Hydrothermal synthesis and tunable luminescence of persimmon-like sodium lanthanum tungstate: Tb$^{3+}$, Eu$^{3+}$ hierarchical microarchitectures

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Abstract

Persimmon-like NaLa(WO$_4$)$_2$ microarchitectures were prepared via hydrothermal process with using trisodium citrate (Na$_3$Cit) as chelated reagent and characterized by X-ray diffraction (XRD), field emission scanning electron microscope (FE-SEM), photoluminescence (PL), and fluorescent dynamics. The influences of Na$_3$Cit concentration, organic additivities, and reaction time on the morphologies of NaLa(WO$_4$)$_2$ phosphor were studied. The results revealed that Na$_3$Cit species had double functions of strong ligand and structure-directing reagent that could efficiently control the formation of persimmon-like NaLa(WO$_4$)$_2$ microarchitectures. The possible mechanism for the growth of persimmon-like NaLa(WO$_4$)$_2$ microarchitectures was attributed to the Ostwald ripening mechanism. The energy transfer from Tb$^{3+}$ to Eu$^{3+}$ in the persimmon-like NaLa(WO$_4$)$_2$ phosphor was observed. The energy transfer efficiencies and emission colors can be tuned by changing the concentration of Eu$^{3+}$. Finally, it was deduced that the electric dipole–dipole interaction (D–D) is the main mechanism for energy transfer between Tb$^{3+}$ and Eu$^{3+}$ in the persimmon-like NaLa(WO$_4$)$_2$ phosphor.

1. Introduction

The synthesis of micro-/nano-sized inorganic materials with special morphologies or hierarchical structures has gained great attention due to the fundamental scientific interest and potential technological applications of these materials in different fields such as luminescence, catalysis, biology.[1–5]. It is well known that the luminescent properties of inorganic materials are affected not only by the composition but also by the morphology, dimension, size, and structure [6]. Therefore, tunable or controllable morphology of nano-/micro-crystals remains an important goal of modern materials chemistry. Many recent efforts have been devoted to the controllable morphology and spatial patterning of various materials, which is a crucial step toward the realization of functional nanosystems [1,2,7–11]. Generally, chemical vapor deposition and solution-phase chemical routes have been used in order to obtain different morphologies [12,13]. However, they usually require catalysts, expensive and even toxic templates or surfactants, high temperature, and a series of complicated procedures. It is still a big challenge to develop simple and reliable synthetic methods for hierarchical architectures with desired chemical components and morphologies, which strongly affect the properties of nano-/micro-materials.

Over the past several decades, optical functional materials have attracted considerable attention because they have played important roles in such fields as display systems, lasers, optoelectronic devices. [14]. As most frequently used luminescent centers, rare earth (RE) ions have been playing crucial roles in modern lighting and display fields owing to the abundant emission colors originating from their 4f–4f or 5d–4f transitions [15–17]. To achieve excellent luminescent performance, the proper host material is often indispensable. It is well known that RE tungstates are essential functional materials and exhibit excellent performance in the scopes of catalysis, lasers, ionic conductors, etc. [5,18–20], and that they are recently considered as promising host materials for RE luminescent centers because of the special properties of WO$_6^{2–}$ group [21,22]. Among all tungstates, alkaline RE double tungstates with the general formula of ARE(WO$_4$)$_2$ (A = Na, K, RE = Y, La, Gd and Lu) can form a wide variety of inorganic compounds having tetragonal or monoclinic symmetries that have attracted great interest in recent years [1,3,21]. As one compound of the alkaline RE double tungstate family, NaLa(WO$_4$)$_2$ has a tetragonal symmetry with the structure of scheelite CaWO$_4$ in which W$^{6+}$ is coordinated by four oxygen atoms in a tetrahedral site, and La$^{3+}$/Na$^{+}$ sites are eight coordinated. It has been demonstrated that
NaLa(WO$_4$)$_2$ is a promising host candidate for RE ions activated luminescent materials because of its broad charge transfer absorption band centered at near-UV wavelengths and excellent thermal and chemical stability [8,23]. Nevertheless, the previous work reported mostly on the single crystal materials to be used as laser crystal materials. This compound with specific morphologies, especially hierarchical structures, for other purposes has received little attention. Lately, stimulated by both the potential applications and the interesting properties, much attention has been directed to the controllable synthesis of RE tungstates with different shapes and the investigation into their size/shape-dependent properties [1]. Indeed, RE$^{3+}$ ions have very similar physical and chemical properties; meanwhile, scheelite-structured tungstates also have the similar crystal structure and properties. However, because of different radii of RE$^{3+}$ ions, the structure of scheelite tungstates with different Ln$^{3+}$ ions is usually different, which may lead to different morphology prepared by wet chemical process. Therefore, to obtain much more different morphologies of scheelite tungstates, we chose NaLa(WO$_4$)$_2$ as studied target in this work.

