Intense ultraviolet photoluminescence at 314 nm in Gd^{3+}-doped Silica

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Abstract: Photoluminescence (PL) of Gd-doped silica in the ultraviolet (UV) is investigated. The efficient emission detected at 314 nm is due to the $^6P_{7/2}$ to $^8S_{7/2}$ transition of a 4f electron of the Gd^{3+} ion.

OCIS codes: (260.7190) Ultraviolet; (250.5230) Photoluminescence; (160.5690) Rare-earth-doped materials

1. Introduction

Light sources emitting in the UV range have numerous applications, such as medical treatment, sterilization and lithography. Current systems mostly rely on gas laser [1] or high-order harmonic generation of longer-wavelength sources [2]. Rare earth (RE) ions have shown interesting luminescence properties, which made them play a key role in many technology applications over the years. Most of RE-doped solid state laser systems reported to date are in the infrared. Only few research papers reported some luminescence of RE-doped materials emitting in the UV spectral regions [3, 4].

Here, we present a study of Gd^{3+} absorption and luminescence in a silica host. The strong UV emission at 314 nm from the $^6P_{7/2}$ to $^8S_{7/2}$ transition of Gd^{3+} ions is extremely efficient when the RE ions are excited with a pump at ~274 nm. Samples with different Gd concentrations have been used. Results show the possibility to use Gd as luminescent ion in solid-state UV lasers.

2. Experiments

The cylindrical Gd-doped silica glass samples were prepared by sol-gel technique. All samples had a diameter of 10 mm and have been cut into small disks with thickness around 1 mm and polished to optical quality with a commercial polishing machine (Logitech). Scanning electron microscope (Zeiss Evo 50) and energy dispersive X-ray (Oxford Instruments INCA PentaFETx3) were carried out to study the sample surface morphology and analyze the full composition at a number of locations on three samples. Results showed excellent dopant uniformity and a Gd atomic concentration of 0.04%, 0.08% and 0.20%, respectively. Absorption measurements were performed using a PerkinElmer lambda-1050 UV-Vis-NIR spectrometer.

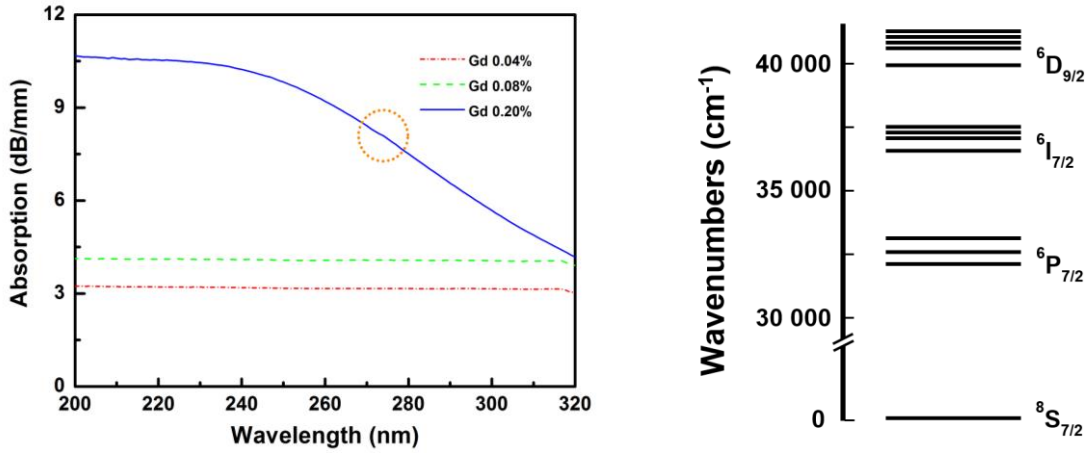

Fig. 1. (a) Absorption of Gd-doped silica samples (b) Energy-level diagram of Gd^{3+} ions in silica

Fig. 1 (a) shows the absorption in the samples with different Gd concentration. Higher absorption is detected in the Gd-doped glass with higher concentration. Absorption decreases for increasing wavelengths and it is more pronounced at higher Gd concentrations. No obvious absorption peak has been found in all samples but a tiny fluctuation around 275 nm in the 0.20% sample was observed. This coincides with the difference (~36500 cm^{-1} in wavenumbers) between the upper level ($^6I_{7/2}$) and the ground state ($^8S_{7/2}$) of Gd^{3+} as shown in Fig. 1 (b).

