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ARTICLE

Novel synthetic route towards monodisperse LaOF:Ln³⁺ (Ln = Eu, Tb) hollow spheres with multicolor luminescence properties

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In this study, monodisperse and uniform LaOF hollow spheres were successfully synthesized through a novel facile synthetic route employing La(OH)CO₃ sphere as a sacrificial template followed by a subsequent calcination process. The structure, morphology, formation process, and luminescence properties were well investigated using various techniques. The possible formation mechanism of evolution from the La(OH)CO₃ spheres to the LaCO₃F precursor, and to the final LaOF hollow spheres can be attributed to Kirkendall effect and the decomposition of LaCO₃F precursor. Under ultraviolet excitation, the LaOF:Ln³⁺ (Ln = Eu, Tb) hollow spheres show their characteristic f–f emissions and give red, green emissions, respectively. Moreover, by codoping the Tb³⁺ and Eu³⁺ ions into LaOF host and tuning their relative concentration ratio, multicolor tunable emissions are obtained due to the efficient energy transfer from Tb³⁺ to Eu³⁺ under 378 nm excitation. This materials may find potential application in color displays fields.

1 Introduction

Synthesis of hollow structure materials with controllable size and shape has attracted great research interest due to their low density, high specific surface areas, surface permeability, and wide spread applications in drug-delivery carriers, catalysis, lithium-ion batteries and so on.^{1–5} And a variety of strategies have been adopted for the design and synthesis of hollow spheres. Template process is the most efficient and common method for such materials. Hard templates such as colloid polystyrene beads,⁶ silica particles,⁷ carbon spheres,⁸ and melamine formaldehyde,⁹ have usually been used as the antecedent templates, and the obtained hollow sphere could be acquired with especially beautiful morphology and pure phase. However, the fabrication and removal of the templates are multistep and time-consuming process. As for soft templates (emulsion droplets, micelles, and gas bubbles)^{10–12}, it is relatively difficult to control the morphology and monodispersity of products. Therefore, many scientists have tended to find simple and easy methods to prepare hollow spheres using the sacrificed template. Among the sacrificed-template synthesis methods, the Kirkendall effect has been proven to be an effective methodology to fabricate the desired hollow spheres. Compared with above approaches, this method can avoid the template removal and simultaneously obtain the controllable and uniform morphology. So far, many metal compound hollow spheres have been synthesized via the Kirkendall effect.^{1,13–17} Despite these efforts, it is still significant and essential to develop more simple, efficient, and low cost methods to synthesize large-scale and well-crystallized hollow nano/microstructures.

Recently, lanthanide ions (Ln³⁺) doped luminescence materials have aroused extensive interest because of their unique electronic and optical properties arising from their intra 4f transitions. In particular, lanthanide oxyfluorides (LnOFs) have attracted fast

growing interest on the basis of their low-energy phonons, high ionicity, and high chemical and thermal stability compared with those oxides and fluorides.^{18–20} Among them, LaOF is a promising host matrix for up-conversion and down-conversion luminescence. Over the past decades, LaOF crystals with different morphologies have been synthesized via various synthesis methods. For instance, Rakov and co-workers described the preparation of LaOF nanocrystalline powders by combustion synthesis.²¹ Lin *et al.* prepared LaOF nanocrystals via a hydrothermal method.²² Lis *et al.* synthesized LaOF nanocrystals through sol–gel method.²³ Moreover, Li *et al.* first fabricated LaOF hollow spheres through a facile template route.²⁴ Nevertheless, quite a few reports touch upon the fabrication of monodisperse and morphology controllable LaOF based phosphors. Moreover, the preparation of the LaOF:Ln³⁺ hollow spheres via sacrificed template method has rarely been reported.

Thus, in this paper we first present a facile, and mass production method for the synthesis of uniform LaOF:Ln³⁺ hollow spheres via the Kirkendall effect followed by an annealing process. The structure, morphology, and formation process of the hollow spheres have been investigated in detail. In addition, the photoluminescence (PL) properties of LaOF:Ln³⁺ samples have been carried out.

2 Experimental Section

2.1 Materials

The rare-earth oxides Ln₂O₃ (99.99%) (Ln = Y, Eu) and Tb₄O₇ (99.99%) were purchased from the Science and Technology Parent Company of Changchun Institute of Applied Chemistry. Ln(NO₃)₃ (0.5 M) stock solutions were obtained by dissolving the corresponding metal oxide in dilute HNO₃ solution under heating with agitation. The other chemicals were purchased from Beijing Chemical Co. All chemicals are analytical-grade reagents and used directly without further purification.

