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Sol–gel preparation and luminescent properties of CeO$_2$:Ln (Ln = Eu^{3+} and Sm^{3+}) thin films

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Abstract

New transparent CeO$_2$:Ln (Ln = Eu^{3+} or Sm^{3+}) thin-film phosphors have been fabricated by a sol–gel method. The CeO$_2$:Ln films with the Ln concentrations of 1 at.% showed the strongest photoluminescence (PL) upon ultraviolet (UV) light excitation. At higher Ln concentrations, the PL intensity decreased because of the nonradiative energy transfer. For Eu^{3+} ions doped in the CeO$_2$ lattice with inversion symmetry, an orangey red emission due to a magnetic-dipole $^5D_0 \rightarrow {}^7F_1$ transition (591 nm) was dominant when excited at a wavelength of 340 nm. In contrast, much stronger orange emissions (573 nm) due to $^4G_{5/2} \rightarrow {}^6H_{5/2}$ were observed for Sm^{3+} ions. Apparently, the Eu^{3+} and the Sm^{3+} ions had different efficiencies of the excitation through the energy transfer from the “Ce^{4+}–O^{2-}″ charge transfer state induced by the UV irradiation.

Keywords: Films; Sol-gel processes; Optical properties; CeO$_2$; Phosphors

1. Introduction

Recent progress in ultraviolet light emitting diodes (UVLEDs) has opened possibility of designing new optoelectronic devices.[1] UV-pumped phosphors are one of the key materials for development of such devices. Luminescence from rare-earth (RE) ions based on intraconfigurational electronic transitions shows a sharp spectrum, which is useful for applications as phosphors in display devices, lighting devices, solid-state lasers, etc. When combined with UVLEDs, phosphors should be in a thin-film form and provide advantages such as high emission efficiencies, good compatibility with semiconductor devices, and low fabrication cost. Furthermore, the excitation at near-UV wavelengths is preferable to the use of LEDs as light source.

It has been reported that RE-doped Sr$_2$CeO$_4$ materials exhibit excellent luminescent properties.[2–4] The excitation of Sr$_2$CeO$_4$:RE is supposed to originate from the initial “Ce^{4+}–O^{2-}” charge-transfer (CT) transition in the host lattice absorbing the excitation light. An efficient energy transfer can then occur from the “Ce^{4+}–O^{2-}” CT state (CTS) to the doped trivalent RE ions having CT excited states (the sensitizer–activator relation) through a nonresonance process involving the exchange interaction.[3] As to cerium dioxide (CeO$_2$), however, few works have been reported on luminescence of the doped RE ions, although it can exhibit strong UV light absorption through the CT from O^{2-} to Ce^{4+}. In addition to this attractive character, CeO$_2$ has both thermal and chemical stability and can be easily deposited on substrates as thin films even at lower heat-treatment temperatures. Recently, we have succeeded in fabricating novel thin-film phosphors based on CeO$_2$:Ln (Ln = Eu^{3+} and Sm^{3+}) by a sol–gel method.[5] It was found that Sm^{3+} doped in CeO$_2$ at the doping level of 1 at.% caused unusual strong $^4G_{5/2} \rightarrow {}^6H_{5/2}$ emissions exhibiting orange color. In this paper, the effects of dopant concentrations on optical properties of CeO$_2$:Ln were investigated to improve their luminescent properties. Luminescence of Eu^{3+} was also discussed by comparing host lattice of CeO$_2$ and EuOF having the similar fluorite-type structure.

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2. Experimental procedure

Eu^{3+} and Sm^{3+} doped CeO_2 thin films were prepared by a sol–gel method using RE acetates. Precursor solutions for CeO_2 were prepared by dissolving $Ce(CH_3COO)_3{\cdot}H_2O$ and trifluoroacetic acid (TFA; CF_3COOH) in ethanol. Separately, $Eu(CH_3COO)_3{\cdot}4H_2O$ or $Sm(CH_3COO)_3{\cdot}4H_2O$ were dissolved in ethanol with addition of TFA. The overall metal concentration was adjusted to 0.25 M. Coating solutions were prepared by mixing these solutions and stirring for 24 h at room temperature. Dopant concentrations in CeO_2 were changed between 0.05 and 100 at.%. The resultant coating solutions were spin-coated on quartz glass substrates and heated at 700 °C for 10 min in air. This coating/heating procedure was repeated three times to increase the film thickness.

Phase identification of the films was performed with an X-ray diffractometer equipped with a thin-film attachment using Cu Kα radiation (Rigaku). Optical transmission/absorption spectra were recorded with a UV–vis spectrophotometer (Hitachi, type U-3300). Photoluminescence (PL) spectra were measured at room temperature with a spectrofluorophotometer (Shimadzu, type RF-5300PC) using a Xe lamp (150 W) as a light source. A filter was used to remove a second-order peak of the excitation light in the PL measurement.

