Caractérisation par cathodoluminescence des défauts ponctuels dans les matériaux à base de silice: fibres optiques et nanoparticules

Imene Reghioua

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Imène Reghioua

Cathodoluminescence Characterization
of Point Defects in Silica-Based
Materials: Optical Fibers and
Nanoparticles

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Introduction

Silicon dioxide, in its amorphous state (a-SiO$_2$) represents a relevant material for optics, photonics and solid state physics. Thanks to its exceptional properties such as its high transparency, low conductivity and low price, silica was selected as a key material for a wide range of applications [1]. Among the well-known silica-based devices we are interested in this work in the optical fiber (OF) technology. Optical fibers consist in a thin wire of functionalized glass able to transport light over long distances opening the way to high bandwidth data links. Optical fibers have then revolutionized the world of communication and they successfully replaced the copper cables thanks to their high performances in terms of transmission speed and low attenuation, among others... [2]. The importance of this field was recognized in 2009 when the Nobel Prize in physics was given to C. K. Kao [3].

The studies of optical fibers were held before 5 decades, and since then, their development has not stopped, their use is now extended from their main application, i.e. telecommunication technologies, to other uses such as optical fiber based sensors [4]. Exploiting the scattering phenomena in a-SiO$_2$ (Rayleigh, Brillouin and Raman), the optical fibers can be used as the sensitive part of distributed temperature and/or strain sensors, offering millions of measurement points along km-long fiber [4]. In addition to these applications, since several decades, the potential of these fibers in harsh environments (radiations and temperature) was investigated. Silica-based radiation tolerant optical fibers are today integrated in photonic devices considered for implementation in several harsh environments: space, nuclear power plants and Large Hadron Collider [5]. Furthermore, some kinds of optical fibers are sufficiently radiation-sensitive to be exploited as dosimeters [5].

Despite the fact that silica-based OFs are promising candidates to be employed under severe conditions, the observed increase of their attenuation under exposure remains a major limitation. The fiber manufacturing process, their profile of use as well as the various environmental conditions of the targeted application cause different levels of signal degradation, which usually noticeably affect the performances of the device. Under irradiation, three main macroscopic effects are induced in the OFs: (i) Radiation Induced Attenuation (RIA), which degrades the transmitted signal; (ii) Radiation Induced Emission (REI), which represents the emission of some parasitic light during the irradiation; and finally (iii) the compaction, or the densification, which induces the change of the refractive index as a
One of the main origins of these previous effects is the radiation induced point defects, sometimes also called color centers, that contribute significantly to the RIA phenomenon, RIE and can cause refractive index variation as a consequence of the Kramers-Kronig relation.

In order to ensure the proper operation of these silica-based devices, a comprehensive understanding of the different mechanisms of creation, conversion and bleaching of point defects is required to imagine ways to control these processes in order to improve the fiber radiation response. In this context, it appeared mandatory to combine several experimental and theoretical investigations to be able to identify the structure and the properties of these point defects [6]–[10]. Indeed, it is necessary to compare the experimental results with the theoretical ones in order to confirm the suggested models, and vice versa, the performed simulations need to be confronted with the experimental data in order to be validated. Hence, it is possible to identify the structure and the characteristics of point defects under several conditions. Regarding the experimental part, usually three different spectroscopy techniques are jointly employed in order to identify point defects: (i) Optical Absorption (OA); (ii) Electron Paramagnetic Resonance (EPR); and (iii) Photoluminescence (PL). By testing with the three techniques different samples having been exposed to external constraints such as temperature or irradiation, it is possible to find correlations between the evolution of a given defect concentration observed by EPR with those of optical properties (OA or PL). Thanks to these experimental works, many point defects have been identified, and their behavior under different conditions are known, see for instance [5]–[7], [9], [11] for reviews. Although the large numbers of papers dealing with this topic, the structure and the properties of many other defects are still debated and their behaviors, as a function of the irradiation and temperature, are not definitively known.

The identification of defects and their properties is not straightforward due to the intrinsic limitations of each of the previously described techniques. In Table 1 we list the main advantages and drawbacks of the most used techniques: OA, EPR and PL:
### TABLE 1: Advantages and drawbacks of EPR, OA and PL techniques

<table>
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<tr>
<th>Technique</th>
<th>Advantages</th>
<th>Drawbacks</th>
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<tr>
<td>EPR</td>
<td>Adapted for paramagnetic defects</td>
<td>• Cannot be used for diamagnetic defects</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Usually not spatially-resolved: global information including the one from the fiber part not supporting the light propagation</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Usually post-mortem measurements: not adapted to the study of transient or metastable defects</td>
</tr>
<tr>
<td>OA</td>
<td>Can be used for all optical active defects</td>
<td>• Global information (limited spatial resolution)</td>
</tr>
<tr>
<td></td>
<td>In-situ measurements</td>
<td>• Overlapping between the multiple absorption bands of the defects</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Affected by the guiding properties of the fibers (especially for single mode fibers)</td>
</tr>
<tr>
<td>PL</td>
<td>Spatially-resolved measurements</td>
<td>• Limited to emitting color centers</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Usually post-mortem measurements</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Very sensitive to photobleaching effects</td>
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</table>

In the present PhD thesis, we evaluate the potential of a complementary technique named cathodoluminescence (CL) to complete the set of available experimental tools for the study of point defects in pure and differently doped silica materials, such as optical fibers and silica-based nanoparticles. Thanks to its excitation system, based on electronic bombardment of the material of interest, CL offers the possibility to perform an in-situ and spatially resolved luminescence measurements, using simultaneously the electron beam as a probe and as an irradiation source able to affect the material. Using an electron beam offers additional advantages in terms of excitation, compared to photoluminescence. For PL experiments, several laser sources are necessary in order to cover the excitation bands of the various emitting point defects generated under irradiation. Whilst cathodoluminescence allows, using electron energies above 1 keV, the excitation of the whole set of luminescent defects present in the silica band gap; the limits are reported to the spectral range allowed by the detector. As it will be deeply discussed in this manuscript, the duality probe/irradiation source in CL will, however,
complicate the analysis of the data, especially if some pre-existing defects are quickly bleached by the electrons.

Some previous investigations have studied bulk samples of silicon dioxide by cathodoluminescence [12]–[23] providing evidence that several emissions exist in silica and quartz. Their kinetics have also been characterized during the electron beam exposure. Fewer works dealt, however, with silica-based OFs. These studies mainly focused the germanosilicate optical fibers as these fibers are the most studied ones in telecommunication applications [24]–[28]. These investigations were principally interested in studying the impact of glass co-doping effects as well as other fabrication processes on the nature and spatial distributions of emitting defects.

In this PhD thesis, the CL technique is used to complete a large number of results obtained on a set of ad hoc optical fibers already characterized by the EPR, CML (Confocal Micro-Luminescence) and OA techniques. In details, numerous ad hoc (sometimes called canonical) samples were specifically designed by the consortium involved in this work to perform a coupled experimental and theoretical approach. This approach was fully explained in [29], [30], with results detailed in [31] [32]. These multimode OFs have been produced by Modified Chemical Vapor Deposition (MCVD) with 65.5 µm diameter cores that are differently doped in their core and cladding. The available set of samples allows studying the radiation effects in various classes of OFs. Three main classes are considered according to their radiation response: (i) telecom-grade germanosilicate OFs; (ii) radiation-hardened OFs, with pure or F-doped silica core fibers and F-doped claddings. These fibers present low RIA at MGy dose levels in the infrared domain and can serve for data links and for distributed sensing; (iii) the third class is the radiation-sensitive OFs including the P or Al-doped fibers offering promising properties for dosimetry applications. In our research group, several investigations have been performed since 2008 using these canonical fibers, revealing the contributions of various intrinsic and extrinsic parameters of the point defect generation: nature of radiation, dose, dose rate, fiber chemical composition, and fiber fabrication processes. The knowledge acquired, through these experiments, is used to validate some ab-initio calculation models that can now be exploited to study the properties of some of the point defects that cannot easily be experimentally investigated. In the following table, we summarize the previous studies done by our group on the samples used in this PhD thesis:
TABLE 2: Classification of canonical optical fibers

<table>
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<tr>
<th>Fibers category</th>
<th>Dopants</th>
<th>References</th>
</tr>
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<tbody>
<tr>
<td>Telecom-grade</td>
<td>Ge, Ge/F, Ge/Ce</td>
<td>[5], [29], [30], [33]–[52]</td>
</tr>
<tr>
<td>Radiation-sensitive</td>
<td>P, P/Ce</td>
<td>[5], [42], [45], [53]–[57]</td>
</tr>
<tr>
<td>Radiation-hardened</td>
<td>Pure-silica, F, N</td>
<td>[5], [29], [41], [42], [45], [58]–[63]</td>
</tr>
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</table>

The manuscript, devoted to the study of point defects in silica-based materials, is divided into five chapters. In the first chapter, a state-of-the-art is provided regarding the amorphous silica glass and the main point defects studied in the literature and discussed in this PhD thesis. The second chapter describes the experimental methods used for the research activities, principally the CL, the PL and EDX (energy dispersive X-ray) techniques that were used to characterize the samples under test. The third chapter consists in an overview of the different point defects that can be detected by CL as a function of silica doping with Ge, P, Ce, N, Al... The fourth chapter will be devoted to deep and ‘complete’ characterization of one defect: the Germanium Lone Pair Center (GLPC) discussing its generation and bleaching mechanisms as a function of the CL test conditions. The final chapter gives a preliminary study by CL of silica nanoparticles produced by an original procedure involving bulk materials and ns pulsed KrF lasers to open the door to future perspectives concerning the employment of this technique.
Chapter I

Background on silica glass

I.1. Silica structure

Based on X-ray and neutron scattering studies [11], the most common microscopic structure of silicon dioxide is tetrahedral formed by a silicon atom bounded to four oxygen atoms for both crystalline (apart from Stishovite) and amorphous states (see figure (I.1)).

![Structure of silicon dioxide according to Zachariasen [11], [64].](image)

In (α-SiO$_2$) or quartz, the typical characteristics of a tetrahedron are: two long bonds 1.62 Å, and two short bonds, 1.60 Å, with an angle Si-O-Si of 144° [11]. The amorphous form of silica (a-SiO$_2$) differs from the crystalline one by the absence of symmetry at long distances. The most adopted model, to describe the amorphous silicon dioxide, is known as Continuous Random Network (CRN) [64]. In this model, the structural unit forming the crystalline SiO$_2$ remains the same for the amorphous one (the same bonds) with some differences in terms of symmetry, which means an identical electronic structure. The main difference is the Si-O-Si
(inter-tetrahedral) angle value that varies between 120° and 180° in the a-SiO₂ instead of being 144° as in quartz.

In order to better describe the glass structure, it was proposed in [11] to use four ranges starting by the basic tetrahedron unit until the long range density:

a. **Range I**: which is the elementary structural unit. It consists of the silicon atom at the center of the tetrahedron bounded to four oxygen atoms. It is necessary while studying the amorphous SiO₂ to define the geometrical parameters that identify its structure. For this range, both the internal Si-O bond lengths and O-Si-O angles need to be known, they are of about 1.6 Å and 109.5°.

b. **Range II**: this range deals with the neighborhood of the basic structures. It consists of the interconnections and the orientations between the fundamental basic units. In other words, we need to provide the angles Si-O-Si (β) and the torsional angles α₁ and α₂ (as above illustrated in Figure (I.2)). It is because of the broad distributions of these parameters that most of the disorder takes place in this range.

c. **Range III**: also called the intermediate range, where the topology of network could be defined. Unfortunately, this is not rigorously possible in the real case due to the disorder of the matrix. However, a shortest path analysis can be performed on the rings constituting the glass network. A ring is represented by the smallest closed path along Si-O bonds, which starts and ends on the same Si atom and, it is also identified by the contained number (n) of tetrahedrons. Differing from the crystalline states of SiO₂, the vitreous one is characterized by a statistic of rings including the four- and the three-membered ones (n=4 and n=3), whose vibrations are detectable using Raman spectroscopy [65], [66].

d. **Range VI**: this fourth range is named the long range and is characterized by density fluctuations, on the scale of several tens of Å.

### I.2. Defect generation in silica

Defects can be present in non-irradiated silica due to many reasons including the presence of impurities, dopants, or some other imperfections caused by the fabrication process.

The defects generated in the OFs are caused essentially by inserting dopants and the production process: preform deposition, fiber drawing process. Another important source of point defects generation remains the irradiation, which is be able to induce a large variety of point defects also from regular sites and/or by converting precursor sites into other radiation induced centers.
Griscom in [67] summarized the different processes taking place when silica-based materials are exposed to ionizing or non-ionizing irradiations. A review scheme of the possible cascade mechanisms is given in figure I.2:

![Figure I.2: Schematic of the different mechanisms of radiation damage in glass [67].](image)

There are two main radiation-matter interactions leading to defect generation: knock-on and ionization processes. The first process, also known as direct atomic displacement, takes place when the incident particles interact with the network atoms, moving them from their initial positions through the network by transferring their kinetic energy [68]. For silica, the needed energies required to induce O or Si displacements are of ~10 and ~18 eV respectively [69]. The second process is ionization, which involves the electrons of the material. By this process, an electron from the valence band is promoted to the conduction band with a certain kinetic energy, creating an electron-hole pair. These electron-hole pairs can recombine in various ways, some of them, illustrated in figure I.2, lead to the generation of point defects. The recombination of the resulting electron-hole pair could be either radiative or non-radiative. The radiative recombination releases photons, whereas the non-radiative one occurs by releasing phonons. In addition, both electrons and holes can be trapped at some pre-existing sites or impurities present in the network.

In this work, we mainly focused our study on the capability of the electron beam to generate, excite and affect the point defect populations. Defects generation under electron bombardment depends on the energy of the primary electrons $E_0$. In particular, if $E_0 > 5$ keV most of the defects are generated through radiolytic processes, whereas the minimum energy needed to
displace an oxygen atom via knock-on process is $E_0 > 65$ keV and $E_0 > 200$ keV for silicon atoms [15], [67], [70]. The maximum available electron energy in this work is $E_0 = 20$ keV, ensuring that the radiolytic process dominates.

It is worth to mention that during the electron irradiation, an electrostatic charging may lead to a localized electrical field, which can cause a migration of the mobile charged defects and their further micro-segregation [16], [71], [72]. In details, it has been predicted in [71] that for a coated glass with a conducting film sample and under the influence of the axial electric field, the negatively charged pre-existing and the radiation-induced-defects will migrate toward the surface, whereas the positively charged ones will migrate to the zones containing a maximum of negative trapped charge. Hence, the electron irradiation causes a subsurface electron field, which may lead to the migration of the charged defects within the interaction volume, as it was shown in [72].

I.3. Intrinsic defects in silica

In this section, we present a non-exhaustive review of the different types of defects that are related to the pure-silica matrix (concerns Si and O atoms) or the fluorine-doped silica as F is not yet associated to specific optically active defect. This topic has been largely studied in the literature, because of the importance of silica in the technological and industrial domains, strongly improving our knowledge about this class of defects even if some defects still have to be better characterized.

I.3.1. the $E'$ center

This famous defect is the most studied in the literature. It belongs to the oxygen vacancy defects family, and it is also known as a silicon dangling bond with an unpaired localized electron. The most common form of $E'$ ($E'_\gamma$) center consists of a Si atom bonded to three oxygen atoms with an unpaired electron [9], [11] (see figure I.3). It was first observed by R.A. Weeks [73] in neutron-irradiated $\alpha$-quartz and in silica.
This defect was extensively investigated using the EPR technique [9], [74]–[78], since it is a paramagnetic center. We also remind that $E'_y$ is characterized by an absorption band at 5.8 eV with full-width at half maximum (FWHM) of 0.8 eV, and no luminescence has been clearly attributed to this defects until now [9], [74], [75]. The EPR studies reveal that there are other varieties of $E'$ defects which differ according to their surrounding environments [76]–[78].

I.3.2. the Oxygen Deficient Center ODC (I)

Also named as oxygen mono vacancy or neutral oxygen vacancy, ODC (I) is a diamagnetic defect formed by two bonded silicon atoms ($\equiv Si \rightarrow Si \equiv$) as described is figure I.4. An absorption band centered at ~7.6 eV with FWHM of ~0.5 eV [9] is ascribed to ODC(I). This attribution was also confirmed by ab-initio calculations such as [10], [30], [31].
I.3.3. the Oxygen Deficient Center ODC (II)

The third oxygen deficient center is the ODC (II) also known as twofold coordinated silicon. This defect is diamagnetic and consists in a silicon atom bonded to two oxygen atoms and owning a lone pair of electrons (\(= \text{Si}: \)) see figure I.5.a) [79].

![Figure I.5.a. The structure of ODC (II) defect b. energetic schema of ODC (II) according to [9].](image)

ODC (II) presents a main absorption band at \(~5\) eV (FWHM \(~0.36\) eV) and one at about \(3.15\) eV (FWHM \(~0.34\) eV), furthermore it is also responsible for two emission bands centered at \(~4.4\) eV (FWHM \(~0.45\) eV, \(\tau \sim 4\) ns) and \(2.7\) eV (FWHM \(~0.35\) eV, \(\tau \sim 10.2\) ms) related to the singlet-singlet and singlet-triplet transitions [9], [80], [17].

The two emission bands that are attributed to ODC (II), were also detected in cathodoluminescence (CL) spectra that have been performed on silica-based materials [12], [17], [19]. It has been shown, in the case of thin film of SiO\(_2\), that the relative intensities of the two emission bands depend on the energy of primary electrons [12], [19], [81]. If the used energy is high \(~200\) keV, this induces more inner secondary electrons that excite the singlet – singlet transition, which by consequence favors the emission of the UV band 4.4 eV). Whereas using a lower incident energy \((1 – 16\) keV), there are less inner secondary electrons that induce singlet – singlet transition than those who induce triplet – singlet transition, so the main observed emission is the blue one (2.7 eV).

I.3.4. the Non-Bridging Oxygen Hole Center (NBOHC)

This defect is composed by a dangling oxygen bond \((\equiv \text{Si} \rightarrow \text{O} \cdot, \) figure I.6) [82]–[84]. It is a paramagnetic center which is characterized by an absorption/excitation band at \(~1.97\) eV (FWHM \(~0.17\) ) [11], in which the absorption spectra can be hardly isolated and can appear with
a larger (FWHM ~0.44 eV) [85] because of the overlap with other component (see the following), and others in the range from 4 to 8 eV [85]–[87]. An emission band peaked at ~1.91 eV (FWHM ~0.17 eV, τ = 10-20 μs) is assigned to NBOHC [85], [88].

![Figure I.6. a. The structure of NBOHC. b. PL and time-resolved excitation spectra of NBOHC adapted from [85].](image)

Different mechanisms can lead to the creation of NBOHC. The first one, under irradiation, consists in the breaking of a Si − O − Si = regular bond, especially the strained ones [89]. The second generation process is through the radiolysis of the OH groups [90]–[92], especially if the investigated silica contains a high amount of hydroxyl groups. A third possible generation process is through the breaking of a peroxy linkage (explained later on) under irradiation [93].

The red luminescent band at 1.9 eV has been observed using CL in different kinds of silica [15], [17] and also in thin layers of SiO₂ [12]. Its kinetics as a function of irradiation have been studied, and it appears that the concentration of this defect increases with the electron fluence [17].
I.3.5. the Peroxy Linkage (POL)

This defect noted as $\equiv \text{Si} \rightarrow \text{O} \rightarrow \text{O} \rightarrow \text{Si} \equiv$ is also called peroxo bridge. This diamagnetic center consists of two silicon atoms that are linked through two oxygen atoms [94]–[96] as described in figure I.7.

Regarding the optical absorption, a weak band centered at $\sim 7.1$ eV (FWHM $\sim 0.7$ eV) is attributed to the POL according to [95]. Whereas in [96] an absorption band peaked at $\sim 3.77$ eV (FWHM $\sim 0.69$ eV) is ascribed to the POL. A recent theoretical paper [97] has correlated the structure of the Peroxy Bridge with its optical properties. In particular, the authors highlighted, using first principles calculations, that in the presence of the bridges broad and weak absorption bands exist between 3.2 and 7.5 eV. Furthermore, it has been shown that the Si $\rightarrow$ O $\rightarrow$ O $\rightarrow$ Si dihedral angle distribution plays an important role to determine the electronic transitions [97].

I.3.6. the Peroxy Radical (POR)

The POR ($\equiv \text{Si} \rightarrow \text{O} \rightarrow \text{O} \cdot$) is a paramagnetic defect formed by a silicon atom linked to oxygen molecule with an unpaired electron delocalized on two adjacent oxygen atoms [11].
This defect is known by its EPR signal [98] and it could be induced by irradiation where a POL may play the role of precursor, or during the fabrication process, such as the drawing of the OFs [99], or by the diffusion of oxygen atoms that can generate this defects as well [98].

The optical absorption bands of POR are still controversial, and there is no definitive attribution to them. For instance, there exist one band peaked at ~5.3 eV (FWHM ~1.3 eV) which is assigned to this center [100], and another at 7.6 eV (FWHM ~0.65 eV) ascribed to this defect too [9], [98]. A theoretical work suggests to attribute the absorption band at ~6.4 eV to POR defects [10]. It is worth to mention that the absorption band at ~2 eV, attributed to this defect, overlaps with the one of the NBOHC, which renders difficult to well determine its spectroscopic features [98]. Further works are needed to better highlight the optical properties of these defects.

1.3.7. Self-trapped holes (STHs)

The STHs are paramagnetic metastable defects. Two types of STHs are distinguished: \( \text{STH}_1 \) and \( \text{STH}_2 \). \( \text{STH}_1 \) consists of a trapped hole on one bridging oxygen atom, whereas \( \text{STH}_2 \) structure consists in a delocalized hole on two oxygen atoms of the same \( \text{SiO}_3 \) tetrahedron [101]. It has been shown that STHs are responsible of most transient red/ near-IR optical absorption in low-OH silica-based OFs at ambient temperature [102]. Optical absorption bands that are centered at ~ 1.63 eV and ~1.88 eV are attributed to \( \text{STH}_1 \) and \( \text{STH}_2 \) respectively in case of silica-based optical fibers [103]. Whilst in bulk silica, these absorption bands are rather centered in ~2.6 eV and ~2.16 eV for \( \text{STH}_1 \) and \( \text{STH}_2 \) respectively [104].
I.3.8. Self-Trapped Excitons (STEs)

STE is an electron-hole pair localized in a self-induced lattice distortion [105]. In silica, the displacement of the oxygen atom has been attributed to the STE [16], [106], [107]. In [108], the authors attributed two optical absorption bands to the STE that are independent from the impurities such as the chlorine and the OH groups. The first one at ~4.2 eV (FWHM = 1.16 eV) and the second one at 5.3 eV (FWHM = 0.78 eV) [108]. The STE can relax radiatively by emitting a luminescent band centered between ~2 eV and 2.3 eV with a lifetime of ~ 1 ms [18], [109] or non-radiatively. The non-radiative decay of STE has been shown to be one of the important mechanisms of the point defects creation in silica, principally by destroying Si ─ O ─ Si linkages. The main defects resulting from the non-radiative decay of STE in irradiated silica (by laser, X or γ rays) are E' and NBOHC [14], [89], [110].

Other defects are existing in silica-based materials which are due to interstitial atomic or molecular species such as oxygen chlorine or hydrogen and so on.

I.3.9. Impurities and interstitial related defects

Chlorine is known to be an undesirable impurity especially for optical fibers since it has been shown that it absorbs in the UV spectral range [11]. It is found in synthetic silica due to the fabrication method [111]. Usually, Cl is an unavoidable impurity that is incorporated in synthetic silica made by MCVD process as Si-Cl groups. Previous investigations were dedicated for the study of Cl impurity effects in synthetic silica using EPR [112], optical absorption and photoluminescence [11], [113, p. 200] and recently, by photoluminescence and Raman spectroscopy [114]. These investigations show that there is an instable, at room temperature, EPR signal that is ascribed to Cl0 [112] in irradiated silica. Optical absorption bands at ~ 3.8 eV (FWHM ~0.67 eV), ~3.65 eV (FWHM ~0.86 eV), ~3.26 eV (FWHM ~1.2 eV) have been attributed to Cl-related defects such as Cl2, Cl2, Cl0 [11], [29], [115] [41]. Furthermore, an emission band that is centered at ~ 1.5 eV was attributed to the Cl2 interstitial molecules [113] and it was related to an 3.8 eV absorption band. The attribution of the optical absorptions to the Cl-related defects, their relation with the other defects, as well as the different mechanisms responsible of their creation are still not totally clear in the literature. Griscom in [116] reported that most of the E' centers were induced by the mechanism of dissociative electron capture at chlorine-decorated oxygen vacancies, and he proposed some models that can explain the creation of some Cl-related defects [116]. A recent investigation [114] demonstrates that at T>160 K, there is a PL band, with excitation at about 3.8 eV, peaked at 1.22 eV (FWHM ~0.42 eV, average lifetime of ~ 5 ms at 13 K) which is ascribed to the Cl2.
The presence of hydrogen in fused silica has attracted the attention of many researchers because of its capacity to increase its photosensitivity [117]–[119]. The H(I) center which is denoted as $= \text{Si} \cdots \text{H}$, is a paramagnetic defect that is similar to the Si E’ (by replacing one oxygen atom by hydrogen one). Skuja in [9] has demonstrated that the ODC centers are an important precursor for generating the H(I) centers. And it was suggested that these centers are generated by an H trapped on ODC center. An optical absorption band at 4.9 eV was attributed to this defect [100] with no related luminescence. Another H-related center is OH group that is known in OFs by their absorption in the NIR spectral domain [120].

