Facile and green synthesis of (La_{0.95}Eu_{0.05})_2O_2S red phosphors with sulfate-ion pillared layered hydroxides as a new type of precursor: controlled hydrothermal processing, phase evolution and photoluminescence

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Abstract
This study presents a facile and green route for the synthesis of (La_{0.95}Eu_{0.05})_2O_2S red phosphors of controllable morphologies, with the sulfate-type layered hydroxides of Ln_2(OH)_4SO_4·2H_2O (Ln = La and Eu) as a new type of precursor. The technique takes advantage of the fact that the precursor has had the exact Ln:S molar ratio of the targeted phosphor, thus saving the hazardous sulfurization reagents indispensable to traditional synthesis. Controlled hydrothermal processing at 120 °C yielded phase-pure Ln_2(OH)_4SO_4·2H_2O crystallites in the form of either nanoplates or microprisms, which can both be converted into Ln_2O_2S phosphor via a Ln_2O_2SO_4 intermediate upon annealing in flowing H_2 at a minimum temperature of ~700 °C. The nanoplates collapse into relatively rounded Ln_2O_2S particles while the microprisms retain well their initial morphologies at 1200 °C, thus yielding two types of red phosphors. Photoluminescence excitation (PLE) studies found two distinct charge transfer (CT) excitation bands of O_2−→Eu^{3+} at ~270 nm and S^{2−}→Eu^{3+} at ~340 nm for the Ln_2O_2S phosphors, with the latter being stronger and both significantly stronger than the intrinsic intra-/transitions of Eu^{3+}. The two types of phosphors share high similarities in the positions of PLE/PL (photoluminescence) bands and both show the strongest red emission at 627 nm (5D_0→7F_2 transition of Eu^{3+}) under S^{2−}→Eu^{3+} CT excitation at 340 nm. The PLE/PL intensities show clear dependence on particle morphology and calcination temperature, which were investigated in detail. Fluorescence decay analysis reveals that the 627 nm red emission has a lifetime of ~0.5 ms for both types of the phosphors.

Keywords: sulfate-type layered rare-earth hydroxides (LRHs), hydrothermal synthesis, (La, Eu)_2O_2S red phosphors, photoluminescence properties
1. Introduction

Lanthanide oxysulfides (Ln₂O₃S, Ln = La–Lu; space group: P3m1) are known as a group of wide bandgap (4.6–4.8 eV) compounds that can be doped with various rare-earth activators for a wide range of luminescence and display applications [1, 2]. Eu³⁺-activated Ln₂O₃S compounds, such as Y₂O₃S:Eu³⁺ and La₂O₃S:Eu³⁺, have been extensively investigated because they are efficient red phosphors finding extensive applications in television picture tubes [1], field emission displays [3] and long-lifetime phosphors [4]. Compared with the traditional Eu³⁺ doped oxide red phosphors [5–7], Ln₂O₃S:Eu³⁺ compounds have Eu–S bonds in their crystal structure, which give rise to an additional Eu–S charge transfer (CT) excitation band, aside from the Ln²⁺ emission bands [8, 9]. As finer phosphor particles of better controlled characteristics are desired in contemporary lighting and display technologies to improve the resolution and luminescence intensity, alternative synthetic methodologies have been reported in recent years for oxysulfide synthesis, including combustion [10], sulfurization of rare-earth oxides by H₂S or CS₂ gas at elevated temperatures [11], solvothermal pressure-relief synthesis [12], two-step solution gel polymer thermolysis [13], gelatin-templated synthesis [14] and gel thermolysis [15]. It should be noted that the above synthetic routes generally need harmful and bad-smelling sulfurization reagents, such as CS₂, H₂S, K₂S and thiourea (CS(NH)₂), and sometimes have difficulties in the morphological control of the final product.

