Study of point defects in as-drawn and irradiated Ge-doped optical fibers using cathodoluminescence

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Abstract. In the present paper, we report an experimental investigation of Ge-doped Optical Fibers (OFs) which were investigated by Cathodoluminescence (CL) measurements. We followed the evolution, under 10 keV electron exposure, of the emissions present in three different samples: the first one was the as-drawn fiber (pristine), the second one was irradiated with a CW UV laser at 244 nm and the last one was irradiated at the dose of 9 MGy (SiO₂) by γ-rays. Moreover, taking advantage of the employed experimental set-up, which allows to perform spatially-resolved (<1µm) CL measures, we were able to investigate the emission evolution in two differently doped zones of the fiber. Our data indicate that (i) the CL spectra of our three samples are dominated by the 400 nm emission band related to the Germanium Lone Pair Center (GLPC), (ii) the spatial distribution of this defect differs in the three fibers and (iii) the electron exposure decreases the GLPC concentration in all samples (pristine, UV and γ irradiated). A comparison between the CL and photoluminescence (PL) measurements shows comparable results.

1. Introduction
Recently, the different harsh environments such as those associated with nuclear power plants, space missions or various research facilities are considered for Optical Fibers (OFs) integration as parts of data transfer or sensing systems (temperature, strain, dose) [1]. Thanks to their high performances, silica based OFs have been shown to be promising candidates for operation in such severe conditions (different types of radiations, temperature…).

When OFs are exposed to either ionizing or non-ionizing radiations like γ-rays, X-rays or electrons, three main effects are induced: the first one is the Radiation Induced Attenuation (RIA), which degrades the transmitted signal via the absorbing point defects; the second one is the Radiation Induced Emission (RIE) that decreases the signal to noise ratio; the third one is the compaction phenomenon that can induce a refractive index change [1].

Among the diversity of the OFs, the Ge-doped ones are of great importance. They are used for the telecom-grade applications thanks to the Ge ability to increase the refractive index of the OF’s cores [2]. Also, their photosensitivity property is used for Fiber Bragg Gratings (FBG) inscription [3]. However,
doping with Ge will induce Ge-related point defects that need to be well controlled under irradiation. Many previous investigations have dealt with the radiation effects on Ge-doped silica [4-7]. Among the Ge-related point defects, the Germanium Lone Pair Center (GLPC) plays a key role for understanding the radiation effects on germanosilicate OFs [8, 9]. This defect consists in twofold coordinated Ge atom owning a lone pair of electrons, and it is characterized by two absorption bands at ~5.1 and ~3.8 eV and two emission bands at ~4.2 and 3.1 eV [10]. Under irradiation, this defect is converted into other point defects such as Ge(1) and Ge(2) [8, 9]. The Ge(1) is formed by an unpaired electron that is trapped in a substitutional tetra-coordinated Ge atom [11, 12]. For Ge(2), a few models have been put forward: the first one in [11] defines the Ge(2) as a variant type of the Ge(1) center, while a second model [12] considers that Ge(2) is an ionized GLPC, a third model suggests that the Ge(2) is a GLPC converted into a threefold forward oriented Ge atom [13].

Cathodoluminescence (CL) is a pertinent technique in order to study the luminescent point defects in dielectric materials like silica, since it allows to perform spatially-resolved in-situ measurements by using both CL spectroscopy and CL imaging. Various studies have been performed before using CL for investigating point defects and electron radiation effects on silica, such as in ref [14-16], but few of them were devoted to Ge-doped OFs [17-20]. In this work, we employed a CL-based apparatus to investigate the effects of different radiations (γ-rays, UV, Electrons) on germanosilicate OFs.

2. Experimental details

2.1. EDX and CL set-up
A field emission Scanning Electron Microscopy (SEM) (JSM 7100f JEOL) equipped with Energy Dispersive X-ray (EDX) detector (X-Max 80, OXFORD) and CL detector (GATAN MONOCL4) has been used for both EDX and CL measurements.

The following results have been obtained using a beam energy of 10 keV and a probe current in the order of 10 nA. These conditions lead to a penetration depth of about 1.3 µm and a spatial resolution of ~1µm.

