Journal of Luminescence 177 (2016) 127–132

Contents lists available at ScienceDirect

Journal of Luminescence

journal homepage: www.elsevier.com/locate/jlumin

Full Length Article

Evidence of different red emissions in irradiated germanosilicate materials

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ARTICLE INFO

Article history:
Received 26 November 2015
Received in revised form
19 April 2016
Accepted 21 April 2016
Available online 27 April 2016

Keywords:
Ge-doped silica
Optical fibers
Point defects
Radiation effects
Photoluminescence

ABSTRACT

This experimental investigation is focused on a radiation induced red emission in Ge doped silica materials, elaborated with different methods and processes. The differently irradiated samples as well as the pristine ones were analyzed with various spectroscopic techniques, such as confocal microscopy luminescence (CML), time resolved luminescence (TRL), photoluminescence excitation (PLE) and electron paramagnetic resonance (EPR). Our data prove that irradiation induces a red luminescence related to the presence of the Ge atoms. Such emission features a photoexcitation spectrum in the UV-blue spectral range and, TRL measurements show that its decrease differs from a single exponential law with a lifetime of tens of nanoseconds. CML measurements under laser at 633 nm evidenced the lack of correlation of the emission here reported with that of the Ge- or Si- non bridging oxygen hole centers. Moreover, our EPR experiments highlighted the lack of correlation between the red emitting defect with other radiation induced paramagnetic centers such as the E′Ge and Ge(2). The relation of the investigated emission with the H(II) defects, previously considered as responsible for a red emission, can not be totally excluded.

1. Introduction

Silica doping (amorphous silicon dioxide SiO_2) is a widely employed procedure to obtain glass with different physical properties. A large part of this dopant engineering is related to the optical fiber technology [1–4]. Ge doping is very common in such fields, since it enhances the refractive index of silica [5], allowing to design the fiber refractive index profile required for the light guidance over kilometers of fiber. Doping however also implies other modifications that involve the glass network [6,7], the presence of point defects [8] and the radiation response of the materials [9–11]. This last topic has been widely studied both from the basic research and the applicative point of view [12–26]. Nevertheless, much research has been conducted into the properties of Ge-related defects, which play a predominant role in the behavior of germanosilicate glasses. Among them, several have been identified such as GLPC (Germanium lone pair center [12,27], $>$Ge:, twofold coordinated Ge atom having two electrons forming a lone pair [8]), Ge(1) ($>Ge^{\bullet}<$, unpaired electron trapped on a tetra-coordinated Ge atom [12,14]), Ge(2) (structural model under debate [12–14]) and E′Ge ($\equiv Ge^{\bullet}$, threefold coordinated Ge atom having an unpaired electron [12,25,26]). Whereas, fewer investigations have focused on the GeX [28,11] that is considered to be a diamagnetic center, the Ge non bridging hole center (Ge–$O^{\bullet}$, unpaired electron localized on an oxygen atom bonded to a Ge one [29], Ge-NBOHC), and on their luminescence at ~680 nm (~1.83 eV). Furthermore, Awazu et al. reported [30] a correlation between the paramagnetic resonance signal of the H(II) ($>Ge^{\bullet}$–H [1,30]) defects and the amplitude of an emission band which peaked at about 680 nm. However, this emission and its origin have not been fully clarified till now. In this work a detailed investigation of the 680 nm emission is carried out employing different Ge-doped silica materials. The samples were prepared by many of the known procedures and irradiated with different irradiation sources to evidence the connection of this band to the presence of Ge atoms and its appearance after irradiation.

2. Experimental

For the present investigation we considered several Ge doped silica samples differing by their manufacturing processes and Ge doping levels. Furthermore, the samples were irradiated at different dose levels and with different type of sources. The corresponding

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http://dx.doi.org/10.1016/j.jlumin.2016.04.044
0022-2313/

Table 1
Nickname of the sample, irradiation source, dose, silica typology and Ge and F contents.

Name	Irr	Dose (MGy)	Type	Ge (wt%)	F (wt%)
SOL	β	10.4	Sol–Gel	1	0
PC20	β	1	PCVD	20	0
PC4	β	1	PCVD	4.5	0
VAD	γ	10	VAD	3.8	0
MC-FGeD	γ	9.7	MCVD	4.5–9	0
MC-FGeF	γ	10	MCVD	8.4	1
MC-FGe	γ	7.8	MCVD	2–11	0
MC-F	γ	7.8	MCVD	0	1.2

characteristics are summarized in Table 1. For all the materials the irradiated specimen will be indicated by name/I, where I stand for irradiated. The sample named SOL was obtained by the sol–gel technique, further details have been reported in [24,31]. The samples PC20 and PC4 were manufactured by Plasma-activated Chemical Vapor Deposition (PCVD) [31] procedure and they are of commercial origin. The VAD is a vapor axial deposition sample with Ge doping of 3.8 wt%. The MC-FGeD is an optical fiber designed with two doping level steps of about 4.5 and 9 Ge wt% respectively; the fiber is obtained with a drawing speed of ~40 m/min and a tension of ~70 g [32].