We report in this work a facile and clean route to synthesize (La, Eu)₂O₃S red phosphors of controlled particle morphologies, with SO₄²⁻ pillared layered rare-earth hydroxides (LRHs) (Ln₂(OH)₄SO₄·nH₂O, Ln = La and Eu, and n ≈ 2) as a new type of precursor. One distinct feature of this technique is that the precursor has already had the exact Ln:S molar ratio of the targeted Ln₂O₃S phosphor, and thus Ln₂O₃S can be directly yielded via proper annealing in a reducing atmosphere without using any of the aforementioned hazardous sulfurization reagents. The method is environmentally friendly, has high efficiency and presents a better morphological control. The Ln₂(OH)₄SO₄·2H₂O compounds were reported as a new family of LRHs in 2010, and elongated platelets of several micrometers in lateral size and tens of nanometers in thickness were successfully crystallized for the intermediately sized Ln³⁺ (Ln = Pr–Tb) via controlled hydrolysis of the corresponding rare-earth sulfates in the presence of hexamethylenetetramine (HMT) [16]. Synthesis via the HMT-based homogeneous precipitation technique, however, has not been reported for the Ln³⁺ larger than Pr³⁺, such as the La³⁺ in this work. It was also noticed that hydrothermal reaction has rarely been attempted in the synthesis of this group of layered compounds. In view of these results, we employed in this work the hydrothermal route to synthesize Ln₂(OH)₄SO₄·2H₂O (Ln = La and Eu) under controlled pH, with Ln(NO₃)₃ as the mother salt and environmentally benign ammonium sulfate ((NH₄)₂SO₄) as the sulfate source, which is then employed as the precursor to generate (La, Eu)₂O₃S red phosphors via proper annealing in flowing H₂. The precursors and the resultant phosphors are thoroughly characterized by the combined techniques of x-ray diffractometry (XRD), Fourier transform infrared spectroscopy (FTIR), field emission scanning electron microscopy (FE-SEM), thermogravimetry/differential scanning calorimetry (TG/DSC) and photoluminescence excitation/photoluminescence (PLE/PL) spectroscopies. In the following sections, we report the phase structure and particle morphology controlled synthesis of SO₄²⁻·LRHs precursors, phase evolution of the precursor upon calcination and PL behaviors of the resultant (La, Eu)₂O₃S red phosphors.

2. Experimental procedure

The starting materials for powder synthesis are La₃O₅ (99.99% pure), Eu₂O₃ (99.99% pure), NH₃, H₂O, (NH₄)₂SO₄ and HNO₃ (Shenyang Chemical Reagent Factory, Shenyang, China). All the chemicals were used as received without further purification. A mixed solution of La and Eu nitrates was prepared by dissolving La(NO₃)₃·6H₂O (La/Eu = 19:1 molar ratio) in concentrated HNO₃, followed by evaporation to dryness at 100 °C to remove superfluous HNO₃ and a final dilution with distilled water to 0.1 M. For each run of the synthesis, 0.792 g of (NH₄)₂SO₄ (Ln³⁺:SO₄²⁻ = 1:1 molar ratio, Ln = La and Eu) was dissolved in 60 ml of the mixed nitrate solution to get a clear solution, and NH₃·H₂O was then added dropwise to reach different pH values in the range 7.0–10. The resultant mixture was homogenized at room temperature in the favor of magnetic stirring for 10 min and was then transferred to a Teflon lined stainless steel autoclave of 100 ml capacity. The autoclave was tightly sealed and was put in an electric oven preheated to 120 °C for a reaction period of 24 h. After natural cooling to room temperature, the hydrothermal product was collected via centrifugation, washed three times with distilled water via repeated ultrasonication and centrifugation to remove by-products, rinsed with absolute ethanol and was finally dried in the air at 50 °C for 12 h to yield a white precursor powder for characterizations and further processing. Calculation of the precursor was performed by following hydrogen (~200 ml min⁻¹) at various predetermined temperatures ranging from 400 to 1200 °C for 1 h, with a heating rate of 10 °C min⁻¹ at the ramp stage. Details of the synthesis are summarized in scheme 1.

Phase identification was performed by XRD (Model PW3040/60, Philips Research Laboratories, Eindhoven,
The Netherlands) operated at 40 kV per 40 mA, using nickel filtered CuKα radiation. FTIR spectroscopy (Model Spectrum RXI, Perkin-Elmer, Shelton, Connecticut, USA) of the precursors was performed by the standard KBr method. Morphologies of the products were observed via FE-SEM (Model JSM-7001F, JEOL, Tokyo, Japan) operated at 10 kV. PL/PLE spectra and fluorescence decay kinetics of the (La, Eu)$_2$O$_5$S phosphors were taken with an LS-55 fluorescence spectrophotometer (Perkin-Elmer, Shelton, Connecticut, USA) at room temperature.

