Synthesis and Formation Mechanism of La_2O_2S via a Novel Solvothermal Pressure-Relief Process

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Recently, a greater importance has been attached to the rare-earth-doped lanthanide oxysulfide (Ln_2O_2S) powder phosphors[1,2] because of their significant commercial applications such as in radiation intensifying screens,[3] fluorescent display tubes,[4] X-ray computed tomography,[5] and local jet impingement heat transfer measurement.[6] In addition, lanthanum oxysulfide either itself or Eu-doped is an effective catalyst for the thermal decomposition of COS and the reduction of SO_2 by CO.[7,8]

Various routes have been explored to synthesize such useful materials.[9−13] Conventionally, Ln_2O_2S (Ln = La, Pr, Nd, Eu, Gd, Tb) could be synthesized by the reaction of rare-earth oxides with S gas in the temperature range 597−1027 °C[9] or with CS_2 at 600 °C.[10] Ln_2O_2S could also be prepared by the hydrogen reduction of $Ln_2(SO_4)_3$ at 550−900 °C.[11] In addition, the Eu-doped Ln_2O_2S phosphor materials were prepared by rare-earth oxides with elemental sulfur and flux (Na_2CO_3) at 1100 °C in a reduced atmosphere for 2 h[12] or by direct thermal decomposition of the respective oxalate compounds under Ar and S vapor.[13] However, all these routes are traditional high-temperature solid-state reaction methods. Currently, a solvothermal method has been found to be an effective route to various compounds under mild conditions.[14] Our group has successfully synthesized Bi_2S_3 nanorods,[15] nanocrystalline β-In_2S_3,[16] nanocrystalline CdE with different morphology,[17] PbE, Bi_2E_3, and Ag_2E semiconductors (E = S, Se, Te)[18,19] via the solvothermal method.

Here, we first report a novel solvothermal pressure-relief (SPR) process for synthesis of crystallized La_2O_2S powders using $La(NO_3)_3{\cdot}nH_2O$ and thiourea as reactants in organic solvents such as ethanol or pyridine. The so-called SPR process is conducted in an autoclave with a controlled relief valve. The detailed procedure for the SPR process is that when the temperature reaches a desired value, the relief valve is immediately opened to conduct the produced gas out of the autoclave slowly. After the reaction proceeds for several hours, the desired products are then obtained under controlled conditions.

Experimental Section. The reaction was conducted in a stainless steel autoclave of 50 mL capacity. In a typical procedure, 1.0 g of analytical $La(NO_3)_3{\cdot}nH_2O$ and 0.4 g of analytical thiourea were put into the autoclave, which was subsequently filled with absolute ethanol up to 75% of the total volume. The autoclave was maintained at 300 °C while the produced gas was slowly conducted out of the system by opening the relief valve during the reaction time of 4 h and then cooled to room temperature. The precipitate was collected and washed with absolute ethanol and distilled water, respectively, to remove impurities. The final product was dried in a vacuum at 70 °C for 2 h.

The samples were characterized by X-ray powder diffraction (XRD) patterns employing a scanning rate of 0.02° in the 2θ range from 10° to 70°, using a Japan Rigaku D/Max-γA X-ray diffractometer equipped with graphite-monochromatized Cu Kα radiation (λ = 0.154178 nm). TEM images and electron diffraction (ED) pattern were taken with a Hitachi Model H-800 transmission electron microscope, using an accelerating voltage of 200 kV. The average particle sizes of powders were measured from microphotographs.