During past decade, the hydrothermal approach has been proved as a promising method for the synthesis of some inorganic micro-/nano-materials due to its flexible conditions including simplicity of equipment and processing, low reaction temperature [24–29]. Consequently, it is possible to obtain homogeneous composites with uniform morphology and phase with stable physical properties via the hydrothermal synthesis. In our previous work, NaY(WO$_4$)$_2$:Eu$^{3+}$ microarchitectures [1], CaWO$_4$:Tb$^{3+}$ microspheres [2], and flower-shaped Y$_2$(MoO$_4$)$_3$:Eu$^{3+}$ phosphors [15] have been prepared via microwave-assisted hydrothermal, sonochemical and co-precipitated routes, respectively. The growing mechanism for each microstructured/nanostructured material has been proposed. Moreover, the fluorescence temperature quenching mechanism and optical transition properties of Eu$^{3+}$ [1], energy transfer behaviors between Tb$^{3+}$ ions and between Tb$^{3+}$ and host [2], as well as the concentration quenching process of Eu$^{3+}$ [3] have been systematically studied.

Herein, in this work, the main objective is to study on the controlled synthesis of persimmon-like NaLa(WO$_4$)$_2$ microarchitectures through a simple hydrothermal process with using trisodium citrate (Na$_3$Cit) as chelated reagent and the energy transfer between Eu$^{3+}$ and Tb$^{3+}$ ions. The effects of Na$_3$Cit concentration, organic additives, and reaction time on the morphology of NaLa(WO$_4$)$_2$ phosphors were studied, and the possible formation mechanism for the persimmon-like microarchitectures was proposed. Finally, the luminescent properties of Tb$^{3+}$, Eu$^{3+}$ codoped persimmon-like NaLa(WO$_4$)$_2$ phosphors were investigated in detail.

2. Experimental section

2.1. Materials

The lanthanide oxides La$_2$O$_3$ (99.99%), Eu$_2$O$_3$ (99.99%), and Tb$_2$O$_3$ (99.99%) were purchased from Shanghai Second Chemical Reagent Factory (China). Trisodium citrate (Na$_3$Cit), Na$_2$WO$_4$·2H$_2$O, oxalic acid (OA), trimethylammonium bromide (CTAB), and disodium ethylenediamine tetraacetic acid (EDTA) were purchased from Tianjin Reagent Chemicals Co. Ltd. (China). Other reagents including NaOH, ethylene glycol (EG), and HNO$_3$ were purchased from Tianjin Kernel Chemical Reagents Development Center (China). All chemicals were used without further purification in this work. In the synthesis process, the lanthanide nitrates including La(NO$_3$)$_3$·6H$_2$O, Eu(NO$_3$)$_3$·6H$_2$O, and Tb(NO$_3$)$_3$·6H$_2$O were used instead of the corresponding lanthanide oxide. These lanthanide nitrates were obtained by a recrystallization process. First, the lanthanide oxide was dissolving in nitric acid of proper amount, and then, the obtained solution was heated to remove the water and excessive nitric acid. The heating process was repeated three times by adding distilled water at each time. Finally, the Ln(NO$_3$)$_3$·6H$_2$O compounds were received.

2.2. Synthesis

In comparison with some inorganic acid groups, for example, WO$_6^{2-}$ group, Na$_3$Cit has very strong chelating ability for coordinating with Ln$^{3+}$ ions; thus, it is often used in synthesis processes of Ln$^{3+}$ containing compounds [1,3]. Therefore, in this study, Na$_3$Cit was used as additive for controlling the morphology of the product. Persimmon-like NaLa(WO$_4$)$_2$ microarchitectures were prepared via hydrothermal process with the ratio of Ln$^{3+}$/Na$_3$Cit of 1. In a typical procedure, 2 mmol of Na$_3$Cit was dissolved in 50 mL distilled water under magnetically stirring. Until Na$_3$Cit was dissolved completely, 10 mL of La(NO$_3$)$_3$ aqueous solution containing 2 mmol of La(NO$_3$)$_3$·6H$_2$O was dropped into the above Na$_3$Cit aqueous solution, and the white precipitation appeared at once. After vigorously stirring for 30 min, 0.2 mol/L of Na$_2$WO$_4$ aqueous solution was dropped into the above suspension slowly. The muddy white suspension dissolved immediately and formed a transparent colloid solution with the pH value of about 6. Then, the pH value of the colloid solution was adjusted to be about 8 by 2 mol/L of NaOH aqueous solution. After additional agitation for 15 min, the obtained colloid solution was transferred into a 100 mL Teflon-lined stainless autoclave and heated at 180 °C for 24 h. As the autoclave cooled to room temperature naturally, the white powders were directly collected by centrifugation then washed with absolute ethanol and distilled water in sequence and finally vacuum-dried at 80 °C for 6 h. In addition, the influences of reaction conditions such as the Na$_3$Cit concentration, reaction time, and organic additives on the morphological evolution of the prepared products were investigated in order to understand the growth mechanism of persimmon-like NaLa(WO$_4$)$_2$ microarchitectures. It should be pointed out that when one of the reaction conditions was varied, the others were kept as constants as used in the typical synthesis. Persimmon-like Tb$^{3+}$/Eu$^{3+}$ single and double doped NaLa(WO$_4$)$_2$ microarchitectures were prepared by the same procedure as above, except for adding a stoichiometric amount of Eu(NO$_3$)$_3$ and Tb(NO$_3$)$_3$ crystals into La(NO$_3$)$_3$ aqueous solution at the initial stage.

