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# Gallium doped $SiO_2$: Towards a new luminescent material

S. Barsanti [a], M. Cannas [b], P. Bicchi [a,*]

[a] Department of Physics, University of Siena, Via Roma, 56, 53100 Siena, Italy
[b] Department of Physical and Astronomical Sciences, University of Palermo, Via Archirafi 36, 90123 Palermo, Italy

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**Abstract**

We show how the interaction between Ga atoms and silica samples in a hot environment gives rise to permanent inclusions of Ga inside the silica matrix which, in turn, produce typical luminescence features. The Ga doped silica is analyzed via laser induced fluorescence, photoluminescence and electron paramagnetic resonance spectroscopies. The results evidence the presence of modifications induced by the Ga inclusions inside the silica matrix and some preliminary hypothesis on their nature are advanced. Possible applications of such Ga doped silica are also mentioned.


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## 1. Introduction

Several properties of silica based materials, and especially those relevant for its wide employment in technological areas such as optics and telecommunications, can be induced by dopant species [1,2]. Substitutional and interstitial impurities cause perturbations in the structural and defect-related properties leading to the appearance of optical absorption and luminescence bands or to the photosensitivity to the ultraviolet (UV) laser radiation [2]. On the other hand, impurity clusters embedded in the silica matrix also manifest optical features linked to their size distribution and matrix interaction that have revealed promising for the development of broad-band wave guiding devices and quantum scale devices for non-linear optics applications [3,4]. Therefore, large attention is currently paid to experience the placement of dopant atoms in required regions aiming to realize new devices with desired performances. In particular the Ga related optical properties in gallium/silica interfaces have been recently studied [5].

While performing experiments of laser assisted collisions in dense Ga vapors confined in fused-quartz cells at temperatures higher than 900 °C, we measured a decrease in the Ga atomic density if compared to its value derived from the saturated vapor pressure [6]. As the cells are sealed, the decrease was attributed to the diffusion of Ga atoms inside the silica network. This effect has important consequences in fundamental physics as it has been proved to be one of the major causes of the quenching of the radiation trapping in dense Ga vapors [7]. Moreover, the potential technological applications have triggered the study of the optical properties induced by these Ga inclusions inside vitreous silica. In the following we report a systematic study on different silica samples thermally treated in absence or in presence of a Ga atmosphere, after the first preliminary observations published in references [8,9]. The samples have been examined by the combined use of several spectroscopic techniques including laser induced fluorescence (LIF), optical absorption (OA), photoluminescence (PL), and electron paramagnetic resonance (EPR). The aim is the characterization of the electronic and vibrational properties induced by the Ga doping.

* Corresponding author. Tel.: +39 0577 234672; fax: +39 0577 234689.
*E-mail address:* bicchi@unisi.it (P. Bicchi).

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## 2. Experimental procedure

We investigated Herasil 3 silica samples ($5 \times 5 \times 1$ mm$^3$) (H3), provided by Heraeus. To obtain the Ga doping, the sample referred as H3/Ga is heated up to 1050 °C, kept at that temperature for 8 h in presence of Ga vapors, whose saturated vapor pressure is 1.4 Pa, and then cooled down to room temperature at which all the measurements are performed. The heating process takes place in stainless steel heat pipe ovens (HPO) [10] whose hot part can reach temperatures up to 1100 °C stabilized to ±1 °C. For comparison, another sample underwent the same thermal treatment in an inert He atmosphere, H3/He.

The LIF spectra are obtained with a typical apparatus whose main features are summarized in the following. The excitation in the near UV, including that corresponding to the fundamental Ga transition $4^2P_{1/2} \rightarrow 5^2S_{1/2}$ at 24 788 cm$^{-1}$, are provided by pulses from a dye laser pumped by the second harmonic of a Nd-YAG laser, with 10 ns duration and a repetition rate of 10 Hz. The laser power density ranges between 150 and 200 KW/cm$^2$. The fluorescence spectra from the samples are dispersed by an 1 m monochromator with 18 cm$^{-1}$ resolution, and monitored at right angles with the exciting beam. The emission is detected by means of a photomultiplier whose output feeds a box-car integrator for frequency resolved signals or a digital oscilloscope (500 MHz bandwidth) in order to get the time resolved signals.

OA spectra in the visible and UV range were detected by a double beam spectrometer (JASCO V-560) with 2 nm bandwidth. PL emission and excitation (PLE) spectra are carried out by a spectrofluorometer (JASCO FP-6500), mounting a 150 W xenon lamp, and both excitation and emission bandwidths are set to be 3 nm. PL profiles are corrected for the spectral response of the detection system while the PLE profiles are corrected for the spectral efficiency of the exciting light by using a Rhodamine B sample in glycerol as a reference.

