Intense hypersensitive luminescence of Eu^{3+}-doped $YSiO_2N$ oxynitride with near-UV excitation

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ABSTRACT

Nowadays highly efficient red phosphors with blue or near-UV excitation are strongly required to improve performance of existing white LEDs. With this aim in view, the Eu^{3+}-doped $YSiO_2N$ ceramics with the pseudo-wollastonite structure was fabricated and thoroughly studied spectroscopically. The presence of two anions – O^{2-} and N^{3-} – around Eu^{3+} ions causes a shift of the host valence band (VB) to lower energy and a certain asymmetry of the impurity sites. After illumination by near-UV excitation light (280–360 nm), the $YSiO_2N:Eu^{3+}$ sample exhibited strong red luminescence at around 620 nm assigned to the hypersensitive $^5D_0 \rightarrow {}^7F_2$ transition of the Eu^{3+} ions. Compared with three Eu^{3+}-doped oxides (α-$CaSiO_3:Eu^{3+}$ which has the same pseudo-wollastonite structure, and α- and y-$Y_2Si_2O_7:Eu^{3+}$ which have the same cation composition), the charge transfer (CT) band was red-shifted by more than $9.5 \times 10^3\,cm^{-1}$ because the VB top increases. From the Judd-Ofelt analysis, it was found out that the $YSiO_2N:Eu^{3+}$ sample has the large Judd-Ofelt intensity parameter, Ω_2, which is correlated with the dopant's site asymmetry. As expected, the mixed-anion coordination which consists of oxide and nitride anions resulted in the strong hypersensitive transition at 620 nm, which is characteristic Eu^{3+} red luminescence at the lower symmetry site. In addition, the fluorescence lifetime of the Eu^{3+} luminescence at 0 K (τ_0) was estimated experimentally to be 0.664 ms, which was shorter than the radiative lifetime (τ_R), 1.32 ms, based on the Judd-Ofelt analysis. The experimental quantum yield measured with an integrating sphere, 32.3%, was lower than the internal quantum efficiency, 50.3%, evaluated from the ratio of τ_0/τ_R. The proposed material can be suitable for applications as a red phosphor.

1. Introduction

As an eco-friendly light source of the next generation of lighting devices, white light emitting diodes (w-LEDs) are getting more and more popular, because of many factors, such as lower energy consumption, longer lifetime, and higher luminescent efficiency [1,2]. The common commercial w-LEDs consist of an InGaN blue LED chip and a yellow phosphor, $Y_3Al_5O_{12}:Ce^{3+}$ [2–4]. In this case, the white light is obtained by combining the transmitted blue light and the yellow light converted by the phosphor. However, this type of w-LEDs shows a weak emission intensity in the red spectral region, with the result of a low color rendering index (CRI) and a high correlated color temperature (CCT) [5,6]. To overcome this drawback by increasing CRI and lowering CCT, many phosphors which supply red luminescence with blue or near-UV excitation light have been developed in recent years [7]. For instance, nitrides activated by divalent europium, Eu^{2+}, such as $CaAlSiN_3:Eu^{2+}$ ($CASN:Eu^{2+}$) [8] and $Sr_2Si_5N_8:Eu^{2+}$ [9], are famous commercialized red phosphors for improving CRI and CCT of w-LEDs.

These phosphors have a broad emission band attributed to the Eu^{2+} $5d \rightarrow 4f$ parity allowed transition from yellow to deep-red light, because the $5d$ energy level is shifted to lower energy due to the nephelauxetic effect of nitrogen with higher covalency. Since $CASN:Eu^{2+}$ exhibits broad emission from 600 nm to 750 nm peaking at 660 nm (which can be excited by blue light), it can be a suitable phosphor for w-LEDs with high CRI. However, because of the big mismatch between the sensitivity curve of photopic vision and the luminescence spectrum of $CASN:Eu^{2+}$, the luminous efficacy in the w-LED system using the $CASN:Eu^{2+}$ phosphor is not so high. In this respect, the phosphors with narrow emission band at around 620 nm are more suitable, since in this case overlap with the human eye sensitivity curve is enhanced, thus leading to the increased efficacy.