3. Results and discussion

3.1. Hydrothermal synthesis and characterization of the precursor

The systematic studies performed in this work indicated that characteristics of the precursor, including chemical composition, phase structure and particle morphology, are significantly affected by the solution pH (7.0–10). For each run of the synthesis, residual La$^{3+}$ and Eu$^{3+}$ ions are hardly detectable in the remnant solution after solid particle removal, suggesting a nearly 100% yield of the hydrothermal reaction.

Figure 1 compares XRD patterns of products synthesized in the pH range 7.0–10. Samples S1 (pH = 7.0) and S2 (pH = 7.5) can be well indexed based on anhydrous La(OH)SO$_4$ (JCPDS No. 00-045-0750). The compound crystallizes in the space group $P2_1/n$ and possesses a layered structure, in which the main layers, composed of LnO$_6$ polyhedra, are confined to the ac plane and the individual ac layers are tied together by the sulfate entities along the b-axis [1, 17]. The S4 (pH = 9.0) and S5 (pH = 10.0) samples, which were obtained under higher pH, are both indexible to the sulfate-type LRHs (SO$_4^{2−}$-LRHs) of Ln$_2$(OH)$_4$SO$_4$·2H$_2$O reported for the intermediately sized Ln$^{3+}$ ions (Ln = Pr–Tb) [16]. The SO$_4^{2−}$-LRHs tend to crystallize in the orthorhombic system, with the SO$_4^{2−}$ anions sandwiched between the hydroxide host layers for charge balance, and the crystal may be viewed as an alternative stacking of the host and SO$_4^{2−}$ layers along the [010] direction (b-axis) [16]. For the five samples of S1–S5, the appearances of (020) and (040) diffractions in the low-angle region are indicative of layered structures. LRHs of the composition Ln$_2$(OH)$_4$A·nH$_2$O (A = NO$_3$, Cl or Br, and n ≈ 1.5–1.7), reported in recent years for a wide spectrum of Ln (Ln = Nd–Yb, including Y), are featured by exchangeable A$^+$ anions and varied hydration number n and interlayer distance with varying Ln$^{3+}$ size and environment humidity [18–20]. The sulfate-type LRHs of Ln$_2$(OH)$_4$SO$_4$·2H$_2$O, however, have bidentately coordinated SO$_4^{2−}$ (un-exchangeable) and an almost fixed hydration number of 2 [16]. From the peculiar crystallization behavior and crystal structure of Ln$_2$(OH)$_4$SO$_4$·2H$_2$O, it can be expected that Ln$^{3+}$ size would bring about no essential difference to the interlayer distance (i.e. peak positions of the (00k) diffractions) but appreciably varied dimensions of the ac plane (the host layer). Calculations from the XRD results shown in figure 1 yielded lattice parameters of $a$ ≈ 0.640 nm, $b$ ≈ 1.626 nm and $c$ ≈ 0.389 nm, and an interlayer distance of ≈ 0.813 nm for the (La, Eu)$_2$O$_5$S phosphor compounds synthesized in this work. The interlayer spacing is close to the value of 0.829 nm reported for Tb$_2$(OH)$_4$SO$_4$·2H$_2$O compounds [16]. The S3 sample, synthesized under the intermediate pH of 8.0, is apparently a mixture of the Ln(OH)SO$_4$ and Ln$_2$(OH)$_4$SO$_4$·2H$_2$O phases. The above results are understandable from the solution chemistry of Ln$^{3+}$ discussed below. The Ln$^{3+}$ cations undergo hydration and hydrolysis in an aqueous solution to form six-fold coordinated [Ln(OH)$_3$(H$_2$O)$_3$(SO$_4$)$_{3−x/2}$(x + y + z = 6)] complex species [21], in which SO$_4^{2−}$ is incorporated because of its high complexing ability. Higher solution pH promotes hydrolysis and thus leads to more hydroxyls while at the same time lessens SO$_4^{2−}$ in these
precursor ions. This accounts for the higher $\text{OH}^-/\text{Ln}^{3+}$ while lower $\text{SO}_4^{2-}/\text{Ln}^{3+}$ mole ratios are observed for the higher pH product and also the phase transition from $\text{Ln(OH)}_2\text{SO}_4$ to $\text{Ln}_2(\text{OH})_4\text{SO}_4\cdot2\text{H}_2\text{O}$.

