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Radiant and Luminous Fluxes of Sm^{3+} Doped Heavy Metal Silicate Glass under The Excitation of Violet Light Emitting Diode

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Abstract: Optical radiative parameters for multichannel visible transition emissions have been determined in Sm^{3+}-doped cadmium-aluminum-silicate (CAS) glass under the excitation of a violet light emitting diode (LED). For the derivation, the necessary fluorescence spectra were measured and calibrated in an integrating sphere, which was connected to a CCD detector with a 400 μm-core optical fiber. The spectral power distribution and luminous flux distribution of the sample under the violet LED excitation have been obtained. And the total radiant flux and total luminous flux for the entire visible region have been calculated to be 712 μW and 12.1 mlm, respectively. The radiant flux and luminous flux for the four visible emission bands of Sm^{3+} were derived to be 36 μW and 9.7 mlm, which occupied 5% and 80% of the whole. The total quantum yield of the visible fluorescence of Sm^{3+} is 2.3%. Investigations on absolute spectral parameters for multichannel visible transition emissions of Sm^{3+} in CAS glass provide a valuable reference for heavy metal silicate glass in developing efficient display and illumination devices.

Key words: radiant and luminous fluxes; samarium ions; heavy metal silicate glass

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紫色发光二极管激发下钐掺杂的重金属硅酸盐玻璃的辐射通量与光通量

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摘要: 采用积分球测试系统配以内芯直径为 400 μm 的功率光纤连接的 CCD 探测器,在紫色发光二极管的激发下,对 Sm^{3+} 掺杂的重金属硅酸盐(CAS)玻璃的荧光光谱进行了表征,实现了以荧光发射特性绝对评价为目的绝对光谱功率分布测定,进一步求得了辐射通量,光通量等荧光特征参数。测试与计算结果表明,在整个可见光谱区域,总的辐射通量和光通量分别为 712 μW 和 12.1 mlm,其中 Sm^{3+} 的 4 个特征发射峰的辐射通量和光通量分别为 36 μW 和 9.7 mlm,占可见区总量的5% 和80% ,其可见特征发射的总量子产率为2.3% 。Sm^{3+} 掺杂 CAS 玻璃可见区多通道辐射跃迁的绝对光谱参数评估为照明和显示器件的研发提供了有益的参考依据。

关　键　词: 辐射通量和光通量; 钐离子; 重金属硅酸盐玻璃

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1 Introduction

In recent years, considerable attentions have been paid to rare earth (RE) ions doped solid-state optoelectronic materials due to their potential applications in display, illumination and laser fields[1-7]. Among various RE ions, trivalent samarium ion (Sm^{3+}) has given rise to extensive interest since its emitting $^4G_{5/2}$ level exhibits high quantum efficiency and shows multifarious radiative emission channels[8]. The abundant multichannel radiation features of Sm^{3+} make it seductive in the applications of optoelectronic devices[9].

Host material with excellent properties plays an important role in developing RE doped optical devices[10-14]. Obviously, oxide glasses have attracted considerable amount of eyes in practical applications due to their small thermal expansion, outstanding chemical-mechanical stability and excellent optical performance[15-16]. In oxide glass, silicate glass has attracted considerable attentions in practical applications due to their low cost, large tensile strength, high chemical durability and excellent thermal stability. Moreover, with the addition of heavy metal elements, the density and refractive index increase almost linearly, therefore higher radiative transition probability and larger emission cross-section in visible waveband are expected[17-18]. Possessing admirable properties in these respects, heavy-metal-silicate glasses are considered to be suitable hosts to obtain the efficient visible transition emissions of Sm^{3+}. In addition, the introduction of aluminum oxide (Al_2O_3) will enhance the dispersion of RE ions and help to limit the effects of concentration quenching on photoluminescence. Combined the advantages of the activators with host materials, Sm^{3+}-doped cadmium-aluminum-silicate (CAS) glass was designed and fabricated.

Luminescence and laser materials are being actively developed for many applications, and it is essential to reveal the optical properties. Generally, the information of emission transitions is given from fluorescence spectrum by the relative intensity. However, an integrating sphere coupled with a CCD detector has been applied to absolute measurements, and shows more reliable data. Therefore, the accurate and reproducible method was applied to characterize optical parameters of Sm^{3+} in silicate glass in this paper. The evaluation of absolute spectral parameters for visible emissions of Sm^{3+} in CAS glass provides a reference for the silicate glasses in developing display and illumination devices.

2 Experiments

Sm^{3+}-doped CAS glass was prepared from high-purity 12.931 g $CdCO_3$ (9.631 g CdO), 2.549 g Al_2O_3 and 4.506 g SiO_2 powders according to the molar host composition of 3CdO-Al_2O_3-3SiO_2 and additional 0.083 g Sm_2O_3 (0.5% of the host weight) was introduced. To make $CdCO_3$ decompose into CdO completely, the raw materials were first preheated in the pure alumina crucible at 450 ℃ for 4 h. After regrinding, the well-mixed powder was put into the pure alumina crucible and then melted in the temperature range of 1 260 ~ 1 300 ℃ for 40 min using an electric furnace in air atmosphere, after that quenched to room temperature onto a cold steel plate. The glass was subsequently annealed in the temperature range of 450 ~ 600 ℃ for 2 h, and then cooled down slowly to room temperature.

