Optical Materials 36 (2014) 1649–1654

Contents lists available at ScienceDirect

Optical Materials

journal homepage: www.elsevier.com/locate/optmat

Two-color emitting of Eu^{2+} and Tb^{3+} co-doped $Sr_2MgSi_2O_7$ for UV LEDs

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ARTICLE INFO

Article history:
Received 29 November 2013
Accepted 13 December 2013
Available online 10 January 2014

Keywords:
Europium
Terbium
$Sr_2MgSi_2O_7$
Energy transfer
Light-emitting diode (LED)

ABSTRACT

An intense bluish green phosphor, $Sr_2MgSi_2O_7$: Eu^{2+}, Tb^{3+}, was synthesized by high temperature solid-state reaction. The photoluminescence excitation and emission spectra, the lifetime, concentration effect and the temperature-dependent properties are investigated in detail. The results show that an efficient nonradiative energy transfer from Eu^{2+} to Tb^{3+} occurs. Tb^{3+} ions give an intense green emitting light by a strong excitation band of Eu^{2+} ions at 350–430 nm, matching well with the dominant emission band of (n)-UV (350∼420 nm) LEDs. These results demonstrate that Tb^{3+} ion with low 4f–4f absorption efficiency in (n)-UV region can play a role of activator in narrow green emitting phosphor potentially useful in (n)-UV GaN-based LED through efficient energy feeding by allowed 4f–5d absorption of Eu^{2+} with high oscillator strength.

1. Introduction

Nowadays, phosphor-converted (pc-) white LEDs are attracting significant attention [1–3]. They can be classified into two approaches: blue (440∼470 nm) InGaN and near (n)-UV (350∼420 nm) GaN chip combined with phosphors. For the blue InGaN chip, the commonly used phosphor is yellow YAG:Ce^{3+}. However, such white LEDs encounter low color-rendering index (Ra < 80) due to the scarcity of red emission. Besides, the white LED based on blue InGaN chip encounter low color reproducibility on mass manufacturing scale [4]. The n-UV pc-LEDs are expected to have great potential application in the field of solid-state lighting due to excellent color-rending index, high color tolerance, high conversion efficiency into visible light [5].

As an efficient activator in phosphors for (n)-UV LEDs, Eu^{2+} ion has been widely investigated because it usually has a strong excitation band covering the emissions from (n)-UV LEDs, and an intense emission band, due to the allowed inter-configurational 5d–4f transitions with high oscillator strength [1–7]. In general, the 5d → 4f emissions of Eu^{2+} can vary from long-wavelength ultraviolet to red light due to its strong dependence on the host composition, crystal structure, the lattice symmetry and so on [8–11]. Also, its emission peak can easily shift and its full width at half maximum (FWHM) can be broader if electron–phonon interaction is stronger [12]. However, to some extent, such a strong host dependence of Eu^{2+} with 5d orbital leads to its poor reproduction quality of optical properties of phosphor especially in the process of mass production and in fabrication of power pc-LEDs with high junction temperature.

Comparatively, the sharp 4f–4f emission peak and its FWHM, for example Tb^{3+} ions, are almost not dependent on the host lattice since the 4f orbital lies inside and is strongly shielded from the outmost filled $5s^2$ and $5p^6$ orbitals. Therefore, it is expected from the viewpoint of emission properties that the sharp 4f–4f emission from Tb^{3+} would be ideal activator for phosphor with excellent reproduction quality of optical properties. Unfortunately, Tb^{3+} ion only has weak absorption peaks at about 300–380 nm and 480 nm, due to the $^7F_6 \rightarrow {}^5D_{4,3}$ transitions, because the 4f–4f absorption transitions are forbidden by the parity selection rule. Furthermore, its FWHM is much narrower and not tolerant to the tiny emission wavelength shift of UV LED chips. From the viewpoint of the absorption properties, these optical parameters make it not perfect as activator. But if one combine the strong 4f–5d broad absorption band of Eu^{2+} and the 4f–4f sharp line emission of Tb^{3+} to form a donor–acceptor pair, the co-doped phosphors would possibly overcome all the drawbacks mentioned above.