PL measurements were carried out using a spectrofluorophotometer (Fluorolog-3, HORIBA Scientific) at room temperature. All the data has been corrected for the spectral response sensitivity of the detection system and referenced spectrum of the Xe-lamp used for excitation.

Fig. 2 (a) exhibits the 2D PL spectrum of the sample with 0.04% Gd recorded from 300 nm to 500 nm under a range of excitation from 250 nm to 300 nm. A strong and sharp line centered at 314 nm is observed when the excitation wavelength is 253 nm and 274 nm with the luminescence associated to the latter being more intense than that associated to the former. The 314 nm emission results from radiative transitions between the first excited state $^6P_{7/2}$ and the ground state ($^8S_{7/2}$) of Gd^{3+}. It is dominant under the excitation $^8s_{7/2} \rightarrow {}^6I_{7/2}$ (274 nm) and $^8s_{7/2} \rightarrow {}^6D_{9/2}$ (253 nm). It is extremely interesting to note the broad intrinsic host emission under shorter excited wavelength, with a maximum around 380 nm that extends to 400 nm and more. This originates from neutral oxygen vacancies and nonbridging oxygen hole centers as typical network defects of the amorphous silicon dioxide.[5, 6]

Detailed spectrum under the excitation of 274 nm is displayed in Fig. 2 (b). As it is clearly evident in the inset of Fig. 2(b), the sideband at 308 nm is probably due to Gd^{3+} transition of $^6P_{5/2} \rightarrow {}^8S^{7/2}$. The other one around 324 nm, is likely vibronic rather than arising from Gd^{3+} ions on other sites.

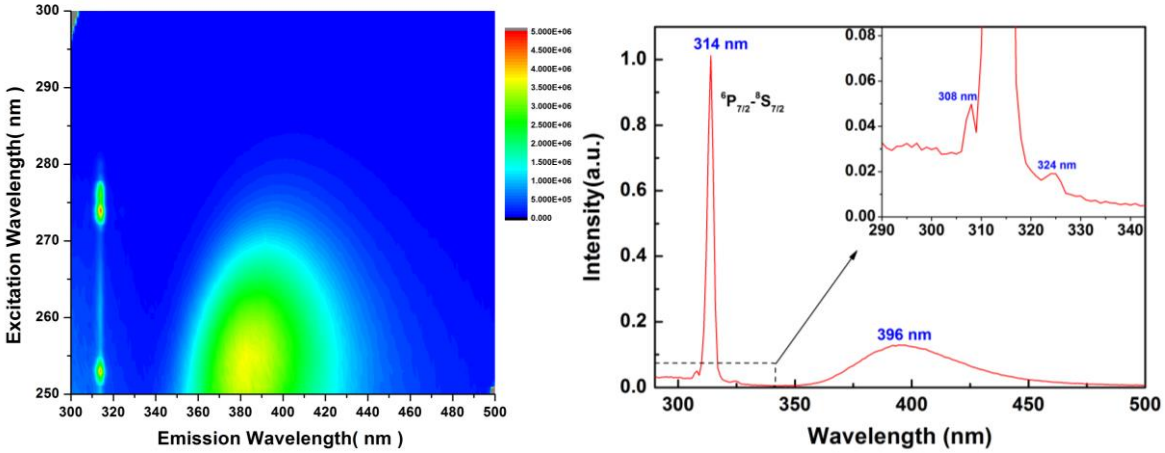

Fig. 2. (a) 2D PL spectrum of Gd-doped silica sample with 0.04% Gd concentration
(b) Spectrum under the excitation of 274 nm, Inset: Enlargement of the 290-342 nm spectral region

In conclusion, the strong PL of Gd-doped silica has been observed. Absorption and luminescence are surveyed in samples with different Gd concentration. The intense UV emission around 314 nm from the the $^6P_{7/2}$ to $^8S_{7/2}$ transition of Gd^{3+} ions was observed when samples were excited under 274 nm or 253 nm pump. The luminescence of Gd^{3+} could be exploited in future research aimed at UV generation in solid-state laser systems.

4. References

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