Inorg. Chem. **2000,** *39,* 3418−3420

Notes

Straightforward Conversion Route to Nanocrystalline Monothiooxides of Rare Earths through a High-Temperature Colloid Technique

Yadong Li,*[†,‡] Yu Huang,[‡] Tao Bai,[‡] and Longquan Li[‡]

Department of Chemistry, Tsinghua University, Beijing,
100084, P. R. China, and Department of Chemistry,
University of Science and Technology of China, Hefei,
Anhui, 230026, P. R. China

Received October 18, 1999

Introduction

There is much recent interest in nanocrystalline materials because of the unique physical and chemical properties resulting from small size and surface effects. The rare earth monothio oxides have high luminescence efficiency and low afterglow and have attracted considerable interest as luminescence materials for a variety of applications.[1] There are reports of their utilization for the X-ray solid-state detector in X-ray crystallography.[2,3] Also, they are common phosphors for optical and lighting applications. Fine particle size, narrow particle size distributions, and large surface areas produce high luminescence quantum yields[4] and high resolution displays. Therefore, preparation of nanocrystallline rare earth monothiooxides is a challenging and valuable research subject.

A conventional route for the synthesis of rare earth monothiooxides is the high-temperature surfurization of solid-state precursors. H. A. Eick[5] reported a method for obtaining a monothiooxide by sulfurizing praseodymium sesquioxide. He proposed a polystep reaction, using CS_2 as sulfurization source, carried out at high-temperature, and the rate of production was low.

Later, to obtain standard diffraction data and supported by a JCPDS Grant-in- Aid, Dr. L. Drafall reported the improved methods[6] for the synthesis of some rare earth monothiooxides.

High temperature always leads to agglomeration and results in a large particle size. The average sizes obtained with the high-temperature method range from 5 to12 μm. In addition, the extreme conditions are not readily amendable to large-scale production.

Recently, a solvothermal procedure (300 °C) in ethanol proposed for the synthesis of La_2O_2S yielded particles with an average diameter of 150 nm.[7] Herein, we report a distinct ion-exchange method for synthesizing nanocrystalline rare earth monothiooxides (10 nm) under much milder conditions.

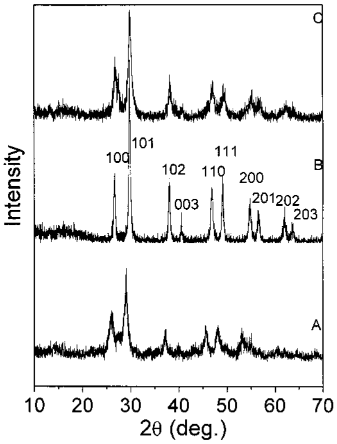

Figure 1. (A) XRD pattern of Pr_2O_2S. (B) XRD pattern of Gd_2O_2S. (C) XRD pattern of Eu_2O_2S.

Experimental Section

An appropriate amount of rare earth oxide (99.9%) powder (Pr_6O_{11}, Gd_2O_3, Eu_2O_3, La_2O_3, Nd_2O_3, Sm_2O_3, Ho_2O_3, Er_2O_3, Yb_2O_3, Lu_2O_3, Y_2O_3, Sc_2O_3), 0.60 g, and sulfur powder(99.9%), in a 20% excess were placed in a 100 mL capacity Teflon-lined autoclave. The autoclave was then filled with analytical pure ethylenediamine up to 70% of the total volume, sealed into a stainless steel tank, and maintained at 150 °C for about 8 h. Then the autoclave was removed from the furnace and allowed to cool to room-temperature naturally. Precipitates were obtained, and the used ethylenediamine could be recycled. The samples were filtered, washed with absolute ethanol, and then dried. Yields based on the amounts of rare earth oxides ranged to 98%.