Figure 2 shows FE-SEM morphologies for the three typical samples of S1, S4 and S5. The S1 sample ($\text{Ln(OH)}_2\text{SO}_4$, pH = 7.0) presents plate-like morphologies, with sizes of up to $4\,\mu\text{m}$ in length, $500\,\text{nm}$ in width and a thickness of $\sim20\,\text{nm}$. It is also seen that some of the plates tend to wrap up and appear curved. The S4 sample ($\text{Ln}_2(\text{OH})_4\text{SO}_4\cdot2\text{H}_2\text{O}$, pH = 9.0) is composed of relatively uniform and thin platelets of approximately $1\,\mu\text{m}$ long, $300\,\text{nm}$ wide and $100\,\text{nm}$ thick. At the even higher hydrothermal pH of 10, the $\text{Ln}_2(\text{OH})_4\text{SO}_4\cdot2\text{H}_2\text{O}$ particles (S5) turn significantly bigger and thicker and appear as microprisms with dimensions of up to $5\,\mu\text{m}$ in length, $1.2\,\mu\text{m}$ in width and $400\,\text{nm}$ in thickness. From figures 2(b) and (c), it is perceived that raising the solution pH from 9.0 to 10.0 appreciably raises the solubility of $\text{Ln}_2(\text{OH})_4\text{SO}_4\cdot2\text{H}_2\text{O}$ in the hydrothermal system, and thus significantly larger particles are resulted via Ostwald ripening (i.e. the dissolution of smaller particles followed by reprecipitation on bigger ones). Nanosized particles are seen to cover surfaces of the microprisms (figure 2(c)), which is believed to be caused by secondary nucleation upon cooling the hydrothermal system. The initially high solubility of $\text{Ln}_2(\text{OH})_4\text{SO}_4\cdot2\text{H}_2\text{O}$, rendered by the high solution pH of 10, decreases with decreasing temperature and thus secondary nucleation of $\text{Ln}_2(\text{OH})_4\text{SO}_4\cdot2\text{H}_2\text{O}$ takes place once supersaturation is reached.

The functional groups built in the hydrothermal products are investigated via FTIR spectroscopy, and the results are shown in figure 3 for the two typical samples of S1 and S4. The fundamental IR vibrations of $\text{SO}_4^{2-}$ are well documented to be located at $1104$ ($\nu_1$), $981$ ($\nu_3$), $618$ ($\nu_2$) and $451\,\text{cm}^{-1}$ ($\nu_2$), and strong bands are usually found in the region $1210$–$1040\,\text{cm}^{-1}$ [22]. When the $\text{SO}_4^{2-}$ tetrahedron is distorted, $\nu_3$ would split to give rise to two or three peaks, the resolution of which depends on the magnitude of the split, and $\nu_1$ would become active usually near $1000\,\text{cm}^{-1}$ [22]. Similarly, the $\nu_4$ absorption may split into three bands [22]. The above-mentioned $\text{SO}_4^{2-}$ vibrations are thus all clearly observable for the S1 sample, that is, $\nu_3$ in the range $\sim1038$–$1250\,\text{cm}^{-1}$ (two splits), $\nu_1$ at $1005\,\text{cm}^{-1}$, and $\nu_2$ in the region $\sim780$–$625\,\text{cm}^{-1}$ (two splits). The sharp absorptions found at $\sim3495, 825$ and $582\,\text{cm}^{-1}$ are all diagnostic of hydroxyls in the molecule. The lack of a clear absorption at $\sim3240\,\text{cm}^{-1}$ and the rather shallow peak at $1650\,\text{cm}^{-1}$ imply that the sample essentially contains no water of hydration but has some surface adsorbed water molecules. The above results suggest that the S1 sample is an anhydrous basic sulfate, in accordance with the results of XRD. The appearance of $\nu_1$ vibration at $\sim1005\,\text{cm}^{-1}$, which is IR inactive in free $\text{SO}_4^{2-}$ ions of highly symmetric $T_d$ point group, together with the significant splitting of both $\nu_3$ and $\nu_4$, strongly suggest the presence of coordinated sulfate anions and also a possible intra-molecular coupling between $\text{SO}_4^{2-}$ and OH$^-$. Sample S4 (spectrum b) presents IR responses similar to the $\text{Te}_2(\text{OH})_4\text{SO}_4\cdot2\text{H}_2\text{O}$ sample reported recently [16]. Compared with sample S1, S4 exhibits additional vibration features, as discussed below, though the hydroxyl absorptions are similarly observed at $\sim3477, 840$
and 531 cm\(^{-1}\). Firstly, water vibrations appear as a strong and broad band at \(~3242\) cm\(^{-1}\) together with a relatively strong one at \(~1678\) cm\(^{-1}\), which suggests that S4 is hydrated. Secondly, more splitting of \(v_3\) into three bands and an expansion of the \(v_4\) band from \(~780–625\) cm\(^{-1}\) for S1 to \(~825–550\) cm\(^{-1}\) for S4 are clearly seen, indicating that the \(\text{SO}_4^{2-}\) tetrahedron in S4 is significantly more distorted. This is further evidenced by the appearances of not only \(v_1\) (at \(~1005\) cm\(^{-1}\)) but also \(v_2\) (~745 cm\(^{-1}\)) vibrations, since, like \(v_1, v_2\) should also be IR inactive for a free \(\text{SO}_3^{2-}\). The enhanced distortion of the \(\text{SO}_4^{2-}\) tetrahedron in S4 was believed to arise from intra-molecular \(\text{H}_2\text{O}/\text{SO}_4^{2-}\) interactions via hydrogen bonding. The coupling would distort the molecular structure of \(\text{H}_2\text{O}\) at the same time, and thus additional hydroxyl absorption appears at \(~3600\) cm\(^{-1}\). The less defined absorption at \(~1445\) cm\(^{-1}\) on spectrum (b) conforms to the characteristic vibration of \(\text{CO}_3^{2-}\), and may be due to chemical adsorption of atmospheric \(\text{CO}_2\) on particle surfaces.