Some results of this thesis will deal with the O$_2$ loaded OFs. Uniform concentration of O$_2$ molecule inside the fiber diameter can be obtained using the diffusion process employing high O$_2$ pressure and temperature treatments in the time scale of weeks [49]. On another side, we remind that molecular oxygen can be generated during irradiation [16], [107], [121], [122]. These molecules are characterized by a luminescent band at 1272 nm (0.975 eV; lifetime ~ 0.8 s) at and a Raman signature at 1549 cm$^{-1}$ [123], [124].

The absorption bands related to intrinsic silica defects can be summarized in the following figure I.8 [5].

![Figure I.8. Summary of the main absorption bands related to intrinsic silica defects [5].](image)

I.4. Ge-doped silica related point defect

In OFs, the Ge incorporation serves to increase the refractive-index of OF’s core, allowing the light guiding with low attenuation at the telecommunication windows. These properties of germanosilicate optical fibers explain that this fiber type is the main one used for data links [125].
Ge-doped silica exhibits two very interesting features: photosensitivity and second harmonic generation [126], [127]. The photosensitivity consists in the possibility to modify the glass refractive index under UV laser insolation [126]. This property is routinely used to manufacture Fiber Bragg Gratings (FBG) [128].

The second harmonic generation is a nonlinear phenomenon based on breaking the centrosymmetry and the generation of a light having a wavelength that is half of the incident one, which is usually a laser [127].

For the above cited reasons, the Ge-doped silica and especially OFs have been largely investigated in the literature, including the Ge related point defects. Both Ge and Si are in the 14th column of the periodic table, the Ge incorporation in the silica glass is then achieved by substituting a silicon atom leading to a Ge atom bonded to 4 oxygen atoms to form a tetrahedron [129], [130]. It is worth to mention that, in the presence of Ge in OFs under irradiation for low doses, the main generated defects are the Ge-related ones rather than those related to Si [41], since the incorporation of the Ge atom that substitute the Si one favors the creation of Ge-related defects.

The following paragraphs present a summary of the today knowledge about Ge-doped silica point defects and their optical properties.

**I.4.1. Ge E’ center**

This paramagnetic defect is analogous to the Si E’ by substituting the Si atom by the Ge one noted as = Ge• [131] (see figure I.9). It has been investigated using EPR measurements, which were correlated with the optical absorption. This latter shows a band peaked at ~ 6.3 eV (FWHM ~1.1 eV) and no known luminescent bands were attributed to this center [132], [133].

![Figure I.9. Structure of Ge E’](image-url)
1.4.2. Ge Neutral Oxygen Mono-Vacancy (NOMV or Ge ODC)

![Image of Ge NOMV defect]

Figure I. 10. The structure of Ge NOMV defect, where T can be either Ge or Si

It is a diamagnetic center in which an atom of Ge is directly bond to another Ge or Si atom instead of an oxygen atom (either $\equiv Ge \equiv Ge \equiv$ or $\equiv Ge \equiv Si \equiv$). An optical absorption peaked at $\sim 5.06$ eV (FWHM $\sim 0.38$ eV) was suggested to be related to this defect, and no luminescence was attributed to it (apart from the bands related to the GLPC) [9], [134]. However, in [31] it has been shown by using the state-of-art first-principle calculations that the associated absorption consists of a weak and broad band between 7-8 eV. The absorption band at $\sim 5$ eV was also attributed to the SiODC (II) according to [52], [135].

It has been demonstrated by performing DFT (Density Functional Technique) calculations in [31], [136] that it is easier to form a NOMV center in the presence of Ge rather than in the presence of Si.

1.4.3. the Germanium Lone Pair Center (GLPC)

Also known as the two fold coordinated Ge or Ge-ODC (II), the GLPC is a diamagnetic defect that can be seen as the counterpart of Si-ODC (II). Its structure is formed by a Ge atom bonded to two oxygen ones and owning a lone pair of electrons (see figure I.11.a) [80].
It is characterized by two absorption bands centered at \(~5.1\) eV (FWHM \(~0.46\) eV) and \(~3.7\) eV (FWHM \(~0.4\) eV) that are ascribed to the singlet-singlet \((S_0 \rightarrow S_1)\) and singlet-triplet \((S_0 \rightarrow T_1)\) transitions respectively. Two emission bands are attributed to this center, the first one is centered at \(~4.3\) eV (FWHM \(~0.43\) eV, lifetime \(~7\) ns at \(10\) K) and the second one at \(~3.1\) eV (FWHM \(~0.48\) eV, lifetime \(~113\) \(\mu\)s). They are due to the singlet-singlet \((S_1 \rightarrow S_0)\) and triplet-singlet \((T_1 \rightarrow S_0)\) transitions respectively [80], [135].

A simplified energy scheme highlighting the different electronic transitions of GLPCs is given in figure I.11.b, where the \(S_0\) refers to the electronic ground singlet state level, \(S_1\) denotes the first singlet electronic state, whereas the first triplet excited state is named \(T_1\). The intersystem crossing process (ISC) is noted as \(K_{ISC}\). This last parameter is a temperature dependent process [135].

This center is considered as one of the most important Ge-related defects, because of its key role in the generation mechanisms of the radiation induced defects [39], [137]–[139]. In particular, the GLPC are present in non-irradiated glasses and these defects can play the role of precursor centers, able to be converted during irradiation into other Ge-related defects. It has been suggested that the bleaching of the absorption band at \(5.1\) eV (also known by \(B_{20}\)) under UV insolation leads to the creation of new absorption bands, attributed to other Ge-related defects such as Ge(1) and Ge(2) (explained later on), that contribute to the refractive index changes [140], [141].
The GLPC defects were studied using CL by Fitting et al in [20] where the authors have investigated Ge-doped silica layers, and they attributed the 3.1 eV emission to the two-fold coordinated Ge.

Ge-doped optical fibers and preforms have been characterized by CL in [24]–[28]. However, the GLPC luminescence at ~3.1 eV was falsely ascribed to the E’ center [24]. These previous investigations highlight the effect of varying the MCVD fabrication process parameters on the distribution of luminescent defects. In details, CL results showed that the luminescence distribution is not only related to the Ge amount, but also to the radial distribution of internal stress induced in the waveguide during its fabrication. These combined effects explain that higher intensity of luminescence is detected at the core/cladding interface and in the central part of the core affected by the collapsing step.

1.4.4. the Ge(1)

Ge(1) is a paramagnetic defect noted as [GeO$_2$]$^\cdot$. It consists of a trapped electron at a substitutional Ge atom [141], [142].

![Figure I.12. The structure of Ge (1) center.](image)

This defect is induced by radiations [6], [39], [143] and has not yet been observed in non-irradiated samples. An optical absorption band at 4.4 – 4.6 eV (FWHM=1.3 – 1.39 eV) has been assigned to this center [131], [141], [144], [145].

1.4.5. the Ge(2)

Ge(2) is also a radiation-induced paramagnetic defect [6], [39], [143]. Its structure appears still controversial and two main experimental models have been suggested in literature (see figure I.12).
Figure I.13.a) The structure of Ge (2) center according to D.L. Griscom [142]. b) The Ge (2) structure according to Fujimaki [133].

The first model proposed by Griscom [142] considers that Ge(1) and Ge(2) are two energetically inequivalent configurations of a single trapped-electron center. These two centers are correlated with their Ge(II) and Ge(I) counterparts in quartz [116]. In this model, the Ge(2) is analogous to the so-called Ge(I) in the quartz, taking into account the fact that the Ge (I) has a glass-like quality in that the orbitals of the unpaired spins do not reflect any quartz-crystal symmetry. The second model of Ge(2) suggested by Fujimaki [133] considers that the Ge(2) is an ionized GLPC.

A third recent theoretical model [48] suggests that the Ge(2) is a three forward oriented Ge atom which is obtained from GLPC conversion.

Regarding the optical absorption of this defect, one band at ~5.8 eV (FWHM=0.9 – 1.2 eV) has been tentatively attributed to Ge(2) [131], [146].This attribution has to be considered not definitive since in other cases a band with similar spectral features has been attributed to the Ge(1) [139, 141].

I.4.6. the Ge NBOHC

This paramagnetic center is similar to the Si NBOHC, noted as ≡ Ge – O •. In literature, two absorption bands are attributed to this center, they are peaked at ~ 4.75 eV (FWHM ~0.49 eV) and 1.97 eV (FWHM ~0.3 eV) [144], [147], [148].
Ge-NBOHC is an emitting defect with a luminescent band centered at \( \sim 1.86 \) eV (FWHM \( \sim 0.18 \) eV, life time \( \sim 5.1 \mu s \) at T between 7 and 80 K) [82]. In the following figure, a summary of the main absorptions bands related to the Ge-doped OFs [5].

![Summary of the main absorption bands related to Ge-related defects](image)

I.4.7. the co-doping with Fluorine

Due to its importance, the Ge-doped silica based optical fibers were largely investigated, and also by adding other elements as co-dopants such as F or Ce.

The F doping is normally used to enhance the radiation resistance of silica-based OFs [149], [150], because of the decrease of the glassy disorder and of the strained \( \text{Si-O-Si} \) bond concentrations. Instead of doping the OF’s core with Ge or P, the cladding is doped with F, allowing to ensure the light guiding as the refractive-index of the cladding remains lower than the one of the pure-silica core [151].
When Ge and F are introduced together in the silica matrix of OFs, the optical losses of the OFs and their dependence on the drawing conditions are reduced according to [151]–[153]. Under irradiation, the F co-doping reduces the excess of losses caused by the radiation induced absorbing defects in the NIR [154] and the UV spectral range [155]. However, in [46], the authors find that the F co-doping does not affect the RIA levels measured during irradiation in the UV spectral range. Furthermore, their CML and EPR measurements showed an increase of the radiation induced NBOHCs related to both Si and Ge atoms and the Ge E’ centers, in the F co-doped samples [46], which is may be due to the small doped region.

I.5. P-doped silica related point defect
Phosphorus is a common dopant for silica-based OFs. Its incorporation has two essential roles. The first one concerns its ability to increase the refractive index of the OF’s core for light guiding [11] with good transparency in the UV domain [11], [156]–[158]. The second role is its capacity to facilitate the incorporation and the pumping of rare earth ions (Erbium, Ytterbium) to design active optical fibers to amplify signals at telecommunication wavelengths [157].

P increases the sensitivity of OFs to radiations, a property that researchers exploit to design punctual or distributed fiber-based dosimeters [159]–[162]. P-doped silica is very interesting for such applications as the growth kinetics of some P-related defects are linear with the radiation dose, at least up to 1 kGy(SiO₂) [55]. At the same time, co-doping phosphosilicate glasses with Cerium was shown to efficiently enhance their radiation tolerance [57], [163].

Unlike Ge-related point defects in silica, the P-related ones have been less investigated in the literature. The P is mainly incorporated in the silica matrix as P₂O₅. While a perfect silica tetrahedron is composed by a Si atom bonded to four oxygen ones, the ideal P₂O₅ consists of one non-bridging oxygen and three bridging oxygens linked to P atom as described in figure I.16. [7]. It is important to mention that from the chemical point of view, the P can make four covalent bonds with four oxygens, whereas its fifth electron of valence makes an ionic bond with one oxygen atom [164].
Figure I.16 the ideal structure of $\text{P}_2\text{O}_5$ according to [7].

The main paper in literature dealing with P-related point defects is the one of Griscom [7]. In this investigation, EPR and optical absorption measurements were performed on irradiated P-doped bulk silica and OFs. Thanks to the recorded data, various P-related defects have been identified and named $\text{P}_1$, $\text{P}_2$, $\text{P}_4$ and Phosphorus Oxygen Hole Center (POHC). Their structures are presented in the following table according to those proposed in [7].

![Chemical Formulas and Structures of Defects](image)

Figure I.17 the main P-related point defects induced by radiation in P-doped silica glass and their precursors, adapted from [7].

### 1.5.1. the Phosphorus Oxygen Hole Center (POHC)

This center presents two different configurations according to the EPR measurements, which were named stable POHC and metastable POHC. Its simplified structure consists in a P atom bonded to four oxygen atoms where three of them are bridging and the fourth one is a non-
bridging oxygen that hosts the unpaired electron. This configuration refers the metastable POHC that is stable only at low temperature but can be easily detected at room temperature too [7]. The second suggested configuration consists in an unpaired electron shared between two non-bridging oxygens bonded to the same P atom. This last configuration has been found to be stable at room temperature [7]. Three optical absorptions peaked at 2.2 eV (FWHM ~0.35 eV), 2.5 eV (FWHM ~0.64 eV) and 5.3 eV (FWHM ~0.74 eV) have been attributed to the stable POHC at room temperature. Whereas an optical absorption centered at ~3.1 eV (FWHM ~0.73 eV) is ascribed to the metastable POHC [7].

Concerning the luminescent features of this center, it was reported in [165] that an emission band centered at ~600 nm (~2.1 eV) may be assigned to POHC defects. This luminescence is excited and photobleached at 488 nm (2.54 eV), see figure I.18.

I.5.2. the P₁ center

This defect, that can be noted as ≡ P^* , is considered as the analogous of the Si-E'. It is formed by a trapped hole in the P₂O₃ precursor as shown in the above table (figure I. 17). According to [7] this defect absorbs at ~0.79 eV (FWHM ~0.29 eV), whilst in [166] an optical absorption centered at ~5.9 eV (FWHM ~1 eV) has been ascribed to P₁. There is no emission band attributed to this defects until now.
I.5.3. the P$_2$ center

The P$_2$ center consists of a trapped electron in P atom bonded to four oxygen atoms (see figure I.17). An optical absorption band peaked at ~4.5 eV (FWHM ~1.27 eV) is assigned to P$_2$ center according to [7]. However, another band centered at ~5.12 eV (FWHM ~1 eV) is assigned to the same defect according to [166]. A formation of POHC-P$_2$ pairs under radiation was reported in [54].

A luminescent band peaked at ~3 eV with lifetime of ~6 ms at RT was detected in P-doped OF in [53] and was tentatively ascribed to the positively charged tetra-coordinated P atom, which is considered as the precursor of P$_2$ center. This luminescence at ~3 eV can be excited at 4.8 eV and 6.3 eV as shown in the figure I.19.

![Figure I.19.a. Luminescence and b. excitation spectra of the tetra-coordinated Phosphorus [53].](image)

I.5.4. the P$_4$ center

Its structure shown in figure I.17. The precursors of this center can be the same than for the P$_1$ that are here converted by trapping an electron instead of a hole or a twofold coordinated P atom after trapping a hole [7]. An optical absorption peaked at ~4.8 eV (FWHM ~0.41 eV) is ascribed to P$_4$ defect [7], [166].

Two luminescent bands centered at ~3.1 eV (400 nm) and 4.6 eV (265 nm) were detected in P-doped core preform [23] under F$_2$ excimer laser (157 nm) excitation. The UV luminescence was assigned to PO$_4^{2-}$ complex ion and it is characterized by two lifetime constants ~30 ns and 5 µs, whereas the blue band at 3.1 eV, which seems similar to the band found in [53], was ascribed to the twofold coordinated phosphorus or P$_4$ center if it captures a hole [23]. This blue
luminescence is characterized by two decay constants $\tau_1 = 5.5$ ms (similar to what was found in [53]) and $\tau_2 = 20$ ns. These two decays were explained by a triplet-singlet and singlet-singlet transitions respectively.

Regarding the cathodoluminescence investigation on P-doped glasses, a comparison between the SiO$_2$-P crystal and 3P$_2$O$_5$.7SiO$_2$ glass at 293 K was performed in [22]. It highlights some differences in their luminescent features. In particular, two bands at ~570 nm (2.17 eV, lifetime ~6-7 µs) and ~300 nm (4.13 eV, lifetime ~2 µs)) were detected in the glass sample. Whereas in the quartz sample, the positions were rather at ~620 nm (~1.99 eV, lifetime ~6-7 µs) and 300 nm (4.13 eV lifetime ~2µs) accompanied with a band at 400 nm (3.09 eV), this later band was suggested to be due to the remains of STE in quartz, and it is almost absent in the glass sample because of the much smaller efficiency of STE in silica glass [22].

![Figure I.20.a CL spectra of SiO$_2$-P crystal and 3P$_2$O$_5$.7SiO$_2$ glass at 293 K [22].](image)

In the following figure, we present the main absorption bands that are related to the P-doped OFs [5].
I.5.6. co-doping with Ce

As we previously mentioned, the P doping helps the introduction of rare earth elements in silica matrix, by limiting their aggregation. In the present work, we will discuss later the electron irradiation effects on P and Ce co-doped OF, so in this section we briefly summarize some previous results. It was found that the Ce co-doping in OF’s core can enhance the radiation response of P-doped silica in the NIR spectral range for doses lower than 1 kGy [163, 167]. The Ce is introduced in silica as Ce\(^{3+}\) [168] and it can be converted into Ce\(^{4+}\) under radiation [168], the released electron then can be trapped at P\(_1\) centers, which are responsible of the absorption in the NIR spectral range [168]. The Ce\(^{3+}\) has an absorption band at \(~3.9\) eV, whilst Ce\(^{4+}\) absorbs light at \(~4.8\) eV [169].

In P/Ce co-doped silica materials, new absorption bands can appear in the UV-Visible spectral domain according to [170]. It has been also shown that the Ce\(^{3+}\) excitation and luminescence spectra were shifted in the P doped silica compared to the pure silica host matrix [170]. An emission band at \(~370\) nm (3.35 eV) is ascribed to the Ce\(^{3+}\) centers, and it has been shown that this luminescence is affected by the rare-earth surrounding environment [169, 170, 171].

I.6. Al-doped silica related point defects

The aluminum doping in silica is generally used for the same reason of the P doping, since the presence of Al atoms facilitates the rare earth ions incorporation.

The aluminum is inserted in the quartz matrix by substituting a Si atom [173, 174], the resulting tetrahedron is then composed by an Al atom bonded to four oxygens, as shown in figure I.22. Since the aluminum replacing the silicon atom has only three electrons on its outer shell, then a fourth electron is needed in order to complete the four bonds with oxygens forming
the tetrahedron. This electron comes usually from some cations such as the alkaline that play the role of charge compensation forming a \( \{\text{AlO}_4^-/\text{M}^+\} \) [174].

![Al tetrahedron](image.png)

Figure I. 22. The resulted tetrahedron structure from the substitution of Si by Al.

Contrary to the other dopants such as Ge, only few papers in literature discussed about the Al as dopant or impurity in quartz or in silica glass (see for example [175]–[177]). In the following section, we present a summary of the Al-related point defects in silica.

I.6.1. the Al - E’ center
As its name indicates, this defect similar to the (Si-E’) is noted as \( \equiv \text{Al} \cdot \) (see figure I. 23.a). It is a paramagnetic defect where its EPR signature is discussed in [175], [178]. An optical absorption centered at \( \sim 4.1 \text{ eV} \) is associated to this defect [175].

I.6.2. the AIOHC center
This defect is analogous to the NBOHC (an intrinsic silica center) which can be noted as \( \equiv \text{Al} - \text{O} \cdot \), where an Al atom is linked to three bridging oxygen atoms and to a fourth non-bridging oxygen that hosts the hole [179] (see figure I.23.b).

Since it is a paramagnetic center, an EPR signal is detected and attributed to AIOHC point defects [180]. Regarding the optical absorption, two bands peaked at \( \sim 2.3 \text{ eV} \) (FWHM \( \sim 0.9 \text{ eV} \)) and \( 3.2 \text{ eV} \) (FWHM \( \sim 1 \text{ eV} \)) were assigned to the AIOHC [175]. Another band centered at \( \sim 2.5 \text{ eV} \) (FWHM \( \sim 1.5 \text{ eV} \)) is assigned to AIOHC in the quartz [181]. Whilst the optical absorption peaked at \( \sim 4.9 \text{ eV} \) (FWHM \( \sim 1.08 \text{ eV} \)) is still not assigned yet [175].
Concerning the luminescent features in Al containing silica, some investigations have been performed in silica [176], [177] and quartz [182]. It has been found that the alkali ions play an important role for understanding the origin of luminescence in such materials. In [176] the authors highlighted that the Al plays the role of hole trap, and it is presumed that alkali ions plays the role of electron trap.

In [182], three emission bands centered at 440 nm (2.82 eV, FWHM −0.64 eV), 425 nm (2.92 eV, FWHM ∼0.75 eV) and 380 nm (3.26 eV, FWHM ∼0.92 eV) were distinguished by their thermal quenching in the quartz. Among these bands only the component at 380 nm (3.26 eV) was assigned to the recombination of an electron with a hole trapped adjacent to an alkali-compensated aluminum ion (Al-M⁺).

In regards to the CL measurements that have been performed on the Al-doped silica, Trukhin et al [176] did not detect new luminescent features (apart from the intrinsic silica emitting centers) in different Al-doped samples, having Al concentration from 0.01 wt% to 1.5 wt% (even if the authors detected an Al-related luminescence at ~3.3 eV using other excitations). The same observation was reported in [27] where Al-doped OF preforms were investigated using CL. Indeed, they only observed the intrinsic luminescence of silica (typically the emission at 460 nm of ODC(II) ). However, the authors highlighted that unlike the Ge-doped preforms, the Al-doped OF preforms (Al content of ~2 – 3 wt%) are less sensitive to the fabrication process, since the spatial distribution of the luminescence did not show a particular sensitivity to the stressed regions.
In [17] different types of silica were studied using CL. Among them, some Herasil and the Infrasil samples (natural silica) that contain the Al as impurity (<50 ppm and <15 ppm respectively). The results show an emission at ~ 3.4 eV in both types of silica. This emission was ascribed to the charge compensated substitutional \( \text{Al}^{3+} \) \((\text{Al}^{3+} - M^+)\) where \( M^+ \) is \( \text{Li}^+ \), \( \text{Na}^+ \), \( \text{K}^+ \) or \( \text{H}^+ \). The behavior of such luminescence under electron beam exposure was shown to decrease as a function of the irradiation time [17].

I.7. N-doped silica related point defect

The nitrogen doping in OFs has recently attracted the attention of the researchers because of its capacity of increasing the refractive index of the OF’s core [183] even with a low dopant content. In details, it has been demonstrated that doping with N, in a way that a small amount of oxygen (1%) is substituted by nitrogen, can provide an increase of refractive index of about 0.015%, which allows to guide the light [184]. In order to elaborate N-doped OF, it is necessary to use the SPCVD method (Surface Plasma Chemical Vapor Deposition) [185].

Some properties of the N-doped silica under radiation have been characterized. These fibers exhibit radiation-induced loss levels comparable to those of the Pure-Silica-Core (PSC) fibers in the NIR spectral range at moderate dose levels (<100 kGy). The N-doped OFs can then be considered as radiation hardened [186], [187].

N-doped OFs are photosensitive allowing to inscribe Fiber Bragg Gratings [188] using pulsed ArF excimer laser at 193 nm. Moreover, the N-doped silica-based FBG were shown to be more resistant to high temperature (900°C) than those written in germanosilicate fibers [184].

The nitrogen is incorporated in the silica network by replacing an oxygen atom and not a silicon [184]. As a consequence, the main microscopic configuration of N in silica is the threefold coordinated one, in which an N atom is bonded to three Si atoms [189]. Although the advantages of using the N-doped OFs, only limited literature work have dealt with the N-related point defects.

The experimental investigations that were held to identify N-related centers were mainly based on EPR, OA and PL. Regarding EPR measurements and simulations, the main detected defect is associated with Si-E’ where one of the three basal oxygen is substituted by an N atom [189]. A second N-related EPR signature has been ascribed to a localized electron on an N atom linked to two Si atoms (noted as \( \equiv \text{Si} -\text{N•-Si} \equiv \)) [189], [190]. Another signal attributed to a trapped electron on a tetra-coordinated N atom (\( =\text{N•} = \)) has been also reported in [190], [191].
We are interested in the present work by the luminescent defects. Few investigations were dedicated to the study of optical absorption and luminescence of the N-doped silica [185, [192], [193] and recently [194]. In the following of this section we summarize the main results obtained by these previous studies.

Figure I.24 show the optical absorption spectrum of an N-doped preform [192]. This spectrum is decomposed into four Gaussian, where the positions of the first three bands are: 4.54 eV (FWHM ~0.4 eV), 5 eV (FWHM ~0.4 eV) and 5.77 eV (FWHM ~0.6 eV). The absorption at 5 eV is ascribed to the Si-ODC(II) [80], and the 5.77 eV is close to the absorption band attributed to Si-E' centers [11]. But due to the weak EPR signal of the Si-E', this attribution was ruled out by the authors of [192]. The origin of the remaining band peaking at 4.54 eV is still unknown.

![Absorption spectrum](image)

Figure I. 24. a. UV absorption spectrum of N-doped preform decomposed into Gaussian bands. b. the PL spectra of the same preform excited at 4.83 eV (solid line represents 10 Hz of modulation frequency, the dashed line represents 300 Hz) Adapted from [192].

Referring to the same figure I.24 in the panel b, PL spectra were recorded under 4.83 eV excitation, and four emission bands can be distinguished.

The bands centered at ~4.45 eV (FWHM ~0.4 eV, lifetime ~4 ns) and 2.7 eV (FWHM ~0.8 eV, lifetime ~10 ms) are known to be associated with the Si-ODC(II) centers [9]. Whereas the emission bands at 3.55 eV (lifetime < 20 ns) and 3.03 eV (lifetime ~ 10 ms) are ascribed to N-related defects [192].