2.3. Characterization

X-ray powder diffraction (XRD) of the prepared samples was measured by a Shimadzu XRD-6000 diffractometer with Cu K$_\alpha$ radiation (x = 0.15406 nm). The XRD data were collected by using a scanning mode in the 2θ ranging from 15° to 70° with a scanning step size of 0.02° and a scanning rate of 4.0° min$^{-1}$. The observation of morphology and structure of the prepared samples were carried out on field emission scanning electron microscope (FE-SEM, Japan, Hitachi S-4800). The excitation, emission spectra, and fluorescent decays were taken on an F-4600 spectrophotometer (Hitachi, Japan) equipped with a 150 W xenon lamp as excitation source. Both the emission and excitation splits are 2.5 nm, and the voltage of photomultiplier tube is 400 V. All the measurements were performed at room temperature.

3. Results and discussion

3.1. Phase, structure, and morphology of the product

In order to identify the crystal structure, XRD patterns for the samples prepared in the presence of Na$_3$Cit were measured, and
that similar diffraction patterns were observed. The typical XRD patterns for the undoped NaLa(WO4)2 sample and 10 mol% Tb3+/5 mol% Eu3+ codoped NaLa(WO4)2 phosphor as representatives which were prepared via hydrothermal process at 180 °C for 24 h with the Ln3+/Na3Cit ratio of 1 are well consistent with that of the pure tetragonal phase of NaLa(WO4)2 [space group: I41/a (88)], which was reported in [Supporting information, Fig. S1]. Additional peaks from other phases were not found even in the sample with highest concentration of Tb3+ and Eu3+. This fact indicates that the pure NaLa(WO4)2 can be formed directly without post-calcination process, and that the crystal structure of the products was influenced little by the introduction of Eu3+ and Tb3+ ions. In addition, it can also be found that the XRD peaks of the prepared samples are intense and sharp, suggesting that the products were well crystallized. This is in the favor of high efficient luminescence of rare earth ions as well. 

Fig. 1 shows the typical FE-SEM images of the prepared undoped NaLa(WO4)2 (Fig. 1a and b) and NaLa(WO4)2:10 mol% Tb3+, 5 mol% Eu3+ (Fig. 1c and d) samples. The low-magnification FE-SEM image in Fig. 1a reveals that the product prepared via hydrothermal process with Na3Cit as chelated reagent consists of uniform persimmon-like hierarchical nanostructures with diameters of about 3 μm. From the high-magnification FE-SEM image shown in Fig. 1b, it is interestingly found that each persimmon-like particle has two holes located, respectively, at the centers of its two-side poles. In addition, every persimmon-like microsphere is built of numerous densely-packed nanosheets aligned perpendicularly to the sphere pointing to the same center and arranged regularly instead of disorderly on the surface and weaved into a hierarchical persimmon-like shape. When 10 mol% Tb3+ and 5 mol% Eu3+ were introduced into the NaLa(WO4)2 crystal, it can be found that the morphology of the product has little change, which indicates that doping concentration has little influence on the morphology of the product in this work because of similar ionic radius between rare earth ions (Fig. 1c and d) [3].

3.2. Growth mechanism

The inorganic crystal growth mechanisms in solution-based system have attracted more and more attention in recent years because of the interest in size- and shape-controllable synthesis [30]. Comprehensive understanding to the growth mechanism of the microstructured/nanostructured materials would be helpful for designing the synthesis routes and controlling the product morphologies on our desired purpose. Although diversified mechanisms have been proposed, the crystallization process still remains a complicated problem. Generally, successful synthesis of nano-/micro-crystals in a solution is not only decided by the crystal structures of the target compounds but also requires more fastidious control of the growth parameters such as reaction time, organic additives, and so forth. Therefore, to clearly reveal the growth mechanism of persimmon-like NaLa(WO4)2 nanostructures, the influences of Na3Cit, organic additives and reaction time were investigated.