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2.2 Preparation of monodisperse $\text{La}(\text{OH})\text{CO}_3$ and $\text{La}(\text{OH})\text{CO}_3:\text{Ln}^{3+}$ spheres

The monodisperse colloid $\text{La}(\text{OH})\text{CO}_3$ spheres were prepared via a urea-based homogeneous precipitation process.²⁵ In a typical process, 1 mL $\text{La}(\text{NO}_3)_3$ and a certain quantity of urea were dissolved in 50 mL deionized water. After stirring for 20 min, the above solution was kept heating at 90 °C for 2 h in the water bath. The resulting precipitates were collected by centrifugation, washed three times with ethanol and deionized water and then dried at 70 °C in air for 12 h. The doped $\text{La}(\text{OH})\text{CO}_3$ samples were prepared by introducing the appropriate amounts of $\text{Ln}(\text{NO}_3)_3$ instead of $\text{La}(\text{NO}_3)_3$ to the solution as described above.

2.3 Synthesis of monodisperse LaOF and $\text{LaOF}:\text{Ln}^{3+}$ hollow spheres

The as-obtained $\text{La}(\text{OH})\text{CO}_3$ sample was dissolved by 10 mL of deionized water by ultrasonic and vigorous stirring for 30 min. Then, a certain amount of NaBF_4 was added followed by further stirring. Subsequently, the beaker was transferred to a water bath kettle at 50 °C for 3 h. The resulting product was centrifuged three times and dried in a baking oven for 12 h. The final LaOF products were retrieved through a heat treatment of the precursors at 400 °C in air for 2 h. The synthesis of $\text{LaOF}:\text{Ln}^{3+}$ hollow spheres was similar to the above procedure.

2.4 Characterization

The samples were examined by powder X-ray diffraction (XRD) measurements performed on a Rigaku D/max-II B X-ray diffractometer at a scanning rate of 10°/min in the 2 θ range from 10° to 80°, with graphite-monochromatic Cu K_α radiation ($\lambda = 0.15406$ nm). The morphology, and composition of as-obtained samples were examined by means of scanning electron microscopy (SEM, S-4800, Hitachi) equipped with an energy-dispersive X-ray spectrum (EDX, JEOL JXA-840). Transmission electron microscopy (TEM) was performed using a FEI Tecnai G₂ S-Twin with a field emission gun operating at 200 kV. The Brunauer–Emmett–Teller (BET) surface area of the powders was analyzed by nitrogen adsorption on a Micromeritics ASAP 2020 nitrogen adsorption apparatus (U.S.A.). The photoluminescence (PL) excitation and emission spectra were recorded with a RF-5301pc equipped with a 150W xenon lamp as the excitation source. All measurements were performed at room temperature.

3 Results and discussion

3.1 Phase structure, and morphology

The composition and phase purity of the samples were first investigated by XRD. Fig. 1A shows the XRD patterns of as-synthesized $\text{La}(\text{OH})\text{CO}_3$, LaCO_3F , and LaOF samples calcined at 400 °C as well as the corresponding JCPDS card, respectively. From the Fig. 1a, we can see that the main diffraction peaks of the precursor are indexed to an orthorhombic $\text{La}(\text{OH})\text{CO}_3$ phase (JCPDS no. 70–1774). As for the LaCO_3F spheres (Fig. 1b), the diffraction peaks can be almost indexed to the hexagonal phase LaCO_3F (JCPDS no. 41–0595). After being calcined at 400 °C for 2 h (Fig. 1c), it can be seen that all the diffraction peaks of the product can be assigned exactly to the pure tetragonal LaOF phase [space group: $P4/nmm$ (129)], which coincides very well with JCPDS no. 05–0470. Fig. 1B shows the schematic view of the structure and coordination environments of LaOF. The La^{3+} cations are coordinated by four O^{2-} and four F^- ions, and occupy sites with C_{4v} symmetry.²³ After doping with Eu^{3+} , and Tb^{3+} ions (Fig. S1), a portion of the La^{3+} ions will be substituted. No other peaks or

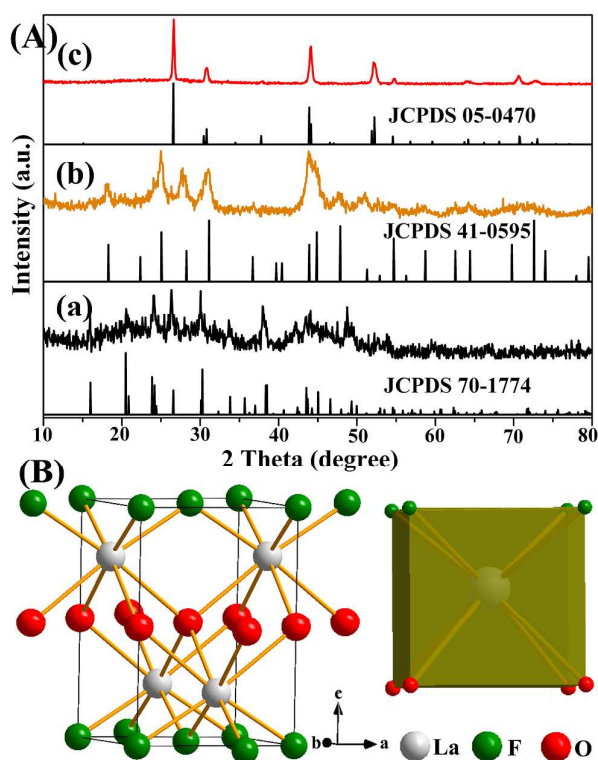


Fig. 1 (A) XRD patterns of the (a) as-prepared $\text{La}(\text{OH})\text{CO}_3$ spheres, (b) uncalcined LaCO_3F precursor and (c) hollow LaOF spheres. (B) Schemes of the tetragonal phase YOF structures.