3. Results and discussion

Two different crystal structures were formed in the $CeO_2:Eu^{3+}$ films depending on the Eu^{3+} concentration, as suggested by the X-ray diffraction (XRD) analysis. Fig. 1 shows the XRD patterns for the films containing 1.00–100 at.% of Eu^{3+}. Diffraction peaks of the films with 1.00–30.0 at.% of Eu^{3+} can be indexed with a cubic CeO_2 structure (JCPDS No. 34-394). On the other hand, we can index a diffraction peaks of the film of 100 at.% of Eu^{3+} as a cubic EuOF structure (JCPDS No. 26-635). The structural change was further supported by the transmission spectra. As shown in Fig. 2, transmittance of the $CeO_2:Eu^{3+}$ films (0–30 at.% of Eu^{3+}) decreases in the UV region below approximately 360 nm, indicative of the inter-band absorption of CeO_2. In contrast, the EuOF film (corresponding to 100 at.% of Eu^{3+}) exhibits an absorption edge at a much shorter wavelength of approximately 290 nm, which is attributed to electronic transitions between the O 2p and the Eu 4f levels.

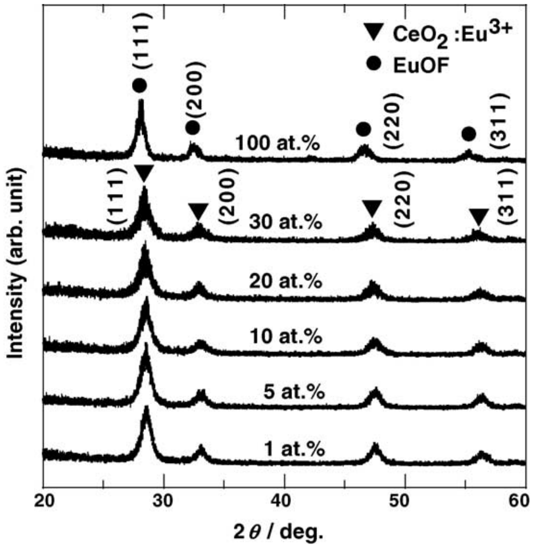

Fig. 1. XRD patterns for $CeO_2:Eu^{3+}$ thin films containing 1.00–100 at.% of Eu^{3+} deposited on glass substrates and heated at 700 °C.

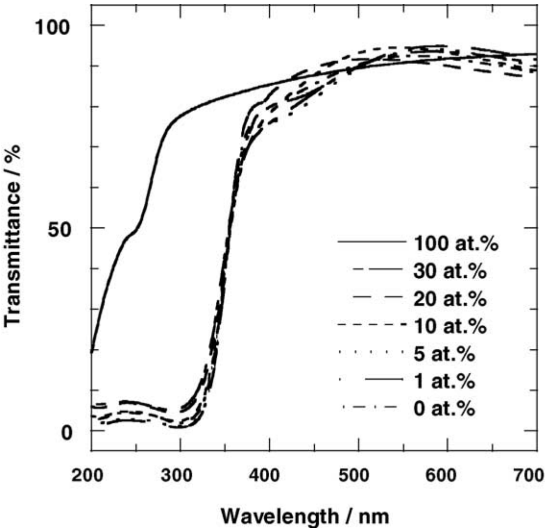

Fig. 2. Transmission for $CeO_2:Eu^{3+}$ thin films containing 0.00–100 at.% of Eu^{3+}.

PL was appreciably observed only for the films with the lower Eu^{3+} concentration between 0.05 and 10.0 at.% at an excitation wavelength of 340 nm. This result is similar to that reported for the Sr_2CeO_4 system.[3] From the PL spectra of the $CeO_2:Eu^{3+}$ films shown in Fig. 3, it was found that an orangey red emission due to a magnetic-dipole $^5D_0 \rightarrow {}^7F_1$ transition (591 nm) of Eu^{3+} was dominant without other strong $^5D_0$-related emissions. The fluorite-type CeO_2 structure has the high inversion symmetry of Ce sites; thereby a forbidden electric-dipole $^5D_0 \rightarrow {}^7F_2$ transition cannot be observed. The emission intensity from the film containing 1.00 at.% of Eu^{3+} was strongest in the present $CeO_2:Eu^{3+}$ system. With the higher Eu^{3+} concentrations of 20.0–100 at.%, the emission was relatively weakened due to occurrence of a non-radiative energy transfer between the luminescent center.[6]