3.3. Effect of Na3Cit content

In the synthesis of inorganic nano-/micro-crystals, many organic additives are frequently employed for the modifications of certain crystallographic surfaces [1,8,21]. Herein, as one kind of organic additives, Na3Cit with various content was introduced into the synthesis of NaLa(WO4)2 to examine the influence of Na3Cit content on the morphology of final product. It is well known that the Na3Cit is a strong chelating agent with three carboxylate groups for metal ions, which can react with metal ions (Mn+) to form stable Mn+–Cit3/C0 complexes through stronger coordination interaction, thus resulting in decreasing the coagulating rate of the ions in solution. The relatively low coagulating rate is favorable for the subsequent growth of 3D hierarchical nanostructures. To investigate the effect of Na3Cit content on the shape evolution, various Cit3/C0/La3+ ratios were adopted, while other experimental
parameters remained constant. The FE-SEM images of the NaLa(WO₄)₂ samples obtained with different molar ratios of Cit³⁻/La³⁺ (0, 0.25, 1, 3) were shown in Fig. S2. It is found that the product obtained in absence of Na₃Cit has dendritic shape (see Fig. S2a), and each dendrite is composed of directly arrayed submicropolyhedrons that are attached to each other in an interesting parallel and scalariform way rather than in a simple manner. When increasing the ratio of Cit³⁻/La³⁺ up to 0.25, nanosheets come out in the product (Fig. S2b). Further increasing the ratio of Cit³⁻/La³⁺ to 1, the obtained sample is composed of persimmon-like microspheres with perfect uniformity and monodispersity (Fig. S2c). When the ratio of Cit³⁻/La³⁺ is 3 (Fig. S2d), the final product is composed of ellipsoid-like microspheres assembled by nanosheets. From the analysis above, it can be concluded that the amount of Na₃Cit is undoubtedly vital factor in the self-assembly of the persimmon-like NaLa(WO₄)₂ microarchitectures in the present reaction system.

3.4. Effect of organic additives

In addition, some other organic additives, such as ethylene glycol (EG), oxalic acid (OA), trimethylammonium bromide (CTAB), and disodium ethylenediamine tetraacetic acid (EDTA) were also introduced individually into the reaction system. Fig. 2a–d shows FE-SEM images of the NaLa(WO₄)₂ samples prepared in the presence of EG, EDTA, CTAB, and OA, respectively. The product prepared in presence of EG is mainly composed of spindle-like particles as shown in Fig. 2a. In the presence of EDTA, the sample contains irregular nanoplates as illustrated in Fig. 2b. Fig. 2c shows the needle-like micro-crystals, which are received when CTAB is employed as an organic additive. The product exhibits submicroparticles with irregular shape when Na₃Cit is replaced by OA as shown in Fig. 2d. These results indicate that the organic additives have a remarkably different impact on the morphologies of the final products, which is related to the differences of the chelating constant with La³⁺ and the adsorption ability of the different crystal facets of the final products [3].

3.5. Time-dependent experiments

Fig. 3 shows the FE-SEM images of the products prepared at 180 °C for 0, 3, 7, and 12 h, respectively. When the initial colloid solution was not treated by hydrothermal process, the product was composed of the nanoparticles with about 30 nm as illustrated in Fig. 3a. When the hydrothermal reaction was carried out for 3 h, many irregular nanosheets appeared. However, a little of nanoparticles still was found. When the reaction time was prolonged to 7 h, several aggregates came forth (see Fig. 3c), and we can see that these aggregates are built from many nanosheets. As shown in Fig. 3d, further prolonging the reaction time to 12 h, the persimmon-like microstructures were dominant in the product. These experimental results suggest that the crystal growth behavior is obviously an Ostwald ripening mechanism [4]. It could also be found that some microstructures are not completely ripened as marked in Fig. 3d. Therefore, these FE-SEM images can clearly demonstrate the shape evolution of the obtained products from nanosheet to micropersimmon. Moreover, in this growth process, more nanosheets are needed to generate and assemble into microarchitecture to make it grow, which means that this is not a one-off nucleation-growth process but a continual nucleation-growth process [31].