Results and Discussion. Figure 1a shows that the XRD pattern of the La_2O_2S powders synthesized by the SPR process in absolute ethanol at 300 °C for 4 h. All the peaks can be indexed as the pure hexagonal La_2O_2S phase with cell constants $a = 0.4047$ nm, $c = 0.6944$ nm, which are close to the reported data (JCPDS Cards File: 27-263). The TEM image in Figure 2a reveals that the powders are nearly spherical with an average size of 150 nm. However, Figure 1b shows that via a normal solvothermal process under the same experimental conditions only $La(OH)CO_3$ powders were obtained. All

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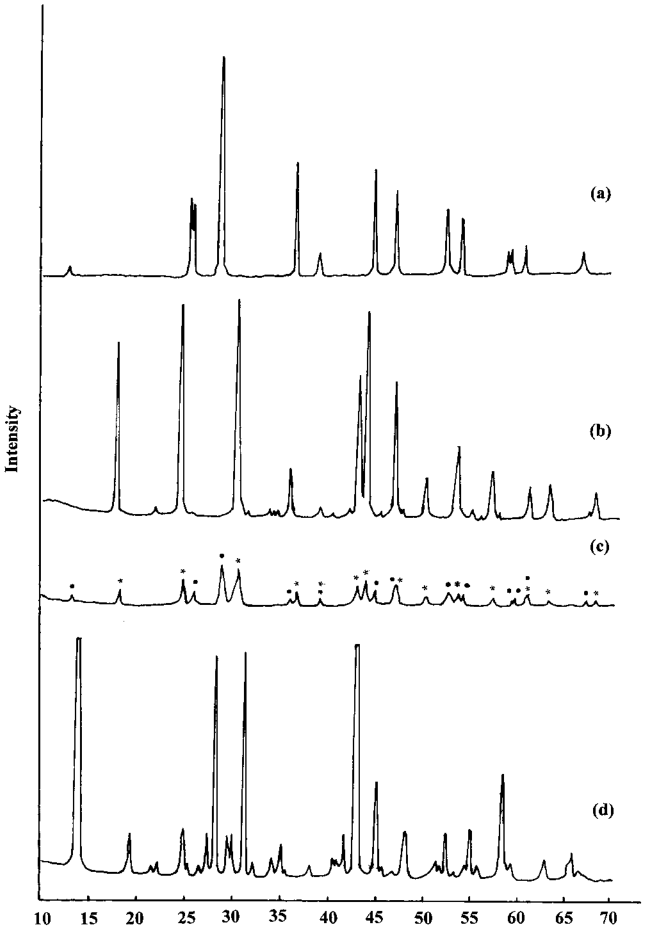

Figure 1. XRD pattern of the samples: (a) La_2O_2S sample prepared in ethanol at 300 °C for 4 h via the SPR process, (b) $La(OH)CO_3$ sample prepared in ethanol at 300 °C for 4 h via the normal solvothermal process, (c) the coexistence of La_2O_2S (marked with black dot •) and $La(OH)CO_3$ (marked with asterisk *) obtained in benzene at 300 °C for 12 h, and (d) single-crystal $La(OH)SO_4$ obtained in water at 300 °C for 4 h via the hydrothermal process.

the peaks in Figure 1b can be indexed as the orthorhombic $La(OH)CO_3$ phase with cell constants $a = 2.1555$ nm, $b = 1.2613$ nm, $c = 1.010$ nm, which are similar to the reported data (JCPDS Cards File: 29-744). The TEM image in Figure 2b demonstrates that as-prepared $La(OH)CO_3$ powders consist of particles varying in size from 40 × 100 nm to 140 × 250 nm with a uniform morphology of short rods, which is much smaller than that prepared at 500 °C for 5 weeks by Haschke.[20]

It was found that different reaction conditions produced different products. The main experimental conditions and results are summarized in Figure 3.

The formation mechanism for La_2O_2S and $La(OH)CO_3$ was proposed. It is well-known that thiourea reacts with water to produce gaseous NH_3, H_2S, and CO_2:

$$NH_2CSNH_2 + 2H_2O \rightarrow 2NH_3(g) + H_2S(g) + CO_2(g) \quad (1)$$

The produced gas NH_3 will react with the crystal water

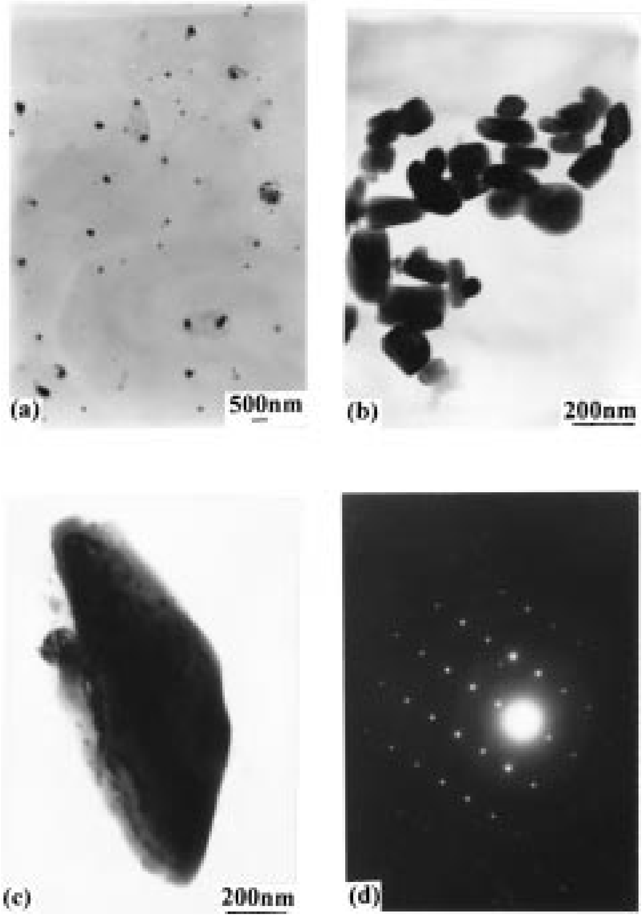

Figure 2. TEM images of the samples: (a) La_2O_2S sample prepared in ethanol at 300 °C for 4 h via the SPR process, (b) $La(OH)CO_3$ sample prepared in ethanol at 300 °C for 4 h via the normal solvothermal process, (c) single-crystal $La(OH)SO_4$ prepared at 300 °C for 4 h via the hydrothermal process, (d) electron diffraction (ED) pattern for 2(c).

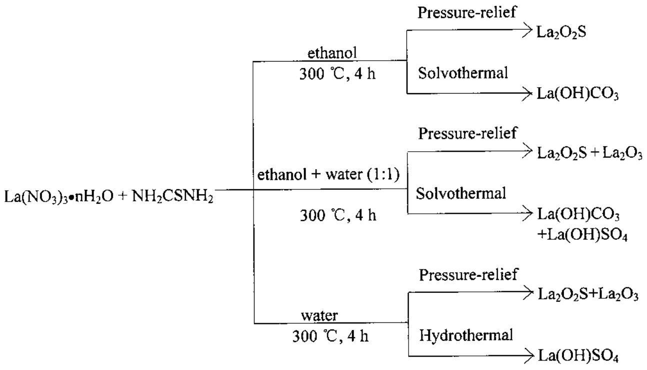

Figure 3. Scheme of the synthetic paths for synthesis of the different products under different conditions.

in the system:

$$NH_3 + H_2O \rightarrow NH_4OH \quad (2)$$

Then, the produced NH_4OH reacts with $La(NO_3)_3$ to form $La(OH)_3$:

$$La(NO_3)_3 + 3NH_4OH \rightarrow La(OH)_3 + 3N_2O(g) + 6H_2O(g) \quad (3)$$

According to the literature,[21] $Pr(NO_3)_3$ reacts with water under hydrothermal conditions to produce $Pr(OH)_3$.

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Therefore, a similar reaction may occur between lanthanum nitrate and the crystal water in the system at elevated temperature to produce $La(OH)_3$:

$$La(NO_3)_3 + {}^3/_2H_2O \rightarrow La(OH)_3(s) + 3NO_2(g) + {}^3/_4O_2(g) \quad (4)$$

Since CO_2 and H_2S are both acidic, reactions between $La(OH)_3$ and them immediately occurred; then the following equilibria were formed:

$$La(OH)_3(s) + CO_2(g) \Leftrightarrow La(OH)CO_3(s) + H_2O(g) \quad (5)$$

$$2La(OH)_3(s) + H_2S(g) \Leftrightarrow La_2O_2S(s) + 4H_2O(g) \quad (6)$$

In case of the SPR process, with the gradual decrease of the pressure in the system, the equilibrium given in eq 6 is more apt to move to the right than that expressed in eq 5. Therefore, the final product was La_2O_2S; no $La(OH)CO_3$ phase was detected by XRD. In contrast, if the produced gas was kept in the autoclave during the whole reaction period, the equilibrium given in eq 6 would be severely constrained and could hardly move toward the right; therefore, the product was highly crystallized $La(OH)CO_3$, as shown in Figure 1b.

