Color tunable emission and energy transfer in LaSi$_3$N$_5$:Ce$^{3+}$,Tb$^{3+}$ phosphors for UV white LEDs†

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A series of new blue-green emitting LaSi$_3$N$_5$:Ce$^{3+}$,Tb$^{3+}$ phosphors were obtained through a high temperature solid-state method. The crystal structure, photoluminescence properties and energy transfer from Ce$^{3+}$ to Tb$^{3+}$ were investigated. The doped ions Ce$^{3+}$ and Tb$^{3+}$ were confirmed to occupy the same crystallographic sites as La$^{3+}$ using a Rietveld structure refinement method. The emission spectra of these phosphors was composed of a blue emission band attributed to the d–f transition of Ce$^{3+}$, together with several sharp lines ascribed to the emission of Tb$^{3+}$ under UV light excitation. Thus a color tunable emission from blue to green was obtained via controlling the doping concentration of Tb$^{3+}$. In addition, the mechanism of energy transfer, efficiency of energy transfer, chromaticity coordinates and thermal stability of these phosphors were investigated. The results indicated that the Ce$^{3+}$,Tb$^{3+}$ co-activated LaSi$_3$N$_5$ phosphors with color-tunable blue-green emission and high quantum efficiency may have potential for UV white LEDs.

1. Introduction

Phosphor-converted white light-emitting diodes (WLEDs) have received considerable attention as a new-fashioned lighting source due to their high conversion efficiency, long lifetime and environment-friendly characteristics compared with the conventional incandescent and fluorescent lamps. Most commercially available WLEDs are fabricated by combining the yellow-emitting Y$_2$Al$_5$O$_{12}$:Ce$^{3+}$ phosphor with (In,Ga)N-LED chips. However, the major shortcoming of this phosphor is the lack of a red spectral component, which results in a low color rendering index ($R_a < 75$) and high color temperature ($T_c > 7000$ K) limiting their application. To further improve the luminescence efficiency of these LEDs, near-UV (380–420 nm, short as n-UV) LED chips combined with blue, green and red phosphors was reported. Especially, W-LEDs fabricated with n-UV chips coated with tricolor (red, green and blue) phosphors are regarded as the main trend in the market of the LED lighting industry. Therefore, it is essential to develop new phosphors that emit blue, green or red light, which can be efficiently excited by the n-UV LED chips.

Recently, Ce$^{3+}$ doped LaSi$_3$N$_5$-based phosphors with blue emission have drawn much attention due to their intense emission and high thermal stability. The structure of LaSi$_3$N$_5$, which was first reported by Inoue et al. in 1980, is composed of a three-dimensional network with vertex-sharing [SiN$_4$] tetrahedral. Moreover, LaSi$_3$N$_5$ are reported to hold similar structure of Si$_3$N$_4$, hinting that LaSi$_3$N$_5$ may have rigid skeleton structure and some other special properties. Thus, LaSi$_3$N$_5$ might be an interesting host for phosphor. In recent years, the luminescence properties of Ce$^{3+}$-activated LaSi$_3$N$_5$ blue phosphors have been studied. In 2011, Park et al. reported that both the excitation and emission bands were getting slightly shift to long wavelength by doping Al. It is well known that Ce$^{3+}$ ions not merely exhibit excellent luminescent properties with broadband emission but also can act as an efficient sensitizer due to its high efficiency of energy transfer. Typically, the energy transfer from Ce$^{3+}$ to Tb$^{3+}$ has been widely studied and the energy could be transferred from the 5D level of Ce$^{3+}$ to the 5D$_{4,4}$ level of Tb$^{3+}$ in the proper matrix. Therefore, it is may be attractive to develop a new phosphor in LaSi$_3$N$_5$ matrix by Ce$^{3+}$ and Tb$^{3+}$ co-doping. To the best of our knowledge, the luminescence properties of LaSi$_3$N$_5$:Ce$^{3+}$,Tb$^{3+}$, as well as the mechanism of energy transfer, have not been reported in the literature.

