Synthesis of multi-type rare earth compounds with RE(OH)SO₄ as a new sacrificial-template and photoluminescence

Xuejiao Wang¹,², Xiaowen Feng², Meng Sun³, Bowen Wang⁴, Ji-tong Wang⁴ and Ji-Guang Li⁴

¹College of Chemistry and Materials Engineering, Bohai University, Jinzhou, Liaoning, China; ²Research Center for Functional Materials, National Institute for Materials Science, Tsukuba, Japan

ABSTRACT

The low OH⁻/RE³⁺ molar ratio of hydroxide sulfate RE(OH)SO₄ (RE = rare earth) makes it a potential good template for the synthesis of rare earth compounds, which is shown in this work by the direct generation of (La,Eu)F₆, (La,Eu)PO₄, Na(La,Eu)(WO₄)₂, and Na(La,Eu)(MoO₄)₂ without further calcination. The template showed irregular and slightly aggregated microparticles morphology, while the products derived from the template showed morphologies of nanoparticles (trifluoride), nanorods (phosphate), aggregate spheres (molybdate), and aggregated polyhedrons (tungstate). The photoluminescence of the derived compounds, including excitation/emission spectra, decay kinetics, quantum yields, color coordinates, and color purities were comprehensively investigated, and the results were well correlated with structures and morphologies. Calcination further improved the luminescence intensity and quantum yield of the obtained phosphors. It is believed that the RE(OH)SO₄ compound proposed in this work may find applications for the synthesis of other rare earth compounds.

ARTICLE HISTORY

Received 18 April 2022
Accepted 17 June 2022

KEYWORDS
La(OH)SO₄ sacrificial-template; photoluminescence; rare earth compound

1. Introduction

Sacrificial phase conversion has been introduced for the controllable synthesis of various compounds [1–10], where the target compound was formed via reacting a pre-made template with an anion source under appropriate conditions [1–3]. Rare earth hydroxides are good templates for the synthesis of other rare earth compounds because the templates themselves can be used as the reactant rare earth sources in the synthesis process. With the reaction proceeding, the template is gradually consumed and plays a decisive role in the reaction process since it often controls reaction kinetics/pathway and determines the yield, chemical composition, and morphology (particle size/shape/dispersion) of the final product. In the strategy, the reaction may proceed via two separate mechanisms: interface chemical transformation and dissolution followed by reprecipitation [5,11–13]. When the template and the target compound have the same crystal structure, the pre-made compound plays a role as both a physical and chemical template, and the final product may well preserve the micro-morphology of the template. One representative example is the synthesis of hexagonal structured β-NaREF₄ from hexagonal RE(OH)₃ via in situ acid corrosion and anion exchange [5]. When the template and final product differ in structure, the dissolution-reprecipitation mechanism may be applied, as exemplified by the synthesis of hexagonal LuBO₃ from monoclinic Lu₂(OH)₃NO₃ via hydrothermal conversion [13]. After a careful literature survey, we summarize the currently used hydroxide templates and their derivatives in Table S1 (in supporting information). It can be seen from Table S1 that a rich family of templates has been investigated, including RE(OH)₃, RE(OH)₂, (NO₃)ₐnH₂O, RE₂(OH)₃ NO₃, RE₂O(OH)₃NO₃, RE₂(OH)₃SO₄ · 2H₂O, and RE(OH)CO₃, and so on. [4–10,14–29]. Various rare earth compounds have been successfully prepared through the templates mentioned above, such as YPO₄:RE³⁺/GdPO₄ phosphate, YVO₄:RE³⁺ vanadate, LaF₃/YF₃ fluoride, tungstate, and so on. The sacrificial conversion based on hydroxide template will gradually release OH⁻ into the reaction system, which competitively coordinates with rare earth ions with the subsequently added reactant anions such as F⁻, PO₄³⁻, WO₄²⁻, and MoO₄²⁻. This will slow down reaction kinetics due to equilibrium reasons, and so a lower OH⁻/cation ratio in the template is desired [20]. The OH⁻/RE³⁺ ratio in the template compound is expressed as R in Table S1. It is found that the R is bigger than 2 for most hydroxide templates. From this point of view, the rare earth hydroxysulfate of RE(OH)SO₄ would be a better template since its OH⁻/RE³⁺ molar ratio (R = 1.0) is lower. In this work, the (La,Eu)(OH)SO₄ compound was used as a sacrificial-template for the synthesis of various rare earth compounds under proper conditions, including...
fluoride ((La,Eu)F₃), phosphate ((La,Eu)PO₄), tungstate (Na(La,Eu)(WO₄)₂), and molybdate (Na(La,Eu)(MoO₄)₂). The effects of reaction temperature, reaction duration, and anion/RE³⁺ molar ratio on phase conversion were systematically investigated. Photoluminescence properties of the derived rare earth compounds were also studied.

