Short Communication

Luminescence properties of Li$_2$Ca$_2$ScV$_3$O$_{12}$ and Li$_2$Ca$_2$ScV$_3$O$_{12}$:Eu$^{3+}$ synthesized by solid-state reaction method

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Li$_2$Ca$_2$ScV$_3$O$_{12}$ and Eu$^{3+}$ doped Li$_2$Ca$_2$ScV$_3$O$_{12}$ have been synthesized by a high temperature solid-state reaction method. The as-prepared compounds have the garnet-type structure by the X-ray diffraction (XRD) analysis. Li$_2$Ca$_2$ScV$_3$O$_{12}$ can be self-excited by the UV light ranging from 200 to 400 nm, and it shows the broad-band greenish yellow emission originating from the Vo$^{3+}$ charge transition (CT), which contains two fitting bands with peaks at 510 nm and 569 nm, corresponding to the $^3T_2$ → $^1A_1$ and $^3T_1$ → $^1A_1$ transitions of VO$^{3+}$. Eu$^{3+}$ doped Li$_2$Ca$_2$ScV$_3$O$_{12}$ phosphor shows characteristic broad-band emission of VO$^{3+}$ and the line-type emission of Eu$^{3+}$ in the red region, which exhibits yellow emission upon the 365 nm UV light. The CIE coordinates and the lifetimes of the samples have been also investigated.

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1. Introduction

The white light-emitting diodes (w-LEDs) has been attached more attention owing to the merits of being environmentally friendly, energy-saving, high brightness, long lifetime and low cost [1–3]. As we all know, the most promising approach to realize white-light LEDs is the combination of a yellow-emitting phosphor with a blue LED chip [4]. But there are many disadvantages such as low color rendering index [5]. Apparently, much increasing attention has been paid to the exploration of new phosphors. Recently many researchers have worked at the development of self-activated phosphors representing by the vanadate compounds, such as Ba$_2$LiMgV$_3$O$_{12}$ [6], Ca$_3$Mg$_4$(VO$_4$)$_6$ [7], and (Ba, Mg, Zn)$_3$(VO$_4$)$_2$ [8], which can be effectively excited by UV radiation and exhibit broadband emission in visible light region due to the charge transition (CT) of VO$^{3+}$ group.

It was accepted that vanadate-based luminescent materials drew much attention for the self-activated emitting properties of VO$^{3+}$ group as well as the sensitization from VO$^{3+}$ to rare earth ions. Furthermore, the good chemical, thermal stability and low temperature make vanadate phosphors the promising phosphor materials [9]. Li$_2$Ca$_2$ScV$_3$O$_{12}$ was first prepared by heating Li$_2$CO$_3$, CaCO$_3$, Sc$_2$O$_3$ and NH$_4$VO$_3$ at 650 °C for 5 days [10], and luminescence properties investigation of Li$_2$Ca$_2$ScV$_3$O$_{12}$ and/or or rare earth ions doped luminescence behaviors have not been reported yet till now. In this paper, high-purity powder samples of Li$_2$Ca$_2$ScV$_3$O$_{12}$ and Eu$^{3+}$ doped Li$_2$Ca$_2$ScV$_3$O$_{12}$ have been synthesized via a conventional solid-state reaction method. The phase structure, photoluminescence excitation (PLE) and emission (PL) properties, luminescence decay and CIE coordinates were discussed in detail, which can be considered as green-emitting or yellow-emitting phosphor in w-LEDs.

2. Experimental

Li$_2$Ca$_2$ScV$_3$O$_{12}$ and Li$_2$Ca$_2$ScV$_3$O$_{12}$:Eu$^{3+}$ phosphors were synthesized by a conventional solid-state reaction. The starting materials were CaCO$_3$ (A.R.), Li$_2$CO$_3$ (A.R.), Sc$_2$O$_3$ (A.R.), NH$_4$VO$_3$ (A.R.), and Eu$_2$O$_3$ (99.99%). Firstly, the starting materials were thoroughly mixed in an agate mortar according to the given stoichiometric amounts. Then, the mixture was put into an alumina crucible and calcined in a muffle furnace at 850 °C for 5 h in air. After the samples were cooled to room temperature, the phosphors were finally obtained.