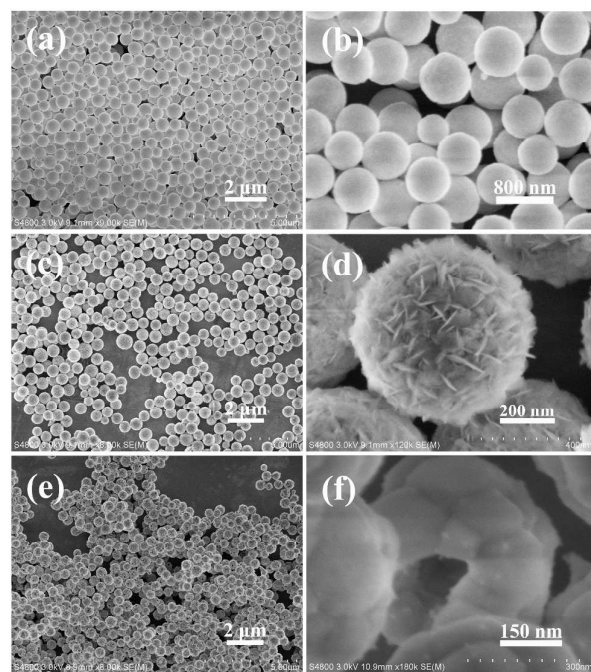


Fig. 2 SEM images of the (a and b) as-prepared $\text{La}(\text{OH})\text{CO}_3$ sphere, (c and d) uncalcined LaCO_3F precursor and (e and f) LaOF hollow spheres.

impurity phase can be found in the Ln^{3+} -doped samples because of the similar ionic radii and valences of the rare-earth elements.²⁶

Fig. 2 presents the SEM image of $\text{La}(\text{OH})\text{CO}_3$, LaCO_3F , and LaOF spheres. In Fig. 2a and b for $\text{La}(\text{OH})\text{CO}_3$ spheres, the sample

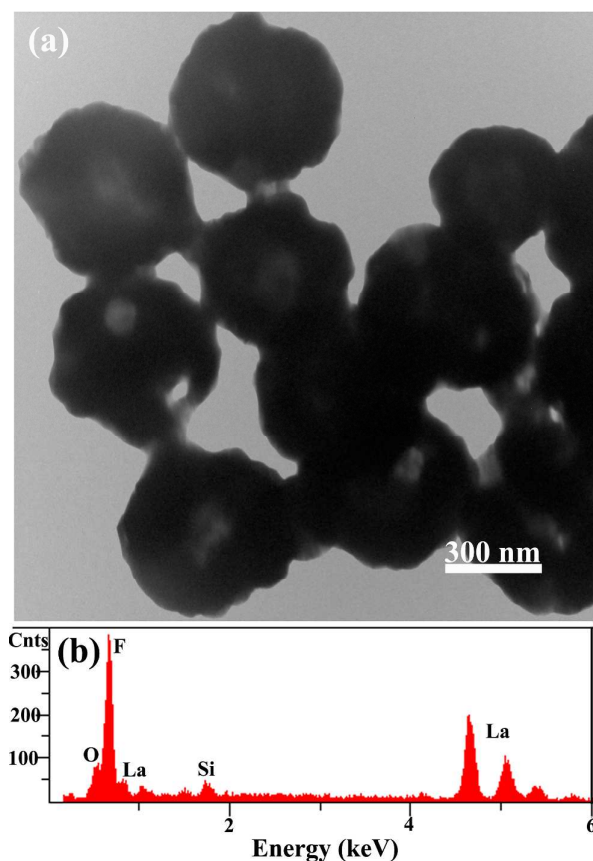


Fig. 3 (a) TEM image, and (b) EDX spectrum of the hollow LaOF spheres.

consists of disperse and uniform spheres with an average size of about 625 nm. The high-magnification SEM image shows that solid spheres have smooth surfaces. As shown in Fig. 2c and d, it can be seen that the LaCO_3F precursor still keeps the uniform spherical morphology with a diameter of about 637 nm. Additionally, it should be noted that the surface of precursor is composed of many nanosheets and exhibits a rough surface, which can be clearly observed from the SEM image (Fig. 2d). Fig. 2e and f illustrate the SEM images of the LaOF spheres after calcination at 400°C . From the SEM images, it is evident that the LaOF sample consists of uniform and well-dispersed spheres with an average diameter of about 556 nm. In addition, one can see that the average diameter of LaOF hollow spheres decreases in comparison with those of the LaCO_3F precursor spheres. The shrinkage of particle size may be due to the decomposition of precursor and crystallization of the LaOF product. The ruptured spheres (Fig. 2f) indicate that the spheres have hollow structures, which can be ascribed to the release of gaseous carbon oxides during the calcination process.

