Irradiation temperature effects on the induced point defects in Ge-doped optical fibers.

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Abstract. We present an experimental investigation on the combined effects of temperature and irradiation on Ge-doped optical fibers. Our samples were X-ray (10 keV) irradiated up to 5 kGy with a dose rate of 50 Gy(SiO$_2$)/s changing the irradiation temperature in the range 233-573 K. After irradiation we performed electron paramagnetic resonance (EPR) and confocal microscopy luminescence (CML) measurements. The recorded data prove the generation of different Ge related paramagnetic point defects and of a red emission, different from that of the Ge/Si Non-Bridging Oxygen Hole center. Furthermore, by comparing the behaviour of the EPR signal of the Ge(1) as a function of the irradiation temperature with the one of the red emission we can exclude that this emission is originated by the Ge(1).

1. Introduction
The understanding of point defects properties and generation in pure and doped silica has been at the center of many experimental and simulative investigations for many years [1-5]. On one side, the study of optical and magnetic properties of point defects in amorphous materials represents a significant field within solid state physics, on the other side, the use of silica as basic material in different application areas as nanostructured systems [6] and optical fibers [7], just to cite some of them, has imposed the understanding of the impact of such defects on the physical properties of silica and as a consequence on silica based devices. Clear examples of this fact are the alterations of the transmission properties of the optical fibers as a consequence of the generation of point defect species having optical absorption bands [7] or the increase of the silica sensitivity to radiation due to absorbing defects related to doping or manufacturing processes [8,9].

Ge related defects in silica have been widely investigated, indeed, Ge atoms can be easily found as impurity in natural silica [10] and the Ge doping is commonly employed to increase the silica refractive index [11] and as a consequence it is used for the production of optical fibers and fiber
based devices [7]. Nowadays it is known that the Ge atoms can form different point defects, one of them is the so-called GLPC (Germanium Lone Pare Center [2]) involved in many radiation induced processes [2,8,9], which are the origin of the photosensitivity of this silica typology. Other known defects are the E’Ge, the Ge(1) and the Ge(2) [1-3]. For these defects various investigations have been performed to elucidate the generation or conversion processes under irradiation at room temperature [2,4,5,8,12] or to identify their thermal stability with post irradiation treatments [13]. On the other side combined temperature and irradiation effects have been poorly studied [14]. Similarly, an emission activity induced in the red spectral domain received low attention. Basing on published data, in this spectral range it is found the luminescence of the Ge/Si Non Bridging Oxygen Hole Center [15], anyway, this luminescence is not isolated. Indeed, the authors of [16, 17] observed in H₂ loaded silica samples another red emission attributing this activity to the H(II) (a GLPC forming a linkage with an hydrogen atom [10,16] through one of the two electrons of the lone pair). More recently [18], we observed a red emission in dissimilar Ge-doped silica. Such luminescence presents some differences with respect to that reported in [16, 17] and it was observed in bulk and fiber samples in which the H(II) EPR signal was not detected. In that study it was shown that this emission is not related to E’Ge or Ge(2) defects, but relation with the Ge(1) center was not rigorously ruled out. In the present study we report on the effects of temperature and irradiation on the generation of Ge-related point defects in Ge-doped fibers. This thermal and irradiation concurrent study enabled to find out the absence of correlation between Ge(1) and red emission paving the way to the attribution of this latter activity to other defects.

2. Experimental

We studied a two steps multimode Ge-doped optical fiber produced by iXBlue Photonics Division. The starting preform was produced by MCVD (Modified Chemical Vapor Deposition) process.

As previously reported [19] the sample has a total diameter of 125 μm with a Ge doped part of ~60 μm. More in details, in the central core, having diameter of ~40 μm, the Ge doping level is ~8 weight per cent (% wt), whereas the second step, being the external ring of the doped part, has a doping level of ~4.5 % wt.

The ARACOR and PROBIX machines located at the French atomic energy center (CEA) were employed to perform X-ray (10 keV) irradiations up to 5 kGy with a dose rate of 50 Gy(SiO₂)/s. The irradiation temperature was imposed by keeping the fibers in contact with a temperature controlled plate.

A Bruker EMX-Micro Bay spectrometer operating at ~9.8 GHz (X-band) with a 100 kHz modulating magnetic field was employed to record EPR measurements. Microwave power and modulation amplitude were opportunely selected to avoid signal distortion.