2. Experimental procedure

2.1. Reagents

The starting materials include rare earth nitrate (RE(NO₃)₃ · 6H₂O, RE = La and Eu, 99.99% pure), ammonium sulfate [(NH₄)₂SO₄, 99.9% pure], NH₃·H₂O (1 M), nitric acid, sodium molybdate (Na₃MoO₄·2H₂O, 99.5% pure), sodium tungstate (Na₂WO₄·2H₂O, 99.5% pure), ammonium fluoride (NH₄F, >96% pure), and ammonium dihydrogen phosphate (NH₄H₂PO₄, 99.5% pure). The rare earth nitrates are from Huizhou Ruier Rare Chemical Hi-Tech Co. Ltd. (Huizhou, China), and all the other chemicals are from Sinopharm Chemical Reagent Co., Ltd (Shenyang, China). All the reagents were used without further purification, and Milli-Q filtered water (resistivity >18 MΩ·cm) was used throughout the experiments.

2.2. Synthesis of (La,Eu)(OH)SO₄

In a typical synthesis procedure, a certain amount of (NH₄)₂SO₄ was dissolved in 60 ml RE(NO₃)₃ stock solution (0.1 M) under magnetic stirring for 10 min. NH₃·H₂O was then dropwise added into the mixed solution to reach a designated pH of ~8. The resultant suspension was either constantly stirred for 24 h at a prescribed temperature (RT or 50°C) under ambient pressure or transferred to a Teflon lined stainless steel autoclave for 24 h of hydrothermal crystallization in an electric oven preheated to 100–200°C (without stirring). The product was collected via centrifugation, followed by washing with distilled water three times to remove by-products, rinsing with absolute ethanol, and air drying at 70°C for 24 h.

2.3. Phase-conversion synthesis of multi-type rare earth compounds using (La,Eu)(OH)SO₄ as the template

In a typical procedure for sacrificial phase conversion, 2 mmol of the above synthesized (La,Eu)(OH)SO₄ was dispersed in 60 ml distilled water, followed by the addition of a certain amount of NH₄F, NH₃·H₂PO₄, Na₂MoO₄·2H₂O, or Na₂WO₄·2H₂O. The obtained suspension was stirred at a designated temperature (below 100°C) or subjected to hydrothermal reaction at different temperatures (above 100°C) for a certain period of time. After natural cooling, the product was collected via centrifugation, followed by washing with distilled water three times to remove by-products, rinsing with absolute ethanol, and air drying at 70°C for 24 h. Calcination was performed in the air at 300–800°C for 1 h, using a heating rate of 5°C/min at the ramp stage.