In this work, we have synthesized a series of LSN:Ce$^{3+}$,Tb$^{3+}$ phosphors and studied the structure, photoluminescence properties, energy transfer mechanism and energy transfer efficiency in detail. The luminescent properties study suggests that LSN:Ce$^{3+}$,Tb$^{3+}$ may have potential application for UV WLEDs.

2. Experimental

2.1 Synthesis

A series of Ce$^{3+}$ and Ce$^{3+}$,Tb$^{3+}$-activated LaSi$_3$N$_5$ (LSN) phosphors were prepared via conventional high temperature solid
state reactions. The raw materials LaN (99.5%), CeN (99.5%), and Tbn (99.99%) were supplied by General Research Institute for Nonferrous Metals, and Girem Advanced Materials Co. Ltd, Beijing, China, together with Si3N4 (>99.9%) bought from Sigma-Aldrich. The starting powders were weighted and mixed in an agate mortar for 15 min per each sample. All these operation were performed in a purified-nitrogen-filled glove box with oxygen and water vapor content maintained below 1 ppm. The mixed powders were placed in BN crucible and heated at 1900 °C for 10 h with pressure of nitrogen gas maintained at 2.0 MPa in the graphite resistance furnace. The prepared phosphors were cooled down to room temperature followed by ball-milling and water washing.

2.2 Characterization

The phase purity of samples was examined by the X-ray diffraction (XRD, Rigaku, Japan) with Co-Kz radiation (λ = 0.178752 nm), performing at 40 kV and 100 mA in the 2θ range from 10° to 80° with scanning speed of 6° per minute. The data for Rietveld structure refinement were collected from D8 Focus diffractometer (Bruker) operating at 40 kV and 40 mA with Cu Kz radiation (λ = 1.54 Å). The morphology of LaSi3N5:0.09-Ce3+,0.08Tb3+ was inspected by using scanning electron microscopy (SEM, S4800, Hitachi, Japan). Diffuse reflection spectra were measured on a UV-vis-NIR spectrophotometer (Shimadzu UV-2550) attached to an integral sphere and using BaSO4 as reference standard. The photoluminescence (PL) and photoluminescence excitation (PLE) spectra were measured on a UV-vis-NIR spectrophotometer (Horiba Jobin Yvon, Japan) with a tunable pulse laser radiation as the excitation source. The Commission International de L’Eclairage (CIE) chromaticity coordinates were obtained from a HAAS-2000 light (Everfine, China). All above measurements were performed at room temperature.

3. Results and discussion

3.1 Crystal structure and morphology

Fig. 1(a) depicts the powder XRD patterns of the as-prepared LSN:0.09Ce3+, LSN:0.08Tb3+, LSN:0.09Ce3+,0.08Tb3+ phosphors. All the diffraction peaks of these samples are consistent with the JCPDS Standard Card No. 86-1858 of CeSi3N5, suggesting phase purities were formed and with the space group P212121. The peaks were shown no obvious shift due to the very close ion radii of La3+ (1.06 Å), Ce3+ (1.03 Å) and Tb3+ (0.923 Å). Here, CeSi3N5 were chosen as references and reasons are following: first, the nitridosilicates LnSi3N5 (Ln = Ce, Pr, Nd) compounds are isostructural with LaSi3N5 as reported by Michael et al. It is worth noting that the lattice parameters of a, b, c and V for LaSi3N5 and CeSi3N5 are basically same; second, the phase purity of LaSi3N5 are obtained by Zhou,12 Ibrahim12 and Suehiro,10 and all of the diffraction peaks of LaSi3N5 accompanying with different doping rare earth Ce3+ are in good agreement with CeSi3N5. However, few peaks in the 2θ range at 47°–52° are observed in the samples prepared by Park et al.14,15 and they are regarded as impurity peaks compared with the JCPDS 42-1144 of LaSi3N5. It is possible that the JCPDS standard pattern of LaSi3N5 should be further confirmed. To further confirm the structure of the obtained samples, Rietveld structure refinement of LaSi3N5 has been performed by using the Fullprof suite software,22 as shown in Fig. 2. The crystal structure data of LSN (reported by Woike23) is used as the initial structure model and the main cell parameters and residual factors are summarized in Table 1. All of the peaks are obtained with goodness of fit parameters Rexp = 11.3, Rp = 8.82, Rexp = 7.33 and χ2 = 2.37, indicating that all atom positions, residual
3.2 Luminescence properties of Ce³⁺,Tb³⁺ doped and co-doped LaSi₃N₅ phosphors