Fig. 3 shows the TEM image and elemental composition of the hollow LaOF spheres. The TEM image of LaOF product exhibits the uniform spherical morphology (Fig. 3a), which agrees with the SEM images. The contrast between the dark edge and the pale center is direct evidence of the hollow nature of spheres. However, the hollow structure of few spheres is not obvious in the TEM image, which may be due to the thick wall of the spheres that the electron beam cannot penetrate. The EDX spectra confirms the presence of characteristic intensity profiles of La, O, and F elements (Si from the Si substrate), which is consistent with the XRD result.

To investigate the specific surface area and porous nature of the LaOF hollow spheres, BET gas-sorption measurements were carried out. Fig. 4 displays the N_2 adsorption–desorption isotherm and pore

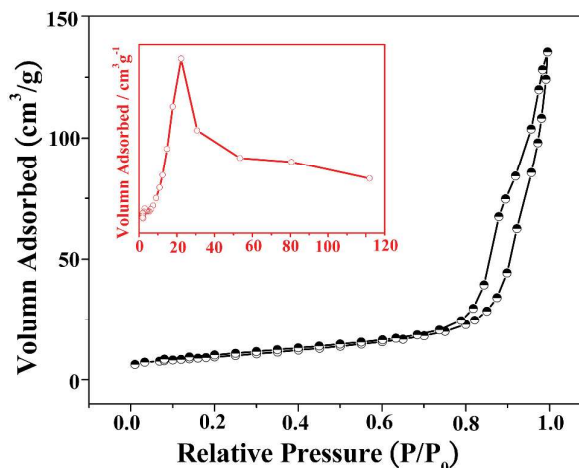
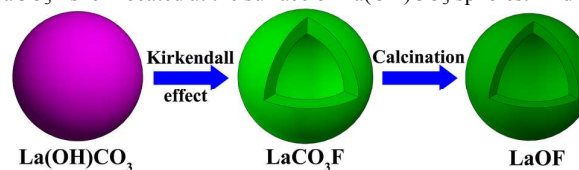


Fig. 4 N_2 adsorption–desorption isotherms for hollow LaOF spheres. Inset: pore size distribution for the hollow LaOF spheres.

size distribution of the as-synthesized LaOF sample. It can be seen that the LaOF hollow spheres show similar N_2 adsorption and desorption isotherms and typical H_1 hysteresis loops, which are properties of typical mesoporous materials. The BET surface area of the sample is about $33.1 \text{ m}^2 \text{ g}^{-1}$, and the pore volume is $0.209 \text{ cm}^3 \text{ g}^{-1}$, and the pore size distribution shows a narrow apex centered at 25.3 nm (inset in Fig. 4). The pores possibly attribute to the interstitial spaces between nanoparticles in the shell, which is in agreement with SEM and TEM observations (Fig. 2 and 3). This result indicates that the as-prepared LaOF hollow spheres have porous structures.

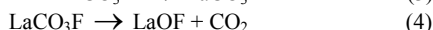
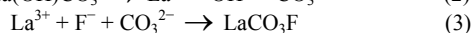
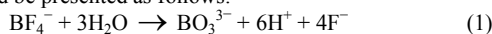
3.2 Formation process

To understand the growth process of the LaCO_3F spheres, time-dependent experiments were carried out by keeping other reaction parameters unchanged. The SEM images of the intermediates obtained at different reaction time intervals are shown in Fig. S2. Before the reaction, the $\text{La}(\text{OH})\text{CO}_3$ precursor is composed of a large amount of monodisperse spheres. At the early stage of the reaction (30 min), the $\text{La}(\text{OH})\text{CO}_3$ precursor is attacked by NaBF_4 , and the surface of the spheres is attached to by many nanoparticles (Fig. S2a). When the reaction time is increased to 1 h, the NaBF_4 continued to react with $\text{La}(\text{OH})\text{CO}_3$ to create much more LaCO_3F nanoparticles on the surface of the spheres (Fig. S2b). In addition, many nanosheets began to appear on the surface of the spheres. After 2 h, the surface of spheres is very rough and comprised of many nanosheets. With further growth, the uniform LaCO_3F spheres are obtained. According to the above analysis, the formation mechanism of the LaOF hollow spheres is proposed, as shown in Scheme 1. In the initial stage, the monodisperse $\text{La}(\text{OH})\text{CO}_3$ spheres employed as the sacrificial template were synthesized via urea-based homogeneous precipitation. In the following process, $\text{La}(\text{OH})\text{CO}_3$ is hydrolyzed to the La^{3+} , OH^- , and CO_3^{2-} ions meanwhile BF_4^- is slowly hydrolyzed to F^- and H^+ ions, which promote the dissolution of $\text{La}(\text{OH})\text{CO}_3$. Then, the La^{3+} ions react with F^- and CO_3^{2-} in the solution to generate LaCO_3F nanoparticles, which form a layer of LaCO_3F shell located at the surface of $\text{La}(\text{OH})\text{CO}_3$ spheres. And the