2.4. Characterization

Phase identification was performed via XRD (Model RINT2200, Rigaku, Tokyo, Japan; λ = 0.15406 nm) under 40 kV/40 mA and a scanning speed of 1°/min. The micro-morphologies of the products were observed via FE-SEM (Model S-5000, Hitachi, Tokyo) under an acceleration voltage of 5 kV. Fourier transform infrared spectroscopy (FT-IR) was conducted on a Scimitar 2000 Near FT-IR Spectrometer (Shimadzu, Kyoto, Japan) using the standard KBr pellet method. The light absorption of the samples was studied via UV–vis spectrophotometry (Model PE-750, PerkinElmer, USA) using BaSO₄ for calibration. Room temperature photoluminescence (PL) spectra were measured with an FLS 1000 fluorospectrophotometer (Edinburgh Instruments Ltd., Herrsching am Ammersee, Germany) with a 450 W Xe lamp as the excitation source. Fluorescence decay kinetics of the main emissions were measured with the lifetime testing unit of the FLS 1000 equipment. The quantum efficiency of luminescence was analyzed with the built-in software of the spectrophotometer by comparing the response of the phosphor to excitation with a diffusive white standard.

3. Results and discussion

3.1. Synthesis of (La,Eu)(OH)SO₄ compound

Figure 1 shows the XRD patterns of the products crystallized at various temperatures (from RT to 200°C). It was found that the products obtained in the RT-50°C range are amorphous. The peaks recorded from the

![XRD patterns](image-url)
products synthesized in the 100–200°C range can all be indexed to (La,Eu)(OH)SO₄ (JCPDS No. 00-045-0750), which is verified by Rietveld refinement for the typical sample (Figure S1(a)). The peak intensity noticeably increased with increasing reaction temperature. It was also noticed that the intensity ratio of the (020) to (111) diffractions increased from 0.86 to 4.31 as the synthesis temperature increased from 100°C to 200°C (Table S2). This phenomenon is originated from the growth habit of (La,Eu)(OH)SO₄ and is also closely related to morphology change of the crystallites in response to the synthesis temperature (Figure S2). (La,Eu)(OH)SO₄ crystallizes in a monoclinic unit cell by alternative stacking of sulfate anions and the [LaO₂] polyhedra containing two-dimensional hydroxide layers along the b-axis (Figure S1(b)). Thus, the non-(0k0) diffractions (such as (111)) reflect the structural features of the host layer, while the (0k0) diffractions reflect the stacking of the host layer along the b-axis. A higher reaction temperature produced thicker and bigger crystallite plates for the product, and thus substantially stronger (020) diffraction was observed. The effects of RE³⁺:SO₄²⁻ ratio on the formation of La(OH)SO₄ were also investigated, and the results are shown in Figure S3.

### 3.2. (La,Eu)(OH)SO₄ as a sacrificial-template for the synthesis of various rare earth compounds

(La,Eu)(OH)SO₄ was used for the first time as a sacrificial-template for the synthesis of rare earth fluoride, and the XRD results of the temperature-dependent fluorination products under a fixed reaction time of 24 h are shown in Figure 2. An immediate increase in pH was observed after F⁻ was added to the template containing suspension, indicating that the reaction is fast. It is encouraging to find from the XRD results that all the diffraction peaks of the reaction product are in good agreement with the standard card of LaF₃ (JCPDS No. 01-074-2415). No impurity can be identified from the XRD patterns even after reaction at room temperature. With increasing temperature, the diffraction peaks gradually become sharper and the (002) and (110) peaks gradually separate, which implies increased crystallization.

When NH₄F is dissolved in water, the following dynamic equilibrium exists:

\[ \text{NH}_4\text{F} \leftrightarrow \text{NH}_4^+ + \text{F}^- \]  

(1)

According to Pearson’s hard and soft acid and base (HSAB) theory [30], La³⁺ and Eu³⁺ are hard Lewis acids, and OH⁻, SO₄²⁻, and F⁻ are hard bases. The basicity of the three types of anions decreases following the order of F⁻ > SO₄²⁻ > OH⁻ [31]. In other words, F⁻ has a stronger ability to coordinate La³⁺ and Eu³⁺ than OH⁻ and SO₄²⁻. As a result, F⁻ will replace the interlayer SO₄²⁻ and attack the OH⁻ containing polyhedrons in (La,Eu)(OH)SO₄ to take out OH⁻ and lead to the collapse of the crystal structure of the template compound. This corresponds well to the instantly increased pH after NH₄F was added into the (La,Eu)(OH)SO₄ containing suspension. The total conversion reaction can be expressed as follows:

\[ (\text{La, Eu})(\text{OH})\text{SO}_4 + \text{F}^- \rightarrow (\text{La, Eu})\text{F}_3 + \text{OH}^- + \text{SO}_4^{2-} \]  

