

The first rare-earth fluoride one-dimensional nanostructures: template synthesis of LnF_3 (Ln = Eu, La) nanotubes

Xiaojing LU and Yin PENG (✉)

Uniformly ordered crystal EuF_3 and LaF_3 nanotubes were prepared using alumina film as a nanochannel reactor, and characterized by scanning electron microscope (SEM), transmission electron microscope (TEM), and X-ray powder diffraction (XRD). These nanotubes have outer diameters in the range of 200–350 nm, inner diameters of 100–250 nm and length up to 30 μm . The fabrication method is simple, efficient and easy to control. It can be used to prepare a wide range of inorganic nanomaterials.

Keywords alumina, rare earth fluoride, synthesis

1 Introduction

Rare-earth fluorides are a class of materials with great potential in optical applications. Fluoride lattices allow high coordination numbers for the hosted rare-earth ions. On the other hand, the high ionicity of the rare-earth-to-fluorine bond leads to a wide bandgap and very low vibrational energies. These two factors in particular contribute to their usability in optical applications based on vacuum ultraviolet (VUV) and near-infrared (NIR) excitation.

The synthesis of rare-earth fluoride (such as LaF_3 , CeF_3 , GdF_3 , YF_3 , $\text{LaF}_3\text{:Eu/Er/Nd/Ho}$, $\text{CeF}_3\text{:Tb}$, $\text{GdF}_3\text{/LaF}_3$, NaREF_4 , $\text{NaYF}_4\text{:Yb}$, Er/Tm) nanocrystals has drawn particular attention [1–14]. As we know, the REF_3 nanocrystals are generally prepared through some limited, wet chemical routes involving modified precipitation [7–10], hydrothermal treatment [11–13], microemulsion [6], and polyol [1] methods, which are based on the liquid precipitation reaction between the rare-earth nitrates/chlorides and $\text{NaF/NH}_4\text{F}$. Recently, Sun et al. presented the systematic synthesis of high-quality REF_3

and REOF (RE = La to Lu, Y) nanocrystals in the shape of triangular, truncated triangular, hexagonal [14]. They also synthesized polygonal nanoplates of trigonal REF_3 , quadrilateral, and zigzag-shaped nanoplates of orthorhombic REF_3 , and nanopolyhedra and nanorods of cubic REOF by using the thermolysis of $[\text{RE}(\text{CF}_3\text{COO})_3]$ in oleic acid/oleylamine/1-octadecene. However, it still remains a challenge to develop a new route towards a general synthesis method of high-quality REF_3 nanocrystals.

Ever since the discovery of carbon nanotubes by Iijima, the synthesis of tubular nanomaterials has aroused worldwide interest both in fundamental studies and in potential applications such as chemical sensors, catalysts and storage and/or release systems [15–18]. However, to our knowledge, the synthesis of tubular structures of rare earth fluorides has not been reported yet. Such materials would be of great significance because of their possible novel properties due to their reduced dimensionality. In this communication, we reported a high-yield synthesis of EuF_3 and LaF_3 nanotubes using porous alumina membrane channel as a reaction vessel, a very simple, low-cost method.

2 Experimental

Porous alumina membranes (Anodise®) purchased from Whatman Inc. (scanning electron microscope (SEM) images revealed a pore diameter range of 200–360 nm) were cleaned for 15 min in an ultrasonic bath using solvents of water, methanol, acetone, chloroform and hexane, respectively. After dried in vacuum, the alumina membrane was put in the middle of two silica half-cells that separate the two cells. $0.02 \text{ mol}\cdot\text{L}^{-1}$ of Ln^{3+} (Ln = Eu, La) and $0.02 \text{ mol}\cdot\text{L}^{-1}$ of F^- aqueous solution of the same volume were poured into each cell. The reaction processed for 48 h at ambient temperature. Ln^{3+} and F^- would enter the pores of the alumina membrane and form nanotubes. After the completion of the reaction, the resulting $\text{LnF}_3/\text{Al}_2\text{O}_3$ composite was washed with de-ionized water for six times. Then it was dipped into $2 \text{ mol}\cdot\text{L}^{-1}$ NaOH aqueous solution for 45 min in order to partially remove alumina membrane, and for 5 h to remove the membrane substrate completely. Finally the product was rinsed with de-ionized water for ten times.

