Enhanced Ultraviolet Photoluminescence of Gd^{3+} in Silica Glass

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Abstract— **Enhancement of photoluminescence (PL) signal from Gd^{3+}-doped silica glass densified by rapid thermal treatment (RTT) in the ultraviolet (UV) is investigated. Significant decrease of the loss covering the UV band is observed. The strong emission detected at 314 nm is assigned to the $^6P_{7/2}$ to $^8S_{7/2}$ transition under excitation of ^6D_J, ^6I_J, and ^6P_J energy levels of the Gd^{3+}.**

Keywords - Rare-earth-doped materials; Ultraviolet; Photoluminescence

I. INTRODUCTION

Ultraviolet (UV) light sources are becoming increasingly important for numerous applications, such as spectroscopy detection, biomedical treatment and lithography. Currently, emission in the UV is mostly generated by halogen lamps, gas lasers [1] or high-order harmonic generation of longer-wavelength sources [2]. Rare earth (RE) ions have shown interesting luminescence properties that spread a wide range of the spectrum. But most of RE-doped laser systems reported to date are in the infrared or even longer wavelength. Only few research papers reported luminescence of RE-doped materials emitting in the UV spectral regions [3, 4]. The pivotal reason for this is the difficulty to achieve combination of the efficient emission of the RE and relative small loss of the host in the UV. Gd^{3+}, in the middle of the lanthanide series, features by far the largest energy gap between its first excited level (^6P_J) and the ground state ($^8S_{7/2}$) of ~32000 cm^{-1} among the triply ionized lanthanides Ce^{3+} through Yb^{3+}[5]. Thus relatively large transition probabilities from excited levels to the ground state are expected to occur within the UV region of the spectrum [6]. Additionally, silica glass has been widely used for the advantages of high physical stability and strong chemical resistance. Pure silica transparency window also extends to short wavelengths of ~ 200 nm [7] so that it can be regarded as a favorable host for active dopants with lasing transitions in the UV.

Here, we present a study of enhanced UV absorption and luminescence in Gd^{3+}-doped silica glass. After imposing rapid thermal treatment (RTT) to the samples, UV emission with at least one order of magnitude stronger intensity than reported before [8] of Gd^{3+} ions at 314 nm is obtained. Significant absorption peak around 274 nm and decreased loss covering the UV band are observed, too. It is shown that Gd^{3+}-doped silica has potential to be the luminescent medium for directly emitting UV lasers.

II. EXPERIMENTAL METHODS

The Gd^{3+}-doped silica glass samples were prepared by sol-gel technique [9] in a cylindrical shape with the diameter of 10 mm. Then the samples were cut into small disks with a thickness around ~1 mm and polished on both sides. Scanning electron microscope (Zeiss Evo 50) and energy dispersive X-ray spectroscope (Oxford Instruments INCA PentaFETx3) were used to characterize surface morphology and analyze the full composition at a number of locations on samples. Loss measurements were performed using Varian Cary 500 UV-VIS NIR Spectrophotometer. Moreover, to optimize the glass matrix and increase the luminescence efficiency in Gd^{3+}-doped sol–gel silica glasses, a RTT was implemented by using an oxidizing oxygen-hydrogen flame [9]. During this treatment, the sample is rapidly heated up to 1700℃, where the sample is kept for few seconds (about 10 s) before cooling in ambient conditions to room temperature.

III. RESULTS ANS DISCUSSION

Loss measurements for samples with Gd concentration of 400 ppm and 2000 ppm were taken before and after RTT (Fig. 1).

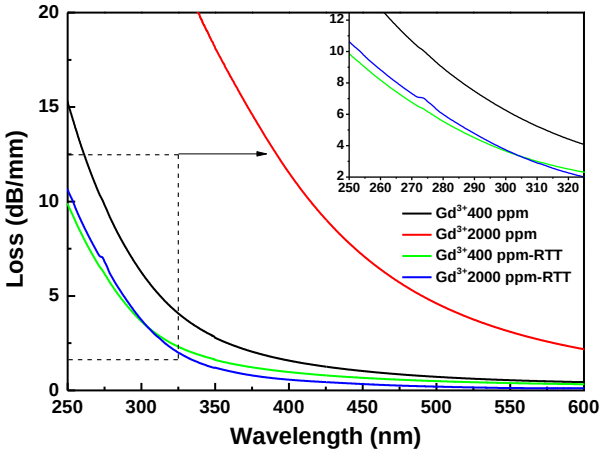

Figure 1. Loss of Gd-doped silica samples with different concentration

It can be seen that after the RTT, there is a significant decrease of the loss across the UV range in both samples, especially for the one with higher Gd concentration. It is because the heat treatment densifies the glass matrix, and that can eliminate scattering inside the sample. Despite five times difference in Gd doping concentration, the curves after RTT tends to be consistent with each other. Besides, it is worth to notice that after the RTT, the absorption peak around 274 nm is much stronger than reported in [8] and it is more pronounced at higher Gd concentrations. This peak coincides with the difference (~36500 cm^{-1} in wavenumbers) between the upper level (^6I_J) and the ground state ($^8S_{7/2}$) of Gd^{3+}.

