High luminescence quantum efficiency of Eu\(^{3+}\)-doped SnO\(_2\)–SiO\(_2\) glasses due to excitation energy transfer from nano-sized SnO\(_2\) crystals

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Abstract

The strong Eu\(^{3+}\) photoluminescence in xSnO\(_2\)–(100–x)SiO\(_2\) derived by the sol–gel method was reported. It was shown that Eu\(^{3+}\) ions were embedded in SnO\(_2\) nanocrystals (tetragonal, rutile) surrounded by a SiO\(_2\) glass matrix. Time-resolved photoluminescence spectra and excitation spectra revealed that Eu\(^{3+}\) ions could receive excitation energy from electron–hole pairs in SnO\(_2\) semiconductor nanocrystal, whose band-gap energy shifted to the higher energy side due to the quantum size effect, and was tuned to an optimum frequency for energy transfer to Eu\(^{3+}\) ions. Absolute quantum luminescence efficiencies were found to be 60.5 (internal) and 26.7% (external).

Keywords: Eu\(^{3+}\); SnO\(_2\) nanocrystals; Energy transfer; Quantum size effect; Sol–gel method

1. Introduction

Human beings around the world are now faced with several problems deeply associated with pollution. Political measures are being taken concerning restriction of the use of cadmium (Cd), lead (Pb), mercury (Hg) ions and organic chemicals, but they are not sufficient to reduce such problems. Since the short-wavelength ultraviolet (UV) light of a Hg vapor plasma is commonly used as an excitation source in the majority of commercially available lamps, the optimization of luminescence quantum efficiency of phosphors is required for 254 nm excitation in fluorescent lighting products [1]. However, the use of Hg vapor has been regarded as giving rise to environmental contamination during disposal. Recent investigation of deep violet light-emitting devices (LED) and lasers [2,3] quite possibly provides an alternative excitation in the range of 340–400 nm. Thus, the development of new lamp phosphors that convert the long-wavelength UV light into a visible light may help replace the mercury currently used in fluorescent lamps and lead to higher net conversion efficiencies. So far, rare-earth phosphors have been developed using such host materials as Y\(_2\)O\(_3\) or Y\(_2\)O\(_2\)S crystals, but it is difficult to effectively excite rare-earth ions with a UV wavelength longer than 254 nm because of the very low oscillator strength (\(\sim 10^{-6}\)) of f–f transitions. A new concept for obtaining highly efficient rare-earth fluorescence under long UV excitation is thus required. This paper reports on high efficient Eu\(^{3+}\) fluorescence combined with the nanometer-sized stannic oxide (SnO\(_2\)) of wide-gap semiconductors in silica (SiO\(_2\)) glass, synthesized by the sol–gel method. The quantum size effect of SnO\(_2\) band-gap and energy transfer from electron–hole pairs in SnO\(_2\) semiconductor to Eu\(^{3+}\) ions has been successfully applied.

2. Experiments

2.1. Sample preparation

The glass composition of xSnO\(_2\)–(100–x)SiO\(_2\) containing normally 1 wt% Eu\(_2\)O\(_3\) were prepared by the sol–gel process of Si(O\(_2\)C\(_2\)H\(_4\))\(_4\), SnCl\(_2\)·2H\(_2\)O and EuCl\(_3\)·6H\(_2\)O. We used SnCl\(_2\)·2H\(_2\)O as a starting material instead of SnCl\(_4\) because SnCl\(_2\)·2H\(_2\)O easily led to the crystallization of SnO\(_2\) in the glassy SiO\(_2\) network. A flow-chart of the sample preparation is shown in Fig. 1. The Si(O\(_2\)C\(_2\)H\(_4\))\(_4\) was first

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hydrolyzed at room temperature with a mixed solution of ethanol and de-ionized water (including 0.15 mol/l HCl) with a molar ratio of 1:1. Separately, SnCl$_2$·2H$_2$O and EuCl$_3$·6H$_2$O were dissolved in 5 g of C$_2$H$_5$OH, which was introduced into the starting solution. After stirring for 30 min, the homogeneous solution was hydrolyzed by adding the mixed solution of ethanol and de-ionized water (including 0.15 mol/l HCl) with a molar ratio of 1:4. After stirring for another 1 h, the resultant solution was placed in a sealed container at room temperature for about 2 weeks to form a stiff gel of 1–3 mm in thickness. To completely hydrolyze the alkoxide, the gel was heated to 150°C in a sealed vessel together with water and held for 30 h. Finally, the gel was heated in air in the range of 500–1000°C for 5 h in order to convert the gel to glass-network and precipitate the nanometer-sized SnO$_2$ crystals.