The phase structures of the as-prepared phosphors were performed by X-ray powder diffraction (XRD-6000, SHIMADZU, Japan) operating with Cu Kzr radiation at 40 kV, 30 mA. Room temperature excitation and emission spectra were recorded by a fluorescence spectrophotometer (F-4600, HITACHI, Japan) with a photomultiplier tube operating at 400 V, and a 150-W xenon lamp used as the excitation lamp. The temperature-dependence luminescence properties were indentified using the same F-4600 spectrophotometer in combination with a self-made computer-controlled furnace. The decay curves were recorded on a spectrofluorimeter (HORIBA, JOBIN YVON FL3-21), and the 370 nm pulse laser radiation (nano-LED) was used as the excitation source. The quantum efficiency values were measured by a C9920-02 model absolute photoluminescence quantum yield measurement system (Hamamatsu-Photonics).
3. Results and discussions

Fig. 1 shows the XRD patterns of as-prepared Li$_2$Ca$_2$ScV$_3$O$_{12}$ and Eu$^{3+}$ doped Li$_2$Ca$_2$ScV$_3$O$_{12}$ phase. The result shows that all diffraction peaks of the as-prepared samples can match well with JCPDS card No. 29-800 of Li$_2$Ca$_2$ScV$_3$O$_{12}$ compound, indicating that the obtained samples have a single-phase cubic garnet-type structure. It is also clear that the doping Eu$^{3+}$ ions did not affect the phase structure of the host matrix. In garnet-type Li$_2$Ca$_2$ScV$_3$O$_{12}$, Ca$^{2+}$, Li$^{+}$, Sc$^{3+}$ and V$^{5+}$ metal ions are surrounded by quantitative oxygen. Ca$^{2+}$/Li$^{+}$ ions are randomly located in eightfold dodecahedral [Ca/LiO$_6$] sites with different occupancies of 1/3 and 2/3, respectively. The Sc$^{3+}$ and Li$^{+}$ ions are in sixfold octahedral [Sc/LiO$_6$] sites. The ion V$^{5+}$ absolutely occupies the fourfold [VO$_4$]Td site. The introduction of a Eu$^{3+}$ ion is completely incorporated into the host lattice by substituting for Ca$^{2+}$ sites located in eightfold dodecahedral sites [6].