PL measurements of the sample with Gd concentration 400 ppm were carried out using a spectrofluorometer (Fluorolog-3, HORIBA Scientific) at a room temperature (Fig. 2). All the data had been corrected for the spectral response sensitivity of the detection system and referenced spectrum of the Xe-lamp used for excitation.

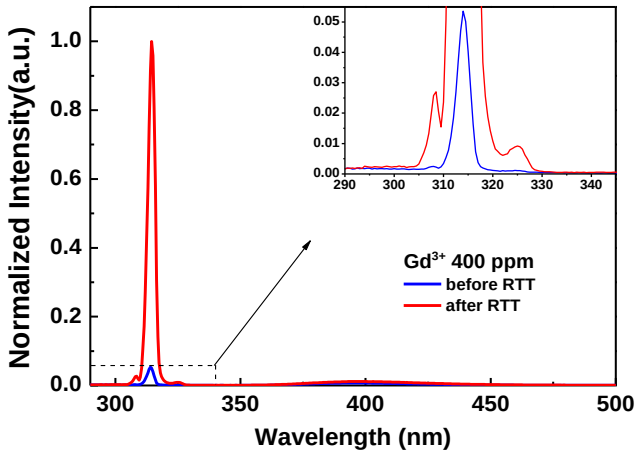

Figure 2. Emission spectrum under 274 nm excitation. Inset: Enlargement of the 290-345 nm spectral region

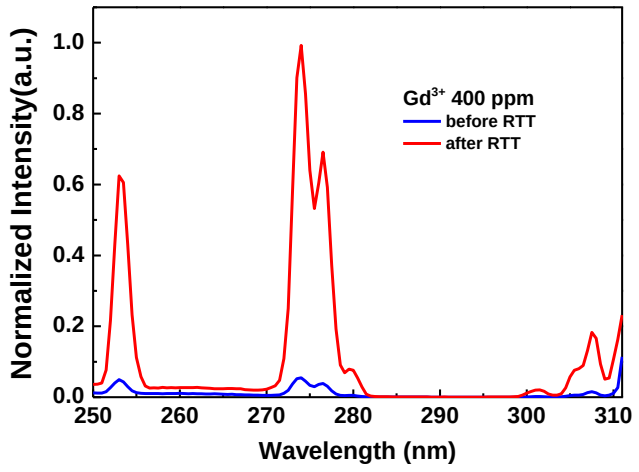

Figure 3. Excitation spectrum for 314 nm emission

The observed strong and sharp line centered at 314 nm results from radiative transitions between $^6P_{7/2}$ and $^8S_{7/2}$ at 274 nm. Detailed spectrum in inset of Fig. 2 shows the sideband at 308 nm is probably due to Gd^{3+} transition of $^6P_{5/2} \rightarrow {}^8S_{7/2}$.

The excitation spectrum for 314 nm emission is displayed in Fig. 3. Excitation wavelength peaking at 253 nm, 274 nm, 276 nm and 308 nm originate from the ^6D_J, ^6I_J, $^6P_{5/2} \rightarrow {}^8S_{7/2}$, where the strongest peaking wavelength is assigned to the 274 nm.

It is extremely interesting to note that both emission and excitation spectrum of the samples have got prominent enhancement after RTT as predicted but the very peaks on each curves are not shifted. In addition, the broad intrinsic host emission under shorter excited wavelength [8], with a maximum around 380 nm that extends to 420 nm in Fig. 2, can't be relieved during the heat treatment.

IV. Conclusion

In conclusion, enhanced UV photoluminescence in Gd^{3+}-doped silica has been observed after glass densification by rapid thermal annealing. Significant decrease of the loss covering the UV band and strengthened absorption peak around 274 nm are observed. The most intense UV emission around 314 nm from the $^6P_{7/2}$ to $^8S_{7/2}$ transition of Gd^{3+} ions is observed when samples are excited under 274 nm pump. The luminescence of Gd^{3+} could be exploited in future research aimed at UV generation in solid-state laser systems.

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