X-ray powder diffraction (XRD) was carried out on an XRD-6000 (Japan) X-ray diffractometer with $\text{Cu-K}\alpha$ radiation ($\lambda = 0.154060 \text{ nm}$) at a scanning rate of $0.05^\circ\cdot\text{s}^{-1}$ in the 2θ range from 10° to 80° . High-resolution transmission electron microscopy (HRTEM) was performed using JEOL 2010 microscope with an accelerating voltage of 200 kV. SEM images and energy-dispersive X-ray (EDX) spectrometry were obtained using a LEO-1350 VP scanning electron microanalysis instrument.

Received December 2, 2009; accepted December 18, 2009
College of Chemistry and Materials Science, Anhui Key Laboratory of Functional Molecular Solids, Anhui Normal University, Wuhu 241000, China
E-mail: kimipeng@mail.ahnu.edu.cn

3 Results and discussion

The phase purity of the products was examined by XRD measurement. The peaks shown in Figure 1(a) are all in good agreement with those of the JCPDS data of EuF₃ with hexagonal and orthorhombic phases. The peaks at 2θ values of 28.58°, 52.45°, 58.61° correspond to the crystal planes of (111), (302), and (114) of EuF₃ with hexagonal phase (JCPDS 32-0373). The peaks at 2θ values of 42.28° and 49.41° correspond to the crystal planes of (221) and (022) (JCPDS 33-0542) of crystalline EuF₃ with orthorhombic phase. All of the peaks of the XRD pattern in Figure 1(b) can be readily indexed to a pure hexagonal phase of LaF₃ with lattice constants $a = 7.2 \text{ \AA}$, $c = 7.375 \text{ \AA}$ (JCPDS 84-0942). The peaks at 2θ values of 24.52°, 27.35°, 43.39°, 50.58°, 52.15° and 70.35° correspond to the crystal planes of (110), (111), (300), (220), (221), and (141) of the crystalline LaF₃, respectively.

Field emission scanning electron microscopic (FE-SEM) images of the products are shown in Figure 2. As can be seen, the products consist of a tubular 1D nanostructure with outer diameters of 200–350 nm, inner diameters of 100–250 nm,

and length up to 30 μm which correspond to the thickness of the used template membrane. The nanotubes were separated from one another. The individual nanotubes were dense and continuous with a uniform diameter throughout their entire length. EDX attached to FE-SEM in Figure 3 further confirmed that the composition of nanotubes were Ln³⁺ and F⁻ with atomic ratios of ca. 1:3.

The HRTEM images shown in Figure 4 indicate that EuF₃ and LaF₃ have single crystal structures. There are two kinds of fringe in Figure 4(a) spacing with 0.35 and 0.39 nm, respectively. They correspond to the interplanar (111), (002) distance of hexagonal EuF₃. In Figure 4(b), the fringe spacings of 0.31 and 0.34 nm correspond to the interplanar (111), (020) distances of hexagonal LaF₃, respectively. These results are in accordance with the results of XRD.

It is noted that similar results were obtained when the concentrations of Ln³⁺ and F⁻ were varied from 0.007 to 0.1 mol·L⁻¹ and from 0.03 to 0.1 mol·L⁻¹, respectively, or when lanthanide chloride was changed to lanthanide nitrate, or when ammonium fluoride was used instead of sodium fluoride.