CML spectra were recorded using the 442 nm laser line of an Aramis (Jobin-Yvon) spectrometer equipped with a micro-translational stage and with a CCD camera. All the data were recorded in a back-reflection geometry using a 50× objective, with a spatial resolution of ~3 μm.

3. Result and Discussion

In figure 1 we report the double integral (normalized to the sample masses and to the instrumental parameters) of the EPR signal acquired in the different samples as a function of the irradiation temperature for the dose 5kGy. The data indicate that the total amount of induced defects decreases with increasing the irradiation temperature. Furthermore, as illustrated by the two spectra, reported as insets in figure 1 and acquired for the samples irradiated at 233 and 570 K, the lineshape of the spectra is not constant.

More in details, the spectra of all the samples result from the combination of the signals of the Ge(1), Ge(2) and E’Ge defects [20] but the relative contributions of the different species depend on the irradiation temperature, in particular we note that increasing the irradiation temperature the signal lineshape tends to the one of the E’Ge. Such data together with the decrease of the EPR signal proves...
the decrease of the amount of Ge(1) defects as a function of the irradiation temperature. Finally, we note that we did not detect the characteristic EPR signal of the H(II) defects [16,17].

**Figure 1.** Double integral of the EPR signal as a function of the irradiation temperature at the dose 5 kGy. Insets EPR spectra recorded for the samples irradiated at 233 and 573 K.

**Figure 2.** Profile along the fiber diameters of the CML signal at 700 nm under excitation at 442 nm in the fibers irradiated at 233 K (○○) and 523 K (●●). Inset PL/Raman signal in the core of the pristine (—) and of the 573 K irradiated fiber (——). Dose 5 kGy.
In figure 2, we report the radial profile of the photoluminescence (PL) signal measured at 700 nm under excitation at 442 nm for the samples irradiated at the lowest and highest temperature. The signal features a maximum at the center of the core. This maximum is related to the presence of an emission band peaked at about 680 nm. In the inset of the same figure we illustrate the PL signals of the pristine and 573 K irradiated samples. All the spectra were normalized to the silica Raman signal [21] located in the range 447-460 nm. We note that these data agree with previous investigations [18].

Figure 3 illustrates the spectra recorded for samples irradiated at different temperatures. Also in this case all the measurements were normalized to the silica Raman signals located at low wavelengths. The data indicate that the relative amplitude (with respect to the Raman signal) of the emission band at 680 nm is independent from the irradiation temperature up to about 420 K. Then, its amplitude increases, we also note that other signal at low wavelengths increases up to 523 K and then it decreases at the highest irradiation temperature. For the aims of the present investigation we focused our attention on the behaviour of the 680 nm component and on possible relation with the Ge(1) defects. In the inset of figure 3, we report the estimation of the relative amplitude at 680 nm as a function of the irradiation temperature after the subtraction of a line tangent to the spectra at about 590 and 825 nm. These data confirm that the amplitude of this band starts to increase for irradiation temperature higher than 420 K. We note that this temperature is very close to the one at which the EPR signal starts to decrease (see fig.1) and that the behaviour of its amplitude is the opposite deduced for the induced concentration of the Ge(1). As a consequence we can conclude that the Ge(1) is not responsible for the 680 nm emission band. On the other side, further investigation should be performed to better clarify the fact that both signals start to change at similar temperature and try to connect this effect to microscopic mechanisms.

Figure 3. PL/Raman signals recorded in the center of core of pristine sample (▬) and of fibers irradiated at 233 K (☐), 423 K (▬), 473 K (○), 523 K (●) and 573 K (△). Dose 5 kGy.

4. Conclusion

We studied the radiation effects on a multimode Ge doped fiber irradiated at different temperatures. In particular, we focused our attention on the behavior of the induced Ge related paramagnetic defects and of a red luminescence activity. Our data indicate that the total amount of the former decreases with increasing the irradiation temperature, whereas the amplitude of the emission increases. Furthermore, since the modification of the line-shape of the electron paramagnetic resonance spectra clearly
indicates the decrease of the induced Ge(1) we can exclude that this type of defects are the origin of the red emission peaked at 680 nm under excitation at 442 nm.

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