3.6. Formation mechanism of the persimmon-like microarchitecture

Based on the above experimental results, it can be confirmed that the growth of the persimmon-like NaLa(WO₄)₂ microarchitectures is directly related to the function of the Na₃Cit molecules [32,33]. Enlightened by our experimental results and the previous
reports [34–37], a plausible growth mechanism of the persimmon-like microstructures is proposed and portrayed in Fig. 4. In the solution, La$^{3+}$ ions can coordinate with Na$_3$Cit to form the La$^{3+}$–Cit$^{3−}$ intermediate complexes, greatly decreasing the free La$^{3+}$ ions concentration. This leads to a relatively slow reaction and transfer rate, which facilitate the oriented growth and self-assembly. When the La$^{3+}$–Cit$^{3−}$ intermediate complexes were treated by hydrothermal process, the La$^{3+}$ ions can be released slowly from the La$^{3+}$–Cit$^{3−}$ intermediate complexes and reacted with WO$_2$$^4$ to form the NaLa(WO$_4$)$_2$ nanoparticles in the solution. Once the NaLa(WO$_4$)$_2$ nanoparticles have been formed, the Na$_3$Cit molecules can selectively adsorb onto certain crystallographic planes of the nanoparticles, which restricted their intrinsic anisotropic growth. This kinetic control results in the formation of the original nanosheets, which are the building blocks. Possibly, the formation process and the assembled process of the nanosheets were simultaneous. Due to the Sillén structure, the WO$_2$$^4$ layers and (NaLa)$^{4+}$ layers can lead to the formation of the nanosheets with polar charges on the top and bottom surfaces [4]. Then, these nanosheets assembled in the layer-by-layer stacking style due to the electrostatic effects.

Fig. 3. FE-SEM images of the as-prepared NaLa(WO$_4$)$_2$ phosphors at 180 °C for different time: (a) 0 h, (b) 3 h, (c) 7 h, and (d) 12 h.

Fig. 4. Schematic illustration of the formation mechanism of the persimmon-like NaLa(WO$_4$)$_2$ hierarchical microstructures.
3.7. Luminescent properties

Fig. 5a shows the PL excitation and emission spectra of persimmon-like NaLa(WO4)2:5 mol% Eu3+ phosphor. The excitation spectrum (Fig. 5a, left) is obtained by monitoring the emission of the 5D0 → 7F2 transition at 615 nm. It can be seen clearly that the excitation spectrum consists of a strong and broadband ranging from 200 to 350 nm with a maximum at about 268 nm and some sharp lines ranging from 350 to 480 nm. The broadband corresponds to the charge transfer bands (CTB) of O2− → Eu3+ and O2− → W6+ transitions [1]. In most cases, the contribution of these two CTB components cannot be distinguished owing to the spectral overlap. The sharp peaks are attributed to the f–f transitions of Eu3+ in the longer wavelength region. Upon the 268 nm UV light excitation, it can be found that the strongest emission peak of NaLa(WO4)2:Eu3+ is located at 615 nm, which originates from the 5D0 → 7F2 transition of Eu3+ (Fig. 5a, right), which indicates that the sites occupied by Eu3+ ions deviate from symmetry center in the NaLa(WO4)2 host [1,29]. Other peaks at 580, 592, 655, and 704 nm are attributed to the 5D0 → 7F6, 5D0 → 7F1, 5D0 → 7F2, and 5D0 → 7F3 transitions of Eu3+, respectively. Although no emission corresponding to the WO2 4 groups is observed, the presence of an absorption band originating from the WO2 4 groups has been detected in the excitation spectrum when monitoring 615 nm emission. This fact suggests that the energy absorbed by the WO2 4 groups can be efficiently transferred to Eu3+ ion levels. So, the emissions corresponding to Eu3+ ions are observed under excitation of the CT band of the WO2 4 groups, and this process has been known as host sensitized energy transfer [1].

Fig. 5b shows the excitation and emission spectra of the as-prepared NaLa(WO4)2:10 mol% Tb3+ phosphor. The excitation spectrum of monitoring Tb4 → Tb5 emission at 545 nm consists of a strong and broadband ranging from 200 to 350 nm with a maximum at about 268 nm (Fig. 5b, left), which corresponds to the transitions of O2− → W6+ (charge transfer band of WO2 4 groups) and 4f → 5d transitions of Tb3+ [3]. Other transitions in the excitation spectrum ranging from 350 to 450 nm are attributed to the f–f transitions of Tb3+. The corresponding emission spectrum excited at 268 nm is shown in right side of Fig. 5b, which consists of f–f transition lines within 4f6 electron configuration of Tb3+. This indicates that an efficient energy transfer also occurs from WO2 4 groups to Tb3+.

The photoluminescence (PL) decay curves of the Eu3+ and Tb3+ doped phosphors were also investigated. The fluorescent decay curves of the NaLa(WO4)2:10 mol% Tb3+ (λex = 268 nm, λem = 545 nm) and NaLa(WO4)2:5 mol% Eu3+ (λex = 268 nm, λem = 615 nm) samples are shown in Fig. 6. It can be found that the fluorescent decay curves for NaLa(WO4)2:10 mol% Tb3+ and NaLa(WO4)2:5 mol% Eu3+ samples deviate from single exponential decay process. Therefore, the average fluorescent lifetime is considered as fluorescent lifetime of Eu3+ and Tb3+ in the NaLa(WO4)2. The average fluorescent lifetime, τ, is defined as follows:

$$\tau = \frac{\int I(t)dt}{\int I(t)dt}$$

(1)