(2)

Figure 3 shows the micro-morphologies of the (La,Eu)F₃ obtained at different reaction temperatures. Though the (La,Eu)F₃ product basically retained the template profile, enlarged views found that nanoplates were actually formed and are the true morphology units of the product (Figure 3(c)). It was found that the nanoplates became bigger and thicker with increasing reaction temperature, collapsed into nanoparticles above 120°C, and became bigger and smoothly rounded nanoparticles at 200°C (Figure 3(d–g)).

The influence of the reaction time was also examined at room temperature, and the XRD/FT-IR results are shown in Figure S4–5. The results indicated that pure products can be obtained after 30 min of reaction. The reaction (RT/30 min) is much faster than that reported for LaF₃ formation from La(OH)CO₃ template that also has low OH⁻/RE³⁺ of 1 (50°C/3 h) [26] and is faster than those for LaF₃ formation from RE₃(OH)₄SO₄ · 2 H₂O (180°C/2 h) and (Y₀.₇₈Yb₀.₂₂E₀.₀₂)F₃ formation from RE₀.₃NO₃ · nH₂O (RT/3 h) [14,22]. Furthermore, the product yield is much higher than that from the direct reaction of La(NO₃)₃/Eu(NO₃)₃ with NH₄F for the same time of 0.5 h (Figure S6–7). It can also be seen from the XRD result (Figure S5) that the direct product of the latter case has a high amorphous background and poor crystallinity. The effects of the F⁻:RE³⁺ ratio on sacrificial phase conversion were also investigated, and the results are shown in Figure S8–9. It can be concluded from the above results that (La,Eu)F₃ can
be readily obtained from (La,Eu)(OH)SO₄ in a wide parameter range of reaction (RT-200°C, 10 min-24 h, R = 3-30).

In view that a higher reaction temperature would better crystallize the product, the synthesis of other rare earth compounds was conducted at 200°C for 24 h. It is seen from Figure 4(a) that phase-pure (La₀.₉₅Eu₀.₀₅)PO₄ can be directly produced via reaction with (La₀.₉₅Eu₀.₀₅)(OH)SO₄ since all the diffraction peaks are in good agreement with the standard card of LaPO₄ (JCPDS No. 00-004-0635). The following dynamic equilibria exist for NH₄H₂PO₄ in an aqueous solution:

\[
\text{NH}_4\text{H}_2\text{PO}_4 \leftrightarrow \text{NH}_4^+ + \text{H}_2\text{PO}_4^- \tag{3}
\]

\[
\text{H}_2\text{PO}_4^- \leftrightarrow \text{HP} \text{O}_4^{2-} + \text{H}^+ \tag{4}
\]

\[
\text{HP} \text{O}_4^{2-} \leftrightarrow \text{PO}_4^{3-} + \text{H}^+ \tag{5}
\]

As the liberated PO₄³⁻ has a much stronger ability to coordinate La³⁺ and Eu³⁺ than H₂PO₄⁻, HPO₄²⁻, OH⁻ and SO₄²⁻ [32], the following conversion reaction would take place to generate (La,Eu)PO₄, like the case of (La,Eu)F₃ formation:

\[
(\text{La, Eu})(\text{OH})\text{SO}_4 + \text{PO}_4^{3-} \rightarrow (\text{La, Eu})\text{PO}_4 + \text{OH}^- + \text{S} \text{O}_4^{2-} \tag{6}
\]