The samples were characterized by X-ray powder diffraction (XRD). The XRD was carried out with a Rigaku D/max-γ A rotating anode X-ray diffractometer, using Ni-filtered Cu Kα radiation. A scan rate of 0.05/s was applied to record the patterns in the 2θ range 10−70°. The morphology and particle size of Ln_2O_2S were determined by transmission electron microscopy (TEM) with a Hitachi H-800 transmission electron microscope.

Results

The color of the samples of Pr_2O_2S, Eu_2O_2S, and Gd_2O_2S are yellow, gray, and light-yellow, respectively. Spectra A, B, and C of Figure 1 are the XRD patterns of the samples Pr_2O_2S, Eu_2O_2S, and Gd_2O_2S, respectively. All the peaks in Figure 1 can be indexed as the hexagonal Ln'_2O_2S ($Ln' = Pr, Eu, Gd$) phase. The calculated unit cell parameters (Pr_2O_2S, $a = 3.97$ Å, $c = 6.82$ Å; Eu_2O_2S, $a = 3.87$ Å, $c = 6.68$ Å; Gd_2O_2S, $a = 3.85$ Å, $c = 6.67$ Å) are comparable with those obtained from JCPDS card files (Pr_2O_2S, 27-479, $a =3.974$ Å, $c = 6.824$ Å; Eu_2O_2S, 26-1418, $a = 3.868$ Å, $c = 6.685$ Å; Gd_2O_2S, 26-1442, $a = 3.852$ Å, $c = 6.667$ Å). Parts A, B, and C of Figure 2 are the TEM micrographs of as-prepared Pr_2O_2S, Gd_2O_2S, and Eu_2O_2S particles, respectively. Though the particles were

---

* To whom correspondence should be addressed. E-mail: ydli@mail.tsinghua.edu.cn.

[†] Tsinghua University.

[‡] University of Science and Technology of China.

(1) Cotter, J. P.; Fitzmaurice, J. C.; Parkin, I. P. *J. Mater. Chem.* **1994**, *4*, 1603.

(2) Yoshida, M.; Nakagawa, M.; Fujii, H.; Kawaguchi, F.; Takeuchi, H.; Hayawa, T.; Ysukuoa, Y. *J. Appl. Phys.* **1988**, *27* (8), 1572−1575.

(3) Ito, Y.; Yamada, H.; Yoshida, M.; Fujii, H.; Tooa, G.; Takeuchi, H.; Tsukuda, Y. *J. Appl. Phys.* **1988**, *27* (8), 1371.

(4) Pede, R. B.; Dhoble, S. J. *Phys. Status Solidi* **1997**, *203B*, 571.

(5) Eick, H. A. *J. Am. Chem. Soc.* **1958**, *80*, 43−44.

(6) As shown in the description of JCPDS cards file 27-479, 26-1422, and 26-1418.

(7) Yu, S. H.; Han, Z. H.; Yang, J.; Zhao, H. Q.; Yang, R. Y.; Xie, Y.; Qian, Y. T.; Zhang, Y. H. *Chem. Mater.* **1999**, *11*, 192.