where I(t) represents the luminescence intensity at time t. By using Eq. (1), the fluorescent lifetime of NaLa(WO4)2:10 mol% Tb3+ and NaLa(WO4)2:5 mol% Eu3+ samples was calculated to be 0.94 and 1.01 ms, respectively. Generally, the fluorescent decay curve could be fitted well to a single exponential function if there is no such an energy transfer originating from the luminescent centers. In the Tb3+ and Eu3+ single doped NaLa(WO4)2 phosphors, the...
fluorescence decay deviation from single exponential function indicates that Tb$^{3+}$ to Tb$^{2+}$ and Eu$^{3+}$ to Eu$^{2+}$ energy transfer processes exist in the Tb$^{3+}$ or Eu$^{3+}$ single doped persimmon-like NaLa(WO$_4$)$_2$ phosphors. It is well known that the exchange interaction is dominant mechanism for energy transfer between the $5D_4$ level of Tb$^{3+}$ or $5D_0$ level of Eu$^{3+}$. In this case, the relationship between fluorescent intensity and time can be expressed as [2,39,40]:

$$I(t) = I_0 \exp \left[ -\frac{t}{\tau_0} - \frac{4}{3} \pi^{3/2} N_a (C t)^{1/2} \times \left( \frac{1 + 10.87x + 15.50x^2}{1 + 8.743x} \right) \right]^{3/4}$$

(2)

where $\tau_0$ is the intrinsic lifetime of the donors in the absence of acceptors, $N_a$ is the number of acceptors, $C$ is the interaction parameter for donor–acceptor interaction, $x = DC^{-1/2}t^{3/2}$, and $D$ is the diffusion constant for ET between rare earth ions. By using Eq. (2), the nonlinear fitting was done, and the fitting results were shown in Fig. 6 as well. It can be observed that the experimental data can be fitted well to Eq. (2). This further confirms that energy transfer mechanism between the $5D_4$ levels of Tb$^{3+}$ ions (or $5D_0$ levels of Eu$^{3+}$ ions) is exchange interaction. In addition, in the fitting processes, the intrinsic lifetimes of Tb$^{3+}$ and Eu$^{3+}$ in the persimmon-like NaLa(WO$_4$)$_2$ microarchitectures were deduced to be 1.94 and 1.07 ms, respectively. Therefore, the inner quantum efficiencies for ET between rare earth ions. By using Eq. (2), the Eu$^{3+}$ phosphors were calculated to be 88% and 52%, respectively.

3.8. Tunable emission colors in Tb$^{3+}$/Eu$^{3+}$ codoped samples

Since the $3D_{4} \rightarrow 7F_j$ emissions of Tb$^{3+}$ are effectively overlapped with the $7F_{0,1} \rightarrow 5D_{0,1,2}$ absorption of Eu$^{3+}$, the energy transfer from Tb$^{3+}$ to Eu$^{2+}$ in phosphors would be efficient. Consequently, the emission colors of phosphors codoped with Eu$^{3+}$ and Tb$^{3+}$ can be adjusted by changing the concentration ratio of Tb$^{3+}$ and Eu$^{3+}$. To investigate the tunable PL properties of the NaLa(WO$_4$)$_2$ phosphor, the NaLa(WO$_4$)$_2$ phosphor codoped with Eu$^{3+}$ and Tb$^{3+}$ ions with different concentrations was prepared, and their luminescent properties were also studied. Fig. 7 shows the emission spectra of persimmon-like NaLa(WO$_4$)$_2$:10 mol% Tb$^{3+}$, NaLa(WO$_4$)$_2$:5 mol% Eu$^{3+}$ and NaLa(WO$_4$)$_2$:10 mol% Tb$^{3+}$, xEu$^{3+}$ (x = 1–7 mol%) phosphors under the 268 nm excitation. In Tb$^{3+}$ single doped NaLa(WO$_4$)$_2$ sample, only the characteristic emissions of Tb$^{3+}$ are observed. With the introduction of Eu$^{3+}$, besides Tb$^{3+}$ emissions, the characteristic emissions of Eu$^{3+}$ corresponding to the $5D_0 \rightarrow 7F_{2,3,4}$ transitions can also be observed. Moreover, with the increase of Eu$^{3+}$ concentration, the emission intensity of Tb$^{3+}$ gradually decreases, which indicates an energy transfer occurs from Tb$^{3+}$ to Eu$^{3+}$. It can also be found that the spectral components can be greatly changed with the increase of Eu$^{3+}$ concentration. As a result, the PL colors can be tuned from red, yellow, and green-yellow, to green by simply adjusting the doping concentrations of the Eu$^{3+}$ and Tb$^{3+}$ ions. In order to more intuitively observe the effect of Eu$^{3+}$ doping concentration on PL colors, the Commission International de l’Eclairage (CIE) chromaticity coordinates of the persimmon-like NaLa(WO$_4$)$_2$:10 mol% Tb$^{3+}$, NaLa(WO$_4$)$_2$:5 mol% Eu$^{3+}$ and NaLa(WO$_4$)$_2$:10 mol% Tb$^{3+}$, xEu$^{3+}$ (x = 1–7 mol%) phosphors were calculated and are shown in Fig. 8. It can be seen that with the increase of Eu$^{3+}$ doping concentration, the PL colors can be tuned from yellowish green, yellow to orange under the 268 nm UV excitation.