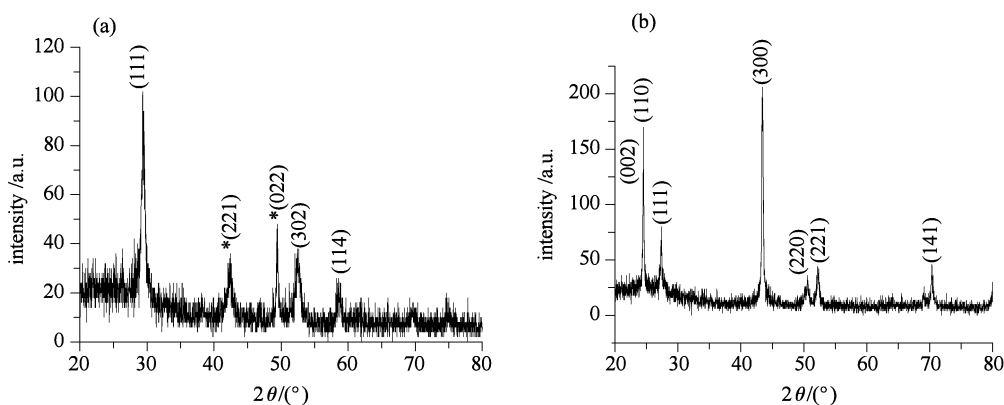


Figure 1 XRD patterns of (a) EuF₃ and (b) LaF₃ nanotubes.

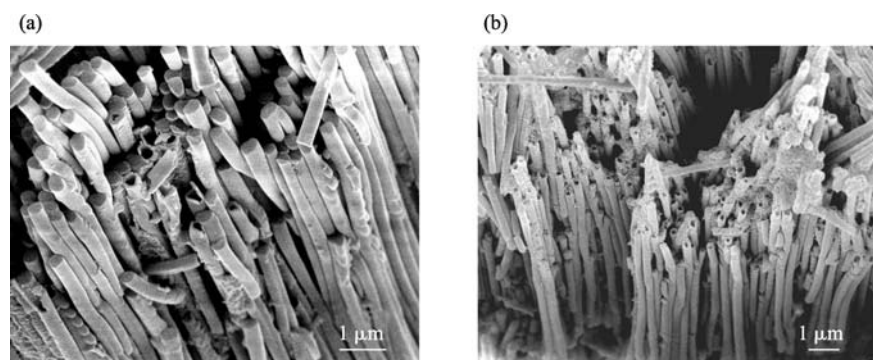


Figure 2 SEM images of (a) EuF₃ nanotubes from the reaction of 0.02 mol·L⁻¹ Eu(NO₃)₃ with 0.06 mol·L⁻¹ NH₄F for 48 h; (b) LaF₃ nanotubes from the reaction of 0.02 mol·L⁻¹ La(NO₃)₃ with 0.06 mol·L⁻¹ NaF for 24 h.

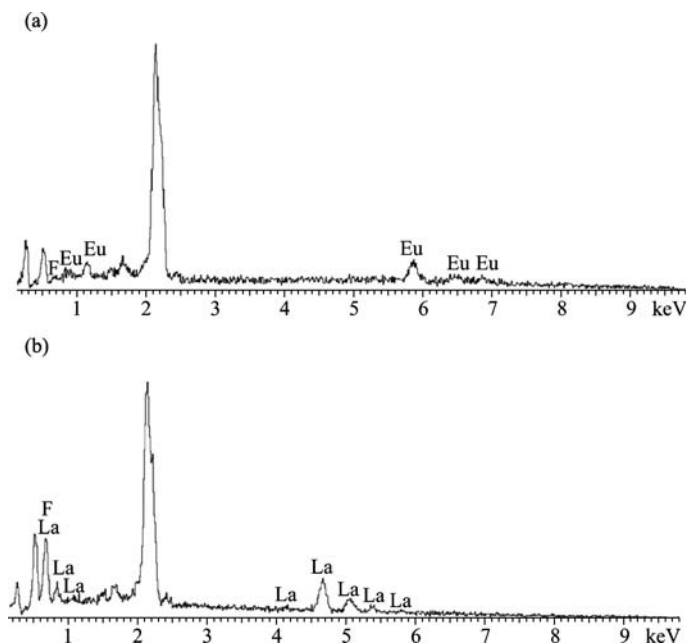


Figure 3 The energy dispersive X-ray spectra of (a) EuF_3 and (b) LaF_3 nanotubes.