Fig. 4(a) shows the PLE and PL spectra of the LSN:0.09Ce³⁺ phosphor. The sample shows a red-shifting from 425 nm to 446 nm, which can be explained by the increased energy transfer between the 5d energy levels and the enhanced crystal-field strength with the increasing Ce³⁺ content. The optimal emission intensity is obtained around 0.09 due to the concentration quenching effect (inset in Fig. 4(b)). The critical energy transfer distance \( R_c \) can be calculated using the following relation: \( R_c = 2 \left( \frac{3V}{4\pi x_c N} \right)^{1/3} \) (1)

where \( V \) is the volume of the unit cell, \( x_c \) is the critical concentration, \( N \) is the number of cations in the unit cell that can be substituted by the activator ions. In this host, \( V = 423.342 \text{ Å}^3 \), \( x_c = 0.09 \) and \( N = 4 \), the critical distance is calculated to be 13.1 Å.

The PLE and PL spectra of LSN:0.09Ce³⁺ (a), LSN:0.08Tb³⁺ (b) and LSN:0.09Ce³⁺,0.08Tb³⁺ (c) are presented in Fig. 5. It can be distinguished directly. Furthermore, the emission spectra can be fitted into two well-separated Gaussian components (the dotted lines) with peak at 428 nm (23 364 cm⁻¹) and 464 nm (21 551 cm⁻¹). The energy gap between two bands is calculated to be 1813 cm⁻¹, which is very close to the theoretical value of \( ~2000 \text{ cm}^{-1} \). This result illustrates that Ce³⁺ ions substitute only one site in host lattice. Fig. 4(b) shows the intensity of PL spectra of LSN:xCe³⁺ with different doping Ce³⁺ contents \( x = 0.03, 0.06, 0.09, 0.12, 0.15, 0.18, 0.21 \). The peak wavelength shows a red-shifting from 425 nm to 446 nm, which can be explained by the increased energy transfer between the 5d energy levels and the enhanced crystal-field strength with the increasing Ce³⁺ content. The optimal emission intensity is obtained around 0.09 due to the concentration quenching effect (inset in Fig. 4(b)). The critical energy transfer distance \( R_c \) can be calculated using the following relation: \( R_c = 2 \left( \frac{3V}{4\pi x_c N} \right)^{1/3} \) (1)
seen that excitation bands of Tb\(^{3+}\) are observed in the region from 300 to 450 nm, which could be referred to the f–f transition absorption of the Tb\(^{3+}\) ions. Under 360 nm excitation, the PL spectra of LSN phosphor singly doped with Tb\(^{3+}\) shows several weak emissions with peaks at 485, 542, 582 and 623 nm, due to the typical 5D\(_4\)/7F\(_J\)\((J = 6, 5, 4, 3)\) multiple transitions of the Tb\(^{3+}\) ions.\(^{29}\) However, as a green phosphor, it is hard to be applied in LED due to the lack of efficiency. In order to enhance the absorption intensity in the n-UV region for the Tb\(^{3+}\) emission, Ce\(^{3+}\) ions can be co-doped as sensitizers to transfer excitation energy to Tb\(^{3+}\) ions. It is observed that there is significant spectral overlap between the emission band of LSN:0.09Ce\(^{3+}\) and the PLE spectrum of LSN:0.08Tb\(^{3+}\) from Fig. 5(a) and (b). Energy transfer is expected to occur from Ce\(^{3+}\) to Tb\(^{3+}\) in LSN host, it can be further confirmed in Fig. 5(c). At the excitation of 360 nm, the emission intensity of LSN:0.09Ce\(^{3+}\),0.08Tb\(^{3+}\) in the region from 375 to 485 nm decreases compared with LSN:0.09Ce\(^{3+}\), while the green lines from Tb\(^{3+}\) simultaneously increases. To further investigate the energy absorption of the LaSi\(_3\)N\(_5\) host lattice, the reflectance spectra of LSN, LSN:0.09Ce\(^{3+}\), and LSN:0.09Ce\(^{3+}\),0.08Tb\(^{3+}\) phosphors are presented in Fig. 6. The LaSi\(_3\)N\(_5\) host exhibits low energy absorption in the UV region, which is assigned as the host absorption. However, two obvious broad absorption bands with peaking at 298 nm and 380 nm of the LSN:0.09Ce\(^{3+}\) are observed due to the f–d absorption of the Ce\(^{3+}\) ions. Moreover, the absorption band of LSN:0.09Ce\(^{3+}\),0.08Tb\(^{3+}\) is similar to LSN:0.09Ce\(^{3+}\). The PLE spectrum and reflectance spectrum demonstrate that LSN:Ce\(^{3+}\),Tb\(^{3+}\) has broad absorption bond, which matches well with n-UV LED chips.