### 3.2. Thermal decomposition of the layered hydroxyl precursors to oxysulfide phosphors

Figure 4 shows thermogravimetry analysis (TGA)/DSC curves of the Ln\(_2\)(OH)\(_4\)SO\(_4\)·2H\(_2\)O precursor (S4) recorded in flowing Ar (5 ml min\(^{-1}\)) at a heating rate of 10 °C min\(^{-1}\). The microprism precursor (S5) exhibits a similar thermal behavior and thus the data are not shown. It is seen that the basic sulfate decomposes via two major stages up to 1100 °C. The small weight loss (~1.26%) from room temperature to \(~200\) °C and the endotherm peaked at \(~185\) °C on the DSC curve are largely due to the evaporation of surface adsorbed water. The weight loss of 6.53% between ~200 and 300 °C is primarily due to the removal of hydration water, and is accompanied by an endothermic peak at ~269 °C. The weight losses occurring in the range of ~300–400 °C, accompanied by a sharp endotherm at ~344 °C, can be attributed to dehydroxylation of the hydroxide layer. No significant weight loss was observed at the even higher temperatures up to 1100 °C, and the broad and ill-defined endotherm above 400 °C is an artifact. From the above TGA/DSC analysis, it can be concluded that the Ln\(_2\)(OH)\(_4\)SO\(_4\)·2H\(_2\)O (Ln = La and Eu) precursor decomposes according to the following procedure:

\[
\text{Ln}_2(\text{OH})_4\text{SO}_4 \cdot 2\text{H}_2\text{O} \rightarrow \text{Ln}_2(\text{OH})_4\text{SO}_4
+ 2\text{H}_2\text{O}(\sim 200 – 300 °C),
\]

\[
\text{Ln}_2(\text{OH})_4\text{SO}_4 \rightarrow \text{Ln}_2\text{SO}_4 + 2\text{H}_2\text{O}(\sim 300 – 400 °C).
\]

In addition, the weight losses of 6.53 and 7.12% observed for the dehydroxylation stages follow closely the values of 7.51 and 8.12% calculated from the chemical formula, respectively.

Figure 5 exhibits XRD patterns of the nanoplate precursor (S4, figure 5(a)) and those calcined from (a) under flowing \(\text{H}_2\) (~200 ml min\(^{-1}\)) for 1 h at (b) 400, (c) 600, (d) 700, (e) 800, (f) 1000 and (g) 1200 °C. The standard diffractions of \(\text{La}_2\text{O}_3\text{S}\) (JCPDS No. 01-075-1930) are included as bars for comparison (h).