When it comes to the synthesis of Na(La,Eu)(WO₄)₂ and Na(La,Eu)(MoO₄)₂, however, reaction at 200°C for 24 h only produced a trace amount of the target compound and the template phase was largely left behind (Figure S10). A pure product of either Na(La,Eu)(WO₄)₂ or Na(La,Eu)(MoO₄)₂ cannot be obtained even if the reaction parameters such as reaction temperature/time and WO₄²⁻/MoO₄²⁻:RE³⁺ molar ratio (R) were regulated in extensive ranges. This is primarily due to the fact that WO₄²⁻ and MoO₄²⁻, being soft bases, are much weakly coordinating than OH⁻ and SO₄²⁻ toward La³⁺ and Eu³⁺ [32]. Although a high WO₄²⁻/MoO₄²⁻:RE³⁺ molar ratio (R = 5) may strengthen the coordination ability of WO₄²⁻/MoO₄²⁻ and promote phase conversion, only trace Na(La,Eu)(WO₄)₂ and Na(La,Eu)(MoO₄)₂ can be formed since the released OH⁻ would immediately restrain the conversion reaction from going on further. Inspired by the synthesis of NaGdF₄ and GdB₃O₇ from Gd(OH)₃ template, in which trace acid was added to balance off the released OH⁻ [3], we adjusted the suspension of (La,Eu)(OH)SO₄ to pH ~6 with nitric acid in this work for the synthesis of Na(La,Eu)(WO₄)₂ (JCPDS No. 01-079-1118) and Na(La,Eu)(MoO₄)₂ (JCPDS No. 00-024-1103) (Figure S10) and pure products were obtained under proper conditions Figure 4(c,d). The involved chemical reactions may be expressed as follows:

\[
(\text{La, Eu})(\text{OH})\text{SO}_4 + \text{Na}^+ + \text{W} \text{O}_4^{2-} \rightarrow \text{Na}(\text{La, Eu})(\text{WO}_4)_{2} + \text{S} \text{O}_4^{2-} + \text{OH}^- \tag{7}
\]

\[
\text{O} \text{H}^- + \text{H}^+ (\text{from the added HNO}_3) \rightarrow \text{H}_2\text{O} \tag{8}
\]

\[
(\text{La, Eu})(\text{OH})\text{SO}_4 + \text{Na}^+ + \text{Mo} \text{O}_4^{2-} \rightarrow \text{Na}(\text{La, Eu})(\text{MoO}_4)_{2} + \text{S} \text{O}_4^{2-} + \text{OH}^- \tag{8}
\]

\[
\text{O} \text{H}^- + \text{H}^+ (\text{from the added HNO}_3) \rightarrow \text{H}_2\text{O} \tag{8}
\]
The absence of $\text{SO}_4^{2-}$ vibrations in the FT-IR spectra (Figure S11) of the products further confirmed a complete consumption of the template and the formation of pure phases. Based on the above results, it can be concluded that four different types of compounds can be successfully synthesized by reacting the per-made $(\text{La}_{0.95}\text{Eu}_{0.05})\text{(OH)}\text{SO}_4$ template with the corresponding anion sources under proper reaction conditions.

Figure 5 shows the FE-SEM morphologies of the $(\text{La}_{0.95}\text{Eu}_{0.05})\text{(OH)}\text{SO}_4$ template and the four types of rare earth phosphors converted from the template via reaction at $200^\circ\text{C}$ for 24 h. It is seen that the $(\text{La}_{0.95}\text{Eu}_{0.05})\text{(OH)}\text{SO}_4$ template has micro-plate-like crystallite morphologies (Figure 5(a)), $\text{Na(La}_{0.95}\text{Eu}_{0.05})\text{WO}_4\text{)}_2$ consists of agglomerated particles (Figure 5(b)), $\text{Na(La}_{0.95}\text{Eu}_{0.05})\text{MoO}_4\text{)}_2$ contains uniform spherical particles of $\sim 300-400$ nm (Figure 5(c)), $(\text{La}_{0.95}\text{Eu}_{0.05})\text{F}_3$ is composed of tiny nanoparticles (Figure 5(d)), while $(\text{La}_{0.95}\text{Eu}_{0.05})\text{PO}_4$ is featured by nanowires (Figure 5(e)). The quite different morphologies between the template and each product imply that dissolution-reprecipitation is the dominant mechanism of phase conversion and the final morphology is primarily determined by the intrinsic crystal structure of the product.