In order to study the relative intensities of the two emissions, a series of LSN:0.09Ce\(^{3+}\),\(y\)Tb\(^{3+}\) phosphors have been prepared. Fig. 7 shows the emission spectra of LSN:0.09Ce\(^{3+}\),\(y\)Tb\(^{3+}\) phosphors with \(y\) varying from 0 to 0.14 excited at 360 nm. With the increase of Tb\(^{3+}\) concentration, it is directly observed that the PL intensity of the Ce\(^{3+}\) decreases monotonically, whereas the green emission peaks of Tb\(^{3+}\) reach a maximum value at \(y = 0.12\), and then decrease due to the nonradiative energy transfer of Tb\(^{3+}\). This result strongly illustrates the energy transfer from the Ce\(^{3+}\) to Tb\(^{3+}\) ions in the LSN host lattice and is shown in the inset of Fig. 7. Therefore, the CIE of the LSN:Ce\(^{3+}\),Tb\(^{3+}\) phosphor could be tuned by appropriately adjusting the relative ratio of Ce\(^{3+}\)/Tb\(^{3+}\). The energy transfer efficiency (\(\eta\)) from the Ce\(^{3+}\) to Tb\(^{3+}\) can be calculated by the following equation: \(^{30,31}\)

\[
\eta = 1 - \frac{I_S}{I_{S0}}
\]

where \(I_S\) and \(I_{S0}\) are the luminescence intensity of the sensitizer (Ce\(^{3+}\) ion in the presence and absence of the activator (Tb\(^{3+}\)), respectively. The inset of Fig. 7 displays the curve of \(\eta\) for Ce\(^{3+}\)–Tb\(^{3+}\) in LSN:0.09Ce\(^{3+}\),\(y\)Tb\(^{3+}\). As Tb\(^{3+}\) content increases, the distance between Ce\(^{3+}\) ions and Tb\(^{3+}\) ions becomes shorter, which enhances the efficient energy transfer. The optimal \(\eta\) (~71%) is obtained when \(y\) reached 0.12.