In a recent work, [194], the PL spectra excited at 325 nm (3.8 eV), given in Fig.I.25 have shown two features; one of the two appearing only after irradiation.
The emission band at 400 nm (3.1 eV) seems to be similar to the one at 3.03 eV observed in [192]. It was suggested that this emission is related to the ODC (II) having N atom as neighboring [192]. According to [194], this center could be assigned to some defects related to N or to Cl or some features involving both atoms. The second luminescence peaked at ~560 nm (2.2 eV, FWHM = 0.52 eV) is appearing only after irradiation and the authors tentatively suggested to consider it as N-related center.

A third emission was detected in the same work [194], but this time using an excitation line at 442 nm. The resulting luminescence is centered at 680 nm (1.82 eV, FWHM ~0.44 eV), and since its cartography follows the N doping profile, it was tentatively suggested to be an N-related center.

The N-doped silica is still limited, and further investigations are required in order to validate the proposed models. Measurements on different samples under different conditions using several techniques such as time resolved luminescence and so on are needed. In this thesis, we will try to provide some new data regarding the N-doped silica using CL technique.
Chapter II

Materials and experimental details

Introduction

This chapter describes the experimental approach and tools used to perform the PhD thesis work. For each technique, the theoretical background principles are briefly explained and the characteristics and performances of the used instruments are detailed.

First, we started by a description of the scanning electron microscope, by giving a theoretical background on the electron beam-matter interaction, energy dispersive X-ray characterization and cathodoluminescence spectroscopy. Another instrument exploited during this work is the confocal luminescence microscope, for which obtained results are compared to those obtained by cathodoluminescence.

Second, the samples that have been investigated along this work are detailed, especially the optical fibers on which most of the work has been focused. The fabrication method of these samples, their main characteristics and the sample preparation before analysis are explained.

The last part concerns the evaluation of the irradiation characteristics (dose, dose rate,..) during the SEM experiments on the different specimens. Geant 4 simulations have been performed to estimate the deposited doses in the two main test configurations that have been the most used during the PhD thesis.
I. Theoretical background of the used techniques

I.1. Scanning electron microscope

Scanning Electron Microscope (SEM) is a known microscopic technique allowing to obtain a 2D characterization of different materials. Thanks to its high resolution, SEM is considered as a powerful tool for studying the topology, the surface morphology, the phases and other characteristics of materials [195]. In general, a SEM consists of three main parts. (i) The electron gun that produces the electrons; (ii) the column where several procedures take place in order to focus the beam and also to allow the sample sweeping; and (iii) the specimen chamber where the generated probe beam interacts with the sample allowing various characterizations of sample properties.

Figure (II.1) simplified schema of scanning electron microscope (SEM)
Figure (II.1) presents a schema describing the different components of a SEM. The electrons can be produced by a thermoionic heater using different methods, the most used ones are: tungsten filament, solid state crystal or field emission gun (FEG).

Most of SEMs can generate a beam with lateral size at focus of less than 10 nm. In order to be able to sweep the sample surface, the electrons passes by the scanning coils, so the beam scans in the X and Y axes of the specimen surface.

When reaching the sample surface, the probe beam interacts with the specimen permitting its characterization using different detectors such as: Secondary Electrons (SE) detector, Backscattered Electrons (BSE) detector, Energy Dispersive X-ray (EDX) detector and Cathodoluminescence (CL) detector. The detected signals are amplified and then displayed on the user screen, so that every swept point in the sample is represented by one pixel in the image displayed in the user screen simultaneously.

I.2. Electron beam-specimen interaction

When a material is exposed to electrons bombardment, various interactions take place. These interactions could be either elastic or inelastic according to the nature of the charged particles involved in the collision with the incident electrons and are essentially governed by electrostatic Coulomb force [21]. If an electron collides with the positive atomic nucleus, then it will deflect without an important loss of energy, because of the big difference of masses between the electron and the atomic nucleus, which induces an elastic scattering [21]. Whereas, if an electron collides with another electron within the sample, here the mass is equal and a transfer of energy takes place, which leads to an inelastic scattering [21]. These interactions are happening at the same time beside each other, resulting in several signals used for the analysis of the material.

The interaction depth of the electrons depends on the employed experimental parameters and on the material under characterization, it is estimated to be in the order of some microns within the surface [195].

Several methods of calculations have been used in order to estimate the electron range (the interaction volume or the penetration depth) [196]. One of them that is widely used is Kanaya Okayama empirical formula:

\[ R = \left( 0.0276 \ A E_0^{1.67} \right) / \left( \rho Z^{0.89} \right) \]  

(2.1)
Where: \( A \) is the atomic weight, \( E_0 \) is the energy of the incident electrons, \( \rho \) is the density of the tested material, \( Z \) is the atomic number.

Figure (II.2) shows the various signals that we can investigate using an SEM apparatus.

![Image of electron range and signals](image)

Figure II.2.a. The electron range. b. The origin of the SE (secondary electrons), BSE (backscattered electrons), AE (Auger electrons) and X-rays, induced by PE (primary electrons), adapted from [196].

Most of the signal used to form the images results from a complete electron diffusion caused by the gradual loss of the electron energy as it crosses the material, and by lateral spreading caused by multiple elastic large-angle scattering [196]. In general, the range of electrons is limited and is from 100 nm to 10\( \mu \)m depending on the density of the material and the energy of the primary electrons. These electrons are losing progressively their energy when spreading inside the target. The different detected signals depend on the depth at which the interactions takes place, and of the ability of the generated signal to travel from the interaction volume to the detector, which makes some signals more surface-sensitive than others.

These regions are not sharply bounded, and sometimes the contribution to the signal decreases exponentially with increasing depth [196]. According to [196], and as shown in figure II.2.b, the characteristics of the different signals which can be obtained using a SEM are:

a. The secondary electrons (SE): The detected SE signal is characterized by a low energy peak that is mostly at energies from 2 to 10 eV. The limit that separates SE from BSE is at \( \sim 50 \) eV by convention. These electrons are released from the sample after absorbing enough energy from the incident beam, in order to go through the surface and reach the detector. They are mainly used for morphology and surface characterization.
b. The backscattered electrons (BSE): The range of the contribution of BSE signal is between 50 eV until the energy of the primary electrons (E=eU in figure II.2). These electrons belong to the beam and are those which were sufficiently deflected by elastic collisions with nuclei of sample atoms during the scattering to cross the surface.

c. Auger electrons (AE): are produced when an electron from the upper shell fills the vacancy in the ionized shell, and the de-excitation energy is transferred to another atomic electron instead of characteristic X-ray emission.

d. The characteristic X-rays: are provided from the volume in which the electron energy is higher than the ionization energy of the inner shell involved. They are used for elemental analysis and they will be more explained later.

e. The continuous X-rays, also known as the Bremsstrahlung or braking radiation. These rays occur when the electrons are decelerated in the interaction volume, and the loss of their energy is emitted as photons. This phenomenon can take place at any event with any energy from 0 to the energy of the incident electrons, forming a continuous electromagnetic spectrum [195].

f. The cathodoluminescence (CL): For semiconductors and insulators, CL is detected when the defects, located in the forbidden band of a material, relax through a radiative way (UV, visible and IR) after being excited by the electrons. The signal detected from this interaction is coming from the near surface until the bottom part of the interaction volume [21]. Further details are reported in the following of this chapter.

The majority of the incident electrons loss of energy is converted into phonons or heat. And since the thermal conductivity of most of materials is very high, this is not a true problem. Among the above cited signals, we are interested in the present work by two main spectroscopic techniques: the EDX (Energy Dispersive X-ray) and the cathodoluminescence (CL) spectroscopies.

I.3. Energy Dispersive X-ray spectroscopy

X-ray spectrometry consists in studying the X-ray emission of atoms ionized by the electron beam and then relaxed to the ground state. Such interaction can provide two kinds of X-ray emission, the continuum one and the characteristic one. The continuum part is a braking radiation or Bremsstrahlung, arising from the deceleration of the electrons due to the Coulombic field of the specimen atoms. The characteristic X-ray is used for the composition analysis of materials. Usually, the electron-probe microanalysis uses the quantum energies in the range between 100 eV and 50 keV [196].
Figure II.3. Example of energy shells and the different possible transitions. The atom energy increases upon ionization of K, L, M and N shell (excitation). Characteristic X-ray is emitted when the atom returns to its initial state [195].

The origin of the characteristic X-ray emission is the relaxation of an electron from an outer shell to a vacancy caused by an ionization of one sample’s atom by the incident electrons. Indeed, two possible process can take place: (i) in the Auger process, the emitted photon, due to the difference between the shell energies, can be transferred to another neighbor electron, which will be ejected with a specific kinetic energy; (ii) in the second process the transition from the excited state to the ground state releases an electromagnetic radiation (photon) that has a characteristic X-ray energy representative of that atomic species. Several series of characteristic X-rays are formed according to the shells (K, L …) from where the ionization took place [197].
Figure II.3 presents a diagram of energy levels of an atom, and possible transitions between the different shells. It is worth to mention that the transitions can take place from subshells, and not all the transitions are allowed, some of them do not provide any characteristic X-ray line.

In figure II.4, we present an example of EDX spectrum of silica nanoparticles. This spectrum shows two main components: silicon and oxygen with some copper and carbon contaminations.

![Figure II.4. An example of EDX spectrum of silica nanoparticles.](image)

We can distinguish an intense peak at the energy of 1.74 keV, which belongs to the Kα series of silicon. Another one at 0.52 keV, which represents the emission from the Kα series of oxygen.

It is possible using EDX spectrometer to calculate the concentration of each component of the specimen using the intensity of each characteristic line.

However, the intensity of the peaks is not simply related with the concentration of the elements, because several parameters can affect the effective number of photons detected in each peak: the ionization cross-section, the probability to relax emitting a photon, the absorption of the photon by the material during the path toward the surface… Mainly three parameters are considered for the correction at the peak intensity, which itself depends on the sample composition: the atomic number (Z), the X-ray absorption by the specimen (A) and the X-ray fluorescence (F). These corrections are needed in order to obtain an acceptable quantitative evaluation of the composition [196].
X-ray elemental mapping is also possible in order to obtain the 2D spatial distribution of the different components of the sample. Another useful tool is the linescan, which is 1D mapping that gives the concentration of each element and its 1D distribution. As an example, figure II.5 shows the EDX mapping and linescan of a Ge-doped optical fiber diameter.

![Image](https://via.placeholder.com/150)

**Figure II.5.** An example of EDX mapping of Ge-doped multimode optical fiber (a) and linescan of Ge concentration along the fiber diameter (b).

From the EDX map presented in figure II.5.a, we can see that the Ge is distributed through 4 levels in the core of the optical fiber. The linescan of the diameter of the same sample is shown in figure II.5.b, where the concentrations of the 4 Ge steps are reported. This technique offers a high spatial resolution allowing for example to highlight the Ge central dip in the fiber core that it induces during the collapsing phase of the preform fabrication.

**I.4. Cathodoluminescence**

Cathodoluminescence (CL), as its name indicates, refers to the luminescent signal emitted in the UV, visible and NIR spectral regions, by a substance under electrons bombardment. The detected signal is used for CL spectroscopy and also CL imaging [198]. CL provides a relevant analytical information that other techniques cannot provide (like SE or EDX). The main employment of CL is for detecting the defects in materials and showing the differences between them as well as detecting dopants and impurities. It is widely used for semiconductors [197] and also minerals [199]. In this work, we are interested to the study of pure and doped silica by CL.

The comparison between CL and other luminescent techniques such as photoluminescence (PL) is possible and it should lead to similar results, with some differences in terms of intensities for example that are associated with the different excitation process. Especially, it should be
emphasized that the incident electrons employed to excite these defects can also create new defects or bleach some of the pre-existing defects, as it is observed for laser probing through photobleaching or photodarkening phenomena. Moreover, using CL, it is possible to excite many defects at the same time (according to the range covered by the detector), whilst the PL needs several laser sources in order to be able to excite the existing point defects. We will highlight these differences in the next chapters.

The luminescence mechanism is produced following three main steps [200]. (i) The absorption of the excitation energy, which brings the investigated system from the ground state to an excited state; (ii) The transfer of this excitation energy; (iii) The emission of the photon that is due to the relaxation on a lower energy level. This emission is a characteristic signal of the luminescent centers of the material.

In semiconductors and insulators (dielectrics), the luminescence (or CL) is resulting from the electronic transitions, and can be divided into two main types [197]:

a. Intrinsic CL: or edge emission indicated as (1) in figure II.6, is due to the recombination of an electron-hole pair. In this case the electron is excited in the conduction band leaving an hole in the valence one, so the energy of the emitted photon is similar to the energy of the forbidden gap \( h\nu_p \approx E_g \), but the exciton binding energy commonly makes the energy of the emitted photon smaller than the band-gap. This intrinsic emission is obtained through the inverse of the fundamental absorption edge mechanism.

b. Extrinsic CL: or characteristic CL, that occurs between intermediate energy levels within the forbidden gap, that are due to impurities, dopants, defects …
Figure II. 6. Mechanisms of CL caused by recombination processes is semiconductors or insulators adapted from [21], [201].

In the case of insulating materials, such as silica, the gap between the valence and the conduction band is large, and the defects are localized in this forbidden band forming new energy levels. The origin of these centers is mainly some imperfections of the network (defects) or the presence of impurities. Some of these defects are luminescent centers, and provide different CL signals. Each CL signal could be attributed to one emitted defect. These defects are distinguished mainly by their energy position, but also as shown in the first chapter, by other parameters such as the full width at half maximum (FWHM) and the life time.

Figure II.4 shows the main luminescence processes possible involving the forbidden band according to [21], [201]:

1. Is the intrinsic CL.
2. A recombination between an electron from the conduction band and an acceptor (an activator that is near the valence band), this recombination can be either radiative or non-radiative.
3. An excited trapped electron to the conduction band may recombine with an acceptor releasing a photon.
4. A trapped electron is relaxed to the valence band by a radiative way.
5. A direct recombination process between the trapped electron and the activator, when the energy between them is small.
(6) A complex excitation process is possible between several energy levels, leading to a luminescence of a single activator after relaxation.

An example of CL spectrum taken in the core of a germanosilicate fiber is given in figure II.7. An important emission band is detected at ~400 nm. According to the literature, this band is ascribed to the Ge Lone Pair Centers (GLPCs) [80].

![Figure II. 7. A typical CL spectrum of the Ge-doped silica-based OF.](image)

**I.5. Photoluminescence**

Besides Cathodoluminescence (CL), Photoluminescence (PL) measurements have been performed on the OF samples, aiming a comparison between the two techniques by confirming the obtained results using the two different techniques from one side, and to highlight the advantages and the drawbacks of both instruments from the other side.

While CL technique uses the electrons to excite the defects, the PL uses photons (UV/visible laser or lamp are the usual sources) in order to excite these defects. Indeed, the PL experiments are based on the illumination of the tested sample by a source of light at a certain wavelength. The photons of the source are absorbed by the sample and if some emitting defects can be excited at the employed excitation wavelength, then they could relax radiatively by emitting photons at wavelengths larger than the one used for the excitation.

Figure II.8 presents a simplified Jablonski diagram [202], where the main excitation and relaxation processes are mentioned. The straight arrows with yellow color represent the absorption process (or excitation), that is a fast (~10^{-15} s) electronic transition from the ground state to a higher excited state by absorbing a photon of certain energy. The arrows in orange indicates the vibrational relaxation. Essentially the nuclei are not in the equilibrium positions
of the excited state and they tend to relax towards these positions, the system losses energy by phonon (nuclear vibration) until to reach the nuclei equilibrium positions of the excited state.

In fig. II.8 the blue arrow indicates the intersystem crossing. This relaxation is less probable (also depends on the selection rules) and it is slower compared to the previously cited mechanisms. It occurs when the spin multiplicity of the system changes.

![Jablonski diagram](image)

**Figure II. 8.** Simplified Jablonski diagram presenting the main electronic transitions within the ground and the excited states. Adapted from [202].

The green and the purple dashed arrows presented in the above Jablonski diagram represent the radiative relaxations, which involve photon emissions. They refer to the fluorescence (allowed radiative transition) and the phosphorescence (‘forbidden’ radiative transition) respectively. It is possible for an excited molecule to relax to a stable lower energy level by releasing a photon of an energy equal to the energy difference between two states. The fluorescence lifetime (∼10⁻⁹ s to ∼10⁻⁵ s) is shorter than the phosphorescence (∼10⁻⁵ s to ∼10⁻¹ s) one, fluorescence processes are more likely than phosphorescence ones.

Photoluminescence, is widely used to investigate point defects in silica [9], since some of them are photon-emitting centers. PL process takes place when some optically-active center is excited by absorbing light of energy $E_{\text{exc}}$ from its ground state to a higher excited one, and then decays back to a lower stable energy level, emitting photons of energy $E_{\text{em}}$, where $E_{\text{exc}} \geq E_{\text{em}}$. 
As an example, a simple Jablonski system contains an electronic ground state level with an energy $E_1$ and population $N_1$, and a first electronic excited state $E_2$ with population $N_2$, where $E_2 > E_1$. According to Boltzmann distribution, $N_2 \approx 0$ when the system is not excited. When absorbing an excitation energy $E_{\text{exc}} \geq E_2 - E_1$, the excited level will be populated, and the number $N_2$ will increase. The system then is in the excited state and it may relax to a lower energy state by two possible means: radiative or non-radiative ways.

The radiative relaxation is a spontaneous process, which takes place with a rate $k_r$ independent of the temperature. The other possible relaxation is a non-radiative one, which occurs with a temperature dependent rate $k_{nr}$. Non-radiative paths include, for instance, the interaction with phonons.

If we assume that the PL intensity spectrum does not present any non-radiative decay, for example in stationary PL experiments, it can be written as according to [11], [135]:

$$I_{PL}(\lambda_{\text{exc}}, \lambda_{em}) = k_r \cdot \frac{N(\lambda_{\text{exc}})}{f_{PL}(\lambda_{em})}$$  \hspace{1cm} (2.2)

With, $\lambda_{\text{exc}}$ is the excitation wavelength, and $\lambda_{em}$ is the emission wavelength, $N$ is the number of the excited centers, $f_{PL}$ is the PL emission lineshape. If we consider that the used excitation source is a continuous one, we obtain a stationary PL, where its intensity $I_{PL}$ is given by

$$I_{PL}(\lambda_{em}) = \eta \cdot I_0(\lambda_{\text{exc}}) \cdot \left(1 - e^{-\alpha(\lambda_{\text{exc}})d}\right) \cdot f_{PL}(\lambda_{em})$$  \hspace{1cm} (2.3)

Where $\eta$ is known by the quantum yield which is defined by the ratio between the emitted and the absorbed photons:

$$\eta = \frac{k_r}{k_r + k_{nr}}$$  \hspace{1cm} (2.4)

The above described relation takes into account the competition between the overall relaxation and emission processes. It is worth to mention that $k_{nr}$ usually depends on the temperature and that it can be neglected from a certain temperature, which depends on the defect species. The relaxation from an excited state of molecules or defects is characterized by its lifetime which is defined as the time in which the emission amplitude decreases by a factor $1/e$ after pulsed excitation, and it is given by $\tau = (k_r + k_{nr})^{-1}$. In the equation (2.3), if $\alpha(\lambda_{\text{exc}})d \ll 1$, then the emission of the defect in a specimen with a thickness $d$ can be considered proportional to its concentration.
In order to analyze the PL spectra, a correction to the system response should be performed. Normally, it is described as following [203]:

\[ I_{PL}^{exp} = R(\lambda_{em}) \cdot I_{PL}(\lambda_{em}) \] (2.5)

Where R is representative of the response function of the used experimental instrument.

Figure II.9 represents an example of PL spectrum taken in the core of a germanosilicate optical fiber. The PL measurement was carried out using an excitation of 325 nm, and an emission band at ~400 nm is recorded. This luminescence is attributed to the GLPCs (the same luminescence that was shown in CL spectrum of Fig. II.7).

![Figure II. 9. PL spectrum of Ge-doped core of silica-based OF.](image)

II. Set-up description

II.1. Field emission scanning electron microscope

The SEM used in this PhD thesis is a JSM 7100f from JEOL. It is a field emission gun scanning electron microscope (FEG SEM) that is known to offer high resolution, good emission and focusing properties. These advantages are due to the very sharp tip (less than 100 nm of diameter) of the tungsten wire consisting its electron source. The voltage provided by this source varies from 1 to 30 keV.
Thanks to its high performances, this SEM-FEG provides a high resolution even at low energy, high current and high magnification. Using the optimal conditions (high voltage, low current and appropriate working distance), the resolution can be better than 2 nm [204].

![SEM-FEG SEM from JEOL](image)

Figure II.10. An image of JSM 7100f FEG-SEM from JEOL. On the left side, a picture of one field emission gun. Image adapted from [204].

The above described FEG-SEM is equipped by several detectors: Secondary Electrons (SE); Backscattered Electrons (BSE); Energy Dispersive x-ray (EDX) and Cathodoluminescence (CL). The main used detectors for this work are: EDX and CL.

II.2. EDX detector

Regarding the EDX measurements, the used apparatus is an X-Max 80 (OXFORD) equipped with silicon drift detector, which allows for a compositional analysis of the specimen with a high energy resolution (about 130 eV), large signal collection and high sensitivity.

![Simplified schema of the detecting principle of EDX signal](image)

Figure II.11. A simplified schema of the detecting principle of EDX signal.
A brief description of the X-ray detection is as following. When an incident X-ray interacts with the semiconductor (Si) of the detector, a number of electron-hole pairs are created due to the absorption of this X-ray by series of ionizations within the semiconductor. The number of generated pairs is proportional to the X-ray energy. These electrons are raised to the conduction band where they can move freely, leaving holes behind them. A high voltage applied between the two faces of the detector’s electrical contact (the front and the back ones) leads to attract the electrons and the holes to the opposite electrodes forming a charge signal that is proportional to the X-ray energy. The obtained pulse charge signal is then converted to a voltage pulse and amplified by a pulse processor and finally evaluated in its energy. The counts are displayed in a counts vs energy histogram, i.e. the EDX spectrum.

II.3. Cathodoluminescence (CL) equipment

The present work is mainly based on the cathodoluminescence (CL) technique for the investigation of the different point defects in silica. The used apparatus is GATAN MONO-CL4 (figure II.14). The spatial resolution for CL measurements is not the size of the electron beam, it is rather related to the interaction volume, which depends on the material density and the energy of the electrons. In general this spatial resolution is in the order of ~1µm, but can be better for low energy electron beam.

Figure II.12 A schema of the principle of work of CL microscopy and spectroscopy [gatan user guide].

The detection system is composed by a parabolic mirror located between the target and the bottom of the electron column allowing the light collection. The electrons are passing through a hole present in the mirror in order to scan the sample. When the specimen is placed at the
focal point of the mirror (~1 mm under the bottom of the mirror), the CL signal is effectively focused onto the detectors, or it will be coupled to the monochromator through entrance slits. The used apparatus can provide two main kinds of measurements, CL imaging and CL spectroscopy.

II.3.1. CL imaging

When the electron beam scans the sample surface, a CL image is formed simultaneously as a function of the beam location by representing the local CL signal intensity detected in given spectral range, which can be decided from the operator. It is possible using the above described SEM to record two or more images synchronously using different detectors (CL, SE…). Usually the recorded CL signal is weaker compared to the signal from electron detectors. For this reason it is preferable to have a quite long acquisition time (tens of seconds) in order to obtain a good signal-to-noise ratio. Another phenomenon that can affect the quality of the recorded CL images is the lifetime ($\tau$) of some luminescent signal, in the mainly employed experimental conditions when $\tau \sim 100$ ms. In this case, the emission lasts significantly more than the integration time over the scanned points, giving rise to large asymmetric broadening of the map. Increasing the acquisition time (slower speed) could be the solution for such emitting defects. Two CL imaging modes can be performed:

a. **CL panchromatic imaging**: which is performed by collecting all the light emitted by the specimen. In this case, the photons are sent to the detector regardless of their energies (wavelengths) and the acquired CL map is representative of the contribution of all the luminescent signals in the sample. Normally, the panchromatic mode of CL imaging is the most efficient one, because of the minimized losses, which give a high quality image.

b. **CL monochromatic imaging**: is able to highlight the features of a unique luminescence. Indeed, this operation mode allows to isolate one single contribution (that corresponds to one wavelength) and obtain its map through the tested area. Such measurements implies a monochromator, in which the light is passed through before reaching the detector. The bandwidth is determined by the entrance slits placed before the monochromator.

In the following of this PhD thesis, CL monochromatic images have been used in order to perform some kinetics measurements. In order to increase the signal-to-noise ratio, an imaging analysis was used to extract the radial profile of the luminescence distribution along the fiber’s
core radius. In details, this imaging analysis consists in calculating the average intensity of each ring we select from the fiber’s transvers cross section, with a certain spatial step (1 μm for example), and then obtaining a spatial distribution of the luminescence along the fiber core radius. As demonstrated in figure II.13, the black squares represent the intensities calculated as a function of the distance from the center of the fiber’s core.

![Graph showing intensity distribution](image)

Figure II.13 schematic illustration of the intensity calculations for the spatial distribution of luminescence in CL monochromatic images [205].