For optical measurements, the annealed glass sample was sliced into pieces and polished with two parallel sides. The density of the glass was derived to be 4.120 g · cm^{-3}, thus the number density of Sm^{3+} ions was 7.081×10^{19} cm^{-3}. Using a Metricon 2010 prism coupler, the refractive indices of Sm^{3+}-doped CAS glass was measured to be 1.691 0 and 1.665 0 at 632.8 and 1 536 nm, respectively. The refractive indices of the sample at all other wavelengths can be calculated by Cauchy's equation $n = A + B/\lambda^2$ with $A = 1.659\ 7$ and $B = 12\ 540$ nm^2.

The spectral power distribution was measured using an integrating sphere of 30 cm diameter, which was connected to a CCD detector (Ocean Optics, USB4000) with a 400 μm-core optical fiber. A stable excitation power of 396 nm excitation was obtained by fixing the current of the exciting violet light emitting diode (LED) at 20 mA. A standard lamp

(EVERFINE, D062) was used for calibrating this measurement system, and its spectral power distribution was obtained through fitting the factory data based on the blackbody radiation law. The excitation source (396 nm violet LED) rounded by a black tape except the emitting surface was mounted in the integrating sphere. The glass sample with dimensions of 6.1 mm × 5.4 mm × 2.6 mm was put on the violet LED and it covered the topside completely. The luminescence photograph of the sample was taken using a Sony α200 digital camera. All the measurements were carried out at room temperature.

3 Results and Discussion

Sm^{3+}-doped CAS glass sample exhibits reddish-orange fluorescence under the excitation of 396 nm violet LED in an integrating sphere. In 360 ~ 780 nm wavelength region, the spectral power distribution $P(\lambda)$ of Sm^{3+}-doped CAS glass under the excitation of the violet LED is presented in Fig. 1. It consists of four emission bands, locating at 560, 604, 650 and 700 nm, which belong to the $^4G_{5/2}\rightarrow{}^6H_{5/2}$, $^4G_{5/2}\rightarrow{}^6H_{7/2}$, $^4G_{5/2}\rightarrow{}^6H_{9/2}$ and $^4G_{5/2}\rightarrow{}^6H_{11/2}$ transitions, respectively. The total radiant flux, Φ_E of the luminescence is calculated by

$$\Phi_E = \int_{360\ \mathrm{nm}}^{780\ \mathrm{nm}} P(\lambda)\,\mathrm{d}\lambda. \qquad (1)$$

In the visible spectral region, the total radiant flux, Φ_E of Sm^{3+}-doped CAS glass under the excitation of the violet LED was integrated to be 712 μW by Eq. 1. In the spectral region of four emission

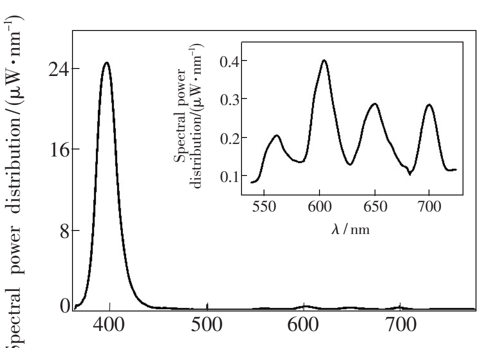

Fig. 1 Spectral power distribution of luminescence in Sm^{3+}-doped CAS glass under the excitation of the violet LED. Inset: Detail of spectral power distribution in the spectral region of 530 ~ 730 nm.

bands (530 ~ 730 nm), it was solved to be 36 μW and occupied 5% of the whole.

The photon distribution provides the fundamental information in optical field and relevant applications, ranging from quantum mechanics to quantum information and quantum metrology. In this paper, the photon distribution $N(\bar{\nu})$ is calculated based on the spectral power distribution $P(\lambda)$:

$$N(\bar{\nu}) = \frac{\lambda^3}{hc}P(\lambda), \qquad (2)$$

where λ is the wavelength, $\bar{\nu}$ is the wavenumber, h is the Planck's constant and c is the speed of light.

The photon distribution $N(\bar{\nu})$ of Sm^{3+}-doped CAS glass under the excitation of the violet LED consists of two components including transmitted violet light from excitation of LED and fluorescence from the sample as shown in Fig. 2. The inset shows four distribution bands corresponding to the $^4G_{5/2}\rightarrow{}^6H_J$ (J = 5/2, 7/2, 9/2 and 11/2) transitions, respectively, which indicates that the Sm^{3+}-doped CAS glass can be excited efficiently by 396 nm violet LED.