2.2. Characterization

The crystalline data were obtained by X-ray diffractometry (XRD; Rigaku RAD-B system using Cu Kα; 40 kV, 20 mA). To determine the lattice parameters of the SnO$_2$ crystal, the diffracted X-ray was collected by scanning between 2θ = 20 and 40° in 0.04 steps and counting for 30 s. Si powder was used as an internal standard. Transmission electron microscopy (TEM) was used to record an image of nanometer-sized SnO$_2$ particles in SiO$_2$ glass, with an accelerate voltage of 200 kV in JEM-2000EX (JEOL).

The optical absorption spectra were measured with a spectrometer (Jasco, V-570). The fluorescence spectra were measured by an image-intensified charge coupled device (ICCD) system (ORIEL Instruments, InstaSpec V system) under long ultraviolet excitation of nitrogen gas (N$_2$) laser (Nippon Laser Co. LN-203C; λ = 337.1 nm). The excitation spectra were recorded using a monochromator (Jobin Yvon, HR-320) and a photomultiplier (Hamamatsu, R955). A 500 W Xenon lamp passed through a monochromator (Jobin Yvon, H-20) was used for excitation. All the measurements were carried out at room temperature.

3. Results and discussion

Fig. 2 shows XRD patterns of xSnO$_2$–(100–x)SiO$_2$ glass heated in air at 700°C, for various SnO$_2$ contents. One can see diffraction peaks at 26.4, 33.4, 38.3, and 51.7°. These peaks indicate the presence of the tetragonal crystal-phase of SnO$_2$ (rutile-type) and the intensities are increased with an increase in SnO$_2$ content. Before the heat-treatment, no peaks were observed except a halo-peak of around 23° that came from the silica matrix. The mean particle size of the tetragonal SnO$_2$ precipitated in SiO$_2$ glass was estimated using Scherrer’s equation to be 3–5 nm. TEM observation supports the estimation, as exemplified in Fig. 3. SnO$_2$ crystal is a semiconductor with a wide bulk band-gap $E_g$ of 3.59 eV, and the nanometer-sizing of these nanocrystals allows us to obtain a quantum size effect of band-gap energy. According to Kayanuma’s theory [4,5] on the quantum confinement of an electron–hole pair in a spherical...
well, the band-gap energy $E_g$ is determined by the characteristic distance (or radius, $R$) in the following equation

$$E_g(R) = E_g^0 + \frac{\hbar^2 \pi^2}{2\mu R^2} - \frac{1.786e^2}{\varepsilon R} - \frac{0.12e^4 \mu}{\hbar^2 c^2}, \quad (1)$$

where $\varepsilon$ is the dielectric constant and $\mu = (1/m_e^* + 1/m_h^*)^{-1}$ is the reduced mass ($m_e^*$ and $m_h^*$ are the effective masses of electron and hole, respectively). The second is the quantum confinement energy for electron and hole in a spherical particle, which is larger than the Coulomb attraction energy (the third term) as $R$ decreases. The fourth is the remnant of the exciton effect. For SnO$_2$ crystal, we obtain the value of $\mu = 0.30m_0$ (mass of free electron) and $\varepsilon = 13.5$ in the calculation, in which the random orientation of tetragonal crystals were considered. On the other hand, since the optical absorption is expressed by $\alpha = \alpha_0(E - E_g)^{3/2}$ based on the assumption of a band-tail of a partially allowed direct transition in the semiconductor, the observed absorption spectra were analyzed in the form of $\alpha^{2/3}$ versus $E$ (= photon energy) [6].

Table 1 summarizes the estimated band-gap energy $E_g$ and particle size $2R$ for various SnO$_2$ contents, using Kayanuma’s equation (1). It is clearly demonstrated that the nanometer-sized SnO$_2$ exhibits a quantum size effect of the blue-shift of band-gap energy with a decrease in the SnO$_2$ content. That is to say, since the decreasing amount of SnO$_2$ content, as expected, leads to smaller sizes of SnO$_2$ particles, it simultaneously increases the gap energy $E_g$. It is also found that the absorption edge can be controlled in the range between 320 ($\sim 3.88$ eV) and 345 nm ($\sim 3.59$ eV).