The used formula to calculate the average of the intensities is:

\[
I_{\text{ring}} = \frac{\sum_{p=0}^{255} (p \times f(p))}{\sum_{p=0}^{255} f(p)}
\]  

(2.6)

Where \( p \) is the pixel intensity that varies from 0 (black pixel) to 255 (white pixel) and \( f(p) \) is the frequency vector, whose components are the number of repetitions of each pixel value in the selected ring [205].

II.3.2. CL spectroscopy
The other principal tool for our investigations is the CL spectroscopy. The used apparatus includes an integrated spectrometer based on monochromator allowing a bandpass filtering of the emitted photons.

Figure II.14 shows the different light paths. First, the collected light is focused onto the entrance slit of the monochromator using achromatic optics. Then, a spherical mirror is used to collimate the light to the diffraction grating that disperses the light. After that, another spherical mirror focuses the light onto the exit slit and then on the detector (photomultiplier). The spectrum is composed wavelength by wavelength while the grating is stepped through a series of rotations. In details, after every wavelength that reaches the detector, the grating rotates once more, and so until completing the spectrum. The spectral range allowed by the detector is from 250 nm to 800 nm, but the apparatus is effective within the range 300-750 nm.

II.4. PL instrumentation
The PL spectra and cartographies used in this PhD thesis were performed by a confocal micro-luminescence (CML) using the LabRAM Aramis (Horiba Jobin Yvon), that includes an integrated Micro-Raman system which allows to obtain Raman spectra as well [207].
The used apparatus is equipped by three different laser sources: HeNe laser which works at 633 nm (1.96 eV), Ar+ laser emitting at 488 nm (2.54 eV) and HeCd laser working at both 422 nm (2.81), and 325 nm (3.82 eV) wavelengths. The laser is focused on the sample using different available objectives (UV 40, 10×, 50× and 100×) providing a beam size of less than 10 µm at the waist point [207]. In order to get a shorter interaction volume, pinholes are available via the software, and they determine together with the employed objective the spatial resolution.

If the sample under examination contains luminescent features that can be excited by one of the four available excitation lines, a luminescent signal is emitted, and passes through a pinhole located in an optically conjugated plane in front of the detector in order to eliminate the out-of-focus signal. Then, the collected light goes to one of the gratings that diffracts it on the CCD multichannel detector.

Spatially resolved measurements are allowed in the three directions (X, Y and Z) by performing 1D, 2D or even 3D cartographies. Since the apparatus is equipped by a translation stage monitored by different motors, the mounted sample can move along the three spatial directions with a precision of ~1 µm.
In the present work, the main used excitation lines are 325 nm and 633 nm. The other experimental conditions were adapted in order to obtain ~2 µm of lateral resolution.

### III. Samples description

#### III.1. Fabrication process of optical fibers

Several optical fibers have been investigated in the present work. They were manufactured by iXBlue Photonics division [208] using the MCVD technique to manufacture the preforms. Most of them were already studied in previous studies by LabHC [5], [45], [194], [209] employing different experimental and theoretical methods, such as Optical Absorption (OA), Electron Paramagnetic Resonance (EPR), Photoluminescence (PL) … The main purpose of producing such kind of canonical samples is to allow the investigation of the different classes of optical fibers: telecommunication, radiation sensitive and radiation hardened. A good comprehension of the radiation effects on these fibers will permit to predict their response under radiation and, to select the most adapted for a variety of applications.

Various fabrication processes exist to manufacture optical fibers: Outside Vapor Deposition (OVD), Axial Vapor Phase Deposition (AVD), MCVD, Plasma Chemical Vapor Deposition (PCVD) and Surface Plasma Chemical Deposition (SPCVD) [2], [125]. These processes are based on a thermal chemical reaction where O$_2$ reacts with a gaseous phase of SiCl$_4$ following this reaction:

\[
\text{SiCl}_4 + \text{O}_2 \rightarrow \text{SiO}_2 + 2\text{Cl}_2
\]  

(2.7)

The fabrication procedure consists in general in two phases, the preform fabrication and its drawing into an optical fiber. In the present work, most of the investigated fibers were produced using MCVD method, which provides high-quality optical fibers. The MCVD process is illustrated in figure II.15. In general, the pure silica consisting the optical fibers is made of small particles (~0.1 µm) which is called soot. This soot is deposited layer by layer on the fused silica tube composing a homogeneous high-quality cladding. The OFs are normally doped in their core or their cladding, in order to control the refractive index, which allows the light guiding. The dopants are integrated in the tube as mixture of gases composed of SiO$_2$ and the other dopants as shown in figure II.16.
The dopant concentration, or the refractive index profile, is monitored by the quantity of the gas added to the mixture. The inner part of the cladding and the core of the preform are formed layer by layer within the tube and vitrified using a burner. The next step, consists to collapse the tube (under ~1700 °C) in order to get a solid preform, which measures some millimeters to few centimeters of diameter and has the same refractive index profile of the optical fiber, but with a higher scale.

After being collapsed, the preform is mounted vertically at the top of the drawing tower (see Figure II.17), and drawn at high temperature (~2000 °C). The coating deposition is performed simultaneously with the drawing process by using liquid prepolymer. Aiming to protect the OF from any damage during the manufacturing or in-site implementation, an inner soft coating and an outer hard one are needed [209]. The fiber then is pulled down and wound on a winding drum [209]. The drawing parameters such as speed, temperature and tension are carefully controlled. All the canonical fibers employed in this thesis measure 125 µm of total diameter. The other characteristics of the employed OFs will be given in the next chapters.
The table here below, reports the main series of canonical optical fibers [5], [45], [194], [209] that have been investigated in this thesis and the type of measurements performed on them. In the following list, the multimode optical fiber will be indicated with MM, whereas the single mode one with SM.

![Fiber drawing process](209).

<table>
<thead>
<tr>
<th>Fiber's name</th>
<th>Total diameter (µm)</th>
<th>Core diameter (µm)</th>
<th>Core dopant</th>
<th>Cladding dopant</th>
<th>EDX</th>
<th>CL</th>
<th>PL</th>
</tr>
</thead>
<tbody>
<tr>
<td>OF_MG_Ge1</td>
<td>125</td>
<td>62.5</td>
<td>4 steps of Ge</td>
<td>pure silica</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
</tr>
<tr>
<td>OF_MG_Ge2</td>
<td>125</td>
<td>62.5</td>
<td>2 steps of Ge</td>
<td>pure silica</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
</tr>
<tr>
<td>OF_MG_Si</td>
<td>125</td>
<td>62.5</td>
<td>pure silica</td>
<td>F</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
</tr>
<tr>
<td>OF_MG_N</td>
<td>125</td>
<td>62.5</td>
<td>2 steps of N</td>
<td>pure silica</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
</tr>
<tr>
<td>OF_MG_P</td>
<td>125</td>
<td>62.5</td>
<td>2 steps of P</td>
<td>pure silica</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
</tr>
<tr>
<td>OF_MG_PCe</td>
<td>125</td>
<td>62.5</td>
<td>P and Ce</td>
<td>pure silica</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
</tr>
<tr>
<td>OF_MG_Al</td>
<td>125</td>
<td>8</td>
<td>Al</td>
<td>pure silica</td>
<td>yes</td>
<td>yes</td>
<td>no</td>
</tr>
</tbody>
</table>
An example of one of the most investigated OF is the Ge-doped one. The chemical analysis performed on OF_MM_Ge2 using EDX measurements shows that it contains, Si, O, two levels of Ge (figure II.19) and a small amount of Cl (~0.2 wt %) resulting from the fabrication method.

![Figure II.18. a. An SE image of OF_MM_Ge2 sample. b. The intensity map of the Ge Lα emission line obtained by EDX [205].](image)

It is clear from the EDX map of OF_MM_Ge2 that the Ge is localized in the core of the optical fiber (~62.5 μm) and its concentration is distributed on 2 steps as expected. A quantitative analysis is obtained by performing a linescan (1D mapping), which highlights, with a resolution below ~0.5 wt%, the amount of each component existing in the specimen.

![Figure II.19. Linescan of the above described specimen showing the 1D distribution of Ge and its amount along the fiber diameter.](image)
According to figure II.18, the first Ge level is ~9 wt% and it is occupying the central part of the core (~40 μm of diameter). The second Ge step, with concentration of ~5wt%, is distributed as a ring measuring ~10 μm surrounding the first region.

III.2. Samples preparation

In order to perform EDX and CL measurements, the tested specimens have been cleaved and mounted on a zinc or aluminum-made circular stub using a carbon tape. The metallic stub measures ~1 cm of height and ~1 cm of diameter, so the samples were mounted vertically and their lengths were also ~1 cm. Figure II.20 shows the used stub containing the OFs.

![Image of sample preparation](image)

Figure II.20 scheme of the used stub for EDX and CL measurements. The grey fiber is a reference which serves to identify the location of the samples.

In order to be able to identify the mounted specimens, we put a reference OF, which is usually a microstructured fiber that is easy to be recognized using secondary electron imaging of SEM.

Since the OFs are made of silica, which is a non-conductive material, large charging effect happens while scanning the samples by the electron beam of the SEM. In the purpose of avoiding this charge effect, normally, a thin layer of carbon or metals is deposited. In our study, we used a thin layer (~5 nm) of Gold/Palladium (Au/Pd) on the surface of all the tested specimens. The choice of this layer was taken based on the EDX measurements, in order to avoid any overlap between the emission X-ray lines of the coating and the ones of the tested optical fiber.

III.3. Radiation effects on the used samples

The present work is considered as a complementary one to other previous investigations that have been done by the same research group. Taking advantage of the already investigated
samples by other techniques, we compare the results obtained via these techniques with ours using Cathodoluminescence. The main reason for which we chose CL is its unique ability to investigate the defect properties and spatial localization while performing electron irradiation of the specimen at the same time. Hence, it is mandatory to study the electron radiation effects on our samples to estimate the dose and dose rate associated to our various experiments.

Figure II.21 illustrates the scanning of one optical fiber by the electron beam. By performing CL imaging, spatially resolved measurements are allowed.

![Diagram of electron beam and fiber cross section](image)

Figure II.21. An illustration of the transverse cross section of one sample under test.

We will present two different cases of electron irradiation effects on silica-based optical fibers according to the two kinds of measurements selected for this PhD thesis. The first one is representative of online-spatially-resolved measurements, where monochromatic images have been used. The second one concerns the CL spectroscopy and the time series for kinetics measures. The main differences between the two measurement kinds is the magnification (equivalent to the dose rate) and the acquisition time.

Monte-Carlo simulations have been performed using Geant 4, in the framework of a collaboration with CEA DAM DIF (Arpajon France, Dr. Mélanie Raine). Figure II. 22 shows the deposited energy in SiO₂ for different electron energies (30, 20, 10 and 5 keV).
Figure II.22 Geant 4 simulation of the interaction volumes caused by 30, 20, 10 and 5 keV energies of electrons in SiO₂ [210].

We observe that the energy deposited by the electron into the material volume is forming a pear shape and higher is the energy, larger is the interaction volume. The penetration depth passes from ~ 0.5 μm for 5 keV to ~8 μm for 30 keV. The deposited energy is much higher in the penetration area of the incident beam, and it decreases as the electrons go deeper in the volume.

Considering the above figure, a dose estimation is possible using the following formula:

$$D = \frac{E}{m}$$  \hspace{1cm} \text{(2.8)}

Where D is the dose in Gray (Gy), E is the deposited energy in Joule (J) and m is the mass of the irradiated material in (kg).

Taking into account the experimental conditions such as the electrons energy, the probe current and the acquisition time, an estimation of the dose for different cases is possible. Let us consider the following experimental conditions: electrons energy $E = 10$ keV and probe current (PC) = 8 nA. For different acquisition times, the irradiation effect (the estimated dose) will not be the same.
a. **CL imaging**: For this case, a large surface is irradiated (low magnification) in order to perform a spatially-resolved and in-situ measurements at the same time. If we consider a magnification allowing to probe the core of the optical fiber (~62.5 μm of diameter), the obtained image has a dimension of (~90 × ~70) μm. The acquisition time for one scan is adapted in order to obtain an acceptable signal-to-noise ratio. The chosen acquisition time for monochromatic images is 19.2 s for one single scan. Since the electron beam is sweeping the sample surface point by point, these points are represented by pixels in the saved images. By dividing the time needed to perform one scan by the number of pixels, we obtain ~16 μs per pixel as irradiation time.

b. **CL spectra**: Usually, the examined area for performing CL spectrum or CL time series (behavior of a single wavelength as a function of irradiation time) is smaller (~4 × ~3) μm, which needs a higher magnification depending on the doped region. The acquisition time here is 0.2 s per scan, but, each measure takes 1 s, this implies 5 successive scans for each obtained point. In this case, the estimated dose is higher since the electron beam scans more times the same area.

Figure II. 23 represents Geant 4 simulations of the deposited energy according to the above described cases.

![Figure II.23 Geant 4 simulation of the deposited energy in one scanned point.](image)

For the CL imaging, the irradiation time is higher, the reason why the deposited energy for a single point is higher. Whereas for the CL spectroscopy and time series, the deposited energy is lower but it is scanned much more times compared to the previous case.
The table hereafter summarizes some information that can help the comprehension of the electron radiation effects on silica for $E = 10$ keV and $PC = 8$ nA.

<table>
<thead>
<tr>
<th></th>
<th>CL imaging</th>
<th>CL spectroscopy</th>
</tr>
</thead>
<tbody>
<tr>
<td>penetration depth (radius and height of the cone) (µm)</td>
<td>1.2</td>
<td>1.2</td>
</tr>
<tr>
<td>Number of irradiated points</td>
<td>1374</td>
<td>111557</td>
</tr>
<tr>
<td>Maximum local dose per point (Gy)</td>
<td>$3.70 \times 10^6$</td>
<td>$2.30 \times 10^6$</td>
</tr>
<tr>
<td>Maximum dose rate per point (Gy/s)</td>
<td>$2.30 \times 10^{11}$</td>
<td>$1.10 \times 10^{13}$</td>
</tr>
<tr>
<td>Average deposited dose per point (Gy)</td>
<td>$3.05 \times 10^3$</td>
<td>$3.8010^3$</td>
</tr>
<tr>
<td>Average dose rate per point (Gy/s)</td>
<td>$1.40 \times 10^7$</td>
<td>$1.70 \times 10^5$</td>
</tr>
</tbody>
</table>

According to these calculations, the overlap between the neighboring points is much higher in the case of CL spectroscopy. This is due to the small scanned area, which makes the distance between two points very small compared to the CL imaging. Considering that for the same experimental conditions (energy, work distance, probe current), the electron beam size is the same, the number of the irradiated points is much higher in the case of CL spectroscopy, since the points are so close to each other, contrary to the CL imaging, where the neighboring points are more spaced from one another, so they are less affected while irradiating.

In order to evaluate the maximum of the deposited dose, we consider that the main deposited dose per point is due to the maximum deposited energy. So the maximum dose is deposited in a cuboid volume, where the size of the surface is the same of the scanned point and the height is the penetration depth (e.g. 1.2 µm for 10 keV).

The method used to calculate the average dose is to use the integral of all the deposited energy by one point simulated by Geant 4 (figure II.23), and then introduce it for calculating the deposited dose per point. In this case we used a volume of cone where both the radius and the height are the penetration depth (see figure II. 22). The choice of this volume was made by considering that a cone is close to the pear shape of the interaction volume.

Aiming to evaluate an estimation of the true deposited dose, that we will use later to present our results, we propose to take into account the overlap between the neighboring points, which is very important especially in the case of CL spectroscopy and time series (see the table above). To do so, we suggest to calculate the overall deposited energy per point and to consider a cuboid volume with the area of the scanned point as the size of the surface and the penetration depth.
as height. This way, we took into account the overlap between the neighboring points, by calculating all the deposited energy in only the volume of the scanned point. The estimated dose in this case is of $3.37 \times 10^7$ Gy for CL spectroscopy.

It is worth to mention that the beam energy is an important parameter for this calculations. If we take $E = 20$ keV, for example, and according to the previous calculations, the interaction volume is $\sim 5 \mu$m, which means a larger depth compared to the surface used for performing CL spectra. The other results concerning the other energies will be presented in chapter 4, where a specific study has been performed as a function of the dose and the dose rate.
Chapter III

Characterization of different classes of silica-based optical fibers

Introduction

This chapter presents the first experimental results acquired during this PhD thesis. It can be considered as an overview on the potential of the CL to study the defect distribution and luminescence properties in differently doped OFs. The objective was to identify for which classes of optical fibers the CL tool can provide valuable complementary information to EPR, OA and PL. Moreover, contrary to PL, CL has the advantage to act simultaneously as a characterization and an irradiation tool, allowing to monitor in situ the spatial distribution of emitting centers in the fiber cross section.

The OFs presented in this chapter are divided into three main classes discussed in Chap 1 according to their interest and applications in harsh environments. The first class is Ge-doped OFs serving for telecommunication applications, which corresponds to the most widely sold type of OFs. For this class of fibers, a 4 steps “canonical” Ge-doped OF was investigated by both CL and PL spectroscopies.

A second type of OFs is used for applications that require the use of radiation tolerant or radiation hardened optical fibers at MGy dose levels of steady state γ-ray irradiations. F-doped and N-doped fibers are within this category, since previous investigations have demonstrated their abilities to tolerate medium to high dose of irradiation [60], [186]. CL and PL measurements on these fibers are presented to highlight the advantages and the drawbacks of both techniques, their complementarity to improve our understanding of the radiation effects on these glasses.

The last category concerns the radiation-sensitive OFs. These fibers are under investigation for possible use as radiation detectors or dosimeters in a variety of radiation environments [55], [159]. Three different samples have been characterized through CL and PL measurements: Al-doped, P-doped and P/Ce co-doped OFs.
For all the results presented in this chapter, the following parameters have been selected to perform the CL and EDX measurements: $E=10$ keV electron beam and a probe current of 8 nA.

I. Telecom-grade optical fibers

Telecom-grade OFs are those doped with Ge and can have various co-dopants in their claddings such as P, F and Ce. In the following section, we report an investigation based on PL and CL measurements by comparing the obtained spectra and discussing their differences. The in-situ kinetics of the GLPC defects are presented during the fiber exposure to the electron beam.

I.1. EDX analysis

The chosen OF to represent the telecom-grade class is a 4-steps Ge-doped OF, an ad hoc sample especially developed by the CEA and LabHC with iXblue for comparison between experimental data and theoretical results. One of the interest of this fiber, produced by MCVD, is that its structure allows to highlight the impact of the Ge concentration thanks to its four levels of Ge, if a spatially-resolved spectroscopy technique is available.

In order to quantify the spatial distribution of Ge concentration in the different fiber parts, EDX measurements were carried out within a precision of 0.5 wt%. The results are presented in figure III.1 for this fiber.

![Image](image_url)

Figure III.1.a. EDX 2D map of Ge amount in OF_MM_Ge1 sample. B. Line scan of the same OF showing the Ge concentration along a fiber diameter [210].
It is clear from the EDX map shown in figure III.1.a that the Ge doping is distributed according to 4 steps, where the central part of the core contains more Ge and the other 3 levels are surrounding this central part forming rings. These results are consistent with those obtained by other types of chemical analysis, such as Electron Micro Probe Analysis (EMPA) [41].

By performing a line scan (1D cartography) it is possible to quantify the amount of Ge along a fiber diameter highlighting the various doping levels. Figure III.1.b denotes the concentration of Ge as a function of the distance from the center of the core. The first step (localized in the central part of the core) measures ~20 µm of diameter and it contains ~11 wt% of Ge. The second Ge level having size of ~10 µm is doped with ~8 wt% of Ge. The third and the fourth steps measure respectively ~7 µm and 5 µm and their Ge contents are of 4.4 wt% and 2.2 wt% respectively. It can be noted that the pure silica cladding can serve as a reference of a MCVD deposited glass without presence of Ge dopant.

I.2. Confocal Micro Luminescence (CML) characterization

CML measurements have been performed on the OF_MM_Ge1 sample using the excitation line at 325 nm. Figure III.2 reports the CML spectra in the different regions of the core (the different Ge steps). In the whole core, we observe the strong luminescence centered at ~400 nm which is assigned to the GLPC defects [see Chap.1 for a detailed description of GLPCs]. The intensity of this band seems to increase with the Ge levels, in particular, the most intense luminescence comes from the highly Ge-doped region and, then it decreases gradually, less is the Ge concentration lower is the intensity of the GLPC.
Regarding the presence of other emission bands, the reported CML spectra under 325 nm excitation line do not show other features, even if the Ge or Si-NBOHC defects can be excited at 325 nm. This is explained by the fact that in the not irradiated sample the concentration of these defects remains lower than the CML detection limit.

I.3. CL characterization

I.3.1. CL imaging
In order to have a first idea about the defects localization in the sample, CL imaging was carried out. A panchromatic image of the sample OF_MM_Ge1 is presented in figure III. 3. a. This image shows a significant luminescence occurring from the fiber core under 10 keV electron exposure. Since the core of this fiber is doped with Ge, a strong contribution from the GLPC centers emitting at 400 nm was expected. To confirm this, a monochromatic image has been recorded at 400 nm with a bandwidth of ~ 5 nm. The obtained image is shown in figure III.3.b. This monochromatic image denotes a similar luminescence distribution than in the panchromatic image, in particular, the central part of the core (highly doped with Ge) appears brighter. It is worth to mention that the parameters used to adjust the contrast and brightness of both images are different, since the image quality is higher for the panchromatic mode.

Aiming a better comprehension of the observed luminescence, CL spectroscopy was held to check out if there are any other emitting features involved. Figure III.4 presents CL spectra acquired by focusing the ion beam into the differently doped zones of the core.

![Figure III. 4. CL spectra of the differently doped parts of the OF_MM_Ge1 (core).](image)

First, the CL spectra in all zones show a significant GLPC luminescence at ~400 nm, which confirms that these defects are the main origin of the measured luminescence. Other lower emission features are present at ~650 nm and maybe at ~560 nm. These later components can originate from some intrinsic silica point defects and they will be discussed in the next sections. However, the reported CL spectra are not in agreement with the images in terms of the spatial distribution of these centers. In other words, if we follow the GLPC intensity as a function of
the Ge concentration, we find that for the images, the luminescence intensity has followed the Ge content. Whereas the CL spectra present an opposite behavior where the signal intensity is higher where the amount of Ge is lower. This behavior is even not correlated with the CML spectra previously reported in figure III.2. This behavior could be explained by an irradiation effect caused by the electron beam exposure during the spectra acquisition, suggesting the possibility of an on-line and spatial resolved study of the GLPC transformation kinetic under electron irradiation.

In order to perform such investigation and to better understand the above reported differences, several on-line measurements were carried out using a series of consecutive CL monochromatic images and are well detailed in the next chapter. In particular, one monochromatic image is saved after a certain number of scans (irradiation with the electron beam). This analysis allows revealing the electron exposure impact on the spatial distribution of the GLPC centers and this as a function of the Ge concentration. The panchromatic and the monochromatic at 400 nm images after 120 scans (~40 minutes of 10 keV electron irradiation) are presented in figure III.5. a and b respectively.

We observe that the luminescence distribution in the fiber’s core has strongly changed compared to the first image (figure III.3). After the 40 min. exposure, the luminescence intensity is higher in the outer part of the core, corresponding to the core region with the lowest Ge concentration. This behavior agrees with the recorded CL spectra given in Figure III.4.

![Figure III. 5. a. panchromatic image of OF_MM_Ge1 sample after being irradiated for 120 scans (40 minutes of 10 keV electron exposure). b. monochromatic image at 400 nm of the core of the same sample after the same irradiation.](image)

To better highlight the difference in the spatial distribution at the beginning and at the end of the irradiation, radial profiles have been extracted from the first and the last monochromatic
images recorded at 400 nm, following the imaging analysis shown in chapter II. The profiles are presented in figure III.6.

Figure. III. 6. Radial profiles of the monochromatic images at 400 nm (GLPC) along the fiber core radius: a. the first recorded image, b. the last recorded image after 120 scans (~ 40 mins of irradiation) [210].

First, in the radial profile of the first recorded monochromatic image, we observe that the maximum of the luminescence signal is located in the center of the core and another maximum is observed in the interface core/cladding. This could be due to the fabrication process of the sample (fabrication of preform, drawing step...) as it was already observed in [26], [27].

Regarding the spatial distribution of the last recorded image, after 40 mins of irradiation, we observe that the GLPC signal has significantly decreased and its radial profile has changed compared to the first image. In particular, it seems than before 40 min of irradiation, the GLPC signal follows the Ge concentration (apart from the stressed regions such as the core/cladding interface), however, this behavior seems inversed by the end of the irradiation, where the luminescence is more intense wherever the Ge concentration is less. The fact that the GLPC intensity has decreased as a function of the electron beam irradiation is not unexpected, since it is known from the literature [36], [46] that the GLPC centers are bleached by irradiation through conversion into other optically-active point defects. On the other hand, our results also reveal that the efficiency of this bleaching effect seems dependent on the Ge concentration: the remaining GLPC signal at the irradiation end is lowered when the Ge amount is higher.

As previously discussed in chapter II, it is important to remind that the deposited dose required to acquire the CL spectra is higher than the one needed to record CL images. So, the GLPC signal distribution is less affected during the CL imaging than during the spectra acquisition. Moreover, the inversion of the relative ratio of the GLPC signals reported in figure 6 for the
different zones clarifies the difference between CL spectra and CML data. As a consequence, we can conclude that CL spectroscopy has to be employed carefully by limiting or controlling the dose effects.

