transmission electron microscopy (HRTEM) (Figure 3c).

Except for $NaRF_4$ (R = La−Pm), other sodium rare-earth tetrafluorides can be synthesized hydrothermally [see Supporting Information Figure 1]. Typically, the powder XRD pattern of $NaSmF_4$ (Figure 1b) confirms its hexagonal structure (JCPDS Card 27-0779), and calculated unit cell parameters are $a_0 = b_0 = 0.6125$ nm and $c_0 = 0.3652$ nm. As compared to that of $NaHoF_4$, the increase in unit cell dimensions is due to the lanthanide contraction. These $NaSmF_4$ crystals also form as hexagonal 1D rodlike prisms with outer diameter of 100−400 nm as displayed in Figure 2b. However, the SEM image is unable to reveal the hollow structure. Bright-field TEM images of the powder sample show the clearly discernable brightness between the inner sides and outer walls of the rodlike $NaSmF_4$ crystals (Figure 4a). A hollow interior in the cross-section TEM image of a representative hexagonal prism (Figure 4b) is apparently observed. The cross-section image clearly confirms this

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(20) (a) Feng, S.-H.; Xu, R.-R. *Acc. Chem. Res.* **2001**, *34*, 239. (b) Xun, X.-M.; Feng, S.-H.; Wang, J.-Z.; Xu, R.-R. *Chem. Mater.* **1997**, *9*, 2966.

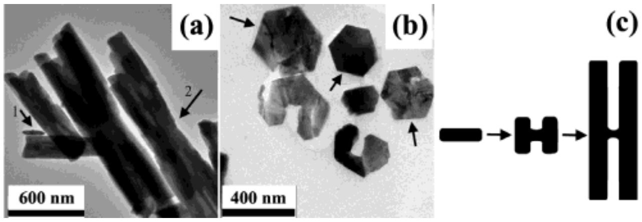

Figure 5. (a) Low magnification TEM image of $NaSmF_4$, showing a hexagonal plate served as a seed (arrow 1) and the poorly grown nanotubes with a nonhollow center (arrow 2), (b) cross-sections showing some sections with holes and some section without holes at the centers, and (c) the model for the growth of the tubular structure, similar to that of Te.[18]

prismatic crystal is tubular. The inner diameters of these hollow $NaSmF_4$ prisms are in the range 10−100 nm. Hexagonal symmetry of SAED pattern from the cross-section sample (Figure 4c) reveals the growth direction along the *c*-axis. The $[0\bar{1}0]$ SAED and HRTEM image further confirm the growth direction (see Supporting Information).

An unusual 1D nanostructure is observed in Figure 4d where there is a concentric $NaSmF_4$ nanorod at the center of a $NaSmF_4$ nanotube. The nanorod is supported by six equivalent but hierarchically grown branches connecting to inner side of the walls. Concentric nanotubes are found in carbon and its related nanotubes, and in some oxides.[1−12] In general, the centers of those nanotubes are hollow along the longitudinal direction except for the ends, and the walls are separated by van der Waals force and/or templates. However, in this one, the nanorod inside the hollow nanochannel at the center is supported by six branches (Figure 4d,e). Both the wall and the central nanorod grow along the *c*-axis. The HRTEM image shows that these branches grow along a^* and shows a perfect match of the lattices between the central rod and outer wall (Figure 4e). This unusual a-rod-inside-a-tube nanostructure has never been reported before in the literature.

In addition to the tubular structure as displayed in Figure 4a, some other typical tubular structures of $NaSmF_4$ are demonstrated in Figure 5a. The growth of some rodlike nanostructures (Figure 5a) is further confirmed to be oriented to along the *c*-axis (see Supporting Information Figure 2). In Figure 5a, there is a thin plate (arrow 1) and filled solid areas at the centers of the tubular structures (arrow 2). In Figure 5b, some typical cross-sections of $NaSmF_4$ crystals appear to be hexagonal plates without holes (arrows) and some appear with holes at the central planes. Compared to TEM images of analogous $NaRF_4$ (R = Eu−Dy) crystals (see Supporting Information Figure 3), the growth procedure is estimated as Figure 5c, similar to that reported for Te nanotubes.[18] The hexagonal plate in Figure 5a (arrow 1) can be thought as a seed. The subsequent growth along the circumferential edges of the seed yields a tubular structure. For the identical feature between (001) and $(00\bar{1})$ of the $P6_3/m$ space group of $NaSmF_4$ (see JCPDF card 27-0779 and Supporting Information Figure 2), the opposite growth toward [001] and $[00\bar{1}]$ proceeds simultaneously. If the local growth along any ⟨001⟩ directions is at same rate, a high quality tubular structure can be formed. The growth orientation of the edges (walls) is perpendicular to {001} plane of the seed. If the local condition around the growth faces is disturbed, the steady growth condition is destroyed, and poor tubes are formed. Also, x-shaped dendritic nanostructures composed of nanorods can be generated (see Supporting Information Figure 3). The joint that connects each part can be considered as the original seed (arrow 2 in Figure 5a and arrows in Supporting Information Figure 3). Sometimes, bow-tie-like architecture results as shown in Figure 3 of the Supporting Information.

Besides the edge growth, an occasional growth from the center site of the seed can occur, accompanied with a second growth of the inner nano-connects along six a^* like the "epitaxial" radial growth of ZnO nanoribbons.[21] This complex growth behavior produces the novel nanostructure: a nanorod inside a nanotube (Figure 4d,e).

In conclusion, a new example of tubular materials composed of sodium rare earth tetrafluorides has been synthesized by using a simple hydrothermal method. A concentric nanorod supported by six equivalent branches is found inside a tube. The growth mechanism shown in Figure 5c is similar to that of Te as proposed by Xia.[18] The present study enlarges the family of tubular nanostructures and leads us to explore other novel nanotubes with various chemical compositions in the future.

Acknowledgment. This work is supported by the Natural Science Foundation of China (20171046), NSF of Guangdong (21423452) for rare earth luminescence and optoelectronic materials, team group program of NSF of Guangdong for optoelectronic materials, and NSF of U.S.A. (EAR-0210820) for chemical reactions in nanopores and nanotubes. We are grateful to Dr. Goparaju Rama Rao, Lysa Chizmadia, and Michael N. Spilde of the University of New Mexico for helpful discussions.

Supporting Information Available: Additional figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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(21) Gao, P.-X.; Wang, Z.-L. *J. Phys. Chem. B* **2002**, *106*, 12653.