Scheme 1 Schematic illustration of the formation process of the LaOF hollow spheres.

equilibrium constant of hydrolysis reaction of the BF_4^- ions is very small, leading to the low concentration of F^- ions in the solution.²⁷ Thus, the diffusion rates of La^{3+} and CO_3^{2-} ions inside are faster than that of F^- ions outside, resulting in net directional flow of La^{3+} and CO_3^{2-} ions through the LaCO_3F shell, which is balanced by an opposite flow of vacancies. Therefore, with the reaction going on, the inner $\text{La}(\text{OH})\text{CO}_3$ core can be completely consumed to form the amount of LaCO_3F nanoparticles, which self-assemble into nanosheets on the surface of spheres due to the minimization of interfacial energy and thus the LaCO_3F hollow spheres were obtained through the Kirkendall effect.^{28,29} Finally, the LaCO_3F precursor was burned and the uniform hollow LaOF spheres were prepared. The main reaction process for formation of LaOF hollow spheres could be presented as follows.



3.3 Luminescence properties

Fig. 5 presents the PL excitation and emission spectra of $\text{LaOF}:0.05\text{Eu}^{3+}$ and $\text{LaOF}:0.05\text{Tb}^{3+}$ samples, respectively. The PL excitation spectrum of $\text{LaOF}:0.05\text{Eu}^{3+}$ (Fig. 5a) consists of a strong broad band ranging from 220 to 300 nm and several sharp peaks, which are assigned to the host absorption and the f-f transitions

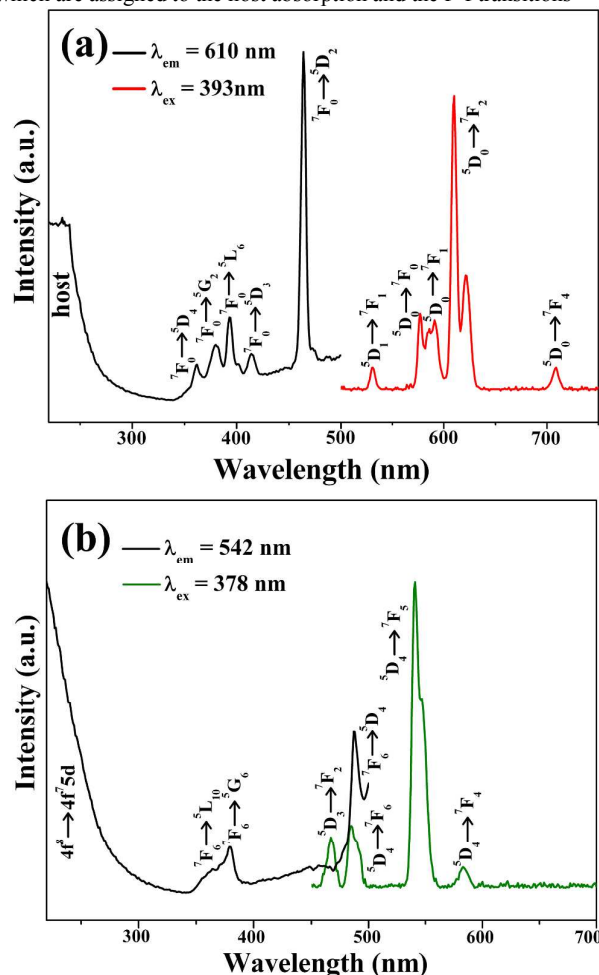


Fig. 5 L excitation and emission spectra of the (a) $\text{LaOF}:0.05\text{Eu}^{3+}$ and (b) $\text{LaOF}:0.05\text{Tb}^{3+}$ samples.

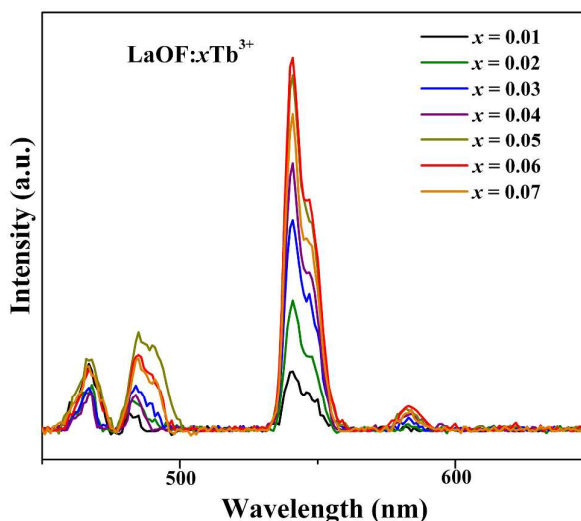


Fig. 6 PL emission spectra of $\text{LaOF}:x\text{Tb}^{3+}$ ($x = 0.01\text{--}0.07$) samples under 378 nm excitation.