To better clarify the relation between the GLPC bleaching and the Ge amount, we plotted in figure III.6 the ratio (GLPC$_f$ / GLPC$_i$) as a function of the Ge concentration, where the GLPC$_f$ refers to the amount of the GLPC at the end of the irradiation and GLPC$_i$ is the initial amount of the GLPC signal. We note that, for the employed experimental conditions, an almost linear dependence is observed between the ratio (GLPC$_f$ / GLPC$_i$) and the Ge amount.

![Figure III. 7. Ratio between the final (GLPC$_f$) and initial (GLPC$_i$) GLPC signal as a function of Ge content, the dashed line indicates the linear fit between the points with a slope of -0.038 ± 0.004.](image)

Such dependence may be explained by the effect of the Ge doping on the stabilization of the silica matrix. In other words, as Ge atoms substitute Si ones, at low concentrations (in the beginning) Ge atoms prevalently occupy the more favorable sites (sites with lowest formation energy) including favorable GLPC defects. With the increase of the Ge amount, the further accommodation of additional Ge atoms may lead to extended modifications of the structure and to a subsequent generation of energetically less favorable (non-stable) GLPC defect. After the electron beam irradiation, as the non-stable sites are easier to destroy or transform than those stable, for low Ge concentrations the final to initial GLPC ratio is higher than for high Ge concentrations.
II. Radiation-hardened OFs

In this section, we report the data on the tested radiation-hardened OFs. The first studied canonical sample is a pure-silica-core (PSC) OF made by MCVD, which is doped with fluorine in its cladding in order to decrease the refractive index, allowing the light guiding. Whilst the second one is a 2 steps N-doped core OF produced by SPCVD.

II.1. EDX Analysis

First we show the chemical analysis of the OF_MM_Si, which is representative of PSC OF, in figure III.8. The fluorine doping is of ~1.5 wt% and it is distributed in the outer ring surrounding the pure silica core, and it measures ~20 μm.

![Graph](image)

Figure III. 8. EDX measurements on OF_MM_Si sample.

In the same figure we illustrate the chlorine concentration, according to our data, it is distributed homogeneously and its amount is low (~0.2 wt%, typical value measured by EMPA in MCVD fibers). The presence of such element in the fiber is related to the fabrication process used to make the preform.

The second employed sample is N-doped OF. As shown in figure III.9, we can distinguish two N levels of doping. The first one contains ~1.5 wt%, whereas the second step’s concentration is ~1 wt%. The central dip is N-free zone, this dip is typical of N-doped fibers for which it appears very difficult to avoid the nitrogen depletion in the core center during the preform collapsing phase.
Contrary to the previous sample, this one contains an extremely high amount of chlorine, which follows in terms of distribution the N doping. The Cl concentration in the first step is of ~4 wt% at the maximum and then reduces gradually till 2.5 wt%, whilst the Cl amount in the second step is of ~1.8 wt%. These high Cl concentrations in such sample are due to the fabrication process of the optical fiber’s preform, which is SPCVD.

II.2. CML characterization

![CML characterization graph](image-url)
The CML measurements for this class of OFs were carried out using the excitation line at 633 nm, because it is more efficient to excite some intrinsic silica defects as the NBOHC.

The obtained spectra for the OF_MM_Si sample are presented in figure III. 10. The three different zones show a similar emission at 650 nm. This luminescence is assigned to the NBOHC defects [86]. In addition, we note the presence of the silica Raman signal at about 650 nm, which justifies some spectral differences with respect to the known emission band of this defects.

Regarding the CML characterization of the OF_MM_N sample, we report again (see first chapter) previous measurements performed on the same sample using the same apparatus using an excitation at 325 nm [194].

![Figure III. 11. CML measurements on OF_MM_N sample [194].](image)

For the pristine sample, an emission band is peaked at ~400 nm, this band increases with irradiation (~10 MGy). At the same time, a new band appears at ~560 nm. A third band was detected at ~680 nm. The band at ~400 nm was ascribed to the ODC (II) centers with N neighboring atom, whereas the other features are still unknown. Their origins could be related either to N atoms, Cl atoms or both.

**II.3. CL characterization**

CL panchromatic images of the OF_MM_Si and OF_MM_N are reported in figure III.12.a and b respectively. For the PSC sample, we can distinguish the F-doped part of the cladding, since the luminescence signal appears a bit more intense compared to the other fiber parts.
Unlike the PSC sample, the N-doped fiber shows more luminescence in the regions doped with N, following the N concentration. The central dip corresponds to the pure-silica part of this fiber core where the N doping features a hole as illustrated in figure III.9. We remind that the parameters used to adjust both images (contrast and brightness) change from fiber to fiber.

Aiming to identify the origin of the observed luminescence in the CL images, CL spectra were recorded in the different regions. The results are presented in figure III.13.

The CL spectra reported in figure III.13. a present three different emissions centered at ~460 (≈2.70 eV) nm, ~560 nm (≈2.21 eV) and ~650 nm (≈1.91 eV) that are typical for the claddings of the OFs. These emissions have almost the same intensity with respect to the different zones, and are originated from some intrinsic silica point defects. Fluorine doping does not change the CL response of the sample, since our data demonstrate that no additional signals are observed.
in the F-doped zone. Regarding the nature of these emissions we can use previous investigation to identify their origin, the luminescence at 460 nm can be assigned to ODC (II) centers [17], [80], and the one at 650 nm can be ascribed to the NBOHC [17], [86].

The emission band at 560 nm could be attributed to either the second order of ODC(II) at 280 nm or to another center such as STE [17]. However, it is quite surprising that, the radiative decay of STE is still observable at room temperature under high electron beam exposure, as non-radiative channels should be dominating. At the same time, our experimental apparatus does not allow to measure the band at 280 nm.

Regarding the N-doped sample (figure III.13.b), the CL spectra of the cladding and the central dip are similar in line shape to the CL spectra of the PSC fiber, since they are made of pure silica. By contrast, some changes are noted in the N-doped regions, where a very low contribution of the NBOHCs is observed. Contrary to fluorine, nitrogen doping increases the luminescence intensity at 460 nm and 560 nm as reported in the spectra of figure III.13.b. This increase does not follow the N concentration (see figure III.9). Anyway, as shown for the GLPC in the previous section (I.3) radiation effects and dopant level can impact the relative ratio of the signals recorded in differently doped zones.

We remind that the CML spectra show the presence of the band at 560 nm in the N-doped regions after irradiation, which agrees with the increase of the signal at this wavelength. The presence of some N (or Cl) related contribution at 560 nm or a relevant increase of the generation of intrinsic defect, due to N (or Cl) doping, can explain the experimental data. Similarly, the increase of the 460 nm attributable to ODC(II) seems to suggest an increase of the generation of intrinsic defects. At the same time, the emission band at 400 nm detected by CML seems not to be present in the reported CL spectra. This means that its contribution could be bleached by the electron beam irradiation. A small contribution seems to be present in the N-doped regions at ~350 nm (the limit of our detector), this luminescence could be due some N or Cl related defects. We remind that a similar contribution at ~3.55 (~350 nm) eV was reported in the literature as an N-related center (see chapter I). Further studies are required to attribute the origin of these bands.

In order to monitor the contribution of each emission band, spatially-resolved measurements were carried out through CL monochromatic images that allow to perform a 2D cartographies at each wavelength, with a bandwidth of ± 5 nm. Unlike the CL spectra, using monochromatic images we avoid to irradiated the samples to very high doses.
The monochromatic image at 460 nm reported in figure III.14.a shows a slightly higher luminescence in the cladding region compared to the core, which explains the distribution of the signal in the panchromatic image reported in figure III.12.a. The intensity of this luminescence will be equal to the other parts, after a sufficient electron beam irradiation as shown in the CL spectra (figure III.13.a). It is remarkable in the same image that the luminescence appears exceeding the sample boundaries, this effect is due to the long lifetime of such emission band, which is in the order of milliseconds. Regarding the other bands at 560 nm and 650 nm, their spatial distributions seems homogeneous through the different parts of the optical fiber.

In figure III.15 we report the three monochromatic images of the OF_MM_N fiber recorded at 460 nm (panel a), 560 nm (panel b) and 650 nm (panel c). The spatial distributions of the emissions at 460 nm and 560 nm show higher luminescence in the N-doped regions in agreement with the CL spectra. This means that the N-doping favors the generation of the ODC(II) centers, and there is an N-related (or Cl-related) contribution in the spectral range around 560 nm or that they increase the content of other intrinsic defects too. Further
measurements as a function of the dose are required to clarify the electron radiation effects on
the behavior of these emission bands. Concerning the band at 650 nm, the luminescence seems
higher in the region doped more with N, which is not observable in the CL spectra.

III. Radiation-sensitive OFs

The third section is dedicated to radiation-sensitive OFs, where three fibers have been
characterized mainly by CL tools: Al-doped OF, P-doped OF and P/Ce co-doped OF. New
insights concerning the emission bands related to the different dopants, as well as their kinetics
as a function of the electron beam irradiation, are reported. The above cited fibers are considered
as good candidates for dosimetry applications, since some of their optical properties vary
linearly as a function of the dose.

III.1. EDX Analysis

Starting with the OF_MM_P, OF_MM_P/Ce and OF_SM_Al fibers, their chemical
compositions are shown in figure III.16.
The first sample, named OF_MM_P, contains only P in its core and the dopant content features a two steps profile as illustrated in figure III.16a. In the first zone the P level is of ~8 wt%, whereas the concentration in the second step is ~3 wt%. The P amount appears less in the central point of the OF’s core because of preform fabrication process.

Unlike the first sample, the second fiber (OF_MM_P/Ce in the following) has a smaller core diameter (~40 μm), which is co-doped with P and Ce, where the P concentration is ~12 wt% whilst the Ce amount is lower, at ~3 wt% (see figure III.16b).

The third sample is a single mode OF (OF_SM_Al) for which the core diameter measures ~4 μm and is doped with aluminum at ~6 wt%.

III.2. CML characterization

We report in figure III.17 the CML spectra of the P-doped and P/Ce co-doped fibers. Using an excitation of 633 nm for the P-doped fiber, the CML spectra show the presence of the NBOHC signal that represents the broad component of the spectra. Furthermore, we can observe that the CML spectra of figure III.17. a. involve the Raman signature of the silica at about 650 nm, and the Raman peak related to the stretching bond of P = O at ~1330 cm⁻¹ (~691 nm), this peak is
clear in the spectra recorded in the P-doped regions of the fiber, and it is higher in the spectrum taken in the highest P-doped zone. By comparing the spectra recorded in the different zones we can conclude that the luminescence intensity decreases with the P concentration.

Figure III. 17. CML spectra of: a. OF_MM_P using the excitation 633 nm. b. OF_MM_P/Ce using the excitation 325 nm.

Using an excitation at 325 nm, CML spectrum was recorded on the P/Ce doped core (figure III.17. b). A large luminescence is detected at ~387 nm that is ascribed to the Ce$^{3+}$ ions [170], the same luminescence was found in [194] where it has been demonstrated that its intensity decreases as a function of the dose. The CML spectrum in the cladding of the same fiber is similar to the one presented in the PSC fiber (figure III.10) with the presence of the NBOHC luminescence at 650 nm.
The Al-doped fiber presents also the same spectrum as the PSC sample. This means that using the available excitation lines (325 nm, 633 nm) we do not observe any new emissions.

### III.3. CL characterization

In the purpose of having a general idea about the existing emission in the different OFs, CL panchromatic images have been taken and are reported in figure III.18.

![Panchromatic images](image)

Figure III. 18. Panchromatic images of the transverse cross section of: a. OF_MM_P fiber, b. OF_MM_P/Ce and c. OF_SM_Al.

The OF_MM_P sample presents dark P-doped zones compared to the cladding (figure III.18.a). Nevertheless, it seems that higher is the P darker is the region, this is also the case in the central dip of the core where the P content is less compared to the surrounded region (see figure III.16). The OF_MM_P/Ce fiber shows a high luminescence in the P/Ce co-doped core, this luminescence is most likely due to the Ce co-doping, since the P-doped regions show no luminescence in the P sample. Finally, the core of the Al-doped single mode OF appears more luminescent than its cladding.

### III.3.1. P-doped OF

To identify the emission bands responsible of the luminescence of the above images, CL spectra were carried out in the different doping regions of different samples. It should be remined that acquiring these spectra implies to deposit high dose levels in the material under test.
Figure III. 19. CL spectra taken in the core of the OF-MM_P sample.

Figure III.19 presents the CL spectra recorded in the core of the P-doped sample. Although the panchromatic image show a dark core, we observe in the CL spectra a new band at ~3 eV (410 nm) for which the origin is still unclear as discussed in [23], [53]. Indeed, it has been tentatively assigned to four-coordinated diamagnetic P impurity substitutional to Si atoms in the SiO$_2$ matrix [53] or to a twofold coordinated P [23].

Besides the new band at 410 nm, we also observe the bands at 560 nm and 650 nm related to intrinsic silica centers. CL monochromatic images have been recorded at the different wavelengths 410 nm, 460 nm and 650 nm, and are shown in figure III.20.

Figure III. 20. CL monochromatic images at: a. 410 nm, b. 460 nm and c. 650 nm.

From the first image, we can see that the spatial distribution of the P related emission at ~410 nm is in qualitative agreement with the reported CL spectra, indeed its amplitude is higher in the region less doped with P. Regarding the ODC(II) centers, the luminescence at 460 nm is
much less intense in the P-doped core compared to the cladding, which indicates that the P doping decreases the ODC(II) centers. Finally, the NBOHC emission at ~650 nm is weak as it is the case in the CL spectra of the claddings of most of the studied OFs.

III.3.2. P/Ce co-doped OF

Concerning the co-doping with Ce, CL spectrum of the core of the OF_MM_P/Ce is reported in figure III.21. Two emission bands are detected at ~370 nm and at ~680 nm.

![CL spectra taken in the core of the OF_MM_P/Ce sample](image)

The luminescence at ~370 nm is similar to the emission detected by CML measurements and assigned to the Ce\(^{3+}\) ions [170]. This luminescence is affected by many parameters, among them, the environment around the Ce\(^{3+}\) ions and their concentration [170]–[172]. In particular, the authors in [171] have demonstrated that the different configurations surrounding the Ce\(^{3+}\) ion, that are caused by the fabrication process of the fiber such as the drawing phase, can modify the luminescence of Ce\(^{3+}\) ions. Furthermore, this luminescence can decrease by increasing the Ce concentration due to clustering phenomena [172]. This clustering phenomena can be avoided by co-doping the glass with Al or P that are usually used to facilitate the incorporation of the rare-earth elements in silica matrix. However, this P co-doping can cause a considerable shift of the emission at ~370 nm compared to the Ce\(^{3+}\) in pure silica [170]. It is worth to mention that Ce-doped optical fiber materials can be used as dosimeters in the different harsh environments [211].

Further investigations are required for this OF in order to clarify the origin of the other luminescent centers related to Ce co-dopant such the one emitting at ~680 nm.
Taking advantage of the CL technique, we followed the kinetic of the emission band at 370 nm as a function of the electron irradiation at different magnifications. In details, we changed the dose (fluence) by changing the size of the irradiated area, smaller is this area higher is the deposited dose. First we present the different kinetics with respect to the irradiation time in order to highlight the effect of the chosen area on the behavior of the emission band under 10 keV electron exposure.

![Graphs of CL intensity versus irradiation time for different areas](image)

Figure III. 22. On line kinetics of the Ce$^{3+}$ luminescence at ~370 nm using different area from the biggest (a) to the smallest (d).

In the first kinetics recorded using the largest area (figure III.22), in the first 100 s the emission of Ce$^{3+}$ decreases as a function of the irradiation time, this behavior was already seen using the same sample in [194], where CML post mortem measurements were carried out at different $\gamma$-raydoses up to ~9MGy. Then, in the same figure III.22.a the luminescence at 370 nm starts increasing slowly after. Figure III.22.b and c show that at the beginning of the irradiation, the intensity decrease is faster when the probed area is smaller and then it starts to increase as a function of irradiation time. In the last figure III.22.d, the investigated area is the smallest, the
decrease of the luminescence was much faster (a few first seconds), after that, the intensity at 370 nm starts to quickly increase until to reach a maximum and then saturate.

In order to better clarify these observed kinetics, we converted the x axis into dose in Gy, and we plot all the kinetics together by rescaling them for a multiplicative factor.

Figure III. 23. a. On line kinetics, normalized to their minimum, of the band at 370 nm in the different areas as a function of the dose. b. CL spectra taken after each set of measurements.

Figure III.23.a show that the luminescence of Ce³⁺ depends principally on the dose, where the smallest area shows the fastest kinetics, in the contrary of the largest area where the kinetic seems slower. In order to check if the different kinetics were recorded for the same emission band, CL spectra have been recorded at the end of each kinetics and the results are shown in the panel b of figure III.23. This figure confirms that the luminescence spectra that we monitored are the same all along the acquisition run.

As hypothesis, the Ce³⁺ centers are bleached under irradiation and converted into other Ce-related centers such as Ce⁴⁺ or Ce²⁺. It has been reported in [212] using UV insolation that the Ce³⁺ is converted into Ce⁴⁺. However, in our case, we are using electrons as source of irradiation, so the electrons in the volume of the irradiated sample can be captured by such centers (Ce³⁺) and converted into Ce²⁺. As a hypothesis, the Ce³⁺ can be converted in the beginning of the irradiation to the Ce⁴⁺ as it is the mechanism for the γ irradiation, but then the backward process is triged because of the available electrons in the volume, until reaching an equilibrium after sufficient irradiation, another conversion into Ce²⁺ can be also involved.
III.3.3. Al-doped OF

The last radiation-sensitive sample investigated in this chapter is the Al-doped single mode OF. The data of figure III.18.c, illustrating a panchromatic image of this sample, proves the presence of an intense CL signal in the Al-doped core of the fiber.

![CL spectrum of the OF_SM_AI sample.](image)

Using the CL spectroscopy (figure III.24), we detected a band centered at ~380 nm. In [182] the authors have tested the quartz and they assigned this luminescence to the recombination of an electron with a hole trapped adjacent to an alkali-compensated aluminum ion (Al-M⁺). On the other hand, Stevens-Kalceff in [17] has reported CL measurements on different types of glasses, where the luminescence at ~380 nm was detected and ascribed to the charge compensated substitutional Al³⁺ (Al³⁺ - M⁺) where M⁺ is Li⁺, Na⁺, K⁺ or H⁺. Other emission bands are detected at 560 nm and 650 nm and are attributed to intrinsic silica related defects.
The in-situ kinetic of the emission band related to the Al at ~380 nm is reported in figure III.25. Under high doses due to electron beam exposure, the intensity of the luminescence at ~380 nm quickly decreases during the first few seconds of irradiation, indeed more than the third of the initial intensity is bleached. Then, after ~40 s the luminescence continues to decrease but with a slower rate. It is worth to mention that the chosen area to perform the kinetic measurements is very small (~12 μm²) due to the small size of the core, since the tested sample is a single mode OF.

The decrease of this luminescence has been reported in [17] and has been attributed to the electron irradiation that tends to dissociate the charge compensating hydrogen or alkali from substitutional aluminum, thus attenuating the luminescence at ~380 nm [14].

However, our sample has been manufactured with high purity silica, i. e. hopefully without alkali impurities. In addition, we compared the obtained luminescence at ~380 nm of the OF_SM_Ai sample, fabricated using MCVD method, with other Al-doped samples, manufactured using the SPCVD. The normalized CL spectra show similar band shape at ~380 nm (see figure III.26).
Figure III. 26. Normalized CL spectra of the different Al-doped samples

Such results indicates that the Al-related luminescence at ~380 nm still exists even in highly pure silica samples that have been manufactured using two different methods, which means that the origin of this luminescence could differ from the one tentatively attributed in the literature.

**Conclusion**

In this chapter we have reviewed different OFs using CL and CML techniques. In particular, we studied the different emission bands related to the incorporated dopants such as the Ge, N, P, Ce and Al.

We have highlighted an important difference between the CL and CML techniques in terms of the variation of the GLPC luminescence intensity as a function of the Ge concentrations. In details, we demonstrated that the CL spectra are highly affected by the electron beam irradiation, which indeed changed the intensity of the GLPC signal as a function of the Ge content. Moreover, we point out a monotonous decrease of the ratio between the final and starting GLPC content as a function of the Ge concentration, in particular, the higher is the Ge amount the lower is the GLPC signal after high electron fluence. This dependence could be related to the role of the Ge doping concentration in modifying the vitreous structure of silica, and the depletion of the stable GLPC sites above a Ge concentration of ~5 wt%.

In the second section dedicated to the study of the radiation-hardened OFs, we put in evidence the capacity of the CL spectroscopy to excite all the emitted defects, in the spectral range of the used detector. This is not the case for the CML technique, where several laser sources are needed to be able to excite all the luminescent defects. Because of this ability, new insights
were given concerning the intrinsic silica defects as well as the N-related centers. In particular, the origin of the luminescent band at 560 nm is still not known yet. According to our measurements, this band could be a contribution of a second order of the ODC(II) defects (at 280 nm) and another species (STE for instance). In the same spectral range, N-related and/or Cl-related features could be present, and their precise origin is still unknown.

The last section dealt with the radiation-sensitive OFs. New insights on the P-related, Ce-related and Al-related emission centers are presented. We have seen that the P dopant induces a luminescence band at ~410 nm, at the same time, the CL monochromatic images show that the P incorporation decreases the amount of the ODC (II) defects. When P doped silica is co-doped with cerium, a significant emission band, ascribed to the Ce$^{3+}$, is observed at ~370 nm. The on-line kinetic of this luminescence as a function the electron irradiation was shown to depend only on the deposited dose. Concerning the Al-doped sample, a luminescence band is detected at ~380 nm and is related to Al species. This emission decreases with the electron irradiation and its origin seems to be different from the (Al$^{3+}$ - M$^+$) compensation-charge centers, assumption suggested in [14]. Indeed, this band is detected in three different samples fabricated using two different methods.
Chapter IV

Study of the GLPC kinetics as a function of different electron beam irradiation conditions.

Introduction

After reporting a CL investigation on differently doped OFs in the previous chapter as an overview, in the present one, a deeper study was carried out on a single emission band related to one of the most important Ge related defect in Ge doped silica: the germanium lone pair center (GLPC).

As a case of study, we have selected the 4-steps Ge-doped canonical OF (iX_MM_Ge1) in order to perform deep CL investigation on the kinetics of the GLPC emission around 400 nm as a function of the germanium concentration. In particular, we characterized the influence of several irradiation parameters such as the energy, the dose (fluence), the dose rate (flux) aiming to better understand the electron-irradiation effects on the Ge-doped OFs. This choice is justified by the fact that germanosilicate fibers are considered as the most widespread ones, and on the other hand, the GLPC defects were shown to play a key role in their radiation responses. GLPC was not deeply investigated by CL in the past, our complementary investigation can enrich the knowledge on the bleaching mechanisms of this defect by irradiation especially at very high equivalent doses, which are difficult to achieve with other irradiation facilities (X-rays, γ-rays).

Moreover, additional CML measurements were carried out at LabHC on the electron irradiated samples and new insights concerning the NBOHC defects are also reported by comparing the results obtained with both techniques (CL and CML).

To complete this study on GLPCs, two pre-treatments were performed on the OF_MM_Ge2 sample in order to reveal, by CL, their effects on the GLPC generation and bleaching
mechanisms. In details, 9 MGy $\gamma$ pre-irradiated sample as well as $O_2$ loaded sample have been investigated using CL and their responses compared to the one of the pristine fiber.

I. Electron beam exposure effects on the GLPC kinetics

In this section we present an experimental investigation on the bleaching processes of the GLPC defects when the fiber is exposed to the CL electron beam. Three different electron energies and two different dose rates (deduced from electron fluxes) were used to investigate the 4-steps Ge-doped OF. Figure IV.1 illustrates the spatial distribution of the Ge content along the fiber radius. In details, we propose an experimental study of the mechanisms of the GLPC bleaching at very high electron doses. Then, by comparing our experimental results with the ab-initio calculations that have recently been published on the conversion mechanisms of the ODC(II) and GLPC centers [52], we propose an explanation of the basic mechanisms at stake.

![Figure IV.1. EDX measurements of OF_MM_Ge1.](image)

First, as we explained in chapter II, two different types of measurements have been performed that are characterized by different dose rates. The lower dose rate configuration consists in the acquisition of a series of monochromatic images at 400 nm ± 5 nm and extracting the radial profiles of the emission intensity after each scan using an imaging analysis (explained in details in [205]). From the next-recorded-images at different delay times we can follow the kinetic of the GLPC in each Ge-doped region (the 4 levels) as a function of the accumulated dose. The measurements dedicated for the higher dose rate configuration were differently carried out. In particular, we used the same monochromator to isolate the GLPC emission with the same bandwidth, but this time using the CL spectroscopy and not the images. In other words, we used the time series option, where only a small area is chosen and irradiated using the same
conditions. The GLPC signal was measured each second (see chapter II). Doing so, we can
follow the electron irradiation induced bleaching of the GLPC in situ. We have pointed out in
chapter II, that using this second configuration, the achieved irradiation dose is much larger
than the one associated with the image measurements. To complete our investigation, the same
procedure was repeated for three different energies of electrons: 5 keV, 10 keV and 20 keV. At
the end of the tests, we obtained several experimental data (several GLPC bleaching kinetics)
in which the analysis can be divided according to three main parameters: the energy, the dose
rate and the Ge concentration. In the following table, we summarize the different estimated
dose-rates for each measurement configuration and for each energy.