In general, the energy transfer efficiency from a sensitizer to acceptor, $\eta_{ET}$ can be expressed as the following equation [42–44]:

$$\eta_{ET} = 1 - \frac{I_s}{I_{0s}}$$

(3)

where $I_s$ is the luminescent intensity of Tb$^{3+}$ in the presence of Eu$^{3+}$ and $I_{0s}$ is the luminescent intensity of Tb$^{3+}$ in the absence of Eu$^{3+}$. In the NaLa(WO$_4$)$_2$:Tb$^{3+}$:Eu$^{3+}$ system, Tb$^{3+}$ is the sensitizer, and Eu$^{3+}$ is the activator. Fig. 9 shows the result of energy transfer efficiency from Tb$^{3+}$ to Eu$^{3+}$ calculated from Eq. (3). As shown in Fig. 9, the energy transfer efficiency increases with increasing Eu$^{3+}$ concentration. However, the increment rate of the emission intensity gradually decreases with the increase of Eu$^{3+}$ concentration. The maximum energy transfer efficiency can reach 90%. The above results indicate that the energy transfer from Tb$^{3+}$ to Eu$^{3+}$ is very efficient.

The energy transfer mechanism can be divided into two main types: one is exchange interaction, and the other is multipolar interaction. It is known that if energy transfer results from the exchange interaction, the critical distance between the sensitizer and activator should be shorter than 3 Å [45]. In many cases, concentration quenching is due to energy transfer from one activator to another until an energy sink in the lattice is reached. The critical
distance \( R_c \) for the energy transfer from the \( \text{Tb}^{3+} \) to \( \text{Eu}^{3+} \) ions can be estimated from the concentration quenching curve. According to Blasse’s theory, the critical distance \( R_c \) can be expressed by [46,47]

\[
R_{\text{TB-Eu}} = 2 \left( \frac{3V}{4\pi KN} \right)^{1/3}
\]

(4)

where \( V \) is the volume of the unit cell, \( N \) is the number of the host cations in an unit cell, and \( x \) is the critical concentration at which the luminescence intensity of the sensitizer (\( \text{Tb}^{3+} \)) is half that in the sample in the absence of activator (\( \text{Eu}^{3+} \)). For the \( \text{NaLa(WO}_4\text{)}_2 \) crystal, the analytical and experimental values were \( x = 0.01, N = 4, V = 657.59 \text{ Å}^3 \). Thus, the \( R_c \) was determined to be 31.6 Å, which is much longer than 3 Å, which suggests that energy transfer via exchange interaction is impossible. Therefore, the energy transfer between the \( \text{Tb}^{3+} \) and \( \text{Eu}^{3+} \) ions mainly takes place via electric multipolar interaction. Based on Dexter’s energy transfer formula of electric multipolar interaction and Reisfeld’s approximation, the following relation can be obtained [48–50]:

\[
\frac{I_o}{I_s} \propto C^{x/3}
\]

(5)

where \( I_o \) and \( I_s \) are the luminescent quantum efficiency of \( \text{Tb}^{3+} \) in the presence and absence of \( \text{Eu}^{3+} \), respectively; \( x \) is the concentration of \( \text{Eu}^{3+} \); and \( x = 6, 8, \) and 10 for electric dipole–dipole (D–D), electric dipole–quadrupole (D–Q), and electric quadrupole–quadrupole (Q–Q) interactions, respectively. The value \( I_o/I_s \) can be approximately calculated by the ratio of related luminescence intensities as

\[
\frac{I_o}{I_s} \propto C^{x/3}
\]

(6)

where \( I_s \) is the luminescent intensity of \( \text{Tb}^{3+} \) in the presence of \( \text{Eu}^{3+} \) and \( I_o \) is the luminescent intensity of \( \text{Tb}^{3+} \) in the absence of \( \text{Eu}^{3+} \).

The \( I_o/I_s \sim C^{x/3} \) plots are illustrated in Fig. 10. Best linear behavior can be observed only when \( x = 6 \), indicating that energy transfer from \( \text{Tb}^{3+} \) to \( \text{Eu}^{3+} \) occurred via the electric dipole–dipole interaction (D–D) mechanism.