The room temperature excitation and emission spectra of Li$_2$Ca$_2$ScV$_3$O$_{12}$ and Li$_2$Ca$_2$ScV$_3$O$_{12}$:0.15Eu$^{3+}$ phosphors are given in Fig. 2. Upon the monitoring wavelength at 528 nm, Li$_2$Ca$_2$ScV$_3$O$_{12}$ shows a broad excitation band covering from 200 to 400 nm with two peaks at 270 and 340 nm corresponding to the $^1A_1 ightarrow ^1T_2$ and $^1A_1 ightarrow ^1T_1$ transition of VO$^{4+}$ group, as given in Fig. 2b [11]. This spectral profile also indicates that the phosphor can be matched well with the UV-LED chips. The emission spectrum of Li$_2$Ca$_2$ScV$_3$O$_{12}$:0.15Eu$^{3+}$ sample shows a broad green emission band with peak at 528 nm corresponding to the typical emission of VO$^{4+}$ ions. It is well-known that the emissions of vanadium garnet arise from the charge transfer transition in the [VO$_4$] tetrahedra. The emission spectrum can be further fitted by two Gaussian components that peaked at Em$_1$ (510 nm) and Em$_2$ (569 nm). The energy gap between the two peaks is 0.26 eV, which is ascribed to the energy separation between $^3T_1$ and $^3T_2$, as reported in many Refs. [6,11,12]. Fig. 2a shows the typical excitation (PLE; $\lambda_{em}$ = 528 and 609 nm) and emission (PL; $\lambda_{ex}$ = 272, 365 and 393 nm) spectra of Li$_2$Ca$_2$ScV$_3$O$_{12}$:0.15Eu$^{3+}$ phosphors. The excitation spectrum ($\lambda_{em}$ = 528) consist of a strong wide hump peaking at about 270 and 360 nm, which belongs to the transitions of the ground state $^1A_1$ to the excited states $^1T_2$ and $^1T_1$ levels of VO$^{4+}$. The PLE spectrum upon 609 nm emission (characteristic transition of Eu$^{3+}$) for Li$_2$Ca$_2$ScV$_3$O$_{12}$:0.15Eu$^{3+}$ phosphor also exhibit a broad excitation band with two peaks centered at around 272 and 319 nm, which is similar as the excitation band of VO$^{4+}$ at 528 nm. Such a phenomenon verified that there is the possible energy transfer from VO$^{4+}$ to Eu$^{3+}$, so that we can find the excitation band of VO$^{4+}$ by monitoring the Eu$^{3+}$ emission. Except for this, we can also find
the characteristic f–f transition of Eu$^{3+}$ at about 393 nm in the excitation spectrum. Fig. 2a also shows the emission spectra excited by different wavelengths of 272, 365 and 393 nm, and there are all similar spectral profile containing the broad emission band and some sharp emission lines attributed to \( ^5D_0 \rightarrow ^7F_J \) (\( J = 1, 2, 3, 4 \)) transitions of the doped Eu$^{3+}$ ions [12]. As shown in Fig. 2a, the most intense emission line of Eu$^{3+}$ peaks at 613 nm is due to \( ^5D_0 \rightarrow ^7F_2 \) forced electric transition of Eu$^{3+}$, suggesting that it occupied a non-centrosymmetric site (Ca$^{2+}$ site) in Li$_2$Ca$_2$ScV$_3$O$_12$ host. Especially, the emission intensities from Eu$^{3+}$ is obviously larger than that of the emission from VO$_4^{3-}$/CO$_4^{3-}$ ions, so that we can observe the yellow emission color compared to the green color of Li$_2$Ca$_2$ScV$_3$O$_12$ under a 365 nm UV lamp.

Fig. 3 exhibits the fluorescence decay of the various emission centers for Li$_2$Ca$_2$ScV$_3$O$_12$ and Eu$^{3+}$ doped Li$_2$Ca$_2$ScV$_3$O$_12$ samples under a 370 nm laser excitation source. It can be seen that all the decay curves are well fitted based on the second order exponential equation [13]:

\[
I(t) = I_0 + A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)
\]

Here \( I \) and \( I_0 \) are the luminescence intensity at time \( t \) and initially, respectively. And \( \tau_1 \) and \( \tau_2 \) are the lifetimes for the exponential components, respectively. \( A_1 \) and \( A_2 \) are constants. In addition, the average lifetime constant (\( \tau' \)) can be calculated as follows [14]:

\[
\tau' = (A_1 \tau_1^2 + A_2 \tau_2^2) / (A_1 \tau_1 + A_2 \tau_2)
\]

Fig. 4. PL spectra (\( \lambda_{ex} = 365 \) nm) of Li$_2$Ca$_2$ScV$_3$O$_12$ (a), and Li$_2$Ca$_2$ScV$_3$O$_12$:Eu$^{3+}$ (b) phosphors under different temperatures in the range of 25–300°C. Integrated intensity as a function of increasing temperature is also given in (c and d).

Fig. 5. CIE chromaticity diagram shows the color coordinates for Li$_2$Ca$_2$ScV$_3$O$_12$ and Li$_2$Ca$_2$ScV$_3$O$_12$:0.10Eu$^{3+}$ phosphors (point a and b) and their corresponding digital photos upon the 365 nm UV lamp. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
On the basis of Eq. 2, the lifetime at 510 and 569 nm in Li$_2$CaScV$_3$O$_{12}$ is determined to be 1.22 ms and 1.20 ms, respectively. Considering that the two emission centers (510 and 569 nm) are corresponding to the transitions of $^3T_2 \rightarrow ^1A_1$ and $^3T_1 \rightarrow ^1A_1$, we can find little lifetime difference between them which means the similar environment and transition probability of the $^3T_2$ and $^3T_1$ level. Similarly, for the Li$_2$CaScV$_3$O$_{12}$:0.15Eu$^{3+}$ phosphors, the lifetime at 510 and 569 nm is calculated as 1.28 ms and 1.23 ms, respectively, and the lifetime of $^3D_0 \rightarrow ^3F_2$ transition at 609 nm for Eu$^{3+}$ is 0.88 ms.