Eu^{2+} activated silicates have been intensively studied due to high chemical stability and various crystal structures. He et al. [13] have reported the luminescence properties of $M_2MgSi_2O_7$: Eu^{2+} (M = Ca, Sr, Ba) in 2007. They exhibited strong absorption in long UV band (370–420 nm), which match well with the (n)-UV GaN chip. Zhang et al. [14] have synthesized $M_2MgSi_2O_7$: Eu^{2+} (M = Ca, Sr) phosphors and fabricated intense yellowish-green (Ca) and blue LEDs (Sr) by combining the as-synthesized phosphors with (n)-UV Ga(In)N chips, respectively. Additionally, $M_2MgSi_2O_7$: Eu^{2+} (M = Ca, Sr) compounds had been investigated as the host materials of long lasting phosphors by co-doping with

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http://dx.doi.org/10.1016/j.optmat.2013.12.026

trivalent rare earth ions in the past decade [15]. But few researchers have focused on their applications in the field of white LEDs.

In this paper, an intense bluish green phosphor, $Sr_2MgSi_2O_7$: Eu^{2+}, Tb^{3+} (SMSO: Eu^{2+}, Tb^{3+}) is synthesized by high temperature solid-state reaction. The efficient energy transfer from Eu^{2+} to Tb^{3+} in SMSO occurs and was systematically investigated by the photoluminescence excitation and emission spectra, the lifetime, concentration effect and the temperature-dependent properties. It suggests that SMSO: Eu^{2+}, Tb^{3+} could be used as a potential candidate in (n)-UV LEDs.

2. Experimental

2.1. Syntheses

Eu^{2+} or Tb^{3+} singly doped and Eu^{2+}–Tb^{3+} co-activated phosphors were prepared by a conventional solid-state reaction technique. The starting materials, $SrCO_3$ (A.R.), Na_2CO_3 (A.R.), MgO (A.R.), SiO_2 (A.R.), Eu_2O_3 (99.99%) and Tb_4O_7 (99.99%) were weighed in stoichiometric amounts. Subsequently the powder mixture was thoroughly mixed in an agate mortar by grinding and was transferred into crucibles. Finally, they were pre-calcined at 600 °C for 2 h in air and sintered at 1250 °C for 6 h under N_2/H_2 atmosphere.

2.2. Measurements

The phase purity of the prepared phosphors was investigated by a Brueckner D8 advance X-ray Diffractometer (XRD) with Cu Kα radiation ($\lambda = 1.542$ Å) at 40 kV and 40 mA. The XRD patterns were collected in range of $15° \leqslant 2\theta \leqslant 46°$.

The room temperature photoluminescence (PL), photoluminescence excitation (PLE) spectra, the decay curves and temperature-dependent photoluminescence spectra in the range of 23–300 K were measured by FSP920 Time Resolved and Steady State Fluorescence Spectrometers (Edinburgh Instruments) equipped with a 450 W Xe lamp, TM300 excitation monochromator and double TM300 emission monochromators and Red PMT in cooled housing. The spectral resolution is about 0.05 nm in UV–VIS.

3. Results and discussion

3.1. Phase characterization

The XRD patterns of SMSO : Eu_x^{2+}, Tb_y^{3+}, Na_y^{+} ($x = 0.03$, $y = 0$, 0.20, 0.25, 0.30, 0.35, 0.40; $x = 0$, $y = 0.02$) are shown in Fig. 1. The results indicate that all the peaks of rare earth ion doped SMSO can be indexed to a pure SMSO (JCPDS 15-0016). The dopants have no obvious influence on the crystalline structure of the host. Considering the effect of ionic sizes of the cations, Eu^{2+} and Tb^{3+} are expected to preferably occupy Sr^{2+} since the ionic radii of Eu^{2+} (1.09 Å) and Tb^{3+} (1.04 Å) are close to that of Sr^{2+}(1.12 Å) [16].

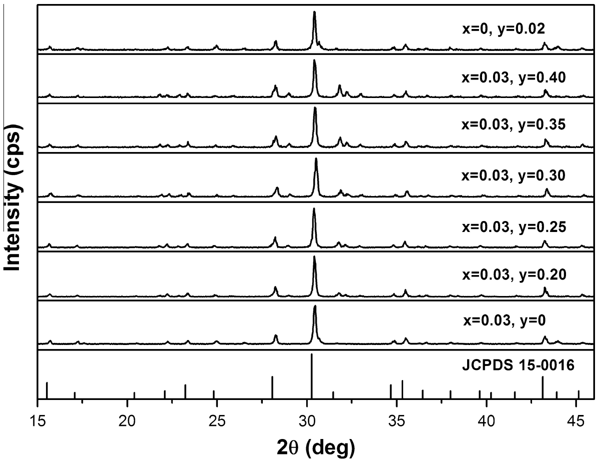

Fig. 1. Powder XRD patterns of SMSO: Eu_x^{2+}, Tb_y^{3+}, Na_y^{+} ($x = 0.03$, $y = 0$, 0.20, 0.25, 0.30, 0.35, 0.40; $x = 0$, $y = 0.02$).