Concerning the CL measurements, the employed instrument works in the 300-750 nm spectral range, and it allows to perform two kinds of CL measurements: CL spectroscopy that is used for the identification of the emitting defects and CL imaging, which is used to investigate the spatial distribution of the defects. The panchromatic imaging is performed by collecting all the emitted light whereas the monochromatic imaging consists in isolating a narrow spectral range (11 nm) in order to single out the associated spatial distribution.

For the kinetics data, an imaging analysis has been used for the intensity calculation which has been already described in ref [20].

2.2. Photoluminescence set-up
In the present investigation, the Photoluminescence (PL) measurements were carried out with an Aramis (Jobin-Yvon) confocal system which employs a HeCd laser at 325 nm as excitation and a ×40 UV objective which allows a spatial resolution of ~1µm.

2.3. Samples description
The employed OFs are multimode with a cladding diameter of 125 µm and a core diameter of 62.5 µm. The samples were manufactured using MCVD (Modified Chemical Vapor Deposition) process and were provided by iXBlue photonic division. As it is shown in Fig.1, the core of these OFs has a 2 steps Ge-doping profile: the highest doping level, ~9 wt%, is situated in the inner part of the core, the second one, ~ 5 wt%, is situated in the outer part of the core.

Two samples of the same OF have been differently irradiated while the third one was left as a pristine reference. The first irradiated sample was exposed to γ-rays up to 9MGy (SiO2) using the Brigitte 60Co source of SCK-CEN. The second sample was irradiated by UV continuum laser at 244 nm with a spot of ~0.5 mm using ~110 mW of power, by moving the sample longitudinally with a speed of 0.13 cm/s. Using the relation employed in [21] the fluence of the laser radiation is ~ 21.5 J/cm². The different samples have been cleaved and their transverse cross sections has been exposed to a normal incident electron beam associated to the CL measurements.
3. Results and discussion

Fig. 2.a reports the CL panchromatic image of the transverse cross section of the pristine OF; it shows that the emitted light is mainly provided by the core part of the OF. The normalized CL spectra reported in the panel (b) of the same figure show the presence of an emission band centered at ~400 nm in the two Ge doped regions. This band is assigned to the GLPC point defects [10]. The pure silica cladding appears darker in the panchromatic image, which means that the intensity of the different intrinsic emitting defects present in this part is much lower compared with the one emitted by the core. Three bands are present in this cladding part, the first one at ~460 nm is attributed to the ODC (II) (oxygen deficient center) [10, 22, 23], the origin of the second band centered at 560 nm is still undetermined, since it could be either the second order of the emission of ODC (II) at 280 nm or a STE (Self-Trapped Exciton) center according to some papers in literature [16] or a sum of both of them. The last band at 650 nm is an emission band of the NBOHC (Non Bridging Oxygen Hole Center) [10, 22, 23]. The same CL spectra have been obtained for the two irradiated samples. These data indicate that the Ge doping induces additional luminescent defects in the studied spectral range.

The Panchromatic images of the 9MGy γ irradiated fiber as well as the UV irradiated one are shown in Fig.3.a, b and Fig.3.c, d respectively before and after being exposed to 10 keV of electron radiation. Please note that different samples of the same OFs were used to perform the panchromatic images and the monochromatic image analysis. For panchromatic images, there are some differences in the used initial conditions for brightness and contrast, which explains the difference in absolute intensity between
the panchromatic images of the pristine, 9 MGy γ irradiated and UV irradiated samples before electron irradiation (Fig.2a, 3a and 3c). On contrary, these conditions were kept constant for the monochromatic images acquisition, which allows to directly compare the profiles presented in Fig.4b and 4c and in the study of the GLPC kinetics (Fig.5).

These data show that for both samples (9 MGy and UV irradiated) the electron irradiation caused a significant decrease of the luminescence in the core of the OFs. According to the previous reported spectra, this luminescence is mainly due to the GLPC. Moreover, before irradiating with electrons, the luminescence was more intense in the inner part of the core, where the Ge concentration is higher, whereas after irradiation, the outer part of the core is brighter. The same behavior was observed for the pristine sample [20].