### 3.3 Energy transfer mechanism of LSN:Ce\(^{3+}\),Tb\(^{3+}\) phosphors

In order to further verify the process of energy transfer from Ce\(^{3+}\) to Tb\(^{3+}\) in LSN:Ce\(^{3+}\),\(y\)Tb\(^{3+}\), the fluorescence decay curves of
Ce$^{3+}$ were measured by monitoring at 430 nm with excitation of 360 nm. As shown in Fig. 8, the decay curve of LSN:Ce$^{3+}$ is agreeable to the single exponential rule with a lifetime of about 38.26 ns, due to single luminescent center in the host. However, the rest of decay curves deviates from the single exponential function and this phenomenon becomes more obvious with increase concentration of the Tb$^{3+}$. Therefore, the experimental curves were fitted by the sum of two exponential decays using the formula:

$$I(t) = I_0 + A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$$  \hspace{1cm} (3)

where the $I(t)$ represents the luminescence intensity at time $t$, $A_1$ and $A_2$ are constants, $\tau_1$ and $\tau_2$ are the decay times for the exponential components. The average decay time ($\tau$) were estimated to be 26.44, 25.37, 21.84, 14.74, 13.06 and 12.98 ns with function for the LSN:Ce$^{3+}$/Tb$^{3+}$ phosphors with $y = 0.02$, 0.04, 0.06, 0.08, 0.10, 0.12 and 0.14, respectively. The lifetimes of the Ce$^{3+}$ ions decreased, which is the direct evidence for energy transfer from Ce$^{3+}$ to Tb$^{3+}$. Moreover, the energy transfer efficiency from Ce$^{3+}$ to Tb$^{3+}$ was also calculated from the decay lifetime by the equation:\(^{(4)}\)

$$\eta_T = 1 - \frac{\tau_5}{\tau_{50}}$$  \hspace{1cm} (4)

where $\tau_5$ and $\tau_{50}$ are the lifetimes of Ce$^{3+}$ ions with and without the presence of Tb$^{3+}$ ions, respectively. As shown in the inset of Fig. 8, the energy transfer efficiency gradually increased and reached 65.86% for Tb$^{3+}$ concentrations at $y = 0.12$, which is closed to the above result (~71%).

Normally, the energy transfer from sensitizer to activator may take place via exchange interaction and electric multipolar interaction.\(^{(22,23)}\) The exchange interaction would take place when the critical distance ($R_c$) between the doping ions was shorter than 4 Å. Base on the eqn (1), $x_c$ is the total concentration of Ce$^{3+}$ and Tb$^{3+}$ ion. For LSN:0.09Ce$^{3+}$/0.08Tb$^{3+}$ sample, $V = 423.342 \text{ Å}^3$, $x_c = 0.17$ and $N = 4$, thus the $R_c$ is determined to be 10.6 Å. It can be inferred that there is no mechanism of exchange interaction because the value of $R_c$ (10.6 Å) is larger than 4 Å. The energy transfer occurs via multipolar interaction based on the Dexter theory:\(^{(4)}\)

$$\eta_0/\eta \propto C^{1/3}$$  \hspace{1cm} (5)

where $\eta_0$ and $\eta$ are the luminescence quantum efficiencies of the sensitizer (Ce$^{3+}$) ion in the absence and presence of the activator (Tb$^{3+}$), $C$ is the sum concentration of Ce$^{3+}$ and Tb$^{3+}$. The value of $\eta_0/\eta$ can be approximated calculated by the $I_{500}/I_5$ (relative luminescence intensity ratio). The value of $n$ is 6, 8, and 10 for dipole–dipole, dipole–quadrupole and quadrupole–quadrupole interactions, respectively. The relationships between $I_{500}/I_5$ and $C^{1/3}$ are illustrated in Fig. 9. It can be observed that the line reaches the optimal when $n = 6$ with $R^2 = 0.987$, indicating that energy transfer from Ce$^{3+}$ to Tb$^{3+}$ in the La$_2$Si$_3$N$_5$ host should mainly through the dipole–dipole interaction. The energy transfer model Ce$^{3+}$–Tb$^{3+}$ in the La$_2$Si$_3$N$_5$ is presented in Fig. S2.\(^{\dagger}\)