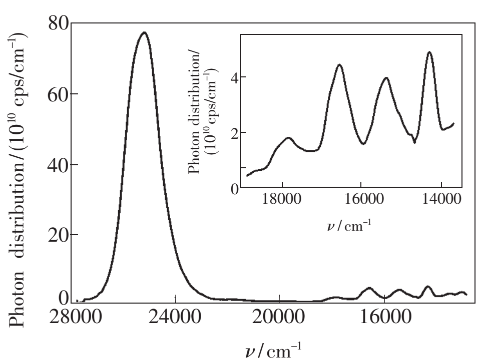

Fig. 2 Photon distribution of luminescence in Sm^{3+}-doped CAS glass under the excitation of the violet LED. Inset: detail of photon distribution in the spectral region of 13 500 ~ 19 000 cm^{-1}.

The quantum yield (QY) of a luminescence material is defined as the ratio of the emitted photo number to the absorbed photon number. The abscissa of distribution spectrum is converted to wavenumber (cm^{-1}) for accurate deconvolution of spectrum. By subtracting the violet LED $N(\bar{\nu})$ from the violet component of LED composite as shown in Fig. 3, the absorbed and emitted photon numbers can be estimated by integrating the net photon distribution with the wavenumber. Hence, the quantum yield is defined by

$$K_{QY} = (E_{on} - E_{side})/(L_{side} - L_{on}), \quad (3)$$

where (E_{on}, E_{side}) and (L_{on}, L_{side}) are the emitted photon numbers from the sample and violet LED, respectively, when the sample located on the top and the side of violet LED. The total K_{QY} of Sm^{3+}-doped CAS glass under the excitation of 396 nm violet LED was calculated to be 2.3%. Although the K_{QY} is not outstanding, the absolute results reported in this paper offer an original referenced data for optimizing the silicate glass, which are employed in developing display and illumination devices.

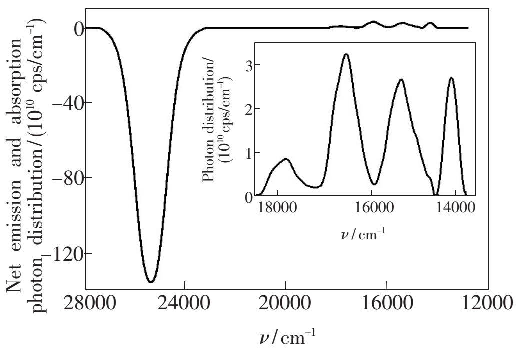

Fig. 3 Net emission and absorption photon distribution of the Sm^{3+}-doped CAS glasses under the excitation of the violet LED. Inset: detail of net emission photon distribution in the spectral region of 13 500 ~ 19 000 cm^{-1}.

Luminous flux is a quantity derived from radiant flux by evaluating the radiation according to its action upon the standard photometric observer. When dealing with the human eye, it is customary to introduce a sensorial physical quantity defined as the radiant flux, which evaluate its capacity to evoke the sensation of brightness. In the visible spectral region, the total luminous flux, Φ_V of the luminescence can be given by

$$\Phi_V = K_m \int_{380\ nm}^{780\ nm} V(\lambda) P(\lambda) d\lambda, \quad (4)$$

where $V(\lambda)$ is the relative eye sensitivity and K_m is the maximum luminous efficacy at 555 nm (683 lm/W).

Luminous flux distribution of Sm^{3+}-doped CAS glass under the excitation of 396 nm violet LED is presented in Fig. 4. In the visible spectral region, the total luminous flux, Φ_V was obtained to be 12.1 milli-lumen (mlm) by Eq. 4. In the spectral region of four emission bands (530 ~ 730 nm), it was calculated to be 9.7 mlm and occupied 80% of the whole. The absolute luminous flux of Sm^{3+}-doped heavy metal silicate glass provides the original reference in developing practical silicate materials applied in display and illumination devices.

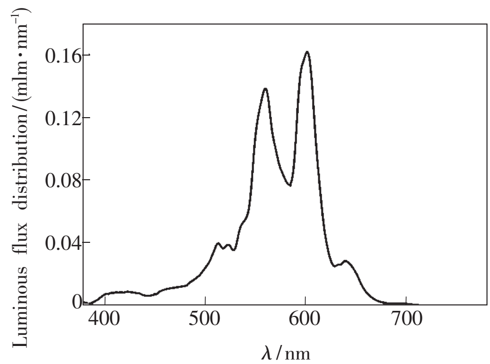

Fig. 4 Luminous flux distribution of luminescence in Sm^{3+}-doped CAS glass under the excitation of the violet LED

4 Conclusion

Optical radiation parameters of Sm^{3+}-doped cadmium-aluminum-silicate (CAS) glass under the excitation of violet LED have been derived from a series of spectral data recorded by an integrating sphere, which was connected to a CCD detector with a 400 μm-core optical fiber, and the calibration of the integrating sphere has been achieved by a standard lamp. In the visible spectral region, the total radiant flux and total luminous flux have been calculated to be 712 μW and 12.1 mlm, respectively, and the values for the four visible transition emissions of Sm^{3+} were solved to be 36 μW and 9.7 mlm, which occupied 5% and 80% of the whole. The total quantum yield of the visible fluorescence of Sm^{3+} has been calculated to be 2.3%. The evaluation of the multichannel radiation parameters for visible emissions of Sm^{3+} in CAS glass provides a criterion for reference in developing display and illumination devices.

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