within the $\text{Eu}^{3+} 4\text{f}^6$ electron configuration. It is a good sign that this phosphor can strongly absorb ultraviolet light (393 nm), which is well consistent with the widely applied output wavelengths of UV LED chips. Upon excitation at 393 nm, the $\text{LaOF}:0.05\text{Eu}^{3+}$ phosphor shows a strong red emission with the Commission Internationale de l'Eclairage (CIE) chromaticity coordinate (0.616, 0.383) (point a) in Fig. 10. The emission spectrum consists of the characteristic transitions at 531 nm, 577 nm, 585 nm, 591 nm, 610 nm, 622 nm, and 709 nm, which are attributed to the ${}^5\text{D}_1 \rightarrow {}^7\text{F}_1$ and ${}^5\text{D}_0 \rightarrow {}^7\text{F}_j$ ($J = 0, 1, 2, 4$) transitions of Eu^{3+} , respectively.³⁰ Obviously, the emission spectrum is dominated by the hypersensitive red transition (${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$) of Eu^{3+} , indicating that the Eu^{3+} ions are located at sites without or deviating from inversion symmetry.^{31,32} The excitation spectrum of $\text{LaOF}:0.05\text{Tb}^{3+}$ (Fig. 5b) mainly consists of a strong absorption and several peaks at 364 nm, 378 nm and 488 nm, which are ascribed to the spin-allowed transition ($\Delta S = 0$) with high energy from the 4f to 5d of the Tb^{3+} ions, ${}^7\text{F}_6 \rightarrow {}^5\text{L}_{10}$, ${}^7\text{F}_6 \rightarrow {}^5\text{G}_6$, and ${}^7\text{F}_6 \rightarrow {}^5\text{D}_4$, respectively. Under 378 nm UV radiation excitation, the as-prepared $\text{LaOF}:0.05\text{Tb}^{3+}$ is composed of a group of lines centered at about 467 nm, 484 nm, 542 nm, and 583 nm, which correspond to the ${}^5\text{D}_3 \rightarrow {}^7\text{F}_2$ and ${}^5\text{D}_4 \rightarrow {}^7\text{F}_j$ ($J = 6, 5, 4$) transitions of the Tb^{3+} ions, respectively.³³ To investigate the effect of concentration on the luminescence properties of the phosphors, a series of $\text{LaOF}:x\text{Tb}^{3+}$ ($x = 0.01\text{--}0.07$) samples were synthesized. Fig. 6 presents the PL emission spectra of the samples with different Tb^{3+} concentrations under the 378 nm irradiation. With the increase of Tb^{3+} content, one can see that the PL emission intensity of the samples first increases gradually to a maximum at $x = 0.06$ and then decreases due to the concentration quenching of the Tb^{3+} ions.

In order to obtain the multicolor tunable luminescence, the Tb^{3+} , Eu^{3+} ions co-doped LaOF samples were synthesized in our work. In Fig. 7a, it can be seen that there is an overlap between the emission spectrum of Tb^{3+} ion and the excitation spectrum of Eu^{3+} ion, indicating that energy transfer may occur among Tb^{3+} and Eu^{3+} ions in the LaOF samples. Upon 488 nm excitation (${}^5\text{D}_4$ of Tb^{3+}), the emission spectrum simultaneously contains the weak ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ (610 nm) of Eu^{3+} ions and the strong ${}^5\text{D}_4 \rightarrow {}^7\text{F}_5$ (542 nm) transition of Tb^{3+} ions in the $\text{LaOF}:0.06\text{Tb}^{3+}, 0.03\text{Eu}^{3+}$ sample (Fig. 7b). However, no emissions appear in the $\text{LaOF}:0.05\text{Eu}^{3+}$ sample. Furthermore, it is evident that the emission intensity of $\text{Tb}^{3+} {}^5\text{D}_4 \rightarrow {}^7\text{F}_5$ transition in $\text{LaOF}:0.06\text{Tb}^{3+}, 0.03\text{Eu}^{3+}$ sample is obviously lower

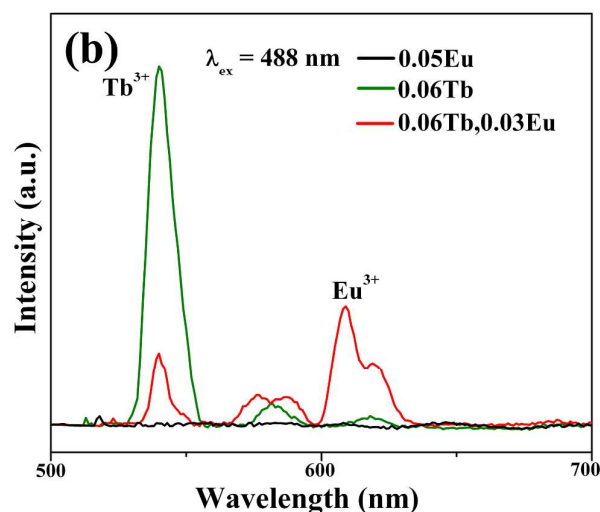
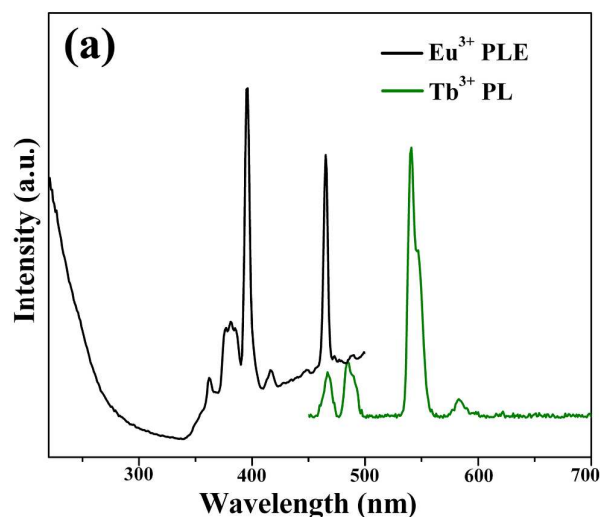