10.1021/ic9912169 CCC: $19.00

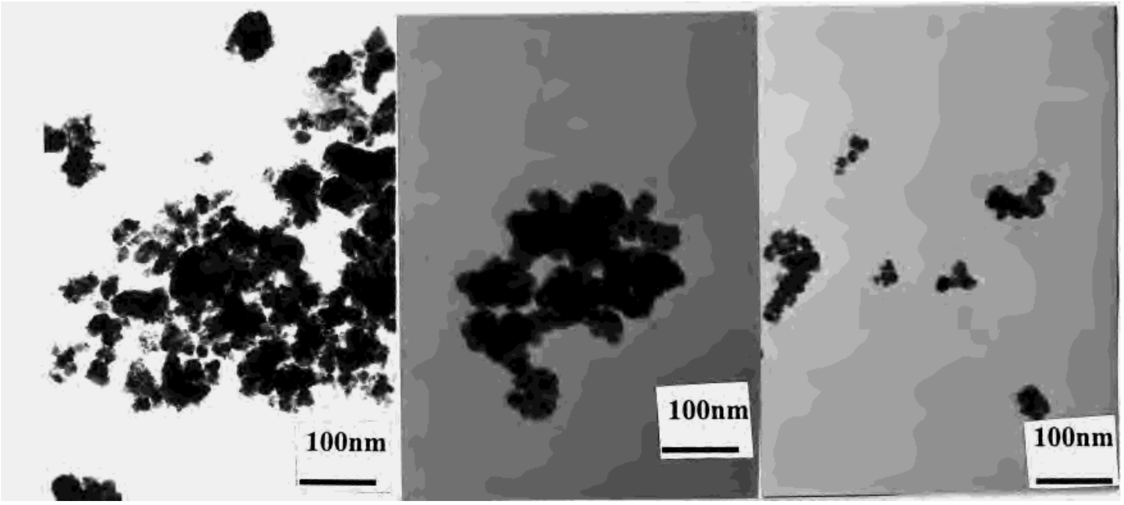

Figure 2. (a, left) TEM images of Pr_2O_2S. (b, middle) TEM images of Gd_2O_2S. (c, right) TEM images of Eu_2O_2S. (1 cm scale bar, 100 nm)

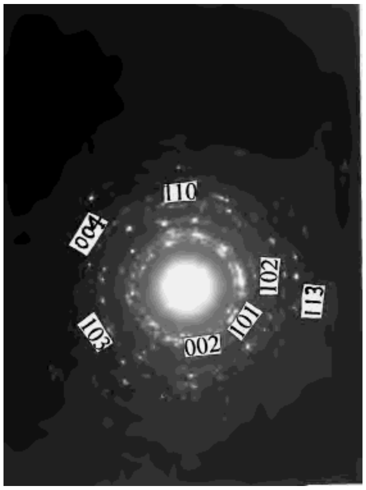

Figure 3. Electron diffraction pattern of Pr_2O_2S.

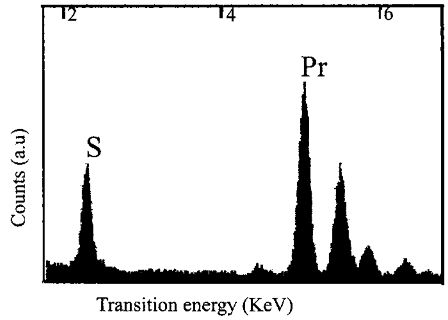

Figure 4. EDAX spectrum of Pr_2O_2S.

not well dispersed, we can clearly see that they are of spherelike morphology with an average size of about 10 nm, which is consistent with the XRD analysis using the Scherrer equation. Figure 3, the electron diffraction photo of Pr_2O_2S, shows a set of diffuse diffraction rings whose diameters are consistent with the hexagonal structure of Pr_2O_2S. From the patterns, the reflections of planes 002, 101, 102, 110, and so on were clearly visible. Figure 4 is the energy dispersion X-ray fluorescence analysis (EDAX) spectrum of the sample Pr_2O_2S. It shows that the atomic ratio Pr to S is near 2:1, consistent with the result (2.00:1.03) of the elemental analysis of the sample.

XRD patterns of products from the reactant Ln''_2O_3 ($Ln'' =$ La, Nd, Sm, Ho, Er) show the peaks of the desired product Ln''_2O_2S and the peaks of the reactant, which indicates that the reactions did not go to completion. Longer reaction times under these conditions do not change the results. We also attempted the synthesis of Ln'''_2O_2S ($Ln''' =$ Yb, Lu, Y, Sc) using the reaction desired above. However, the XRD patterns of the samples showed only the pattern of the pure rare earth oxide.