### 3.3. Photoluminescence properties of rare earth compounds derived from $(\text{La},\text{Eu})(\text{OH})\text{SO}_4$

The photoluminescence properties of Eu$^{3+}$ have long been reported, and this work mainly studies the performance of Eu$^{3+}$ in correlation with crystal structure and crystallite morphology. The PL excitation and emission spectra of derived $\text{Na(La}_{0.95}\text{Eu}_{0.05})\text{WO}_4\text{)}_2$, $\text{Na(La}_{0.95}\text{Eu}_{0.05})\text{MoO}_4\text{)}_2$, $(\text{La}_{0.95}\text{Eu}_{0.05})\text{F}_3$, and $(\text{La}_{0.95}\text{Eu}_{0.05})\text{PO}_4$ phosphors are shown in Figure 6, with the quantum yield (QY), color coordinates (CIE), and color purity (CP) of luminescence being inserted in the corresponding figure. As can be seen from Figures 6(a,b) the excitation and emission spectral features of $\text{Na(La}_{0.95}\text{Eu}_{0.05})\text{WO}_4\text{)}_2$ and $\text{Na(La}_{0.95}\text{Eu}_{0.05})\text{MoO}_4\text{)}_2$ are similar. The PLE spectra of the two compounds consist of a broad band in the UV region of $200-350$ nm and a series of sharp peaks at $350-500$ nm region. The broad band is overlapped from $\text{WO}_4^{2-}/\text{MoO}_4^{2-}$ excitation and $\text{O}^2- \rightarrow \text{Eu}^{3+}$ charge transfer (CT), while the sharp peaks are arising from intra-4f transitions of Eu$^{3+}$. The PL spectra of $\text{Na(La}_{0.95}\text{Eu}_{0.05})\text{WO}_4\text{)}_2$ and $\text{Na(La}_{0.95}\text{Eu}_{0.05})\text{MoO}_4\text{)}_2$ consist of sharp peaks located at $590, 615, 650$, and $700$ nm, which are assigned to $\text{4D}_0 \rightarrow \text{4F}_j$ transitions of Eu$^{3+}$ ions. The peak at $\sim 615$ nm is the strongest, which is well consistent with the fact that Eu$^{3+}$ has a $\text{C}_4$ symmetry, which is distorted from $\text{C}_{4v}$ due to the statistical distribution of Na$^+$ and RE$^{3+}$ ions in the two hosts. Considering that the two hosts have similar crystal structure and site symmetry of luminescence centers Figure 7(a,b) their similar photoluminescence behaviors can be well understood.

For $(\text{La},\text{Eu})\text{F}_3$, the excitation spectrum consists of a series of sharp peaks in the range of $280-500$ nm, with the $397$ nm excitation ($\text{4F}_0 \rightarrow \text{4L}_6$) being the strongest. $\text{F}^- \rightarrow \text{Eu}^{3+}$ CT was not observed because the large bandgap of LaF$_3$ ($\sim 6.2$ eV) makes it occur below $200$ nm. Under $397$ nm excitation, the $\text{5D}_0 \rightarrow \text{7F}_j$ transitions of Eu$^{3+}$ were produced with the $\text{4D}_0 \rightarrow \text{7F}_1$ one ($590$ nm) being the strongest. This is different from that observed from Eu$^{3+}$ in the tungstate and molybdate hosts, where the $\text{4D}_0 \rightarrow \text{7F}_2$ transition is the strongest. This, however, is consistent with the fact that Eu$^{3+}$ is at the higher symmetric $\text{C}_{2v}$ site in hexagonal LaF$_3$. Besides, low symmetry surface-site Eu$^{3+}$ may contribute to the strong $\text{5D}_0 \rightarrow \text{7F}_2$ and $\text{5D}_0 \rightarrow \text{7F}_4$ transitions for the tungstate and molybdate phosphors, and this corresponds well with the biexponential decay behaviors of the $\sim 615$ nm main emission (Figure S12).