**TABLE 1: The estimated dose-rates for time series (TS) and image configurations**

<table>
<thead>
<tr>
<th>Energy (keV)</th>
<th>Images (Gy/s)</th>
<th>TS (Gy/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>$1.1 \times 10^5$</td>
<td>$5.6 \times 10^7$</td>
</tr>
<tr>
<td>10</td>
<td>$6.4 \times 10^4$</td>
<td>$3.4 \times 10^7$</td>
</tr>
<tr>
<td>20</td>
<td>$3.8 \times 10^4$</td>
<td>$2.0 \times 10^7$</td>
</tr>
</tbody>
</table>

I.1. Bleaching kinetics of the GLPC signal at high dose rate

In this section, we present the different GLPC kinetics as a function of the irradiation time
recorded using the TS configuration in the different Ge-doped regions of the OF.

Figure IV.2 shows the GLPC kinetics at 5 keV, 10 keV and 20 keV as a function of the
irradiation time. We observe that whatever the concentration of Ge or the probe beam energy,
the GLPC signal decreased as a function of the irradiation time before reaching a constant value.
This decrease is similar to what we reported in the first section of the previous chapter. In
particular, we have seen in chapter III, where the kinetics measurements were held using the
imaging configuration, that the Ge amount may control the minimum constant value observed
for the GLPC emission after a sufficiently long electron irradiation. This observation remains
valid when using the TS option of CL. Indeed, we observe that by the end of the irradiation,
higher is the Ge concentration lower is the constant value of the GLPC signal.

It is necessary to clarify that the selected approach to record the intensity at 400 nm implies a
low confidence level on the first points of each kinetics. In details, we first record the
background signal without the electron beam and then, at a certain time, we switch on the beam.
Since the time used to perform one scan is 0.2 s, and the acquisition time of the TS is 1 s, this
implies that the TS measurements collect the intensity of 5 scans from the same small area in
order to obtain one point. The error on the first point depends strongly on the synchronization
between the instant in which the beam is switched on and the instant in which the intensity is collected. In other words, the first point can be recorded only after 1 or 2 or 3 or 4 scans and the irradiation was not fulfilled the 5 scans, the reason why large error bars are associated to the first point. However, the amplitude of this error continuously decrease as the irradiation duration increases. We conclude that the intensities measured for varying parameters may not be comparable in the very beginning of the exposition but will be directly comparable at the end of the irradiation. To overcome this limitation, it should be remembered that the intensities at the beginning of the irradiation are comparable using the CL imaging technique, since in this case, the four steps are simultaneously recorded, as it will be discussed later.
Figure IV.2. GLPC kinetics recorded in the different Ge steps at E= 5 keV, 10 keV and 20 keV
As we previously observed, the remaining GLPC signal at the end of the irradiation seems to be controlled by the amount of the Ge. In order to better visualize the different bleaching processes existing while exposing the fiber surface to the electron beam, we have subtracted the saturation values recorded by the end of the irradiation, and plot in figure IV.3 the data in semi-logarithmic scale.

Figure IV.3. GLPC bleaching kinetics, after subtracting the saturation values, of OF-MM_Ge1 fiber recorded in the 4th step using a. 10 keV of beam energy, b. 20 keV of beam energy.

More in details, figure IV.3 reports the bleaching kinetic of the GLPC signal, after subtracting the saturation values, in the less Ge-doped region (4th step) using 10 keV (panel a) and 20 keV (panel b) electron irradiations.

From these curves plotted in semi logarithmic scale, it is easy to suggest the existence of at least two exponential processes. The first is very fast, mainly contributing in the first tens of second, whereas the second is slower and appears dominant after several hundreds of seconds. A deeper study of the dependence of these processes on the Ge content and on the electron energy is reported in the following.
Taking other data giving the GLPC intensity in the first doping level of Ge (~11 wt%) under 10 keV electron exposure, we tried to fit the data using 2 exponentials and 3 exponentials. Figure IV.4 presents the different obtained curves.

![Graph showing GLPC intensity and fits](image)

Figure IV.4. Experimental data and their fits of the GLPC intensity measured in the ~11 wt% region using 10 keV electron beam. The inset presents the residual of both 2 and 3 exponentials fits.

From figure IV.4, we can notice that using 3 exponentials plus a constant value, the reported data are better reproduced than with the 2 exponentials plus a constant value. In the inset we highlight the residuals between the data and the fits for both cases, we pass from ~13% of maximum residual using 2 exponentials to ~ 5% using 3 exponentials.

Indeed, to characterize the bleaching process of the GLPC intensities, we fitted the experimental data using a multi-parameter exponential functions with a nonlinear least-squares curve fitting algorithm. The best mathematical fit to the curves shown in figure IV.2 is expressed as:

\[ y_{fit}(t) = A_1e^{-t/\tau_1} + A_2e^{-t/\tau_2} + A_3e^{-t/\tau_3} + y_0 \]  

(4.1)

Where:
\( A_1, A_2 \) and \( A_3 \) are the intensities of the signals at \( t = 0 \) and \( 1/\tau_1, 1/\tau_2, 1/\tau_3 \) are the first order rate constants of the kinetics of each process, \( y_0 \) corresponds to the part of GLPC that are not bleached at the end of the irradiation (ie. the GLPC saturation level).

Aiming a better representation of the data, and in order to facilitate the comparison between the different variables, we have seen before that the Ge concentration determines the minimum value of the GLPC signal observed after the irradiation. In this context, the different curves were fitted group by group according to the used electron beam energy, assuming that for one used energy, the various processes are very similar (with the same kinetic constants) and that only their relative contributions can vary as a function of the Ge concentration. So we fitted the first 4 curves (referring to the 4 Ge levels) at \( E = 5 \) keV using the same \( \tau_i \) but different \( A_i \) and \( y_0 \), and we repeated the same protocol for the two other electron energies (10 keV and 20 keV). This procedure allows not only comparing the effect of the used electron beam on the different bleaching processes, but also to identify which process has the main impact as a function of the Ge concentration and of the irradiation parameters.

Figure IV.4 shows the experimental data that were fitted using equation (4.1). We report in particular the different kinetics recorded in the different Ge levels using energies of 5 keV (the right side of the figure), and 20 keV (the left side of the figure). We observe that for the lowest and the highest energies, the experimental data are well fitted with the above equation (4.1), which support our assumption that three exponential processes are responsible for the GLPC bleaching.

Aiming to reveal the energy effect on the bleaching kinetics, we summarized the parameters used to perform these fittings in the table 2.
Figure IV.5. GLPC bleaching kinetics of OF_MM_Ge1 fiber recorded in the zones containing different Ge levels using electrons of E = 5 keV in the right side, and E= 20 keV in the left side.
TABLE 2: Values of $\tau_i$ allowing to achieve the best fits shown in figure IV.5. The errors were evaluated as the standard deviation.

<table>
<thead>
<tr>
<th>Energies (keV)</th>
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<th>$\tau_3$ (s)</th>
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<td>5</td>
<td>1.5 ± 10%</td>
<td>8 ± 10%</td>
<td>72 ± 3%</td>
</tr>
<tr>
<td>10</td>
<td>2 ± 2%</td>
<td>13 ± 2%</td>
<td>95 ± 1%</td>
</tr>
<tr>
<td>20</td>
<td>3.6 ± 1%</td>
<td>20 ± 2%</td>
<td>186 ± 2%</td>
</tr>
</tbody>
</table>

We observe that the kinetics constants differ as a function of the electron beam energy. In particular, three bleaching mechanisms with different kinetics are observed, where the first one is very fast and the last one is slow. The three $\tau$ values are lower at lower energy, which means that the duration of the different processes is shortened when the electrons are less energetic. This finding leads to wonder if the dose could be the main factor affecting the kinetics constants, since according to table 1 reported in this chapter, lower is the energy higher is the dose. In other words, if the dose is the main factor who controls the different processes, then, using 5 keV, the required time to reach a certain dose is shorter than at 20 keV.

Additionally, in order to take the energy parameter into account, we can replot the data as a function of dose instead of the irradiation time using the relation (4.2) to compare the various results.

$$D = d \times t$$  \hspace{1cm} (4.2)

Where $D$: is the deposited dose in Gray (Gy), $d$: is the dose rate in (Gy/s) and $t$ is the irradiation time in (s). The expression (4.1) becomes:

$$y_{fit}(D) = A_1 e^{-dt/p_1} + A_2 e^{-dt/p_2} + A_3 e^{-dt/p_3} + y_0$$  \hspace{1cm} (4.3)

In this case, the estimated kinetics constants converted into dose have been calculated by taking into account the different energies, and the new constants $D_i$ become:

TABLE 3: The new values of the kinetics constants $D_i$ used to perform the fits of the GLPC intensity evolution with respect to the accumulated dose.

<table>
<thead>
<tr>
<th>Energies (keV)</th>
<th>$D_1$ (Gy)</th>
<th>$D_2$ (Gy)</th>
<th>$D_3$ (Gy)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>8.4 × 10^7 ± 10%</td>
<td>4.5 × 10^8 ± 10%</td>
<td>4 × 10^9 ± 3%</td>
</tr>
<tr>
<td>10</td>
<td>6.7 × 10^7 ± 2%</td>
<td>4.4 × 10^8 ± 2%</td>
<td>3.2 × 10^9 ± 1%</td>
</tr>
<tr>
<td>20</td>
<td>7.3 × 10^7 ± 1%</td>
<td>4 × 10^8 ± 2%</td>
<td>3.8 × 10^9 ± 2%</td>
</tr>
</tbody>
</table>
The table reported above shows the values of the constants $D_i$ converted into Gy unit. We observe that for each bleaching process, the kinetics constants are comparable regardless of the energy, which may indicate that the three bleaching mechanisms are the same for the three energies, and that they are following the evolution of the dose. In order to check any changes in the spectra’s shape after irradiation, we have recorded CL spectra after each irradiation, and we normalized them to their maxima, to check if any radiation-induced spectra modifications.

Figure IV.6. Normalized CL spectra of the GLPC signal taken at $E = 10$ keV: a. as a function of Ge concentration at the beginning of the irradiated for 600s, b. as a function of Ge concentration after being irradiated for 600s, c. the 1st Ge doping level before 600 s electron exposure and after 600 s electron exposure.

Figure IV.6 demonstrates that the lineshape of the GLPC band does not changed during irradiation with electrons at $E = 10$ keV regardless of the Ge content. Similar results were obtained for the other 3 doping levels and for both other electron energies (5 keV and 20 keV). Such information indicates that at least from the spectroscopy point of view, the bleached features seem to be the same whatever the Ge amount or the used energy, which may indicate that the bleaching processes are not generated by the decrease of some sub-features of the band.
at ~3.1 eV. It is worth to mention that the obtained spectra “before” 600 s of irradiation, have also been irradiated because of the technique operating principle. However, in [213], it has been shown using photoluminescence, that up to 20 wt%, the Ge doping content does not strongly change the lineshape of the GLPC emission spectrum at ~3.2 eV.

Assuming that the bleaching processes found above are independent from the three employed energies and the starting GLPC-concentration values, and they are following the dose variations, it remains to reveal which process is the dominant by varying the dose and the Ge amount. The table 4 summarizes the values of the ratios between the intensities of the bleaching kinetics $A_i$ extracted from the model (4.1).

TABLE 4: Contributions of each intensity with respect to the sum of all the intensities $(A_i/(\Sigma A_i + y_0)) \times 100$ for the different energies and Ge concentrations.

<table>
<thead>
<tr>
<th>Contribution of amplitudes</th>
<th>((A_1/\text{sum})\times 100)</th>
<th>((A_2/\text{sum})\times 100)</th>
<th>((A_3/\text{sum})\times 100)</th>
<th>((y_0/\text{sum})\times 100)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5keV_4th step</td>
<td>43%</td>
<td>3%</td>
<td>17%</td>
<td>36%</td>
</tr>
<tr>
<td>5keV_3rd step</td>
<td>40%</td>
<td>16%</td>
<td>14%</td>
<td>30%</td>
</tr>
<tr>
<td>5keV_2nd step</td>
<td>51%</td>
<td>17%</td>
<td>11%</td>
<td>21%</td>
</tr>
<tr>
<td>5keV_1st step</td>
<td>66%</td>
<td>17%</td>
<td>8%</td>
<td>9%</td>
</tr>
<tr>
<td>10keV_4th step</td>
<td>60%</td>
<td>6%</td>
<td>11%</td>
<td>24%</td>
</tr>
<tr>
<td>10keV_3rd step</td>
<td>63%</td>
<td>10%</td>
<td>6%</td>
<td>20%</td>
</tr>
<tr>
<td>10keV_2nd step</td>
<td>66%</td>
<td>16%</td>
<td>4%</td>
<td>14%</td>
</tr>
<tr>
<td>10keV_1st step</td>
<td>77%</td>
<td>14%</td>
<td>3%</td>
<td>7%</td>
</tr>
<tr>
<td>20keV_4th step</td>
<td>47%</td>
<td>14%</td>
<td>12%</td>
<td>27%</td>
</tr>
<tr>
<td>20keV_3rd step</td>
<td>53%</td>
<td>21%</td>
<td>7%</td>
<td>19%</td>
</tr>
<tr>
<td>20keV_2nd step</td>
<td>60%</td>
<td>22%</td>
<td>6%</td>
<td>12%</td>
</tr>
<tr>
<td>20keV_1st step</td>
<td>52%</td>
<td>27%</td>
<td>7%</td>
<td>13%</td>
</tr>
</tbody>
</table>

As general observations, we notice that the faster process in which the amplitude is called $A_1$ dominates whatever the Ge concentration or the used energy. The other two processes are closer, their relative contributions seem dependent on the Ge content. Regarding $y_0$ which represents the amplitude of the remained GLPC signal after irradiation, this amplitude appears more dominant compared to $A_2$ and $A_3$ at lower Ge concentration.

To better visualize the table above, we present in figure IV.7 an example of the evolutions of the contributions of the different processes at the energy 10 keV as a function of the Ge content.
Figure IV. 7 gives clearer visualization of the data and reveals further information concerning the relation between the different processes and the Ge concentration. For example, we can see that the $y_0/\text{sum}$, representative the stable for of GLPCs, decreases linearly with the increase of Ge amount. Also, the most dominant process, which is the first and the less stable form of GLPCs, seems to increase with the Ge concentration. As well as for the second which shows a saturation tendency. In regards of the last process, represented by the amplitude $A_3$, its contribution tends to decrease at larger Ge concentration. These observations remains true for the other employed energies (5 keV and 20 keV) for which the behavior of each process appears similar to the one reported in figure IV.7.

To explain these bleaching kinetics, it is worth to remind that the GLPC defects were shown to be a precursor centers of other Ge-related radiation induced point defects. In particular, while exposing Ge-doped OF to X or $\gamma$-rays up to MGy dose, their concentration decreases as the GLPC defects are converted into new defects such as Ge (1) and Ge (2) centers [36], [139]. However, in our case, the deposited doses are very high, which may lead to other conversion mechanisms. It is worth to mention that using electrons at high doses, the amount of the remained (non-bleached) GLPC by the end of the irradiation seems to be controlled by the Ge concentration. Such finding could be explained by the fact that at low Ge-doping concentrations, the Ge atoms substitute the Si atoms and occupy the stable available sites.
However, when increasing the Ge amount, the global silica structure may be modified by these Ge atoms, and the occupied sites are less stables. When irradiating with electrons, it is easier to bleach the GLPC defects that occupy the non-stable sites (related to the higher Ge concentration), and harder to destroy those related to the stable sites (in the case of lower Ge concentration). This can explain the fact that the remained (non-bleached) GLPC observed after the electron beam irradiation, which was observed to be higher in the lowest Ge concentration.

In order to strengthen our hypothesis, we compare our experimental measurements with a recent theoretical work that investigated the conversion processes of the oxygen deficient centers (ODCs) in pure and Ge-doped silica [52]. Here again, we report figure IV.8 that shows the theoretical results of the different conversion mechanisms of the ODC(II).

![Diagram showing different conversion mechanisms of ODC (II) centers](image)

**Figure IV. 8.** The different conversion mechanisms of ODC (II) centers. X can be Si in case of Si-DOC (II) or Ge in case of GLPC (which is our case) where dimer corresponds to ODC(I) and Forward Oriented (FO) refers to $E_{	ext{OX}}$ or Ge(2). Adapted from [52].

According to [52], there exists at least three bleaching channels of the GLPC: (i) is the bleaching through ionization that transforms GLPC into Ge(2); (ii) direct conversion to (≡ Ge - Si ≡) through rotation mechanism (RM) and (iii) direct conversion to (≡ Ge - Si ≡) through puckering mechanism (PM). Because of the amorphous nature of silica, the activation energies for the conversion may differ from site to site. We remind that when more Ge atoms are present in the
silica network the activation energies of the defects tend to decrease, hence favoring the bleaching process as reported in [52]. Such finding seems in agreement with the multi-processes performed in our experimental data. In particular, we have shown that the obtained experimental data can be well fitted with three exponentials, and we found out that increasing the Ge amount efficiently increase the bleaching process impact and lower the remaining GLPC level at the end of the electron exposure.

I.1. Bleaching kinetics of the GLPC signal at low dose rate

In this section, the kinetics measurements were differently carried out, by employing the CL imaging option, which allows to characterize in situ the spatial distribution of the emitting centers during the beam exposure.

Such image measurements are associated with less aggressive constraints in terms of dose rate (electron flux). In details, the investigated zone is much bigger in size (90 μm × 70 μm) instead of (4 μm × 3 μm) than the one used for the TS configuration. Moreover, each point is irradiated after a large time between two consecutive scans. In details, every point represented by one pixel in the image has been irradiated for ~16 μs, and is not irradiated for more than 20 s before being exposed to the next irradiation.

We first show the first recorded monochromatic images at 400 nm of the OF_MM_Ge1 fiber, using 20 keV of beam energy (figure IV.9).

Figure IV.9. a. CL monochromatic image at 400 nm measured using electrons of 20 keV in energy. b. The radial profile of the GLPC emission extracted from this image.

Contrary to the TS configuration, by using the imaging one, we are able to compare the GLPC signal of the different Ge-doped zones at the beginning of irradiation. We observe that the
maximum of luminescence is at the center of the core where the Ge concentration is the highest. However, a second maximum is obtained at the core/cladding interface. These higher intensities of the GLPC signal are probably due to the fiber fabrication processes (preform deposition and drawing process). Similar observations were done in [26], [27] where the authors claim that such increase of luminescence is caused by the fabrication process of the OF. The same luminescence distribution was shown for $E = 5$ keV and $E = 10$ keV (the results regarding 10 keV are shown in chapter III). Because of the weak signal to noise ratio in the case of the $E = 5$ keV, we will focus our discussion on the $E = 10$ keV and $E = 20$ keV.

The three samples were exposed to electron exposure (irradiated using $E = 5$ keV, 10 keV and 20 keV) for about 40 mins, their monochromatic images were recorded after each scan (19.2 s), so we can deduce the bleaching kinetics of GLPCs. In figure IV.10 we present the last monochromatic image recorded after 40 minutes of 20 keV electron exposure.

![Image](image.png)

Figure IV.10. a. CL monochromatic image at 400 nm taken after 40 mins of 20 keV electron irradiation. b. The radial profile of the GLPC emission extracted from this image.

After about 40 mins of 20 keV electron irradiation (~122 scans), the spatial distribution of the luminescence has changed. As it can be seen in the radial profile of this emission reported in the panel b of figure IV.10, the remaining GLPC-luminescence is higher in the zones with the lower Ge concentration. These results confirm again that the Ge concentration affects the final amount of GLPC signal and agree with previous results for the previous section. Similar radial profiles were obtained for $E = 5$ keV and $E = 10$ keV.

The bleaching kinetics obtained by recording series of monochromatic images, show similar behavior as the data previously reported in the first section (see chapter III for the kinetics using $E = 10$ keV).
Following the same procedure as in the first section, we converted the experiment time into equivalent doses. In particular, we have seen in the previous section (TS) that the bleaching kinetics of the GLPC signal depend on the dose and not on the dose rate. Basing on these results, we applied the same procedure for this section (images) where the dose rate is less important, and because of this low dose rate, the accumulated dose by the end of the irradiation is lower than using the TS configuration. As a consequence, the last two processes (2 and 3) of the TS measurements have a very weak contribution in the case of the images measurements and they are included in the $y_1$ values. Also, because of the low dose rate, the bleaching of the GLPC in the beginning of the irradiation is better observed here (images), and it is called process 0 in the following.

Figure IV.11 shows the results of the fitting of the CL imaging data using the following model:

$$y_{fit}(D) = A_0 e^{-dt/D_0} + A_1 e^{-dt/D_1} + y_1$$  \hspace{1cm} (4.4)

Figure IV.11. GLPC bleaching kinetics of OF_MM_Ge1 fiber recorded in the fiber parts with different Ge levels using $E = 20$ keV.

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The parameters found using the model described by the equation (4.1) are summarized in the table 5:

**TABLE 5:** The values of the kinetics constants $D_i$ used to achieve the best fits of the experimental data. The errors were evaluated as the standard deviation.

<table>
<thead>
<tr>
<th>Energies (keV)</th>
<th>$D_0$ (Gy)</th>
<th>$D_1$ (Gy)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>$4.9 \times 10^6 \pm 6%$</td>
<td>$6.7 \times 10^7 \pm 10%$</td>
</tr>
<tr>
<td>20</td>
<td>$4.2 \times 10^6 \pm 4%$</td>
<td>$7.3 \times 10^7 \pm 10%$</td>
</tr>
</tbody>
</table>

We observe lower $D_i$ values using the CL imaging configuration compared to the TS one. In particular, using the imaging mode for $E = 10$ and $20$ keV, a new process is activated at $D_0 \sim 4.5 \times 10^6$ Gy which was not observed in the previous TS measurements. The second process with a constant $D_1 \sim 7 \times 10^7$ Gy, seems the same like the first process using the TS configuration for both energies. Such finding could be explained by the lower deposited dose in the case of CL images. As a consequence, a “hidden” process in which the constant is $D_0$ is observed using the imaging mode. This process needs a lower dose value to be bleached compared to the one deposited in the TS measurements, at the same time, the other two processes that need more accumulated dose, cannot be observed in the imaging data and a very longer irradiation time is needed to observe the bleaching mechanisms characterized through the TS measurements.

From this, we could assume that at least 4 mechanisms are involved in the GLPC kinetics over the whole dose range. The values of the kinetic constants in Gy seem similar for both $E = 10$ keV and $E = 20$ keV, which indicates again that the bleaching processes are mainly affected by the dose rather than by the energy or dose rate. It is worth to mention that the recorded images have a weaker signal-to-noise ratio compared with the TS configuration, which explains the fact that the errors are larger in the case of the images configuration. A comparison of the contributions of the two bleaching mechanisms to the global emission is reported in the table 6:

**TABLE 6:** Contributions of each process amplitude with respect to the sum of all the amplitudes $\left(\frac{A_i}{\sum A_i + Y_0}\right) \times 100$ for the different energies and Ge concentrations.
The fitting results show that the first bleaching process is the most dominant contributor regardless of the used electron energy or Ge amount. The remaining GLPC signal after irradiation ($y_1$ values) dominates the second process when the Ge concentration is lower, this behavior is inversed at higher Ge concentration (> 8 wt%). These $y_1$ values can include the contributions of the two other processes observed in TS measurements as well as the remaining GLPC after irradiation ($y_0$). The behavior of these $y_1$ values can be compared with the ones of the TS configuration in terms of their dependences to the Ge amount. As we observed in the first section, the non-bleached GLPC signal after irradiation, represented by the ($y_0$/sum), seems to be strongly related to the Ge amount. Once again, we remind the hypothesis of the stable GLPC sites at lower Ge concentration that generates more stable defects compared to the ones generated at higher Ge concentration, that are harder to bleach.

To conclude this section, the two used methods (TS and imaging) to follow the kinetics of the GLPC signal as a function of electron irradiation reveal the existence of different bleaching processes (at least 4) for this defect. Regarding the CL imaging, the irradiation process was held in a chopped way (successive irradiation separated by periods of recovery) whereas the TS measurements were carried out almost continuously. In particular using the CL imaging, each irradiated point for 16 µs needs to wait for ~ 20 s to receive the next irradiation, whilst for the TS measurements this duration is only ~0.2 s. Considering that the bleached GLPC centers are converted into other Ge-related point defects, the ratio between the initial amount of GLPC (recorded at the very beginning of beam exposure) and the one at the irradiation end varies linearly as a function of the Ge concentration, which means that the Ge amount controls this remaining and constant GLPC signal. Further investigations, with other spectroscopic techniques, are required in order to identify the defects in which the GLPCs are converted under electron-beam irradiation, since the information reported in the literature concerns other types of irradiation, principally $\gamma$-rays and X-rays at doses up to a few MGys. In particular, several

<table>
<thead>
<tr>
<th>Contribution of amplitudes</th>
<th>$(A_0$/sum)$\times$100</th>
<th>$(A_1$/sum)$\times$100</th>
<th>$(y_1$/sum)$\times$100</th>
</tr>
</thead>
<tbody>
<tr>
<td>10keV_4th step</td>
<td>46.2%</td>
<td>8.6%</td>
<td>45.2%</td>
</tr>
<tr>
<td>10keV_3rd step</td>
<td>56.8%</td>
<td>11.5%</td>
<td>31.6%</td>
</tr>
<tr>
<td>10keV_2nd step</td>
<td>69.5%</td>
<td>12.9%</td>
<td>17.6%</td>
</tr>
<tr>
<td>10keV_1st step</td>
<td>71.0%</td>
<td>19.7%</td>
<td>9.3%</td>
</tr>
<tr>
<td>20keV_4th step</td>
<td>48.4%</td>
<td>10.5%</td>
<td>41.1%</td>
</tr>
<tr>
<td>20keV_3rd step</td>
<td>61.7%</td>
<td>9.8%</td>
<td>28.5%</td>
</tr>
<tr>
<td>20keV_2nd step</td>
<td>75.2%</td>
<td>11.2%</td>
<td>13.6%</td>
</tr>
<tr>
<td>20keV_1st step</td>
<td>76.7%</td>
<td>18.2%</td>
<td>5.1%</td>
</tr>
</tbody>
</table>
investigations (for example [39] where the same sample was used) showed that under X-rays the radiation induced Ge-related defects are mainly the so called Ge(1) and Ge(2), their concentrations saturating at MGy dose levels. However, in the current investigation, both the nature of irradiation as well as the doses are sufficiently different to open the door for the involvement of other types of defects in the GLPC conversion mechanisms.