For the excitation wavelength of 340 nm used above, no emission was detected for the EuOF film. Upon the excitation at 259 nm, however, strong red emissions were observed from the Eu^{3+} ions in EuOF. PL spectra of $CeO_2:Eu^{3+}$ and EuOF are compared in Fig. 4 with the excitation at 331 and 259 nm, respectively. The dominant emissions from EuOF are centered at 610 and 624 nm. It is known that EuOF has no inversion symmetry in the Eu^{3+} sites, providing much higher probability of the hypersensitive $^5D_0 \rightarrow {}^7F_2$ transitions.[7]

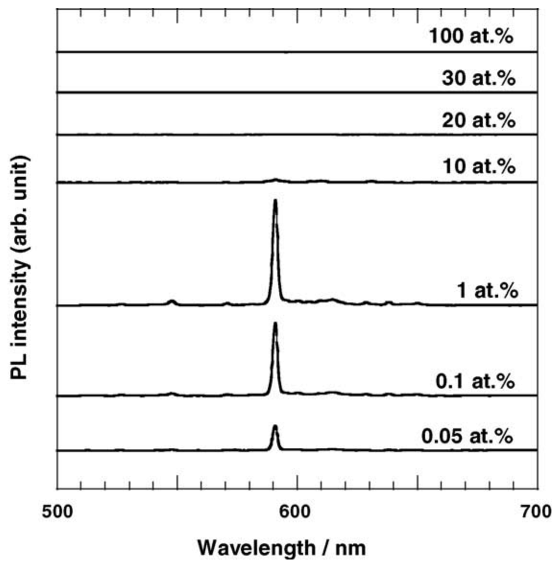

Fig. 3. PL spectra for $CeO_2:Eu^{3+}$ thin films containing 0.05–100 at.% of Eu^{3+}.

PL excitation (PLE) spectra of the $CeO_2:Eu^{3+}$ film (1 at.% of Eu^{3+}) for the 591 nm emission and those of the EuOF film for the 610 nm emission are shown in Fig. 5 together with their absorption spectra. A broad-band excitation peak centered at 330 nm is observed in the PLE spectra of Fig. 5(a). An absorption edge observed in the absorption spectrum, approximately 360 nm, corresponds to a band-gap of CeO_2 reported as 3.4 eV (365 nm).[8] EuOF shows, on the other hand, a narrower excitation band centered at 260 nm (Fig. 5(b)). In addition, the absorption spectrum of EuOF shows an absorption edge around 280 nm, as described above for the transmission spectra. These spectral data support that the efficient energy transfer from the "Ce^{4+}–O^{2-}" CTS to the doped Eu^{3+} could be achieved in the $CeO_2:Eu^{3+}$ system.

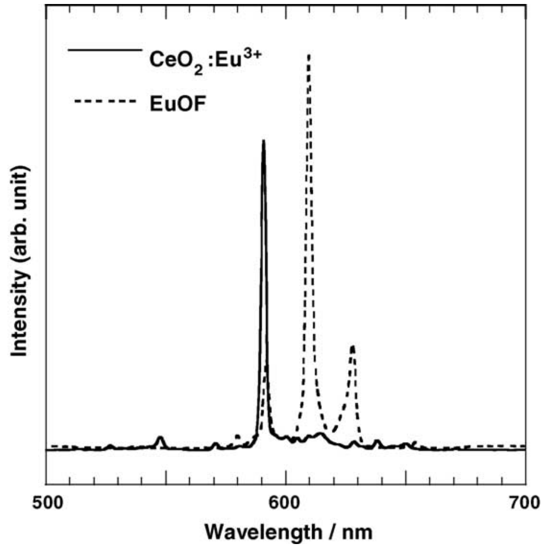

Fig. 4. PL spectra for $CeO_2:Eu^{3+}$ (1.00 at.%) and the EuOF film excited at 331 and 259 nm, respectively.