Fig. 7 (a) PL excitation spectra of LaOF:Eu³⁺ and PL spectra of LaOF:Tb³⁺ phosphors, (b) PL spectra of the LaOF:0.05Eu³⁺, LaOF:0.06Tb³⁺ and LaOF:0.06Tb³⁺, 0.03Eu³⁺ samples under excitation at 488 nm.

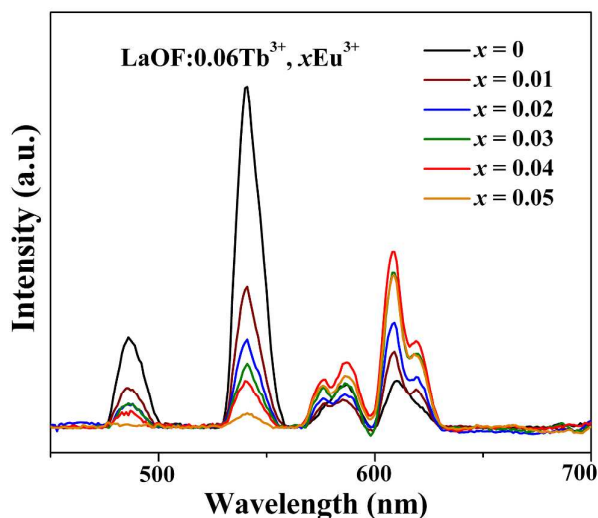


Fig. 8 PL spectra for LaOF:0.06Tb³⁺, xEu³⁺ phosphors as a function of the Eu³⁺ doping concentration (x).

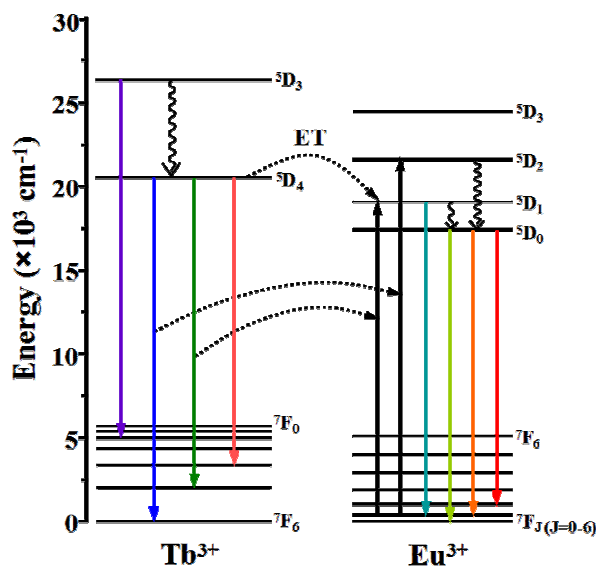


Fig. 9 Energy level scheme representing the energy transfer and energy transfer mechanism in the Tb³⁺, Eu³⁺-codoped LaOF phosphors.

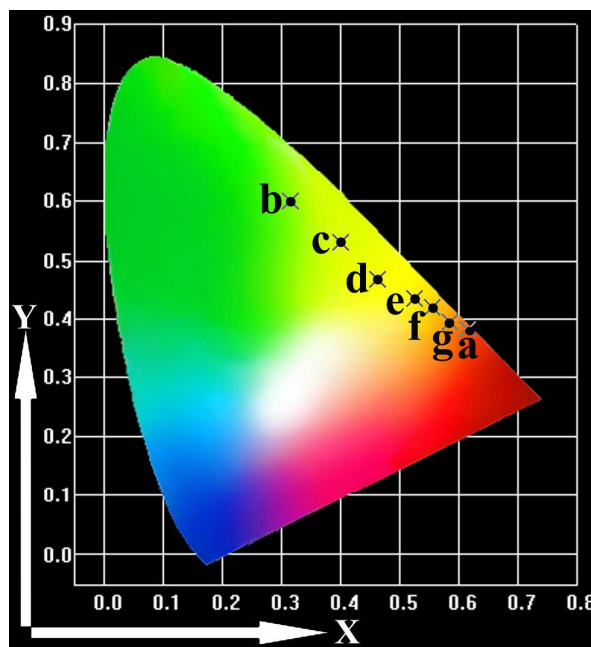


Fig. 10 The CIE chromaticity diagram of the LaOF:0.05Eu³⁺ and LaOF:0.06Tb³⁺, xEu³⁺ ($x = 0, 0.01, 0.02, 0.03, 0.04, 0.05$) phosphors.