III. Electron irradiation induced effects on the NBOHC defects

After being irradiated up to high doses (~ $10^8$ Gy) using the CL imaging, the fiber samples were characterized post irradiation (weeks later) by confocal micro luminescence (CML) in order to reveal the permanent effects of such irradiation. It was quite difficult to investigate the GLPC luminescence bleaching using the CML after electron irradiation, since the volume of interaction of the electrons with the material is of only a few microns below its surface. In details, the later resolution of the used CML instrument is ~ 2 µm cross section and some microns in depth. So the detected signal will not be only from the irradiated zones, but also from the pristine ones, where the GLPC signal is much higher, affecting largely the reliability of the GLPC measurements.

However, investigating the NBOHC centers is easier, since it was proved that its amount is very low before irradiation. So it should be possible to investigate the NBOHC induced by the electron beam irradiation [214] during the CL experiments by CML, through the 2D monitoring of their luminescence at ~645 nm [85] (see chapter III for the spectrum).
Figure IV.12. Ex-situ 2D CML cartographies of the emission at 650 nm (NBOHC) in the electron irradiated samples of fiber OF_MM_Ge1. The big rectangular zones are those where the CL imaging irradiation were held, and the small intense ones refer to the regions where the CL spectra were recorded.

The reported maps in figure IV.12 clearly show the traces of the zones that have been irradiated using CL imaging. In particular, the NBOHC signal is higher in the regions that have been irradiated (rectangular area around the core of the fiber and a part of its cladding). The NBOHC signal is more intense for higher electron energies. This can be explained by the fact that higher is the energy, deeper and larger is the interaction volume. As example, in the case of $E = 5$keV,
the electrons penetrate only ~0.5 µm in the volume, which indicates that the detected signal shown in the map is the sum of the signals from 0.5µm of the irradiated volume and the pristine one located deeper in the sample. This effect is less considerable if we increase the used energy to irradiate the samples, for instance using E = 20 keV the penetration depth is ~ 4µm leading to consider a larger irradiated volume to perform the measurements with a higher signal to noise ratio.

Regarding the radial distribution of the NBOHC luminescence, we observe that, the luminescence level is lower in the center of the core, and it increases getting closer to the cladding. This means that the NBOHC defects are more generated by electrons in the less Ge-doped regions. It is worth to remind that there should be the contribution of both defects: the Si-NBOHC emitting at ~650 nm and the Ge-NBOHC emitting at ~660 nm [46], [82], and since the central positions of both peaks are so close, it is difficult to determine which luminescence is more present.

These results sounds surprising, since using γ-rays, an opposite behavior is observed. To confirm so, we tested the same fiber (OF_MM_Ge1) but irradiated up to 9 MGy doses. The obtained 2D map is reported in figure IV.13.

![Figure IV.13. 2D CML cartography of the emission at 650 nm (NBOHC) in the γ irradiated sample.](image)

For the γ irradiated sample, the spatial distribution of the NBOHC luminescence is clearly different, larger is the Ge amount higher is the NBOHC signal. These results could be explained by the difference of the irradiation nature, since the electrons are more aggressive in a small volume, they may cause some structure changes [215] that are related to the presence of the Ge, thus the differences of the spatial distributions of the defects. Additionally, as we reported in the first chapter, the electron beam has been shown to have a particular defects distribution due
to a localized electronic field that can cause an immigration of the mobile charged defects and their micro-segregation [16], [71], [72].

In order to complete the data recorded by the CML technique, in-situ CL measurements were held to follow the evolution of the NBOHC luminescence in the core as well as in the cladding of the OF. These measurements were carried out using the TS configuration on two different samples.

![Figure IV.14. CL kinetics of the NBOHC emission: a. at 645 nm, b. 660 nm.](image)

Figure IV.14 shows the kinetics of the NBOHC luminescence signal as a function of the irradiation time, using 10 keV of electron beam energy. Employing a bandwidth of ± 5 nm, we recorded the CL signal at 645 nm and 660 nm reported in the panels (a) and (b) respectively.

First, we observe that the behavior of the NBOHC signals appear to be very similar regardless of the chosen wavelength, this is due to the very close central positions, even if a spectral deconvolution is needed to confirm such observation; the weak NBOHC CL spectrum prevented us to have a complete analysis. Second, the kinetics recorded in the core of the OF differ from the ones of the cladding in both cases. These kinetics agree with the previously reported CML ex-situ maps. In details, the lowest intensity of the NBOHC luminescence is detected in the cladding, and it is almost equal to the NBOHC intensity in the highest Ge-doped region by the end of the irradiation. Regarding the core regions (the Ge-doped ones), the results show that the higher is the Ge concentration, the less is the NBOHC signal, even at the beginning of the irradiation.

We conclude that e origin of the red luminescence is may be due to the coexistence of the Si-NBOHC and the Ge-NBOHC, further investigations are required to distinguish their
contributions to the global emission. Regarding the impact of the nature of the irradiation, γ rays and electrons induce different NBOHC distributions as a function of the Ge amount.

III. Pre-treatment effects on the GLPC kinetics

To complete our CL investigation of the GLPC luminescence and the electron beam effects on its amplitude, we investigated different Ge-doped samples on which we applied some pre-treatments before its exposure to the electrons.

The used sample for this study is a 2-steps Ge-doped OF provided by iXBlue Photonics division [208]. Its EDX characterization is reported in figure IV.15 that presents the radial distribution of the Ge concentrations. The highest Ge amount is found in the central part of the core with ~9 wt% of Ge concentration, whereas the second step contains ~5 wt% of Ge.

![Figure IV.15. EDX measurements of OF_MM_Ge2 [216].](image)

III.1. 9 MGy γ-rays pre-irradiation

OF_MM_Ge2 OF was irradiated up to 9 MGy (SiO₂) γ-rays using the Brigitte $^{60}$Co source of SCK-CEN. First, we perform CML characterization to highlight the gamma irradiation effects. As we reported in the previous chapter, the main luminescence detected in the core of the fiber under 325 nm excitation is the GLPC emission band at ~ 400 nm. We have also shown that, before irradiation, the intensity of this luminescence increases with the Ge amount. In the purpose of highlighting the γ-ray effect on the emission at 400 nm, a cartography along the fiber radius was carried out basing on the PL measurements.
The radial profiles along the core radius of the 400 nm emission presented in figure VI.16 show a decrease of the GLPC emission after $\gamma$ irradiation up to 9 MGy. We can notice that the profile of the GLPC emission is affected not only by the Ge concentration, but also by the fabrication process which induces some stressed zones especially in the center of the core favorable to this defect generation.

![Graph showing radial profile](image)

Figure IV.16 Radial profile along the core radius of the emission at 400 nm using CML.

The ratio between the intensities of the GLPC luminescence in the pristine and the 9 MGy $\gamma$ irradiated sample is about 0.63 which indicates that this irradiation reduces about a third the GLPC intensity.

The same sample was characterized using CL technique. The CL spectra have shown the presence of the GLPC emission at ~400 nm in the core of the pre-irradiated fiber. We report in figure IV.17 the panchromatic images of the first and the last scans, the last scan being recorded after 30 minutes of 10 keV electron beam exposure.

![CL images](image)

After 30 mins of 10 keV electron beam exposure
Figure IV.17. CL panchromatic images of the 9 MGy γ irradiated sample of a. the first scanned image, b. after 30 minutes of electron beam exposure.

From the panchromatic images (representative of the GLPC emission in this fiber), we can clearly see the decrease of the luminescence caused by the electron beam exposure. Even after pre-irradiating with γ rays up to 9 MGy, the luminescence is higher where the Ge concentration is lower after a sufficient electron irradiation. This behavior could be due to the very high doses associated with the electron beam and the nature of this irradiation (electrons). It is worth to mention that the panchromatic images before and after 30 minutes of irradiation of the non-pre-treated sample, present the same tendency [205].

Regarding the study of the GLPC kinetics, CL monochromatic images (at ~400 nm ± 5nm), were recorded after each scan (imaging configuration) and then radial profiles along the core radius were extracted. These profiles were compared to the non-pre-irradiated sample. In figure IV.18 we show the first (panel a) and the last (panel b) radius profiles before and after 30 minutes of irradiation.

![Figure IV.18 CL radial profile along the core radius: a. before 30 minutes of electron beam irradiation, b. after 30 minutes of irradiation.](image)

The CL radius profiles before 30 minutes of irradiation reported in the left panel of figure IV.18 present a decrease of the GLPC intensity in the case of the γ pre-irradiated fiber. This decrease is about 0.23 of the initial luminescence recorded in the first scan of the pristine fiber which is in agreement with the previously reported CML profiles.

After a sufficient electron beam exposure (30 minutes), both samples show a similar radial distribution of the GLPC luminescence (figure IV.18.b). The intensity of the emission at 400 nm decreased significantly and its signal is higher in the lowest Ge-doped region, confirming
both the panchromatic images of figure IV.17 and the results obtained on the OF_MM_Ge1 sample.

Aiming to highlight the impact of the Ge amount on the bleaching process of the GLPC luminescence, an in-situ investigation under electron beam exposure in the different parts of the OF’s core is reported in figure IV.19 The presented kinetics were obtained by acquiring a series of CL monochromatic images at 400 nm. The GLPC signal was bleached in the whole core reaching a minimum value by the end of the irradiation (~90 scans).

![Figure IV.19. In-situ bleaching kinetics of the GLPC signal under electron irradiation. 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).](image)

After 20 scans (~6 mins) the intensity of the GLPC signal has decreased from ~150 to ~50 counts 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. The bleaching behavior of the emission at 400 nm observed in both samples under radiation could be explained by a conversion process of the GLPC to other Ge-related centers [139] as we already reported in the first section of this chapter. After a sufficiently long electron irradiation, the GLPC kinetics reached a saturation level. It is worth to mention that the available studies in literature up to now are mostly dealing with doses up to 10 MGY and there are no enough investigations that have been performed at larger doses (in the order of GGy), thus some other mechanisms of conversion are probable to be involved besides the ones already reported in the literature.
III.2. O₂ loading pre-treatment

The second pre-treatment that was performed on the OF_MM_Ge2 is its O₂ loading. Such treatment of the OFs has been shown to strongly change the response of the OFs especially under irradiation. In particular, the O₂ loading turned out to passivate the oxygen deficient defects such as the GLPC, thus enhancing the RIA (Radiation Induced Attenuation) of the OFs at specific wavelengths [49].

In this section, we provide a complementary study of the O₂ loaded Ge-doped OF by cathodoluminescence. CL monochromatic images at 400 nm were recorded after each scan for 30 minutes of electron beam exposure. Figure IV.20 show the first and the last recorded images respectively.

![Image of CL monochromatic images](image.png)

Figure IV.20. CL monochromatic (@ 400 nm ± 5 nm) images of the O₂ loaded sample of a. the first scanned image, b. after 30 minutes of electron beam exposure @ 10 keV.

We observe that the GLPC signal is still detected but it is weaker in the central part of the core. By exposing the sample to 10 keV electron beam irradiation for 30 minutes, the monochromatic image is brighter which means that the GLPC signal increases indicating the creation of these centers by irradiation, contrary to the all previous cases where the GLPC signal was decreasing during the electron irradiation.
Radial profiles along the core radius have been extracted from the first and the last recorded monochromatic image at 400 nm to better visualize the spatial distribution of the luminescence. Figure IV.21 shows that for the first performed scan, the GLPC signal is slightly weaker in the highest Ge-doped zone. After 30 minutes of electron irradiation, the intensity of the GLPC has increased and it is always higher in the lower Ge-doped region.

Figure IV.22. GLPC CL kinetics during 10 keV irradiation for the two-core zones of the O₂ loaded sample.
The spatially resolved in-situ measurements reported in figure IV.22 reveals the on-line evolution of the GLPC signal as a function of the electron irradiation with respect to the Ge amount. We can see that the intensity of the GLPC grows as a function of the irradiation in both zones until reaching a stable level after 30 minutes. However, the generation process of the GLPC is more important in the outer part of the core (the lower Ge-doped region).

To explain such results, we first remind that the \( \text{O}_2 \) loading converts an important amount of GLPC centers [49], which explains the initial weak GLPC signal. After electronic exposure, the GLPC defects are generated with the irradiation contrary to the non-loaded sample and also the pre-irradiated one. This phenomenon could be explained by a competition between the generation and destruction processes of the GLPC. On the other hand, basing on the previous measurements, we have seen that the ratio between the final and the starting GLPC content is lower in the higher Ge-doped zone, which suggests a higher bleaching efficiency and as a consequence can explain the fact that in this region the saturation level is lower in the highest doped zone in the \( \text{O}_2 \) loaded fiber. In other words, in the lower Ge-doped region, the stable sites form more stable GLPCs, the other sites are less stable in the case of higher Ge concentration. When the GLPCs are passivated by the \( \text{O}_2 \) loading, and those who occupied the stable sites are easier to be regenerated after electron irradiation.

The centers in which the GLPC is converted after the \( \text{O}_2 \) are still undetermined yet, two configurations are possible. For instance, the germanone (\( > \text{Ge} = \text{O} \)) which is an oxygen-excess defect or dioxsilirane-like defect (\( > \text{Ge} < (\text{O}_2) \)) [49]. Also, the radiation induced centers are still unknown since the mechanisms of conversion at such huge doses and using electrons can differ from the ones already studied in the literature at lower doses.

**Conclusion**

This chapter deals with the electron beam irradiation effects on Ge-doped OFs. The luminescence signal at 400 nm which is attributed to the GLPC defects, has been investigated in details as a function of the beam energy, the dose rate and the Ge concentration. A simple descriptive model was used in order to better understand the bleaching mechanisms of this luminescence. We have suggested that there exist at least four bleaching processes that are associated with kinetic constants which seem independent of the dose rate. In other words, there exist four different bleaching-kinetics of instable GLPC defects. The remained GLPCs are stable and can be regenerated even when bleached by the \( \text{O}_2 \) loading. The presence of multi-processes is in agreement with some recent theoretical ab initio calculations [52]. The Ge
concentration has shown to influence some of these processes leading to reach at the irradiation end different saturation levels. The saturation level is higher when the Ge content is lower. These bleached GLPCs are converted into other Ge-related point defects.

The CML measures taken after the electron irradiation as well as the in-situ CL investigations have shown some new insights regarding the spatial distribution of the NBOHC centers. In particular, the NBOHC defects are slightly present in the pristine fibers, and they are largely created by the irradiation. Our measurements indicate that the γ-ray induced and the electron induced NBOHC defects differ as a function of the Ge concentration. In other words, while the NBOHC centers follow the Ge concentrations in the γ-irradiated sample, this behavior is the opposite in the case of electron beam irradiation, more is the Ge amount, less is the NBOHC signal. The main difference between the two kinds of irradiation is due to the nature of the irradiation (electrons) and the very high deposited dose, which is not the case for the γ rays, which seems to result in different defect distribution.

Finally, we have tested other Ge-doped samples that were pre-treated before being exposed to electrons. The results concerning the pre-irradiated sample (γ rays up to 9 MGy) confirm the bleaching of the GLPC centers under γ rays as for electrons. The second pre-treatment consists of the O₂ loading of the sample. Previous study has demonstrated that such treatment leads to decrease the GLPC amount in the core of the OF. Nevertheless, after the electrons beam irradiation, some GLPCs are regenerated. Qualitatively the spatial distribution of the stable GLPC as a function of the Ge concentration has not changed, since they were from the beginning more abundant in the regions less doped with Ge. Then, by the electron beam exposition, the GLPC defects are regenerated again. This regeneration is favored in the case of low Ge concentration, since it contains more stable sites to create GLPC defects that are difficult to bleach by irradiation but easier to create once passivated by the O₂ loading.

The results reported in this chapter are considered as new insights that may help to better understand the response of the Ge-doped OFs under electron irradiation and the role of GLPCs defects in the radiation response of germanosilicate optical fibers. Furthermore, the presented pre-treatment such as loading with O₂ has been shown to passivate the GLPC centers, and the re-generation of some centers was favored by the electrons. Further investigations are needed to identify the centers in which the GLPC is converted after irradiation, but appear difficult to design especially due to the low volume of material irradiated with electrons preventing EPR, or absorption measurements. On the other hand, with the recent advance about the ab-initio calculations of structural and optical defects-properties, it may be possible in the future to
progress on this topic by combining more experimental and theoretical approaches. Furthermore, it would be interesting to perform a study of the GLPC bleaching kinetics at low Ge-doping levels, to check the hypothesis related to the stable sites.
Chapter V

Characterization of silica-based nanoparticles

Introduction

This last chapter presents the potential of the CL technique to characterize the same pure- and Ge-doped silica materials but this time at the nanometer scale as nanoparticles were produced from bulk materials. SEM, EDX, TEM (Transmission Electron Microscopy), STEM (Scanning Transmission Electron Microscope) measurements have been coupled to the CL experiments to better highlight its potential for studying such nanoscale systems.

In details, two different samples containing either Ge-doped or pure-silica nanoparticles have been investigated. We first demonstrate the feasibility to produce amorphous silica nanoparticles employing nanosecond pulsed UV laser focused on bulk Ge-doped preform or silica bulks. We then evaluate the ability of CL apparatus to characterize the luminescent features of the produced samples. CL provides an additional information besides the morphological ones provided by SEM and TEM. Furthermore, the chemical analysis obtained using EDX measurements can be performed using the same SEM apparatus to improve the understanding of the investigated samples. As an example, such results confirm the presence of high amounts of Ge atoms in the nanoparticles produced starting from Ge-doped commercial preforms.

In terms of morphology SEM and TEM images give an idea regarding the size and shape of the produced nanoparticles, the TEM images allow to give insights about their amorphous nature. Then, EDX measurements were performed to confirm the chemical composition of the nanoparticle. Finally CL imaging as well as CL spectroscopy were carried out to investigate the emitting defects present in these nanoparticles, showing the emission features of the investigated systems.
I. Motivations

Nanotechnology is a domain that attracts a great attention of scientists in the last decades, with the aim to reduce the size of the devices and to exploit the peculiar properties of nano-systems which usually differ from those of bulk materials [217]. Such field involves several disciplines such as physics, biology, chemistry, medicine and electronics [217] from the basic research and the applicative point of views. Indeed, the nanoscience and nanocomposite systems cover relevant roles in the biosensing, bioimaging, and many other medical fields [218]–[223]. Among the diversity of the nanoparticles or core-shell systems, those made of silica have shown several advantages, because of their low cost and their non-toxic nature [224] which make them a good candidate for medical applications. The diminution of the silica bulk size to the nanoscale can change its structure [224]. One of the fundamental roles is played by the specific surface since the ratio between the surface and the volume is higher [224] and the functionalization of their surface often rich of SiOH groups [225].

Several methods exist in literature in order to produce silica nanoparticles [219], one of them uses lasers [226], [227] to remove material through ablation process [228], [229]. Production of nanoparticles using laser irradiation is based on the absorption of high energy from the laser source by the investigated material. It is worth to remind that such operation remains possible even if the absorption coefficient of the material, at the laser wavelength, is quite weak, and it is furthermore possible to enhance this coefficient by co-doping the glass [229]. Different mechanisms are responsible for the absorption, their relative contributions depend on the target, its optical properties, and also the characteristics of the used laser pulse. The laser light can be absorbed by the material either by a linear or nonlinear processes [228]. The linear process dominates if the material is opaque and if the laser pulse is characterized by a low intensity and a long pulse duration (≥ ns). Whereas the nonlinear mechanisms dominate the absorption of the transparent targets (at the wavelength of the laser), in this case they can lead to the optical breakdown of the material. Unlike the linear mechanisms, these nonlinear processes are more likely to occur if the laser’s intensity is high, and its duration is short (sub-picosecond) [228].

Regarding the laser ablation of pure silica, Ihlemann et al [229] have investigated the effect of different wavelengths and pulse durations varying from hundreds of fs up to tens of ns. The authors focused their attention on the ablation induced modifications at the surface of the target and they did not study the nature and properties of removed material. The effects of the laser pulse duration as well as the important role of its intensity were investigated by [230], [231]. These authors studied the break-down of silica and especially the damages induced at its
surface. On the other hand, a coupled theoretical/experimental investigation of the silica breakdown was carried by Stuart et al [232] using pulse durations ranging from ns to the fs. The authors observed a multiphoton ionization process induced by very short and intense pulses. According to [232] if the laser pulse duration exceeds 50 ps, the induced damage is due to the melting, boiling or fracture of the target surface. Whereas, if the laser pulse duration is shorter than 10 ps then the target modification is caused by the ablation. Once again, in their study, the authors did not investigate the nanoparticles produced by such process.

It is possible to enhance the absorption coefficient of the material by adding dopants, which facilitates the material removal from the sample. These dopants induce new defects in addition with those intrinsic to the pure material. At high concentrations, these dopants can also decrease the band gap. On one side, the defects can play an important role to initiate the avalanche ionization process by providing additional electrons [228] changing the response of the material under laser pulse exposure [228], [232]. On the other side the band gap reduction can facilitate the nonlinear absorption. In this context, we present an investigation of silica-based nanoparticles produced by KrF laser irradiation and characterized by SEM, EDX, CL and TEM. This study is considered as a complementary to the one performed in [233].

II. Materials and methods

Two samples have been prepared from a silica glass containing 20 mol% of Ge, and fabricated using the PCVD method. The third sample has been produced from a pure wet silica bulk. All the glass pieces were maintained with the sample holder presented in figure.V.1 immersed in distilled water during the laser exposition, this procedure allows to easily collect the removed particles. The used laser is a pulsed KrF (COMPex 110 from Lambda Physik) that emits light pulses at 248 nm, with a duration of 30 ns, a frequency of 10 Hz and a spot of ~1 mm. The first sample, that was produced from the Ge-doped glass is named A in the following, and has been exposed to the laser beam energy of 33 mJ/pulse. The second one, called B, was prepared from the same glass using 165 mJ/pulse of laser energy, and the last sample (C) was exposed to 400 mJ/pulse. After a certain number of pulses, the material started to be removed, so the laser focus was adjusted whenever the samples are moved longitudinally in order to keep it in focus for the whole operation.
In order to better organize out data, we used a holey carbon-coated grids onto 200 mesh copper from SPI (Structure Probe Inc). These grids are made of copper, their diameter is 3 mm and the width of the holes is ~90 μm. They are mainly used to permit the characterization of the same micro or nano-particles using different techniques. The center of these grids is asymmetric and each square contains a stretched carbon film that forms different shapes, which help to recognize the investigated particles.
The solutions obtained by the laser processing of materials (distilled water + silica particles) contain particles of different sizes from micrometer down to nanometer. Before being able to investigate the silica nanoparticles, we have to immerse one grid into the solution, and then to heat it at about 60 °C. After that, we waited for ~10 minutes in order to dry the water, and finally mount the grid on an aluminum-made stub.

The prepared samples have been studied using: SEM that includes EDX and CL, TEM that includes STEM. The used SEM, EDX and CL apparatus are those presented in chapter II. We selected an electron energy of 20 keV and a probe current of 8 nA for this set of experiments. Regarding the TEM measurements, we used a JEM-2100F UHR from JEOL that is equipped with the same EDX detector than the SEM. The employed energy was 200 keV and the used mode was the dark field (DF).

III. Results:

III.1. Sample A

In figure.V.3 we report some of the SEM images recorded for the sample A, in order to characterize its morphology. In these pictures we observe the presence of some micro particles and of several nanoparticles with size ranging from tens to hundreds of nm (see panel (b) as example), forming agglomerate/aggregate. The two red squares in panel (a) provide evidence for two sample regions that have been further characterized by EDX or CL measurements. Panels (c) and (d) illustrate two smaller groups of nanoparticles having sizes of about 30 nm. In these panels we note the presence of some spherical nanoparticles, whereas others have irregular shapes. Anyway, a better understanding of such details will be obtained by TEM experiments as a consequence of the higher resolution of this latter technique.
Aiming to know the chemical composition of these particles, EDX maps have been performed in some of the observed clusters. Figure.V.4 shows the EDX results of the part framed in red and marked as 1 in figure V.3.a.