![Figure 3](image-url)

**Figure 3.** CL panchromatic images, a and b: the 9 MGy γ pre irradiated sample before and after electron irradiation respectively. C and d: the UV pre irradiated sample before and after electron irradiation respectively.

Concerning the pure silica part of the samples (cladding), the reported panchromatic images show no significant changes in the intrinsic luminescent defects in the investigated spectral domain. This could be due to the experimental conditions (adjustment of the image acquisition) which prevent us to detect the intrinsic pure silica luminescent defects compared to the Ge related ones.

Fig.4 shows the different radial profiles along the core radius of the different samples at 400 nm: for PL measurements (a), and for CL measurements before (b) and after (c) electron radiation. These profiles have been obtained by performing a mapping for PL measurements and by acquiring monochromatic images for the CL measurements. Fig.4.a and fig.4.b report the spatial distributions of the GLPC before irradiation with electrons, obtained with two different techniques. We can note that the ratio between the pristine and the 9 MGy γ irradiated samples is ~0.77 for CL measurements and ~0.63 for the PL ones, which means that the pre irradiation with γ-rays up to 9 MGy has induced a reduction of the GLPC signal of about 30%. Regarding the UV irradiated sample (fig.4.b), we note that according to the CL measurements, no significant change was induced in the GLPC intensity compared with the pristine sample. This could be due to the small accumulated dose deposited in the sample during irradiation.

After being exposed to 10 keV of electron beam for 30 mins, the three samples show a similar radial distribution of the GLPC luminescence (see Fig.4.c). This luminescence decreased significantly and its signal is higher in the lower Ge-doped region, confirming the previous panchromatic images reported in Fig.3.
In order to clarify the Ge impact on the bleaching process of GLPC, an in-situ investigation under electron exposure in the different parts of the OF’s core is reported in Fig.5. The GLPC kinetics has been obtained by acquiring a series of monochromatic images at 400 nm. We observe that the GLPC signals were bleached in both the inner and the outer regions of the core and reached a minimum level by the end of the irradiation. After 20 scans (~6 mins) the intensity of the signal at 400 nm has been decreased from ~150 to ~50 in the 9 wt% Ge-doped part, while it has been reduced from ~90 to ~40 in the 5 wt% Ge-doped zone. Also, the 9 MGy irradiated sample showed a lower GLPC concentration in the first recorded image (the first scan) confirming a bleaching effect induced by the γ pre irradiation. This bleaching behavior under radiation could be explained by a conversion process of the GLPC to other Ge-related centers [8]. After a sufficiently long electron irradiation, the GLPC kinetics reached equilibrium due to the radiation induced conversion and the back conversion of these centers.

**Figure 4.** Radial distributions along the core radius of the luminescence at 400 nm. a. PL measurements. b. CL measurements before electron exposure. c. CL measurements after 30 mins of electron exposure.

![Graph](image1.png)

**Figure 5.** In-situ bleaching kinetics of the GLPC signal under electronic radiation. a. at 3µm away from the center of the core (zone doped with 9 wt% of Ge). b. at 25 µm away from the center of the core (zone doped with 5 wt% of Ge).

![Graph](image2.png)

4. Conclusion

We reported an in-situ CL investigation of two irradiated samples of germanosilicate OF and we compared their behaviors with a pristine one. Our data indicate that the luminescence observed in all samples is dominated by the emission band at 400 nm attributed to the GLPC point defects. The pre-irradiation with γ-rays up to 9 MGy induced a bleaching of the GLPC intensity of about 30%. Moreover, the GLPC kinetics of the different samples showed that after a sufficiently long electron irradiation, the GLPC concentrations reach a saturation level which is independent from the pre-irradiation. This means
that an equilibrium is reached between the conversion and the back conversion processes involving GLPC and the other radiation induced Ge-related defects. Furthermore, we observed that after being exposed to electronic radiation for 30 mins, the GLPC concentration are lower in the Ge-doped region of the core with the higher Ge concentration.

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