### 3.4 Thermal stability and chromaticity coordinates of LSN:Ce$^{3+}$/Tb$^{3+}$ phosphors

The thermal stability of phosphor is one of key parameters for practical phosphors. The temperature dependence of the luminescence for the LSN:0.09Ce$^{3+}$/0.12Tb$^{3+}$ phosphor under 360 nm excitation was investigated as a function of temperature in the range of 50–200 °C, as shown in Fig. 10. As the temperature is increased to 200 °C, the PL intensities of Ce$^{3+}$ and Tb$^{3+}$ decrease to 44% and 80% of the corresponding initial value (50 °C), which suggests that LSN:Ce$^{3+}$/Tb$^{3+}$ is a promising green phosphor for UV white LED. The shift of CIE coordinates is neglectable ($x = 0.2788$, $y = 0.4439 \rightarrow x = 0.2788$, $y = 0.4452$) due to the relative weak component of blue emission. As the essential of thermal quenching is the result of interaction between electron and lattice under varying temperatures, leading to nonradiative transitions. Since the f–f transition of Ce$^{3+}$ is more affected by crystal field environment than f–f transition of Tb$^{3+}$, thus, the reason for different degradation rate of Ce$^{3+}$ and Tb$^{3+}$ is due to different degree of interactions between transition electron and lattice.

The CIE chromaticity diagram and a series of digital photographs of LSN:0.09Ce$^{3+}$/0.12Tb$^{3+}$ phosphors upon 365 nm
UV lamp excitation are presented in Fig. 11. The values of CIE $(x, y)$ for LSN:0.09Ce$^{3+}$,0.12Tb$^{3+}$ phosphors with different doping contents are listed in Table 2. It can be found that color-tunable of LSN:0.09Ce$^{3+}$,yTb$^{3+}$ phosphors can be obtained with increasing content of Tb$^{3+}$ due to efficient Ce$^{3+}$–Tb$^{3+}$ energy transfer. The corresponding features of the chromaticity coordinates for the LSN:0.09Ce$^{3+}$,yTb$^{3+}$ phosphors could be changed from blue (0.1842, 0.0947) to green (0.2845, 0.4653) by adjusting the different emission compositions of the Ce$^{3+}$ and Tb$^{3+}$ concentration. Based on the results, it is clear that new blue-green emitting LSN:0.09Ce$^{3+}$,yTb$^{3+}$ phosphors can be efficiently excited in the UV range. It is suggesting that LSN:Ce$^{3+}$,Tb$^{3+}$ phosphor can act as a potential blue-green phosphor for WLEDs.

4. Conclusions

A series of Ce$^{3+}$/Tb$^{3+}$ co-activated LaSi$_3$N$_5$ phosphors were synthesized through high temperature solid state reaction. The obtained phosphors show a broad excitation spectral range from 280 to 400 nm, which can meet the application requirements for UV LED chips. The energy transfer from Ce$^{3+}$ to Tb$^{3+}$ in LSN host has been investigated by PL and PLE spectra, together with the contents of Tb$^{3+}$, and the decay curves of Ce$^{3+}$. The energy transfer from Ce$^{3+}$ to Tb$^{3+}$ was mainly via a dipole–dipole reaction. The critical distance of energy transfer was calculated and has also been evaluated by the concentration quenching method. By adjusting Tb$^{3+}$ doping concentration in LSN:0.09Ce$^{3+}$,0.12Tb$^{3+}$ phosphors can be tuned appropriately from blue (0.1824, 0.0947) to green (0.2845, 0.4653) and the luminescence efficiency of green emission reached the maxima at the Tb$^{3+}$ concentration of 0.12. The LaSi$_3$N$_5$:Ce$^{3+}$,Tb$^{3+}$ phosphor could be potentially used as a green emitting phosphor for WLEDs.

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