The EDX experiments show the presence of the three main elements composing our starting material. In particular, we observe an homogeneous distribution of Si (figure.V.4.a), O (figure.V.4.b) and Ge (figure.V.4.c) elements through the entire group of nanoparticles. Such
information indicates that the produced nanoparticles have an homogeneous chemical composition that seems qualitatively comparable to the one of the starting material.

CL imaging and CL spectroscopy data have been recorded in different zones of the prepared sample corresponding to various groups of nanoparticles. As example, we present in figure.V. 5 the particles shown previously in the square number 2 of figure.V.3.a. Here we compare between the SEM image (panel (a)) and the CL panchromatic image (panel (b)) of the same region. This way we can compare the morphology of the investigated particles with the CL signal distribution. The CL signal features a very good correspondence with the presence of the nanoparticles. Indeed, the recorded CL panchromatic image indicates the presence of some emitting centers within the particles and this luminescence seems to increase with the nanoparticle concentration. Minor deviations can be present as a consequence of a too low mass of the samples, which implies a very low (under the detection limit) amount of defects.

![SEM and CL images](image)

Figure. V. 5.a. SEM image of nanoparticles; b. CL panchromatic image of the same particles.

In order to determine if the luminescence detected in the panchromatic images is related to intrinsic or extrinsic defects, CL spectrum has been recorded in the red framed part of figure.V.5.a and the results are presented in figure.V.6. A clear emission activity is seen at about 400 nm that can be attributed to the GLPC defects. Obviously, the signal-to-noise ratio is lower with respect to those observed in previous chapters as a consequence of the low amount of mass in the case of the nanoparticles.
Our sample was characterized also using TEM associated with higher resolution level. Figure V.7 shows different parts of the cluster already investigated by SEM (square number 1 in figure V.3). Panel (a) illustrates the entire cluster, whereas panels (b), (c) and (d) are zooms of some specific zones. Panel (b) highlights the state of agglomeration/aggregation showing that in almost all cases the nanoparticles are close to each other, the merging of some of them cannot be excluded. Such suggestion is also supported by the zooms reported in panels (c) and (d).
In panel (c) we report a TEM image in which we recognize the presence of nanoparticles with very different shapes (spherical and irregular). In this image we report the estimated sizes of such nano-systems ranging from some tens up to some hundreds of nanometers. Such results confirm the SEM and CL data. We also note that in this sample spherical nanoparticles are almost always detected near irregular ones. Finally, we note in the very high magnification picture the absence of order structure in the nanoparticles suggesting that they are in amorphous state.
Taking advantage of the apparatus, we acquired some STEM results, STEM being the scanning mode of TEM using the dark field. Two examples of such data are reported in figure.V.8, in details, panel (a) shows the image recorded for one of the spherical particles (with size of about 100 nm) detected in sample A, whereas panel (b) shows the one acquired for a group of irregular nanoparticles having sizes of tens of nm. In both cases we note the presence of brilliant spots. The nature of such spots needs further investigations, but their presence evidences the structured morphology of the produced nanoparticles. In addition, this feature seems independent on the particle sizes. Also, their presence seems independent on their agglomerate/aggregate or isolate state. Finally, such spots seem absent in the external part of the particle as shown in figure.V.8.a, since this external part is indicative of the surface we can tentatively suggest that they are more located inside the particles than in their surfaces.

III.2. Sample B

The second sample (B) was produced using the same type of glass. However, in this case, the laser energy was increased up to 165 mJ/pulse in order to investigate the effect of the employed laser energy on the nanoparticle production. Some SEM images of the sample B are shown in Figure.V.9. In particular, panels (a) and (b) show a large aggregate/agglomerate of nanoparticles, whereas the panels (c) and (d) illustrate examples of a small groups of nanoparticles. In both cases, the images suggest that the nanoparticles are aggregated/agglomerated, that they have size of at least tens of nm, and that both spherical and not spherical particles can be observed. Further details have been obtained using the TEM measurements as previously done for the A sample.
In order to check the chemical composition of sample B, EDX measurements were performed on the cluster of particles presented in the panel (a) of figure V.9. The results are presented in figures V.10.a, b and c for the Si, the O and the Ge respectively.
According to the EDX maps of sample B, the chemical composition of sample B is almost uniform, similar to sample A and to the starting preform. In particular, the relative Si, O and Ge contents in this group of particles do not feature relevant dependence on the positions.

CL measurements were also employed in order to characterize sample B. CL panchromatic images and spectra have been recorded. In figure.V.11, we report the data obtained for the same group of particles that were studied by EDX experiments. As for the sample A, the CL panchromatic image shows clear luminescence indicating the presence of some emitting centers. Furthermore, we observe a correspondence between the morphology given by the SEM image (figure.V.11.a) and the intensity of the CL signal (figure.V.11.b)

Figure.V.11. a. SEM image nanoparticles. b. CL panchromatic image of the same particles.

To identify the origin of the CL signal detected in the above reported image we recorded the CL spectrum in the region framed in red in figure.V.11.a, and the results are reported in figure.V.12. Also in this case, the signal is dominated by an emission activity peaked at about 400 nm, which appears to be due to GLPC emission.
Figure V.12. CL spectrum of the sample B.

Figure V.13. Some TEM images of the segregated nanoparticles already characterized by the SEM. Figure V.13.a illustrates the TEM image of the same group of particles that we characterized by SEM, EDX and CL experiments. Panel (b) of this figure shows a zoom of one part of this nanoparticles and in particular highlights the presence of a large amount of almost spherical
particles with sizes of tens of nm side by side with others having sizes of hundreds of nm. Panel (c) gives another zoom of a different zone of panel (a). Here again, the nanoparticles size ranges from tens to hundreds of nm and the shape is spherical in the majority of cases. Finally, in panel d we report a further zoom recorded on few nanoparticles that we will further investigate with STEM experiments. In this image (figure.V.13.d) in some cases they could be merged (black arrow), whereas in others they seem just near or superimposed one to the other (white arrow). Furthermore, we do not note any order structure in the investigated particles which allow us to suggest that they are amorphous. In order to confirm so, we report diffraction measurements in figure.V.14 revealing no ordered structures in the tested zone (the same zone marked in red in figure.13.b). As for the sample A irregular nanoparticles have been observed in TEM and SEM images, but contrary from the previous sample, in sample B we detected groups of particles in which the spherical shape is predominant.

Figure.V.14. TEM image of the diffraction test on the region marked in red in figure.V.12.b.

Figure V.15 illustrates the STEM images of some of the nanoparticles previously investigated by TEM images (figure.13). As for the sample A, we note the presence of brilliant spots embedded in the particles. This indicates that such features are not dependent on the laser energy in our tested range. In figure.V.15 the white spots seem to be absent on the external part of the particles. So similar to the sample A it seem more probable that they are inside the particles rather than on their surface. Furthermore, in agreement with the previous morphological data the STEM confirms the state of agglomeration/aggregation of the produced nanoparticles.
III.3. Sample C

After investigating the Ge-doped samples, it was necessary to study one pure silica sample as a reference to better understand the role of Ge. In the following, we present the results of the particles produced by the laser irradiation of pure wet silica sample at an energy of 400 mJ/pulse. Indeed, up to energy of 200 mJ/pulse we did not observe (at naked eye) any removal of matter from the sample as for the Ge doped preform. Furthermore, the number of pulses needed to remove the material is higher in the case of pure silica sample (C). For pure silica, several pulses were needed and the irradiated parts become very white before observing the removal of matter. Such phenomenon, if present, was too fast in the Ge doped samples to be observed.
We report in Figure.V.16 some examples of the SEM images recorded for this sample. In these images we note the presence of a large agglomerate/aggregate of particles, in addition we note the presence of some flakes. In the purpose of checking the chemical composition, EDX measurements have been performed on the zone shown in panel (b) of figure.V.16, and the results are presented in figure V.17.a for Si, b for O and c for Fe (iron).

![SEM images of the sample C. a) Si b) O and c) Fe distributions](image)

The chemical analysis of one cluster of the sample C demonstrates the presence of the iron (Fe) in all the tested particles of the sample C. This unexpected result is probably be due to the used sample holder, since it contains some iron-based screws. By increasing the employed energy of the laser to 400 mJ/ pulse, some material from these screws was removed too and detected within the produced particles. This is also probably the main reason for the observed change of morphology shown in the previous figures. Further samples need to be prepared differently in order to complete this preliminary study. It is worth to mention that CL measurements were held for this sample as well, and the spectra showed no particular detected emission. However, the other techniques (TEM and STEM) were not used for this sample because of the high contamination caused by the iron (Fe).

IV. Discussion

The above obtained results demonstrate the possibility to produce silica-based nanoparticles using laser irradiation. Such particles exhibited luminescent propriety related to the Ge atoms if the starting material was doped with Ge. The employed procedure causes the production of micro-particles besides the nanoparticles, which needs improvement of the used method in order to better exploit the starting material. Nevertheless, the resulting particles with a size of hundreds of nm could be employed in some biological applications, such as the ones discussed in [234], [235].
In regards to the Ge-doped samples, we remind that the used laser power was much lower than the one used for the pure-silica sample. Such difference is based on the optical absorption of Ge-doped silica, since the Ge doping decreases the band gap of silica, as it is reported in the optical absorption spectrum shown in figure. V.16. [233]. This spectrum has been recorded up to the VUV spectral domain on the same here employed starting sample.

The spectrum reported in figure. V. 18 shows a significant absorption coefficient with a clear difference compared with a pure-silica material [236]. Such effect can be considered a key factor that enhanced the absorption of the UV and VUV photons. In particular, the presence of the Ge doping lowers the band-gap and improves the multi-photons processes through reducing the number of photons required to induce the transition from the valence to conduction band. Another factor that could significantly contribute to the absorption of energy from the laser is the presence of the point defects, these later, are involved in the transfer of the laser energy to the glass network via their absorption bands. All these properties can favor the avalanche and the multi-photons ionization, besides the high sensitivity of the Ge-doped silica materials to the UV laser that causes not only the creation of point defects but the matrix reorganization as well [143]. On the other hand, the wavelength of the used laser (248 nm) belongs to the spectral
range of the GLPC optical absorption, which strengthen the obtained results in [237] where the authors suggest that using similar lasers, it is possible to induce the multi-photon processes in Ge-doped materials. In this context, we note that in our sample the 5.12 eV [233] absorption band of the GLPC is present in the starting preform. Their presence was probably more relevant for the 8 wt% GLPC rich sample investigated in [233], but it cannot excluded for the here reported data.

It is worth to mention that we expect that the laser energy is transferred to a volume deeper than the one in which the laser is focused and the material was removed mainly after the heating of the target, taking into account the long duration of the laser pulse and the study reported in [228]. Hence the presence of some micro particles that could be generated due to some explosions during the laser exposition caused by the thermal gradient, as-made stress or inhomogeneities of the investigated material.

Regarding the laser energy effects, both employed energies (33 mJ/pulse and 165 mJ/pulse) show similar results in terms of the morphology, the size, CL activity and the homogeneity in chemical composition of the resulted particles. Nevertheless, we have noted some differences in terms of the shape of the particles, since they appear as more spherical in the case of high energy (165 mJ/pulse) production. The CL measurements of the Ge-doped particles, have shown the presence of an emission activity at ~400 nm which may be attributed to the GLPC defects, the absence of CL signal in the pure sample puts in evidence another important role of the Ge doping to obtain emitting silica based nanoparticles.

Regarding the TEM experiments, we have confirmed the morphology of the produced particles, and their sizes, which varies from tens to hundreds of nm. Furthermore, the amorphous structure was confirmed according to the TEM high resolution images as well as the diffraction tests. The STEM images have highlighted the presence of some brilliant spots embedded in the particles of sample A and B, such spots could be due to some densification points caused by the irradiation, or some segregated atoms such as Ge since it is the biggest atom composing the samples. These variations of density or Ge content are too small to be detected with the EDX measurements performed with the SEM apparatus so if confirmed they do not contradict the chemical uniformity on a larger scale as those that we were able to investigate. Anyway, further measurements are needed to perform a systematic study of the laser energy effects on the obtained particles.
Conclusion

This last chapter is dedicated to the characterization of silica-based nanoparticles by SEM, CL, EDX, TEM and STEM. We have followed the procedure of laser irradiation used in [233] in order to produce silica-based nanoparticles. We have used two different starting materials, the first was a Ge-doped silica-based glass, whereas the second was a pure silica one. Unfortunately, we were not able to complete the characterization of the particles obtained from the pure silica material because of the iron contamination resulted from the used sample holder, and we focused our attention on the Ge-doped sample. We have shown that the Ge doping of the starting material helps the laser ablation operation, by improving the absorption of the laser pulse energy.

Concerning the morphology of the obtained particles, the SEM as well as the TEM images showed the presence of different agglomerate/aggregates containing nanoparticles with size of tens to hundreds of nanometers. The chemical composition of these particles tested by EDX shows the presence of Si, O and Ge. The amorphous state of the material seems maintained after laser irradiation, according to the TEM experiments on the produced nanoparticles. The results are similar for the two employed energies (33 mJ/pulse and 165 mJ/pulse). The investigation of the samples using the scanning mode of TEM (STEM) shows the presence of small brilliant spots (few nanometers) embedded in the big particles. These small features could be attributed to segregated Ge atoms, considering that the Ge is the biggest present atom, or densified regions induced by the laser irradiation. Anyway, such preliminary observations need further measurements in order to reveal the origin of such components. The spots are present in both the Ge doped samples independently of the nanoparticles sizes.

The resulting particles from the Ge-doped glass have shown to be luminescent as it was confirmed by CL panchromatic images. By recording CL spectrum, this luminescence was attributed to the GLPC emission band at 400 nm. These results put in evidence the possibility to use CL to perform characterizations on the nanoscale and the relevance of the Ge doping to obtain emitting nanoparticles since in the pure sample no significant signal was detected. The investigation presented in this chapter opens the door to produce other silica-based nanoparticles that are differently doped or co-doped with other luminescent elements.
Conclusions and Perspectives

This PhD work focused on the study of point defects in silica-based materials, particularly into optical fibers. For this, the experimental measurements were mainly based on the cathodoluminescence spectroscopy and imaging. These techniques are considered as complementary to the other spectroscopy techniques, such as electron paramagnetic resonance, optical absorption and photoluminescence that are usually combined to investigate the optical and structural properties of point defects in amorphous materials. The main advantage of cathodoluminescence is its ability to simultaneously probe and irradiate the material under test allowing to perform in-situ and spatially-resolved luminescence measurements.

The tested fibers are canonical samples that have been especially designed, by iXBlue Photonics, for addressing basic mechanisms studies. These samples were already investigated by the same research group using the other techniques and their responses to X-rays and γ rays radiations are well-known. These fibers have been made using their MCVD process and are all differently doped in their cores and claddings. Regarding their radiation responses, these fibers could be divided into three main classes: telecom-grade OFs, radiation-hardened OFs and radiation-sensitive OFs. We have shown the ability of the cathodoluminescence technique to investigate these different types of optical fibers that were doped with either Ge, F, N, P or Ce. In particular, several emissions were detected using CL spectroscopy and their spatial distribution along the fibers cross sections have been discussed. Furthermore, the obtained CL results were compared with their PL counterparts putting in evidence the similarities as well as the main differences between both techniques. A deeper investigation was performed on one sample which is 4-steps Ge-doped OF, for which we tried to better clarify the effects of varying the electron beam irradiation conditions on the Ge-related GLPC defect growth and decay kinetics. The last chapter of this PhD thesis was dedicated to another form of silica samples. We characterized the morphological and optical properties of different silica-based nanoparticles that have been made at Lab. Hubert Curien using an UV laser ablation process. Such study aims to open the door to other kinds of materials that can be characterized using CL.

We present in the following, a summary of the most interesting results:
First of all, it was very important to estimate the deposited dose associated to the various electron beam probing configurations. These calculations have shown that the deposited doses are large (in the order of MGys up to GGy). In particular the electron beam irradiation causes a higher doses whenever the irradiated area is smaller and the energy of the primary electrons is lower, due to the interaction volume characteristics.

Regarding the telecom-grade germanosilicate OFs, we have highlighted an important difference between the CL and the CML techniques in terms of the intensity of the GLPC signals as a function of the Ge content. Our CL measurements show that the recorded emission spectra are strongly affected by the electrons. Depending on the irradiation time, the dependence of the GLPC signal intensity as a function of the Ge amount evolves. Furthermore, we provide evidence for a monotonous decrease of the remaining GLPC signal as a function of the Ge concentration after irradiation: larger is the Ge amount, less is the GLPC signal after electron exposure.

The capacity of the CL technique to excite all the existing defects, emitting in the spectral range allowed by the detector, was shown for the different types of OFs and new insights are given for intrinsic and extrinsic point defects. Particularly, a green luminescence at ~560 nm was detected in the pure-silica samples, and its origin is still unknown, since it could be either a second order of ODC (II) defects (at 280 nm) or another center such as STE for example. However, another contribution peaking in the same spectral range was detected in the N-doped samples. This indicates that some N or Cl-related centers should be active in this spectral domain too.

For the radiation-sensitive OFs, the P-doped OF are associated with an emission band at ~410 nm which is attributed to a P-related defect. Moreover, we have noticed using CL monochromatic images that the P incorporation in the core of the OF reduces the concentration of the ODC (II) centers. When a Ce-codoping is done, an emission band at ~370 nm appears that is assigned to the Ce$^{3+}$ centers. The intensity of this luminescence was shown to depend on the deposited dose. The Al-doped fiber that belongs also to this radiation-sensitive section, has shown an emission band centered at ~380 nm, which is associated with an Al-related defect. This band is assigned in the literature to the (Al$^{3+}$ - M$^+$) features, however, our measurements on different samples that are known for their high purity levels, indicate that the origin of such luminescence may differ from the (Al$^{3+}$ - M$^+$) centers.
A deeper study was carried out on one of the main Ge-related point defects, the so-called GLPC, which emits light at 400 nm. These centers play a key role in the comprehension of the radiation effects on Ge-doped OFs, since they act as precursors for the generation of other Ge-related defects. A CL investigation has been performed on the iX_MM_Ge1 sample as a function of the beam energy, the flux and the Ge concentration. We tried to establish a descriptive model in order to better understand the bleaching mechanisms of this luminescence under these test conditions. Our results suggest that there exist five different sites: a stable one and four others who bleach according to first-order kinetics independently of the dose rate. Such results were shown to agree with some theoretical work done in parallel by researchers at Nova Gorica, CEA and Trieste. Changing the Ge concentration can favor or disadvantage one process against another, allowing to reach by the irradiation end, various steady-state levels. This level is higher when the Ge content is lower.

CML measures performed after the electron irradiation of the iX_MM_Ge1 sample as well as the in-situ CL investigations have shown some new insights regarding the spatial distribution of the NBOHC centers. In details, the NBOHC defects are present at low concentrations in the pristine fibers, and they are easily created by the irradiation. Our measurements indicate that the γ-rays and electrons efficiencies to generate NBOHC differ. Furthermore the Ge concentration impacts these efficiencies too. Indeed, the NBOHC amount follows the Ge concentrations if the sample is irradiated with γ-rays, however, the opposite behavior is observed in the case of an electron beam: larger is the Ge content, less is the NBOHC signal. The main difference between the two kinds of irradiation concerns the nature of the interaction. It can be assumed that electrons could lead to some structural changes in the irradiated zones that result in different defect distributions.

Some samples of a second Ge-doped fiber named iX_MM_Ge2 with 2 levels of Ge-doping were pre-treated before being exposed to electrons. The results concerning the γ-rays treatment up to 9 MGy confirm the results obtained with the first fiber. Whilst the second pre-treatment consisting of the O₂ loading has demonstrated its ability to passivate the GLPC defects. However, in the later case, after the electrons beam irradiation, the GLPC signal increases, and its spatial distribution, as a function of the Ge concentration, has not evolved, since it was from the beginning larger in the regions with the smaller Ge levels. Such results could be explained by the passivation of the GLPC defects by the oxygen molecules. Then, by the electron beam exposition, only
The stable GLPC defects are regenerated again: those who were not bleached under electron irradiation.

- The last chapter of the present PhD thesis treated the case of another form of silica, which are the silica-based nanoparticles, in order to demonstrate the ability of CL to characterize such nanoscale materials. The nanoparticles were produced by the laser ablation method using Ge-doped preforms as starting material. The morphology of the obtained particles, characterized by the SEM as well as the TEM images, shows the presence of different agglomerate/aggregates of particles with sizes from of tens to hundreds of nanometers. The chemical composition of these particles tested by EDX reveals the presence of Si, O and also Ge. The results are similar for the two employed energies (33 mJ/pulse and 165 mJ/pulse). STEM investigation of the samples A and B (The Ge-doped ones) shows the presence of small heterogeneities (few nanometers) in the particles independently from their sizes. These heterogeneities may represent the Ge-rich areas or laser-densified regions. Such preliminary observation needs further studies in order to reveal the origin of such components. It is worth to mention that the TEM measurements confirm the amorphous state of the produced nanoparticles.

- The resulting particles from the Ge-doped preform have shown to be luminescent particles as it was confirmed by CL panchromatic images. By recording CL spectrum, this luminescence has shown to be similar to the GLPC emission band at 400 nm. These results confirms the possibility to use CL to perform characterizations on the nanometric scale.

The results obtained in this PhD thesis opens the way to new research axis. For example, it could be interesting to perform a spectral decomposition studies on the spectra acquired for the different classes of fibers. Several of the observed emission bands have been already studied in the literature. Combining our original results with those from other techniques could be very important to reveal the origin of the remaining “unknown” bands. Furthermore, the methodology reported in chapter 4 could be applied to the emission bands related to other centers (or other dopants) than GLPC (Ge). Combining the CL measurements and different pre-treatments may be useful to help the identification of the nature of the bands not yet assigned to known defect structures. A deeper investigation on the GLPC bleaching kinetics can be hold on the very low Ge concentrations in order to check the stable sites hypothesis.

Regarding the silica-based nanoparticles, we demonstrated the possibility to produce them using laser ablation, and characterizing them using, among others, the CL technique. Future
work will be done to produce other types of silica-based nanoparticles that are differently doped or co-doped with other emitting elements and may have practical applications.
List of related papers and communications

List of articles in international journals


List of communications

International conferences


Attenuation of Ge-Doped Fibers”, RADiation Effects on Components & Systems Conference (RADECS), Bremen, Germany, September 2016, Poster Contribution.

**National conferences**

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Abstract

The recent use of silica-based optical fibers (OFs) in harsh environments associated with severe conditions pushed the researchers to accelerate their vulnerability and hardening studies. Such challenges are strongly linked to the good understanding of the macroscopic as well as the microscopic effects of different types of radiations on the silica-based OF’s response. This PhD thesis presents a complementary study to previous researches on the properties of different point defects in silica-based OFs by Cathodoluminescence (CL). Such technique offers the ability to both detect the luminescent centers and to follow their spatial distribution, their growth and decay kinetic as a function of the electron beam characteristics. In the present manuscript we first summarize the current knowledge regarding point defects in pure silica or silica glass doped with Ge, P, Ce, N or Al. Details of the experimental procedure are discussed in the 2nd chapter in which we highlight that the equivalent dose deposited during the various configuration of CL measurements are very large (from MGys up to GGys). In the 3rd chapter, we perform an overview study of the CL responses of different classes of OFs (telecom-grade, radiation-hardened and radiation-sensitive) in which many emission bands related to the different dopants were detected and are discussed. The 4th chapter focuses on the study of the effects of varying beam conditions on the signature of Germanium Lone Pair Center (GLPC), one of the most important Ge-related point defects. Finally, in chapter V, we demonstrate the possibility to produce silica-based nanoparticles by laser ablation process, and the ability of the CL technique to characterize such materials, which opens the door to other employments of this technique for future studies on nanoparticles.

Résumé

L’utilisation récente des fibres optiques (FOs) à base de silice dans des environnements extrêmes associés à des conditions sévères, a incité les chercheurs à accélérer leurs études de vulnérabilité et de durcissement. De tels défis sont fortement liés à la bonne compréhension des effets à la fois macroscopiques et microscopiques des différents types de radiations sur la réponse des FOs. Cette thèse de doctorat présente une étude complémentaire aux études précédemment menées sur les différents défauts ponctuels dans les FOs à base de silice par Cathodoluminescence (CL). Cette technique offre la possibilité de détecter les centres luminescents mais aussi de suivre leurs distributions spatiales, leurs cinétiques de création et de guérison en fonction des caractéristiques choisies pour le faisceau d’électrons. Dans ce manuscrit, nous introduisons tout d’abord un résumé des connaissances actuelles sur les défauts ponctuels liés à la silice pure ainsi que la silice dopée avec Ge, P, Ce, N et Al. Les détails de notre procédure expérimentale sont discutés dans le 2ème chapitre où nous mettons en évidence que les doses déposées lors des mesures CL sont très importantes (de l’ordre du MGy jusqu’au GGy). Dans le 3ème chapitre nous présentons une étude systématique de la réponse en CL des différentes classes de FOs (télécom, durcies aux radiations ou sensibles aux radiations) dans lesquelles différents bandes d’émission ont été détectées et sont discutées. Le 4ème chapitre est dédié à l’étude de l’impact d’une variation des conditions d’irradiation électronique sur les centres émetteurs GLPC, l’un des défauts liés au Ge les plus importants. Enfin, dans le 5ème chapitre, nous avons montré la possibilité de produire des nanoparticules à base de silice par ablation laser, et la capacité de la technique de cathodoluminescence de caractériser ce type de matériaux, ce qui ouvre la porte à d’autres utilisations de cette technique pour la caractérisation de nanoparticules.