The microprism precursor (S5) exhibits a similar thermal behavior and thus the data are not shown. It is seen that the basic sulfate decomposes via two major stages up to 1100 °C. The small weight loss (~1.26%) from room temperature to \(~200\) °C and the endotherm peaked at \(~185\) °C on the DSC curve are largely due to the evaporation of surface adsorbed water. The weight loss of 6.53% between ~200 and 300 °C is primarily due to the removal of hydration water, and is accompanied by an endothermic peak at ~269 °C. The weight losses occurring in the range of ~300–400 °C, accompanied by a sharp endotherm at ~344 °C, can be attributed to dehydroxylation of the hydroxide layer. No significant weight loss was observed at the even higher temperatures up to 1100 °C, and the broad and ill-defined endotherm above 400 °C is an artifact. From the above TGA/DSC analysis, it can be concluded that the Ln\(_2\)(OH)\(_4\)SO\(_4\)·2H\(_2\)O (Ln = La and Eu) precursor decomposes according to the following procedure:

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\text{Ln}_2(\text{OH})_4\text{SO}_4 \cdot 2\text{H}_2\text{O} \rightarrow \text{Ln}_2(\text{OH})_4\text{SO}_4
+ 2\text{H}_2\text{O}(\sim 200 – 300 °C),
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\[
\text{Ln}_2(\text{OH})_4\text{SO}_4 \rightarrow \text{Ln}_2\text{SO}_4 + 2\text{H}_2\text{O}(\sim 300 – 400 °C).
\]

In addition, the weight losses of 6.53 and 7.12% observed for the dehydroxylation stages follow closely the values of 7.51 and 8.12% calculated from the chemical formula, respectively.

Figure 5 exhibits XRD patterns of the nanoplate precursor (S4, figure 5(a)) and those calcined under flowing \(\text{H}_2\) at various temperatures for 1 h. The powder calcined at 400 °C (figure 5(b)) can be well indexed to the monoclinic structured \(\text{Ln}_2\text{O}_3\text{S}\) phase (JCPDS No. 01-085-1534), and the XRD result is in accordance with TG/DSC analysis (figure 4). The 600 °C powder is primarily of monoclinic \(\text{Ln}_2\text{O}_3\text{S}\), with the presence of trace \(\text{Ln}_2\text{O}_3\text{S}\) (figure 5(c)), and hexagonally structured \(\text{Ln}_2\text{O}_3\text{S}\) (JCPDS No. 01-075-1930) has resulted as a pure phase at 700 °C (figure 5(d)). As TG/DSC analysis revealed no composition change of \(\text{Ln}_2\text{O}_3\text{S}\) up to 1100 °C in Ar, the above XRD results thus indicate that the \(\text{H}_2\) atmosphere used for calcination has a strong capability to take out oxygen atoms from \(\text{SO}_4^{2-}\) even at a low temperature of 600–700 °C. Since no hazardous sulfurization reagents were used for precursor synthesis and the only exhaust gas during calcination is water vapor, the synthetic route developed in this work for \(\text{Ln}_2\text{O}_3\text{S}\) phosphor can be regarded as a green one. The powders calcined at even the higher temperatures of up to 1200 °C show identical positions of the XRD peaks but successively more refined peak shapes and improved peak intensities, indicating lattice perfection and crystallite growth. Compared with the standard JCPDS file (No. 01-075-1930) for \(\text{La}_2\text{O}_3\text{S}\), the diffraction peaks of \(\text{Ln}_2\text{O}_3\text{S}\) slightly drifted to larger angles, indicating a contracted unit cell.

By applying equations \(1/d^2 = (h^2 + k^2 + l^2)/a^2\) and \(2d \sin \theta = n \lambda\), the lattice parameters of \(\text{Ln}_2\text{O}_3\text{S}\) were calculated to be \(a = b = 0.399\) 38 nm and \(c = 0.685\) 38 nm for...
the 1200 °C sample, which are indeed smaller than those of pure La$_2$O$_2$S (JCPDS No. 01-075-1930; $a=b=0.4040$ nm and $c=0.6890$ nm). This is due to the smaller ionic radius of Eu$^{3+}$ than La$^{3+}$ (for seven-fold coordination in hexagonal Ln$_2$O$_2$S, La$^{3+}$ and Eu$^{3+}$ have their respective sizes of 1.10 and 1.01 nm) [1, 23], and is a manifestation of solid solution formation.