Generally, in the working process of w-LEDs, the temperature of LED chip increases up to about 150 °C, therefore the thermal stability of phosphor is an important consideration for the application of phosphors in w-LEDs. Temperature dependent emission spectra for Li$_2$CaScV$_3$O$_{12}$ and the selected Li$_2$CaScV$_3$O$_{12}$:Eu$^{3+}$ under excitation at 365 nm were investigated and shown in Fig. 4. Both the VO$_4$ emission lines and the Eu$^{3+}$ emission lines can be found from the PL spectra, and the emission intensity decreases significantly with increasing temperature. Fig. 4c presents the variation of temperature-dependent emission intensity of VO$_4$ emission under 365 nm excitation. At 150 °C, VO$_4$ emission intensity of Ca$_2$NaZn$_2$V$_4$O$_{12}$ decreased by 14.3% of the initial value. The emission spectra have not obvious shift with variable temperature. Meanwhile, the characteristic of VO$_4$ and Eu$^{3+}$ emission intensity of Ca$_2$NaZn$_2$V$_4$O$_{12}$:Eu$^{3+}$ decreased by 12.1% and 74.8% of the initial PL intensity at 150 °C, respectively, as shown in Fig. 4d. From the above results, the present phosphors have not good thermal stability, and some modified work will be done in the future. Furthermore, the quantum efficiency (QE) values of the selected Ca$_2$NaZn$_2$V$_4$O$_{12}$ and Ca$_2$NaZn$_2$V$_4$O$_{12}$:Eu$^{3+}$ phosphors have been measured and determined as 5.5% and 6.8%, respectively, under 365 nm excitation. As a kind of rare earth free self-activated phosphors, the present phosphors show the competitive QE values in the potential practical applications.

Fig. 5 displays a summary graphic of the CIE 1931 chromaticity of Li$_2$CaScV$_3$O$_{12}$ and Li$_2$CaScV$_3$O$_{12}$:0.15Eu$^{3+}$ phosphors under 365 nm excitation. It can be seen that the (x, y) chromaticity coordinate of Li$_2$CaScV$_3$O$_{12}$ is (0.3049, 0.4484) in the green region. However, Eu$^{3+}$ doped Li$_2$CaScV$_3$O$_{12}$ exhibits CIE coordinates of (0.3643, 0.4372), which is shifted from green to yellow region. The corresponding digital photos of the phosphors upon a 365 nm UV lamp have also been given in Fig. 5. The above obtained results indicated that garnet-type vanadate representing by Li$_2$CaScV$_3$O$_{12}$ has favorable potential for the application in WLEDs.

4. Conclusions

Pure-phase Li$_2$CaScV$_3$O$_{12}$ and Eu$^{3+}$-doped Li$_2$CaScV$_3$O$_{12}$ phosphors have been obtained via solid-state reaction. The structure was analyzed by the XRD and the corresponding crystal structure analysis. The self-activated green emission can be obtained for Li$_2$CaScV$_3$O$_{12}$, which have broad emission band with peak at 528 nm corresponding to the typical emission of VO$_4$$^{3-}$ ions. The emission band of Li$_2$CaScV$_3$O$_{12}$:0.15Eu$^{3+}$ contains a decreasing broad green-emitting band and the strong and sharp f–f transitions of Eu$^{3+}$, which shows yellow emission upon the 365 nm UV excitation. The fluorescence decay of different emission centers and color coordinates of the Li$_2$CaScV$_3$O$_{12}$ and Eu$^{3+}$-doped Li$_2$CaScV$_3$O$_{12}$ phosphors have also been presented. The results indicate that garnet-type vanadate compounds may be potential in developing the color-tunable phosphors for w-LEDs.

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References