If the donor and acceptor ions are uniformly distributed in the host, and the migration process are negligible in comparison with the electric multipolar energy transfer between donors and acceptors, then according to the Inokuti–Hirayama (I–H) model, the luminescence intensity of donors can be written as [51,52]

\[
I(t) = I_0 \exp \left( -\frac{t}{\tau_0} - x \left( \frac{t}{\tau_0} \right)^{3/5} \right)
\]

(7)

where \( I(t) \) is the luminescence intensity at time \( t \), \( I_0 \) is the luminescence intensity at \( t = 0 \), and \( \tau_0 \) is the intrinsic lifetime of the donors in the absence of acceptors. \( x \) is a index of energy transfer type, for electric dipole–dipole (D–D), electric dipole–quadrupole (D–Q) and electric quadrupole–quadrupole (Q–Q) interaction, \( x = 6, 8, \) and 10, respectively. \( x \) is a parameter containing the energy transfer probability. To better understand the energy transfer process, the I–H model was utilized for the analysis of the fluorescent decay of \( \text{D}_4 \) level of \( \text{Tb}^{3+} \) in the \( \text{NaLa(WO}_4\text{)}_2:10 \text{ mol}\%\text{Tb}^{3+}, 5 \text{ mol}\%\text{Eu}^{3+} \). Fig. 11 shows the fluorescent decay of \( \text{D}_4 \) level of \( \text{Tb}^{3+} \) in the \( \text{NaLa(WO}_4\text{)}_2:10 \text{ mol}\%\text{Tb}^{3+}, 5 \text{ mol}\%\text{Eu}^{3+} \) under the 268 nm excitation by monitoring at 545 nm. It can be seen that the decay curve shows non-exponential dependence of emission intensity on the decay time. The non-exponential decays are resulted from the energy transfer process from \( \text{Tb}^{3+} \) to \( \text{Eu}^{3+} \). In order to determine the nature of the possible interaction mechanism from \( \text{Tb}^{3+} \) to \( \text{Eu}^{3+} \), the I–H model is applied to the analysis of the decay curves. According to Eq. (7), using nonlinear fittings to deal with the experimental data, the fitting results are shown in Fig. 11 as well. In the fitting process, the \( s \) is further confirmed to be 5.77, which approximates the theoretical value 6 for the D–D interaction. This further indicates that the energy transfer mechanism from \( \text{Tb}^{3+} \) to \( \text{Eu}^{3+} \) is a dipole–dipole (D–D) interaction type, which is well in accordance with that derived from Dexter’s energy transfer formula. In addition, the intrinsic radiative transition lifetime \( \tau_0 \) of \( \text{D}_4 \) level of \( \text{Tb}^{3+} \) is also confirmed via the fitting process to be 1.10 ms, which is in a good agreement with the theoretical value 1.10 ms.

![Fig. 9. Dependence of energy transfer efficiency between \( \text{Tb}^{3+} \) and \( \text{Eu}^{3+} \) in the persimmon-like \( \text{NaLa(WO}_4\text{)}_2 \) phosphor.](image)

![Fig. 10. Dependence of \( I_o/I_s \) of \( \text{Tb}^{3+} \) ions on (a) \( \text{C}^{6/3} \), (b) \( \text{C}^{8/3} \), and (c) \( \text{C}^{10/3} \).](image)

![Fig. 11. Fluorescent decay curve of the as-prepared of \( \text{NaLa(WO}_4\text{)}_2:10 \text{ mol}\%\text{Tb}^{3+}, 7 \text{ mol}\%\text{Eu}^{3+} \) phosphor (\( \lambda_{\text{em}} \) = 268 nm, \( \lambda_{\text{em}} \) = 545 nm). Solid lines are the fitting results.](image)
agreement with the value derived from the analysis on the fluorescence decay of Tb\(^{3+}\) single doped sample by using Eq. (2).

4. Conclusion

Persimmon-like NaLa(WO\(_4\))\(_2\) microarchitectures have been synthesized through a hydrothermal process in the presence of Na\(_2\)Cit. The experimental results showed that the Na\(_2\)Cit plays a key role in the formation of persimmon-like microarchitectures. The possible formation mechanism for the persimmon-like microarchitectures was proposed based on the analysis of time-dependent experiments to be Ostwald ripening mechanism. In the Tb\(^{3+}\) and Eu\(^{3+}\)-codoped persimmon-like NaLa(WO\(_4\))\(_2\) phosphors, the energy transfer process from the Tb\(^{3+}\) to Eu\(^{3+}\) was observed. Moreover, the energy transfer efficiencies and emission colors can be tuned by changing Eu\(^{3+}\) concentration. The energy transfer type between Tb\(^{3+}\) and Eu\(^{3+}\) was proved as electric D–D based on the analysis of emission spectra and fluorescence dynamics.

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Appendix A. Supplementary material

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References