The MC-FGeF is a silica optical fiber obtained using drawing speed of ~40 m/min and drawing tension of ~65 g. In this fiber the Ge doping level was of about 9 Ge wt% and the external part of the doped zone was co-doped with ~1 wt% of F [33]. The MC-FGe is a Ge doped fiber with four steps profile from 2 to 11 wt% and the preform was drawn with a speed of ~40 m/min and a tension of ~70 g [16]. Finally, the MC-F is a pure silica core optical fiber produced with drawing tension and speed of ~47 g and ~35 m/min respectively. All the fibers were produced by iXFiber SAS [34] and the original preforms were obtained using the MCVD (modified chemical vapor deposition) process.

The samples were irradiated in different conditions and with different sources as described below.

The β irradiations were carried out using a linear accelerator (National Institute for Laser, Plasma and Radiation Physics, Magurele, Romania) or pulsed RF S-band Linac (ENEA C.R. Frascati, Italy). For the former the mean electron energy was 6 MeV and dose rate ~120 kGy/h, while for the latter the mean electron energy was 3 MeV and the dose rate ~430 kGy/h.

The γ irradiations were performed by exposing the samples to the BRIGITTE ^{60}Co source of the SCK-CEN (Mol, Belgium), the maximum applied dose rate was ~80 kGy/h. All the irradiations were performed at room temperature.

The Confocal Micro Luminescence (CML) experiments were carried out with an Aramis (Jobin-Yvon) confocal spectrometer. The probe laser sources at 442 nm and 633 nm were focused on the samples using a 100 × objective and light coming out from the samples was diffracted by a 150 grooves/mm grating on a CCD camera. In addition, the system is equipped with a translational stage, which allows to change the position in the X, Y and Z directions with micrometric precision.

Time resolved luminescence (TRL) measurements and photoluminescence excitation (PLE) spectra were acquired using an optical parametric oscillator equipped with a II harmonic generation nonlinear crystal pumped by the third harmonic of a Nd:YAG laser with pulse width of 5 ns and repetition rate of 10 Hz. The light emitted by the samples was spectrally resolved by a grating with 300 grooves/mm and recorded by a gated intensified CCD equipped with a delay generator. The system allows us to set the acquisition time width t_w and delay time t_d with respect to the probe laser pulse. For the TRL measurements the t_w was kept constant while the t_d was changed. For the PLE experiments both parameters were fixed to the values of 650 ns and 50 ns respectively, the incident laser power was measured to normalize the spectra recorded at the different excitation wavelengths.

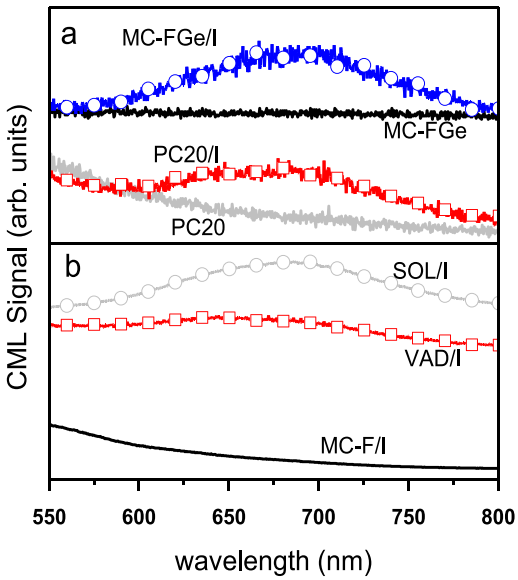

Fig. 1. CML spectrum recorded in (▬) MC-FGe, (▬○▬) MC-FGe/I, (▬□▬) PC20/I (▬) PC20 (panel a) and (▬) MC-F/I (core), (▬□▬) VAD/I and (▬○▬) SOL/I (panel b). The spectra have been recorded under excitation at 442 nm and were vertically shifted for presentation clarity. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)

Electron paramagnetic resonance (EPR) measurements were recorded with an X-band (9.8 GHz) Bruker EMX-Micro Bay spectrometer employing a 100 kHz modulating magnetic field.

All the measurements were recorded five years after irradiation and at room temperature.

3. Results and discussion

3.1. Radiation induced red emission under 442 nm probe laser

Fig. 1a illustrates the CML spectra recorded, under excitation at 442 nm, on the samples MC-FGe before (black line) and after irradiation (blue line) up to 7.8 MGy and on the samples PC20 before (gray line) and after irradiation (red line) up to 1 MGy. The data provide evidence, in the irradiated samples, for the presence of an emission band peaking at ~680 nm (~1.82 eV), with a full width at half maximum (FWHM) of ~120 nm. This emission is detected in all the investigated Ge doped samples after irradiation, regardless of their manufacturing process or irradiation sources used. Similar emission band is found in the irradiated SOL and VAD materials (Fig. 1b). Importantly, this band is absent in Ge-free MC-F fiber.

3.2. Characterization of lifetime and excitation spectrum of the 680 nm emission band

To further characterize the properties of the emission band reported in Fig. 1 we performed time resolved luminescence (TRL) and photoluminescence excitation (PLE) experiments.

In Fig. 2, we report the natural logarithm of the ratio between values of the emission area (range 600–770 nm) measured at different delay times from the laser pulse (380 nm) and the one measured at 40 ns (I_0). The data indicate that the emission area decreases following a non-single exponential law. In detail, we