Fig. 4 shows a decay curve of $^5D_0-^7F_1$ fluorescence and time-resolved spectra of Eu$^{3+}$ doped in 5SnO$_2$–95SiO$_2$ glass. Immediately after pulsed excitation of N$_2$ laser (pulse width < 1 ns), $^5D_0-^7F_2$ emission ($\sim 620$ nm) is stronger than $^5D_0-^7F_1$ emission ($\sim 590$ nm) (see the insertions). $^5D_0-^7F_1$ transition is magnetic dipole in character and is independent of crystal fields, while $^5D_0-^7F_2$ transition is electric dipole in character and forbidden in the center-symmetric site because of the parity law of f–f transitions. Generally therefore, Eu$^{3+}$ ions in the glass phase (disturbed sites) have a strong $^5D_0-^7F_2$ emission. The time-resolved spectrum of Eu$^{3+}$ ions following the pulsed excitation shows that Eu$^{3+}$ ions in the glass phase initially emit fluorescence. On the other hand, 10 ms after the excitation, the spectral shape of Eu$^{3+}$ fluorescence is greatly changed and $^5D_0-^7F_1$ emission dominates, indicating that Eu$^{3+}$ ions are also located in SnO$_2$ nanocrystals, since the cation sites of tetragonal SnO$_2$...
crystal have a center-symmetric 6-coordination to nearest neighboring oxygen ions. The excitation spectra of Eu\(^{3+}\) emission monitored at 618 nm of \(^{5}D_0-^{7}F_2\) transition, depicted in Fig. 5, show the increasing absorption band around 340 nm, which is confidently matched with band-gap energy of nanometer-sized SnO\(_2\) shifted by quantum size effect, as well as the typical \(^{7}F_0,1-^{5}D_2,5^{2}L_6,5^{2}G_2,4^{1}D_4\) absorption lines of Eu\(^{3+}\) ions [7]. From these results, it was concluded that the excitation energy of electron–hole pairs generated by interband transition of SnO\(_2\) is non-radiatively transferred to Eu\(^{3+}\) ions located near or inside SnO\(_2\).

The obtained decay curves can be analyzed using a double exponential function

\[
I(t)/I_0 = \alpha \exp(-t/\tau_1) + (1-\alpha) \exp(-t/\tau_2).
\]  

(2)

The parameter \(\alpha\) denotes the ratio of Eu\(^{3+}\) ions in the nanocrystal and \(\tau_1\) is the lifetime of Eu\(^{3+}\) ions in the nanocrystal. \(\tau_2\) is the lifetime of Eu\(^{3+}\) ions in the glass matrix. Fig. 4 also includes the fitting result by a least-square method. The lifetimes of Eu\(^{3+}\) ions with different glass matrixes were observed, where the grain-sizes of the powdered SnO\(_2–SiO_2\) glasses, ranging from 100 to 1000 nm, were somewhat dependent on the grain-sizes of the powdered samples.

The results of the photoluminescence quantum efficiency of Eu\(^{3+}\) under excitation at 337.1 nm are summarized in Table 2 in comparison with a commercial Eu\(^{3+}\) phosphor of \(Y_2O_3:Eu^{3+}\). Although the internal quantum efficiency \(\eta_{\text{int}}\) is 60.5%, lower than \(81.7\%\) of \(Y_2O_3:Eu^{3+}\), the external quantum efficiency \(\eta_{\text{ext}}\) is 26.7% which is improved in comparison with the reference (19.2%). Under 253 nm excitation by Hg vapor plasma, \(Y_2O_3:Eu^{3+}\) has the high external efficiency of 56% [11], but the long UV excitation does not always give rise to a highly efficient photoluminescence. It is clear that SnO\(_2\) nanocrystals embedded with Eu\(^{3+}\) ions exhibit more advantages in the condition of long UV excitation. Bear in mind here that the adopted sol–gel synthesis results in the preferential doping of Eu\(^{3+}\) ions in SnO\(_2\) nanocrystals. The Eu\(_2O_3\) concentration of 1 wt% used in this investigation, however, showed that 57.3% of Eu\(_2O_3\) is, as a result, dispersed in the SiO\(_2\) glass phase, where the \(^{5}D_0\) level of Eu\(^{3+}\) ions is less emissive due to energy migration among Eu\(^{3+}\) ions, and subsequently energy capture by optical killer sites [8]. The excess concentration of Eu\(_2O_3\) should be restricted. In order to improve the external quantum efficiency, optimization of Eu\(_2O_3\) content is required, which will be reported elsewhere.