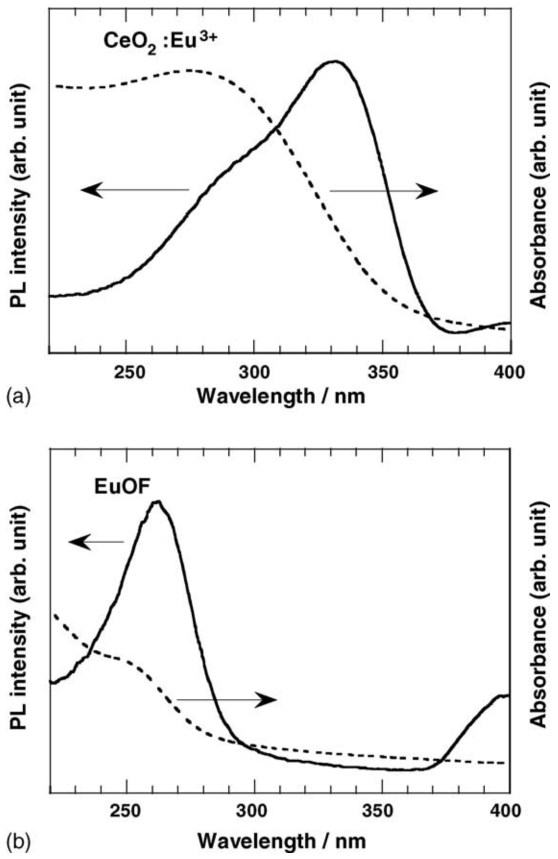

Fig. 5. PLE and absorption spectra for (a) $CeO_2:Eu^{3+}$ containing 1 at.% of Eu^{3+} and (b) EuOF film. The 591 nm and the 610 nm emission was used for the PLE measurement of the $CeO_2:Eu^{3+}$ and the EuOF film, respectively.

Fig. 6 shows PL and PLE spectra of the $CeO_2:Sm^{3+}$ film at the dopant level of 1.00 at.%. The structure of the PLE spectra for the $CeO_2:Sm^{3+}$ film is similar to that of the $CeO_2:Eu^{3+}$ film shown in Fig. 5(a), suggesting the same excitation mech-

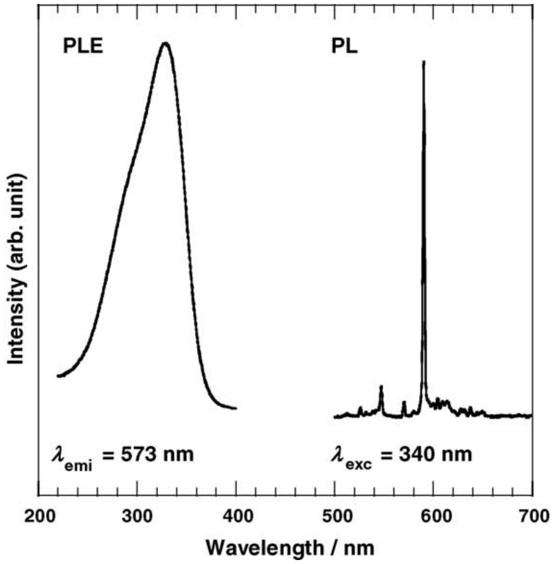

Fig. 6. PL and PLE spectra of the $CeO_2:Sm^{3+}$ (1.00 at.%) thin film deposited at 700 °C.

anism. The PL spectra show orange emissions (with the strongest peak at 573 nm) due to the $^4G_{5/2} \rightarrow {}^6H_{5/2}$ transition of Sm^{3+}. The intensity of the 573 nm emission of Sm^{3+} was observed to be four times higher than that of the 590 nm emission of Eu^{3+} at the same dopant level of 1.00 at.%. The different emission intensities between Eu^{3+} and Sm^{3+} can be explained as follows. The excitation of CeO_2:Ln is supposed to originate from the initial "Ce^{4+}–O^{2-}" CT transition in the host lattice absorbing the excitation light. Then the efficient energy transfer can occur from the "Ce^{4+}–O^{2-}" CTS to the doped Eu^{3+} or Sm^{3+} ions having CT excited states. The Eu^{3+} and the Sm^{3+} ions may have different efficiencies of the energy transfer from the "Ce^{4+}–O^{2-}" CTS, which leads to the different overall excitation efficiency.

4. Conclusions

A series of transparent and luminescent thin films, namely CeO_2:Ln (Ln = Eu^{3+} and Sm^{3+}) and EuOF, were fabricated by the sol–gel method. In the fluorite-type CeO_2 host, photoluminescence was observed only for the films with the lower Ln concentrations. The orangey red emissions (591 nm) due to the magnetic-dipole $^5D_0 \rightarrow {}^7F_1$ transition of Eu^{3+} was dominant without other strong $^5D_0$-related emissions at the excitation wavelength of 340 nm in the CeO_2:Eu^{3+} films. This is because CeO_2 provides inversion symmetry with the doped Eu^{3+} site. The CeO_2:Sm^{3+} showed the orange emissions (573 nm), the intensity of which was much higher than that of the emission from Eu^{3+}, due to the $^4G_{5/2} \rightarrow {}^6H_{5/2}$ transitions. The excitation mechanism was suggested to be the energy transfer from the "Ce^{4+}–O^{2-}" CTS to the doped Eu^{3+} and Sm^{3+} ions.

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