For $(\text{La}_{0.95}\text{Eu}_{0.05})\text{PO}_4$, the excitation spectrum consists of a strong and broad $\text{O}^2- \rightarrow \text{Eu}^{3+}$ CT band in the $200-300$ nm range (centered at $\sim 268$ nm) and a series of sharp peaks arising from intra-4f transitions of Eu$^{3+}$. It should also be noted that the position of the CT for $(\text{La}_{0.95}\text{Eu}_{0.05})\text{PO}_4$ appeared at a shorter wavelength.
than those observed for Na(La_{0.95}Eu_{0.05})(WO_4)_2 (~285 nm) and Na(La_{0.95}Eu_{0.05})(MoO_4)_2 (~291 nm). This is due to the fact that the position of CT is strongly dependent on the length of (La/Eu)-O bond, and the longer the bond would red-shift the CT band [33,34]. The positions of the CT bands observed in this work
Table 1. A summary of crystal structure information for the four types of phosphors.

| Phase           | Space group | Structure | Site symmetry | Rare earth polyhedron | La-O bond length | Position of CTB |
|-----------------|-------------|-----------|---------------|-----------------------|------------------|-----------------|
| Na[La,Eu](WO₄)₂ | I₄/a        | Tetragonal | C₁            | REO₆ (Figure 7(a))    | ~2.3532 Å        | 285 nm          |
| Na[La,Eu](MoO₄)₂ | I₄/a       | Tetragonal | C₁           | REO₆ (Figure 7(b))    | ~2.5129 Å        | 291 nm          |
| (La,Eu)F₃      | P6₃c       | Hexagonal | Cᵥ           | REF₆ (Figure 7(c))    | ~2.3384 Å        | ~    268 nm      |
| (La,Eu)PO₄     | P6₃c       | Hexagonal | D₂           | REO₆ (Figure 7(d))    | ~2.6531 Å        |                |

4. Conclusions

(La,Eu)(OH)SO₄ was used as a novel sacrificial-template in this work for direct synthesis Na[La,Eu](WO₄)₂, Na[La,Eu](MoO₄)₂, (La,Eu)F₃, and (La,Eu)PO₄ phosphors. The synthesis of the template, the phase conversion process for each type of the phosphors, and the photoluminescence properties of the products were systematically investigated. The main conclusions are as follows:

1. The (La,Eu)(OH)SO₄ template phase can be hydrothermally obtained in the temperature range of 100–200°C (pH = 8, RE³⁺:SO₄²⁻ = 1) and RE³⁺:SO₄²⁻ molar ratio range of 1–2 (120°C, pH = 8).

2. (La,Eu)F₃ and (La,Eu)PO₄ can be directly and readily obtained via reacting the template with the corresponding anion source, while a small amount of nitric acid is needed to balance off the OH⁻ generated via phase conversion so that pure Na[La,Eu](WO₄)₂ and Na[La,Eu](MoO₄)₂ can be derived.

3. Na[La,Eu](WO₄)₂ and Na[La,Eu](MoO₄)₂ similarly showed a strong red emission at ~615 nm (D₉₀ → F₂) under 395 and 465 nm excitation, respectively, while (La,Eu)F₃ and (La,Eu)PO₄ showed strongest red emissions at 592 nm (D₉₀ → F₄) and 697 (D₉₀ → F₄) nm under 397 and 395 nm excitation, respectively. Calcination further improved photoluminescence, and the quantum yields of the 800°C calcined (La,Eu)F₃, (La,Eu)PO₄, Na[La,Eu](WO₄)₂, and Na[La,Eu](MoO₄)₂ reached ~72.72%, 87.59%, 53.06%, and 87.08%, respectively.

Disclosure statement

No potential conflict of interest was reported by the author(s).

Funding

This work is supported by the Natural Science Foundation of Liaoning Province (Grant No. 2020-MS-286).

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