EPR measurements are carried out by means of a spectrometer (Bruker EMX) working at frequency $\nu \approx 9.8$ GHz (X band) with 100 kHz magnetic-field modulation frequency and 0.4 mT peak to peak amplitude, and by detecting the first-harmonic signal. The concentration of EPR active defects is determined, with relative accuracy of 10%, by comparing the intensity of their signal with that of $E'$ center in a reference sample. The defects concentration in the latter was evaluated, with absolute accuracy of 20%, using the instantaneous diffusion method in spin-echo decay measurements carried out in a pulsed EPR spectrometer [11].

## 3. Results

The appearance of peculiar fluorescence signals from the sample thermally treated in Ga atmosphere is evident in Fig. 1 where a portion of the LIF spectra following excitation at 24 788 cm$^{-1}$ is reported for three different situations.

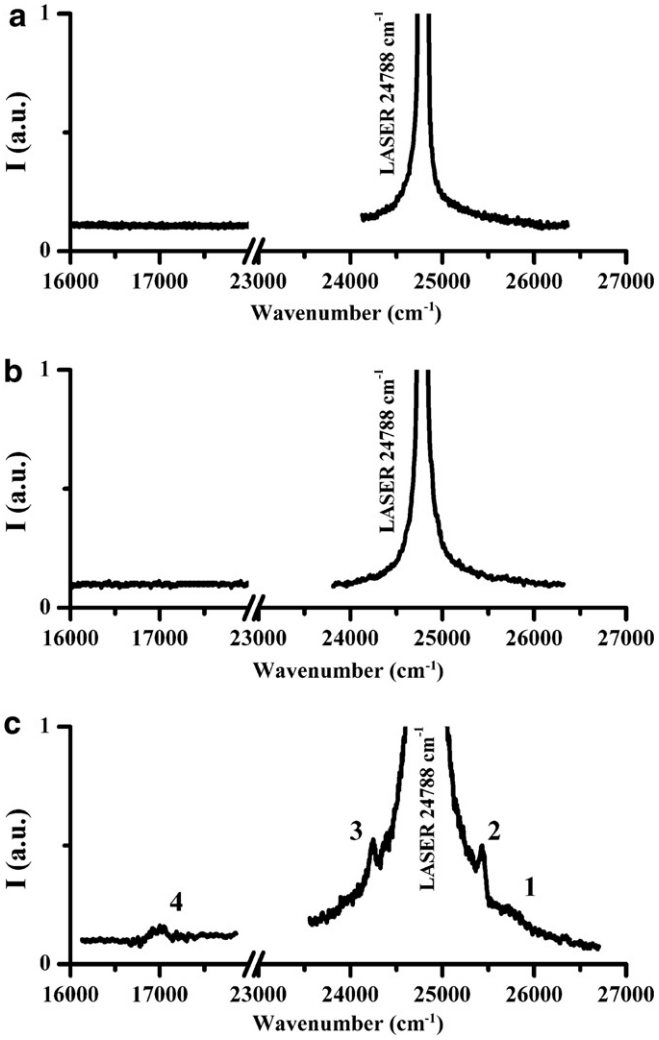


Fig. 1. Portion of the LIF spectra recorded at room temperature from a Herasil 3 silica sample excited at 24 788 cm$^{-1}$ before the thermal treatment (a), after the thermal treatment in an inert He atmosphere (b), and after the thermal treatment in Ga atmosphere, (c).

Fig. 1a shows the spectrum from the brand new H3 sample, which was recorded to check that the observed features were not due to contaminants in the sample. The spectra recorded in H3/He and H3/Ga samples are plotted in Fig. 1b and c, respectively. The modification induced in the silica samples by the presence of the Ga vapor manifests in the rise of peaks 1 (~940 cm$^{-1}$ to the *blue* of the excitation), 2 (~640 cm$^{-1}$ to the *blue* of the excitation), 3 (~540 cm$^{-1}$ to the *red* of the excitation) and 4 (at 17 000 cm$^{-1}$). Some of these features are shown in Fig. 2 where the same portion of the LIF spectrum obtained from the H3/Ga sample is reported for different excitations. In Fig. 2b the excitation is at 24 788 cm$^{-1}$, as in Fig. 1c, while in Fig. 2a and c, the excitation is shifted by 185 cm$^{-1}$ to the *red* and to the *blue* respectively. It is clear that the group of peaks 1, 2, and 3 behave differently from peak 4. The first three peaks, when the laser is detuned either to *red* or to *blue*, are shifted by the same energy, while the last peak remains at 17 000 cm$^{-1}$ for laser detuning to *red* and disap-