On the basis of the reaction modes and the obtained products discussed above, we believe that a transition reaction from $La(OH)CO_3$ to La_2O_2S most probably exist in the present SPR process, as expressed in eq 7. The equilibrium given in eq 7 is also more apt to move to the right in the SPR process than in a normal solvothermal process. Unfortunately, the coexistence of these two phases was not observed in ethanol, which may be due to the quickness of the transition reaction. However, if we used benzene instead of absolute ethanol via the SPR process at 300 °C for 12 h, these two phases were observed in the final products as shown in Figure 1c. This might be attributed to the nonpolar solvent effect on the transition reaction.

$$2La(OH)CO_3(s) + H_2S(g) \Leftrightarrow La_2O_2S + 2H_2O(g) + 2CO_2(g) \quad (7)$$

Meanwhile, the following reaction may occur to produce a small amount of La_2O_3:

$$2La(OH)CO_3(s) \Leftrightarrow La_2O_3(s) + H_2O(g) + 2CO_2(g) \quad (8)$$

These results demonstrate that the SPR process is more favorable for the formation of La_2O_2S.

Instead of using $La(NO_3)_3 \cdot nH_2O$, $Ce(NO_3)_3 \cdot 6H_2O$ was employed to react with thiourea in ethanol under similar conditions. Three phase, Ce_2O_2S, $Ce(OH)CO_3$, and CeO_2, were observed to coexist in the product obtained by the present SPR process. Similarly, only $Ce(OH)CO_3$ phase was detected by XRD for the product obtained by the normal solvothermal process. These results coincide with our conjecture mentioned above, which proved that the transition from $Ln(OH)CO_3$ to Ln_2O_2S did occur in the SPR process.

The influence of temperature and solvents on synthesis of La_2O_2S, $La(OH)CO_3$, and $La(OH)SO_4$ was also studied. It was found that lower temperature (<250 °C) is unfavorable for the formation of them. Crystallized La_2O_2S powders can also be obtained using pyridine as solvent, except that higher temperature (400 °C) was needed. When the solvent was the mixture of ethanol and water with a volume ratio of 1:1 instead of absolute ethanol, La_2O_2S was the dominant product, together with some La_2O_3 via the SPR process. This result demonstrated that the excess water content in the system did not influence the formation of the La_2O_2S but led to the increasing amount of La_2O_3 in the final product. In addition, the water content in the system was found to play a key role in the phase transition between $La(OH)CO_3$ and $La(OH)SO_4$ via the normal solvothermal process, as shown in Figure 3. The content of $La(OH)SO_4$ will also increase with the increase of the water content in the system. If the solvent was completely substituted by distilled water, in other words, via the conventional hydrothermal process, a monoclinic $La(OH)SO_4$ single crystal was produced from the same reactants at the same temperature, as shown in Figures 1d and 2d. The detailed results and formation mechanism of $La(OH)SO_4$ under different operating conditions are still under research and will be reported later.

In summary, a new solvothermal pressure-relief (SPR) process was successfully developed for the synthesis of La_2O_2S at relatively low temperature (300 °C) in ethanol media. In contrast, the normal solvothermal and hydrothermal process can only produce $La(OH)CO_3$ and $La(OH)SO_4$, respectively. Both solvents and the process employed have significant influence on the formation of La_2O_2S. The formation mechanism was proposed. The present SPR process provides a favorable low-temperature reaction pathway for synthesis of other lanthanide oxysulfides.

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