than that in single Tb³⁺-doped LaOF sample and the emission intensity of Eu³⁺ ⁵D₀ → ⁷F₂ transition in LaOF:0.06Tb³⁺, 0.03Eu³⁺ sample increases apparently compared with that in LaOF:0.05Eu³⁺ sample. All the spectrum result indicate that the Tb³⁺ ion may act as an energy donor in the LaOF host.^{34,35} Fig. 8 depicts the dependence of PL spectra for LaOF:0.06Tb³⁺, xEu³⁺ ($x = 0-0.05$) samples. Under 378 nm UV radiation excitation, the characteristic emission of both Tb³⁺ and Eu³⁺ are observed. With increasing the Eu³⁺ concentration, the emission intensities of the Tb³⁺ ion decreases monotonically whereas the emission intensities of Eu³⁺ firstly increases, reaching a maximum value at $x = 0.04$, then decreasing due to the concentration quenching effect.

Table 1 The CIE chromaticity coordinates (x , y) for the LaOF:0.06Tb³⁺ $_x$ Eu³⁺ samples upon excitation at 378 nm

| Sample no. | Sample compositions | CIE (x , y) | CCT (K) |
|------------|---|-------------------|---------|
| b | LaOF:0.06Tb ³⁺ | (0.315, 0.599) | 5803 |
| c | LaOF:0.06Tb ³⁺ , 0.01 Eu ³⁺ | (0.399, 0.531) | 4315 |
| d | LaOF:0.06Tb ³⁺ , 0.02Eu ³⁺ | (0.462, 0.468) | 3118 |
| e | LaOF:0.06Tb ³⁺ , 0.03Eu ³⁺ | (0.525, 0.436) | 2164 |
| f | LaOF:0.06Tb ³⁺ , 0.04 Eu ³⁺ | (0.554, 0.420) | 1874 |
| g | LaOF:0.06Tb ³⁺ , 0.05Eu ³⁺ | (0.586, 0.396) | 1711 |

Fig. 9 illustrates energy diagrams of Tb³⁺ and Eu³⁺ and the sensitized Eu³⁺ luminescence mechanism. One can see that the energy level of Tb³⁺ (⁵D₄) is a little higher than that of Eu³⁺ (⁵D₁ and ⁵D₀), which makes energy transfer possible. Moreover, the ⁵D₄ → ⁷F₆, or ⁵D₄ → ⁷F₅ emission of Tb³⁺ is effectively overlapped with the ⁷F₁ → ⁵D₂, or ⁷F₁ → ⁵D₁ absorption of Eu³⁺, thus the energy transfer from Tb³⁺ to Eu³⁺ is efficient in general.^{36,37} For the emission of phonons in the ⁵D₄ energy level of Tb³⁺, part of energy transfers to the ⁵D₂ and ⁵D₁ energy levels of Eu³⁺. Subsequently, the excitation energy relaxes to ⁵D₀ energy level, and finally transfers to the ⁷F₁ or ⁷F₂ level of Eu³⁺ by radiative transition, which enhances the characteristic emission of Eu³⁺.

Fig. 10 shows the CIE chromaticity diagram for the emission spectra of LaOF:0.05Eu³⁺ and LaOF:0.06Tb³⁺ $_x$ Eu³⁺ as a function of the Eu³⁺ doping concentration. It can be clearly seen that the color tone of samples changes from green (0.315, 0.599) to red (0.586, 0.396) by doping different Eu³⁺ concentration. The correlated color temperature (CCT) as one of the characteristics of samples has also been obtained and the results are presented in Table 1. These results show that the as-obtained phosphors with multicolor emissions might find potential applications in light display systems.

4 Conclusion

In summary, we proposed a novel, facile, and mass-production method to synthesize the LaOF:Ln³⁺ hollow spheres via a sacrificial template followed by a further heat treat. The LaCO₃F precursor was fabricated through the Kirkendall effect using La(OH)CO₃ as the sacrificed template. Subsequently, the LaOF hollow spheres were obtained during a calcination process. Furthermore, under ultraviolet excitation, the Eu³⁺ and Tb³⁺ ion doped LaOF samples show strong red and green emission, respectively. By codoping the Tb³⁺ and Eu³⁺ ions into LaOF host, the emission colors of the as-prepared codoped LaOF:Tb³⁺ $_x$ Eu³⁺ hollow spheres were changed from green to red by a simple adjust Eu³⁺ doping concentrations. These results indicate that this kind of materials with the variable colors could potentially be used in the light display fields.

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