Discussion

We herein propose an ion-exchange mechanism that is described as below:

$$\text{rare-earth oxide} + S^{2-} \xrightarrow[\text{ethylenediamine}]{150\ ^\circ\text{C, 8 h}} Ln_2O_2S + O^{2-}$$

The solubilization process of sulfur in liquid ammonia had been the focus of much research. It has been pointed out that this process can give various imido anions (S_2N^-, S_3N^-, S_4N^-) and H_2S (or sulfur polyanions, e.g., $S_6{}^{2-}$, $S_4{}^{2-}$) resulting from the disproportionation of nucleophilic product $S_8NH_2{}^{8-}$. Parkin and co-workers[9] successfully utilized this behavior of sulfur to fulfill the synthesis of metal sulfides at room temperature. We also recall that sulfur dissolves in organoamine solvents and can produce colored *N*,*N*′-diaminepolysulfide solution, hydrosulfide solution, and hydrosulfuric acid.[10] Ethylenediamine is also a good solvent for sulfur. It may act in roles similar to the above-mentioned amines in our process. As temperature is elevated to 150 °C, the disproportionation of sulfur increases and more polyanions can be produced. This high-energy imput (heat at 150 °C) can also cause the dissociation of polyanions, from which required S^{2-} can be released.[11−13]

The newly produced active S^{2-} (or sulfur polyanions) collides in the high-temperature solution. We suppose that by substitution of S^{2-} for O^{2-}, the product Ln_2O_2S flakes off from the rare earth oxide crystal, generating a fresh interface for the succeeding reaction. That is, the breakage of the old bonds and the formation of the new bonds may take place simultaneously. The two principles, newly produced S^{2-} (or sulfur polyanions)

---

(8) Dubois, P.; Lelieur, J. P.; Lepoutre, G. *Inorg. Chem.* **1989**, *28*, 195.

(9) Henshaw, G.; Parkin, I. P.; Shaw, G. A. *J. Chem. Soc., Dalton Trans.* **1997**, 231.

(10) Cotton, F.A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 3rd ed.; John Wiley & Sons: New York, 1972.

(11) Li, Y. D.; Ding, Y.; Liao, H. W.; Qian, Y. T. *Chem. Mater.* **1998**, *10* (9), 2301.

(12) Li, Y. D.; Ding, Y.; Liao, H. W.; Qian, Y. T. *Inorg. Chem.* **1999**, *38*, 1382.

(13) Li, Y. D.; Liao, H. W.; Ding, Y.; Qian, Y. T. *J. Phys. Chem. Solids* **1998**, *66*, 965.

and a fresh interface, facilitate the process, lead the reaction to completion, and form Ln_2O_2S.

Since the radii of the Y, Sc, Yb, Lu are smaller than those of the other atoms, the bonds between the oxygens and the rare earths are presumably stronger. This may be the reason that we did not get any product in these reactions. What we want to emphasize here is a new synthesis route to the nanocrystalline rare earth monothiooxide. This liquid-phase reaction is expected to yield other luminescence materials of nanometer scale and to provide an industrial scale approach.

Conclusion

In conclusion, a straightforward conversion procedure from rare earth oxide to nanocrystalline Ln_2O_2S at low temperature (150 °C) in ethylenediamine by a high-temperature colloid technique is presented. The solvent plays an important role in the formation of S^{2-}(or sulfur polyanions), and further studies are needed to investigate the solubilization process of sulfur in ethylenediamine and the ion-exchange process in this reaction. This conversion method is very convenient to carry out because it requires a low temperature and is fast and easily controlled. This route also is expected to be applicable to the fabrication of other nanoparticles and to be applied on the scale of industrial use.

$$\text{rare earth oxide} + S^{2-} \xrightarrow[\text{ethylenediamine}]{150\ ^\circ\text{C, 8 h}} Ln_2O_2S$$

$$(\text{Ln} = \text{Pr, Eu, Gd, etc.})$$

Acknowledgment. We acknowledge the support of the National Natural Science Foundation of China, the Presidential Foundation of Chinese Academy of Science and State Key Project of Fundamental Research.

IC9912169