3.3. Morphology analysis of the (La, Eu)$_2$O$_2$S red phosphors

Figure 6 shows morphology evolution of the nanoplate (S4) and microprism (S5) precursors upon calcination. It is seen from the FE-SEM micrographs that the powders derived from S4 well preserved the original thin-platelet morphologies up to 700 °C (figure 6(b)), at which point the powder had turned into pure Ln$_2$O$_2$S (figure 5). The platelets partially collapse into much smaller particles at 1000 °C (figure 6(c)), followed by an almost complete disintegration at 1200 °C to form submicron-sized particles of relatively good dispersion and somewhat irregular shapes (figure 6(d)). The prismatic particles of S5 are highly stable in morphology against calcination of up to 1200 °C, due to their much larger lateral sizes and particular thickness, although cracks arising from thermal decomposition and crystallite growth are observable (figures 6(e)–(h)).

3.4. Luminescence behaviors of the (La, Eu)$_2$O$_2$S red phosphors

Figure 7 reveals the effects of calcination temperature on emission and excitation properties of the (La, Eu)$_2$O$_2$S red phosphors derived from precursor S4. The PLE spectra are obtained by monitoring the strongest red emission at 627 nm, and the PL spectra are measured under UV excitation at 340 nm. It is seen from the PLE spectra (figure 7(a)) that a higher calcination temperature, particularly above 1000 °C, produces significantly stronger excitation bands. The paired broad peaks at ~275 and 340 nm are ascribed to different transitions by CT. To be more specific, the one located at ~275 nm is owing to the electron transition from the 2p orbital of O$^{2-}$ to the 4f orbital of Eu$^{3+}$ ($O^{2-}$ → Eu$^{3+}$) [24] and the stronger one centered at ~340 nm is attributed to S$^{2-}$ → Eu$^{3+}$ CT transition. The higher covalency of S–Eu than O–Eu bonds (S and O have their respective electronegativities of 2.58 and 3.44) allows much easier electron transfer to Eu$^{3+}$, and thus the S$^{2-}$ → Eu$^{3+}$ CT band appears at a longer wavelength (lower energy) with an appreciably higher intensity. In each spectrum, the weaker and sharper peaks observed in the wavelength region of ~390–500 nm belong to the intra f–f transitions of Eu$^{3+}$, and are originated from the $^{7}F_{0}$ → $^{4}L_{6}$ transition at 395 nm, the $^{7}F_{0}$ → $^{5}D_{1}$ at 418 nm, the $^{7}F_{0}$ → $^{5}D_{2}$ at 468 nm and the $^{7}F_{1}$ → $^{5}D_{2}$ at 475 nm.

Figure 7(b) shows the emission spectra recorded under 340 nm excitation. The observed PL bands are ascribed to the transitions from the $^{5}D_{2}$ excited sates to the different $^{7}F_{J}$ levels of Eu$^{3+}$ ground states. More specifically, the emissions at lower energies (597, 619/627 and 706 nm) arise from the $^{5}D_{0}$ → $^{7}F_{J}$ ($J=1, 2$ and 4) transitions while the higher energy ones (541, 559 and 590 nm) from the $^{5}D_{1}$ → $^{7}F_{J}$ ($J=1$, 2 and 3) transitions, respectively. The Eu$^{3+}$ activators are expected to replace La$^{3+}$ and thus inherit the $C_{3v}$ point symmetry of La$^{3+}$ in hexagonal La$_2$O$_2$S [1]. The low site symmetry of Eu$^{3+}$ thus allows the forced electric dipole
Figure 7. PLE and PL spectra of the (La, Eu)$_2$O$_2$S phosphors calcined from the nanoplate precursor (S4) at various temperatures for 1 h. The inset in panel (b) is the average crystallite size as a function of calcination temperature.

Figure 8. (a) PLE and (b) PL spectra of the (La, Eu)$_2$O$_2$S phosphors shown in figure 6(d) (rounded particles) and figure 6(h) (microprisms). The PLE spectra were recorded by monitoring the 627 nm emission while the PL spectra were taken under 340 nm excitation. The inset in part (b) is the appearance of red emission (digital photograph) of the phosphor powder shown in figure 6(d). The picture was taken under 254 nm irradiation of the phosphor from a hand-held UV lamp.