4. Conclusion

The photoluminescence of Eu\(^{3+}\) ions in SnO\(_2–SiO_2\) glasses fabricated by the sol–gel method was obtained a value proportional to the number of photons in excitation, \(I_{\text{ex}}\).
investigated. Nanometer-sized SnO$_2$ crystals (tetragonal, rutile) were precipitated in SiO$_2$ glasses and exhibited blue-shift of band-gap energy $E_g$ due to the quantum size effect. It was demonstrated that a strong Eu$^{3+}$ photoluminescence under the long UV wavelength of 337.1 nm could be obtained. Time-resolved fluorescence spectroscopy and excitation spectra clarified that Eu$^{3+}$ ions could accept excitation energy from electron–hole pairs in SnO$_2$ semiconductor nanocrystals. Absolute luminescence efficiencies were estimated using Wrighton–Ginley–Morse’s method. The external quantum efficiency of 26.7% was larger in comparison with a commercial Y$_2$O$_3$:Eu$^{3+}$ phosphor in the excitation condition at 337.1 nm, indicating that the newly developed sol–gel glass is promising as a highly efficient light emitter under long UV excitation, which may lead to a discontinuance of the mercury vapor plasma as a short-wavelength UV excitation source.

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References

[1] S. Kubota, M. Izumi, H. Yamane, M. Shimada, Luminescence of Eu$^{3+}$, Tb$^{3+}$ and Tm$^{3+}$ in SrLaGa$_3$O$_7$, J. Alloys Compd. 283 (1999) 95–101.
[2] T. Nishida, N. Kobayashi, 346 nm emission from AlGaN multiple quantum-well light emitting diode, Phys. Status Solidi A 176 (1999) 45–48.
[3] S. Nakamura, M. Senoh, S. Nagahama, N. Iwasa, T. Yamada, T. Matsushita, H. Kiyoku, Y. Sugimoto, T. Kozaki, H. Umemoto, M. Sano, K. Choocho, InGaNaGaN-based laser diodes with modulation-doped strained-layer superlattices, Jpn. J. Appl. Phys. 36 (1997) L1568–L1571.
[4] Y. Kayanuma, Wannier exciton in microcrystals, Solid State Commun. 59 (1986) 405–408.
[5] Y. Kayanuma, Quantum-size effects of interacting electrons and holes in semiconductor microcrystals with spherical shape, Phys. Rev. B 38 (1988) 9797–9805.
[6] T. Hayakawa, T. Enomoto, M. Nogami, Nanocrystalline SnO$_2$ particles and twofold-coordinated Sn defect centers in sol–gel-derived SnO$_2$–SiO$_2$ glasses, J. Mater. Res. 17 (2002) 1305–1311.
[7] M. Nogami, T. Enomoto, T. Hayakawa, Enhanced fluorescence of Eu$^{3+}$ induced by energy transfer from nanosized SnO$_2$ crystals in glass, J. Lumin. 97 (2002) 147–152.
[8] T. Hayakawa, M. Nogami, Energy migration of the local excitation at the Eu$^{3+}$ site in a Eu–O chemical clustering in sol–gel derived SiO$_2$:Eu$^{3+}$ glass, J. Appl. Phys. 90 (2001) 2200–2205.
[9] M.S. Wrighton, D.S. Ginley, D.L. Morse, Technique for the determination of absolute emission quantum yields of powdered samples, J. Phys. Chem. 78 (1974) 2229–2233.
[10] T. Hayakawa, A. Hiramitsu, M. Nogami, White light emission from radical carbonyl-terminations in Al$_2$O$_3$–SiO$_2$ porous glasses with high luminescence quantum efficiencies, Appl. Phys. Lett. 82 (2003) 2975–2977.
[11] K. Ohkubo, T. Shigeta, Absolute fluorescence quantum efficiency of NBS phosphor standard samples, J. Illum. Eng. Inst. Jpn 83 (1999) 87–93.