In this work, the trivalent europium, Eu^{3+}, is used as the luminescent activator. Usually, Eu^{3+} ions show the characteristic luminescence with narrow bands in the red spectral region (590–640 nm), attributed to the $4f$-$4f$ parity forbidden transitions. However, conventional Eu^{3+}-doped oxide phosphors have an intense excitation band only in the

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deep-UV (~ 250 nm) region [9,10], where very few commercialized LEDs with high power and efficiency are yet available. As this excitation band depends on the energy of the VB top [12], red phosphors activated by Eu^{3+} for w-LED applications require the upward energy shift of the VB. In oxides, the VB is mainly formed by the O $2p$ orbitals, and many oxide compounds have a similar VB top energy. On the other hand, in oxynitrides, the VB consists of both O $2p$ and N $2p$ orbitals, and the VB top is dominated by the N $2p$ states, because the electronegativity of nitrogen is smaller than that of oxygen. As a result, the VB top of oxynitrides is located higher than that of oxides [13]. Hence, it is expected that, in oxynitrides, the Eu^{3+} red luminescence can be obtained with lower excitation energy. Moreover, in some cases of the Eu^{3+}-doped oxynitrides, enhancement of red luminescence intensity can be anticipated. Red phosphors activated by Eu^{3+} show several characteristic narrow bands assigned to the $^5D_0 \rightarrow {}^7F_{2,4,6}$ electric dipole (ED) transitions, whose transition probability largely depends on the local environment around Eu^{3+} [14,15]. In some oxynitrides, Eu^{3+} is coordinated not only by oxide anions but also nitride anions, and the local environment with such a mixed-anion coordination affects the Eu^{3+} luminescence.

In this paper, we report the photoluminescent properties of the Eu^{3+}-doped yttrium silicon oxynitride, $YSiO_2N$, with the pseudo-wollastonite structure [16]. This compound was chosen because of anticipated upward energy shift of the VB top, on one hand, and low symmetry local structure around Eu^{3+} ions due to the mixed-anion coordination, on the other hand. To evaluate the mixed-anion effect, three Eu^{3+}-doped oxides, α-$CaSiO_3$:Eu^{3+}, α-$Y_2Si_2O_7$:Eu^{3+}, and y-$Y_2Si_2O_7$:Eu^{3+}, were also prepared with the aim of comparing their luminescent properties with the selected oxynitride. These oxides were chosen because of their structural and compositional features strongly related with those of $YSiO_2N$: α-$CaSiO_3$ is isostructural with $YSiO_2N$ [15]; α-$Y_2Si_2O_7$ has the same cation composition and coordination number of Y^{3+} sites (8-fold) [17–19]; y-$Y_2Si_2O_7$ has the same cation composition but different coordination number of Y^{3+} sites (6-fold) [17,18]. The photoluminescence spectra were analyzed based on the Judd-Ofelt theory [20–22], which allows for quantitative estimations of the radiative transition probabilities of the lanthanide ions emission transitions. Since the Judd-Ofelt intensity parameters, Ω_2, is strongly correlated with the site asymmetry around lanthanides [13,23,24], comparative analysis of these Ω_2 parameters in all prepared samples was performed to discuss the mixed-anion effect on the Eu^{3+} $4f$-$4f$ red luminescence.

2. Experimental procedure

2.1. Synthesis

Eu^{3+}-doped and non-doped yttrium silicon oxynitride samples with the compositions of $Y_{0.99}SiO_2N$:$Eu_{0.01}^{3+}$ and $YSiO_2N$ were fabricated by the solid-state reaction method. The starting materials, Y_2O_3(99.99%), SiO_2(99.9%), Si_3N_4(99.9%), and Eu_2O_3(99.99%), were weighed in the glove box filled by high-purity argon gas and mixed homogeneously by ball milling with ethanol for an hour. The mixed powder was dried at 100 °C for 24 h. After the mixture was pressed into a pellet, the pellet was covered with BN pellets and laid in an alumina crucible. This crucible was put into another larger alumina crucible with carbon powder, and then the sample pellet was sintered at 1600 °C for 24 h under nitrogen gas flow. Upon cooling to room temperature, the as-made Eu^{3+}-doped sample was annealed at 700 °C for 24 h under nitrogen gas flow. In addition, to compare the photoluminescence properties, three Eu^{3+}-doped oxide phosphors, α-$CaSiO_3$:Eu^{3+}, α-$Y_2Si_2O_7$:Eu^{3+}, and y-$Y_2Si_2O_7$:Eu^{3+}, were prepared by the solid-state reaction method with rapid cooling (1250 °C, 6 h, in air), by the sol-gel method (1100 °C, 6 h, in air) [16], and by annealing the $YSiO_2N$:Eu^{3+} sample in air atmosphere (1000 °C, 24 h), respectively.