$^5$D$_0$ → $^7$F$_2$ transition to appear significantly stronger than the magnetic dipole $^5$D$_0$ → $^7$F$_1$ transition according to the Judd–Ofelt parity law [25, 26]. The most intense emission was observed as splits at 619 and 627 nm, and thus the phosphor emits a bright red color. Color coordinates of the emission were calculated from the PL spectra to be around (0.61, 0.39), irrespective of the synthesis temperature, conforming to a vivid red color in the Commission Internationale de L’Eclairage (CIE) chromaticity diagram. The PL bands do not change obviously in their positions but exhibit appreciably improved intensities at a higher synthesis temperature of the phosphor. To be more precise, an 87% increase was yielded with a 200°C temperature increase from 800 to 1000°C, and another 200°C temperature increase from 1000 to 1200°C improves the emission intensity by 99%. The enhancements may mainly be due to the removal of surface dangling bonds and particularly hydroxyls, crystal perfection and crystallite growth (the inset in figure 7(b)). It is noteworthy that the significant improvement from 1000 to 1200°C may also arise from the complete collapse of plate-like particles into relatively rounded ones. The morphology change may appreciably reduce the scattering of excitation light, and thus improves excitation absorption to yield higher CT and emission intensities.

Particle morphology may appreciably affect the luminescence properties of a phosphor [27]. Figure 8 compares PLE/PL behaviors of the two phosphor powders shown in figures 6(d) and (h) (both calcined at 1200°C). Clearly, the rounded particles (figure 6(d)) exhibit a stronger S–Eu CT band (figure 8(a)) and more intense emission (figure 8(b), ~10.5% stronger for the 627 nm peak) than the microprisms shown in figure 6(h). Phosphors of bigger particles are normally observed to exhibit stronger luminescence since their smaller specific surface area allows less scattering and hence better absorption of the excitation light. The reverse finding in this work may mainly be due to the different extents of crystallization. Since the microprismatic precursor particles are significantly larger, they may not be as evenly heated from the particle surface to the interior as compared to their nanoplate counterparts under identical calcination. That is, the relatively low crystallinity in the center region of the prismatic phosphor particles may have led to the observed inferior luminescence. Such an explanation is supported by the PLE results shown in
Calcining the phosphors above 1000 °C results in non-uniform crystallization. These may indicate that the Ln–O bonds (Ln = Eu) are equally well developed in the two phosphors but the Ln–S ones, formed after Ln–O at higher temperatures, are less well developed in the microprism phosphor owing to the Ln–S bonds having almost identical intensities for the two phosphors. The decay data can be fitted to single exponential decay behavior, and the fluorescence lifetime of the hydrothermal product was determined to be ∼0.5 ms for both the phosphors.

4. Conclusions

Facile and clean synthesis of (La0.95Eu0.05)2O3S red phosphors with controlled particle morphologies has been achieved via calcination in hydrogen of Ln2(OH)4SO4·2H2O (Ln = La and Eu) layered hydroxyl sulfate precursors prepared via hydrothermal reaction at 120 °C. Characterizations of the products via XRD, DSC/TG, FTIR, FE-SEM, PLE/PL and fluorescence decay analysis have yielded the following main conclusions:

(1) Solution pH is the decisive factor controlling properties of the hydrothermal product. Low pH up to ∼7.5 yields La(OH)SO4 while higher pH values of 9.0 and 10 produce pure phases of the intended Ln2(OH)4SO4·2H2O. A mixture of the two compounds is observed at the intermediate pH of 8.0. The crystallites of Ln2(OH)4SO4·2H2O change from thin platelets to submicron-sized Ln2O3S particles of rounded shapes while the microprisms well retain their initial shapes up to 1200 °C, yielding phosphor powders of two distinctive particle morphologies.

(2) The Ln2(OH)4SO4·2H2O precursor compounds decompose to Ln2O3S via hydrogen annealing at a minimum temperature of 700 °C via a Ln2O3SO4 intermediate. The precursor platelets collapse into submicron-sized Ln2O3S particles of rounded shapes while the microprisms well retain their initial shapes up to 1200 °C, yielding phosphor powders of two distinctive particle morphologies.

(3) The resultant (La0.95Eu0.05)2O3S phosphors exhibit the typical emissions of Eu3+ in a hexagonal host lattice, with the strongest red emission (the 5D0 → 7F2 transition of Eu3+) located at 627 nm irrespective of particle morphology. The 627 nm red emission exhibits a single exponential decay behavior, and the fluorescence lifetime was determined to be ∼0.5 ms for both the phosphors.

(4) Calcining the phosphors above 1000 °C significantly improves intensities of the PLE/PL bands for both the phosphors. After identical processing at 1200 °C, the rounded phosphor particles show better luminescence than the microprismatic ones owing to their higher extent of crystallization and better development of Eu–S bonds.

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