3.2. Luminescence properties of SMSO

The PLE and PL spectra of SMSO: Eu^{2+}/Tb^{3+} are showed in Fig. 2. For SMSO: $Tb_{0.02}^{3+}$, $Na_{0.02}^{+}$, the emission spectrum under the excitation at 378 nm shows the characteristic optical transitions of Tb^{3+} ion at about 486 nm, 540 nm, 585 nm, 619 nm, due to $^5D_4 \rightarrow {}^7F_J$ (J = 6, 5, 4, 3). The weak $^5D_3 \rightarrow {}^7F_J$ (J = 5, 4) emissions of Tb^{3+} at 412 nm and 432 nm, respectively, are also observed in SMSO : $Tb_{0.02}^{3+}$, $Na_{0.02}^{+}$ which may be due to the lower vibration frequency υ_{max} of phonon in this host [17]. Monitoring the emission at 540 nm, the PLE spectrum consists of an intense band at 245 nm, assigned to the allowed 4f → 5d transition of Tb^{3+}, and many weak sharp peaks in the wavelength range of 310–500 nm, due to the forbidden 4f → 4f transitions of Tb^{3+} ions. Though there are some absorption bands between 300 nm and 380 nm, these optical absorption transitions are very week since they are strongly forbidden by the parity selection rule. So it is very difficult to absorb the emitting lights of n-UV LED chips. Moreover, there is no any absorption band between 385 nm and 475 nm, suggesting that Tb^{3+} singly doped sample cannot be efficiently excited by UV/blue LED chip.

The PLE spectrum of SMSO : $Eu_{0.03}^{2+}$ contains an intense broad band at 250–450 nm, as shown in Fig. 2 (b), which can be attributed to 4f → 5d allowed transitions of Eu^{2+} ions in the host [14]. The intense broad excitation band at 250–450 nm suggests that this phosphor can be effectively excited by UV LED chip. The blue emission band peaked at 471 nm is assigned to the typical 5d → 4f transition of Eu^{2+} ion. It overlaps with some excited levels of Tb^{3+}, as shown in Fig. 2. Therefore, it is expected that energy transfer between Eu^{2+} and Tb^{3+} would occur [18,19].

Fig. 3 shows PL and PLE spectra of Eu^{2+}–Tb^{3+} co-activated SMSO phosphor and the PL spectra of Tb^{3+} singly doped SMSO phosphor. Under 400 nm excitation, intense green emission peaks as well as one broad blue emission band are observed in Eu^{2+}–Tb^{3+} codoped SMSO phosphor. The former is attributed to 4f → 4f transitions of Tb^{3+} ions and the latter is due to 5d → 4f allowed transitions of Eu^{2+} ions. For comparison, Fig. 3 also gives the PL spectra of Tb^{3+} singly doped SMSO phosphor. It is obviously seen that the green emission intensity of Tb^{3+} in the codoped phosphor (curve 2) is about 11 times as intense as that of Tb^{3+} in singly doped phosphor (curve 1) under 400 nm excitation. As shown in the inset of Fig. 3, the PLE of SMSO : $Eu_{0.03}^{2+}$, $Tb_{0.02}^{3+}$, $Na_{0.02}^{+}$ contains one broad band centered at 368 nm when the green emission of Tb^{3+} at 540 nm is monitored. Compared with the PLE spectra of singly doped Eu^{2+} in SMSO phosphors (as shown in Fig. 2), the broad band is attributed to 4f → 5d allowed transitions of Eu^{2+} ions. The appearance of 4f → 5d absorption transitions of Eu^{2+} ions in the PLE spectrum ($\lambda_{em} = 540$ nm) and of 4f → 4f emission transitions of Tb^{3+} ions in the PL spectrum ($\lambda_{ex} = 400$ nm) of SMSO : $Eu_{0.03}^{2+}$, $Tb_{0.02}^{3+}$, $Na_{0.02}^{+}$ suggest that the efficient energy transfer from Eu^{2+} to Tb^{3+} occurs. It is therefore expected that Tb^{3+} ions can serve as potential activator of green-emitting phosphor that can be directly excited by 350–420 nm emission of UV LED, by energy feeding of Eu^{2+} ions.

3.3. The energy transfer from Eu^{2+} to Tb^{3+}

The spectral overlap between the broad band emission of Eu^{2+} and the excitation peak of Tb^{3+} at 484 nm (shown in Fig. 2) indicates that the energy transfer from Eu^{2+} to Tb^{3+} is probably the radiative or non-radiative energy transfer [19,20]. In order to