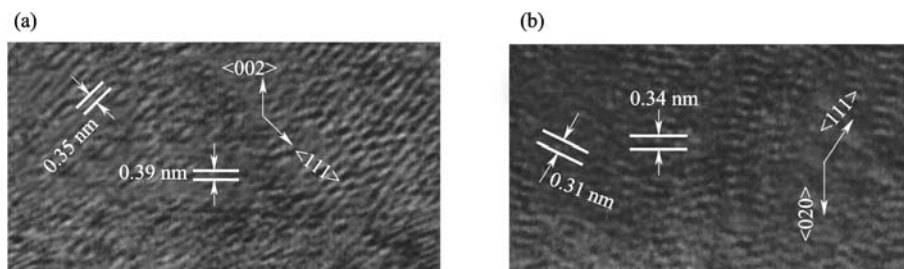


Figure 4 HRTEM images of (a) EuF_3 and (b) LaF_3 nanotubes.

4 Conclusions

In summary, we reported the preparation of long and dense EuF_3 and LaF_3 nanotubes using nanoporous alumina membrane as the reactor vessel. The method is simple, efficient and easy to control, and hence can be used for the preparation of a wide range of inorganic nanomaterials. Further investigation on the properties of as-prepared EuF_3 and LaF_3 nanotubes are in progress.

Acknowledgements This project was supported by the Department of Education of Anhui Province (Grant. No. 2006KJ006TD).

References

1. Wang, Z. L.; Quan, Z. W.; Jia, P. Y.; Lin, C. K.; Luo, Y.; Chen, Y.; Fang, J.; Zhou, W.; et al, *Chem. Mater.* **2006**, *18*, 2030–2037
2. Heer, S.; Kömpe, K.; Güdel, H. U.; Haase, M., *Adv. Mater.* **2004**, *16*, 2102–2105
3. Zhang, Y. W.; Sun, X.; Si, R.; You, L. P.; Yan, C. H., *J. Am. Chem. Soc.* **2005**, *127*, 3260–3261
4. Sudarsan, V.; van Veggel, F. C. J. M.; Herring, R. A.; Raudsepp, M., *J. Mater. Chem.* **2005**, *15*, 1332–1342
5. Mai, H. X.; Zhang, Y. W.; Si, R.; Yan, Z. G.; Sun, L. D.; You, L. P.; Yan, C. H., *J. Am. Chem. Soc.* **2006**, *128*, 6426–6436
6. Lemyre, J. L.; Ritcey, A. M., *Chem. Mater.* **2005**, *17*, 3040–3043
7. Diamente, P. R.; van Veggel, F. C. J. M., *J. Fluoresc.* **2005**, *15*, 543–551
8. Wang, F.; Zhang, Y.; Fan, X.; Wang, M., *J. Mater. Chem.* **2006**, *16*, 1031–1034
9. Stouwdam, J. W.; van Veggel, F. C. J. M., *Nano. Lett.* **2002**, *2*, 733–737
10. Evanics, F.; Diamente, P. R.; van Veggel, F. C. J. M.; Stanisiz, G. J.; Prosser, R. S., *Chem. Mater.* **2006**, *18*, 2499–2505
11. Wang, X.; Zhuang, J.; Peng, Q.; Li, Y., *Nature* **2005**, *437*, 121–124
12. Li, P.; Peng, Q.; Li, Y. D., *Adv. Mater.* **2009**, *21*, 1–4
13. Zhang, F.; Wan, Y.; Yu, T.; Zhang, F. Q.; Shi, Y. F.; Xie, S. H.; Li,

- Y. G.; Xu, L.; et al, *Angew. Chem. Int. Ed.* **2007**, *46*, 7976–7979
14. Sun, X.; Zhang, Y. W.; Du, Y. P.; Yan, Z. G.; Si, R.; You, L. P.; Yan, C. H., *Chem. Eur. J.* **2007**, *13*, 2320–2332
15. Li, J.; Lu, Y. J.; Ye, Q.; Cinke, M.; Han, J.; Meyyappan, M., *Nano Lett.* **2003**, *3*, 929–933
16. Sun, Y.; Fuge, G. M.; Fox, N. A.; Riley, D. J.; Ashfold, M. N. R., *Adv. Mater.* **2005**, *17*, 2477–2481
17. Lawrence, J.; Xu, G., *Appl. Phys. Lett.* **2004**, *84*, 918–920
18. Kam, N. W. S.; Jessop, T. C.; Wender, P. A.; Dai, H. J., *J. Am. Chem. Soc.* **2004**, *126*, 6850–6851