2.2. Characterization

X-ray diffraction (XRD) measurements were carried out with a diffractometer (XRD-6000, Shimadzu) with Cu K_α radiation. Thermogravimetry (TG) and differential thermal analysis (DTA) of the non-doped $YSiO_2N$ sample was performed with a TG-DTA analyzer (TG8120, Rigaku). The sample and the reference compound, α-Al_2O_3, were weighed in the platinum pan and heated up to 1000 °C at a rate of 10 K/min. Diffuse reflectance spectra of samples were measured by a spectrophotometer (UV-3600, Shimadzu) equipped with an integrating sphere. Photoluminescence (PL) and photoluminescence excitation (PLE) spectra of all Eu^{3+}-doped samples were measured by using two monochromators (SP-2300i and SP-300i, Acton), a PMT detector (R11041, Hamamatsu Photonics), and a xenon lamp (R300-3 J, Eagle Engineering Aerospace). To observe the PL and PLE at low temperature (~ 90 K), the spectra were measured with a temperature-controlled stage (10035 L, Linkam). For the fluorescence lifetime measurement, a fluorescence lifetime spectrometer (Quantaurus-Tau-C11367, Hamamatsu Photonics) was used. To estimate the PL quantum yield (QY), a Si CCD spectrometer (USB-2000+, Ocean Optics), a 10 inches integrating sphere (LMS-100, Labsphere), and a 325 nm He-Cd laser (IK3452R-F, Kimmon Koha) were used. All the spectra were calibrated with a standard halogen lamp (CSFS-600, Labsphere).

2.3. Judd-Ofelt analysis

In the framework of the Judd-Ofelt theory, the spontaneous emission rate of lanthanide ions for the ED transition (A_R^{ED}) and the magnetic dipole (MD) transition (A_R^{MD}) from initial states $|(S', L')J' >$ to final states $|(S, L)J >$ is described by Eqs. (1) and (2), respectively [13,22,23]:

$$A_R^{ED}[(S'L')J'; (SL)J]$$
$$= \frac{64\pi^4 e^2 \nu^3}{3h(2J'+1)}\left(\frac{n(n^2+2)^2}{9}\right)\sum_{t=2,4,6}\Omega_t |\langle (S', L')J'\|U^t\|(S, L)J\rangle|^2$$

(1)

$$A_R^{MD}[(S'L')J'; (SL)J] = \frac{64\pi^4 n^3 \nu^3}{3h(2J'+1)}S_{MD}$$

(2)

where e is the charge of electron ($= 4.803 \times 10^{10}$ esu), ν is the centroid frequency of the transition, h is the Planck constant ($= 6.626 \times 10^{-27}$ erg/s), n is the refractive index of the host material, Ω_t ($t = 2$, 4, and 6) are the Judd-Ofelt intensity parameters, which are sensitive to the local environment of lanthanide ions, and $|\langle (S', L')J'\|U^t\|(S, L)J\rangle|^2$ terms are the doubly reduced matrix elements (RMEs) of the unit tensor operators, U^t, which are almost constant in all compounds. The value of S_{MD}, the line strength of the MD transition, is constant because the MD transition probability does not change largely in any host material. In the case of the Eu^{3+} $4f$-$4f$ emission S_{MD} was calculated to be 9.6×10^{-46} esu^2 cm^2 [26]. If Eu^{3+} ions are the luminescence center, the Judd-Ofelt intensity parameters, Ω_2 and Ω_4, can be calculated easily from the PL spectrum by using these two equations and the following equation, Eq. (3) [23]:

$$\frac{A_R(^5D_0 \rightarrow {}^7F_{2,4})}{A_R(^5D_0 \rightarrow {}^7F_1)} = \frac{I_{area}(^5D_0 \rightarrow {}^7F_{2,4})}{I_{area}(^5D_0 \rightarrow {}^7F_1)}$$

(3)

where I_{area} is the area under the corresponding peak in the PL spectrum, whose vertical axis is proportional to the photon flux. By using Eq. (1)–(3), not only the Judd-Ofelt intensity parameters, Ω_2 and Ω_4, but also the spontaneous emission rates, A_R (^7F_J) ($J = 1$, 2, 4), were calculated. The Judd-Ofelt parameter Ω_6 is usually calculated for the $4f$-$4f$ transitions of lanthanides except for trivalent europium. The $^5D_0 \rightarrow {}^7F_6$ emission transition of Eu^{3+} is too weak to be detected and the $|\langle (S', L')J'\|U^6\|(S, L)J\rangle|^2$ REM is much smaller than other RMEs, $|\langle (S', L')J'\|U^t\|(S, L)J\rangle|^2$ ($t = 2$, 4) [13,23,24]. This is why Ω_6 and A_R