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Vacuum ultraviolet absorption spectrum of photorefractive Sn-doped silica fiber preforms

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Vacuum ultraviolet absorption data have been obtained up to 8.3 eV on Sn-doped silica preforms of optical fibres. Measurements have been carried out before and after exposure to 248 nm radiation from KrF excimer laser. The absorption spectrum is composed of three structures peaking at about 4.9, 5.8 and 7 eV, with the absorption edge at about 8.2 eV. The main effect of 5 eV irradiation is the decrease of the spectral components at 4.9 and 7 eV, whereas a small increase of absorption intensity is only observed just below the band at 4.9 eV. According to the observed negative absorption changes in the whole region of point-defect bands one would expect a negative refractive index change, contrary to the positive change previously reported in optical fibres of the same composition. The role of structural modifications accompanying the defect photoconversion process is briefly discussed.

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1. Introduction

The ultraviolet (UV) absorption spectrum of Ge- and Sn-doped silica is current matter of investigation because of the controversial role of optically active defects in the photosensitivity of silica-based optical fibres [1,2]. Many works in the past looked for a possible justification of the photoinduced refractive index change caused by UV induced photoconversion of optically active defects [1]. In germanosilicates, absorption changes in the energy range above 6 eV were found to be consistent with the observed refractive index changes in optical fibres, although only few measurements in the vacuum ultraviolet (VUV) absorption region were reported supporting this view [1]. The fact that Kramers-Kronig relations are satisfied using only the VUV spectral range of absorption changes indicates that the photosensitivity in germanosilicates is mainly due to photoconversion of optically active defects. Other mechanisms involving structural changes have been proposed to contribute to the photosensitivity of doped silica, such as the densification of the material (compaction), suggested by various experimental evidences [1-3]. In particular, these mechanisms might be dominant in Sn-doped silica since recent measurements in the near UV on fibre preform samples showed different results with respect to germanosilicates [4]. In fact the absorption change below 6 eV after excimer laser irradiation is negative, whereas a positive change of refractive index was measured in fibres obtained from the same samples. No VUV absorption data on Sn-doped silica samples was reported to our knowledge confirming this point.

In this work we report the absorption pattern of Sn-doped silica fibre preforms prior and after UV laser exposure in the whole defect-related spectral range, up to the absorption edge of the material. Kramers-Kronig analysis confirms the different role of optically active defects in Sn-doped silica with respect to germanium silicates. In fact, UV irradiation causes a decrease of all the main components of absorption bands up to the absorption edge. Only after prolonged UV laser exposure a minor component grows at about 5.9 eV, probably

related to radiation induced E'-Sn centres detected by electron paramagnetic resonance measurements.

2. Experimental procedure

Slices about 100 μm thick were cut from $Sn:SiO_2$ optical fibre preforms obtained by modified-chemical-vapour-deposition method, with the core diameter of about 0.8 mm and an average core doping of 0.15 mol% SnO_2. Different samples were exposed to increasing number of pulses (from 300 to 30000) from a KrF excimer laser (emission wavelength 248 nm, pulse fluence 80 mJ/cm^2, repetition rate 20 Hz). Electron paramagnetic resonance (EPR) measurements were carried out at room temperature with a EMX Bruker spectrometer operating in X band (about 9.6 GHz). VUV measurements were carried out in the spectral range from 130 to 300 nm with a MgF_2 sealed D_2 lamp (Hamamatsu mod.L1835) dispersed with a crossed Czerny-Turner monochromator (MacPherson mod.218) with a bandwidth of 0.5 nm. The signal was synchronously detected by a MgF_2 sealed photomultiplier operating into the VUV range (Hamamatsu mod.6836). Clean vacuum conditions (better than 10^{-3} Pa) were obtained by a contaminant-free turbo molecular vacuum system. Two kinds of uncertainties mainly affected the evaluation of the absorption coefficient: the sample thickness (about 5 %) and the composition inhomogeneity due to the core profile and the cladding-core interface. The latter effect, minimized by suitable masks (0.9 mm diameter), results in an underestimation of the absorption coefficients.

3. Results

In figure 1 the absorption spectrum of the Sn-doped fiber preform before irradiation is shown and compared to the spectrum after exposure to 10^4 UV laser pulses. Main features of the spectrum are the following: a strong band peaked at 4.9 eV, a shoulder at 5.9 eV and a broad

intense structure centred at about 7.0 eV, followed by the absorption edge starting from 8.2 eV. As a result of excimer laser exposure the intensity of the absorption spectrum decreases. Major effects are observed on the band at smallest energy (4.9 eV) and just below the absorption edge (7.0-8.0 eV), whereas minor effects occur around 6 eV. The difference between the two spectra is reported in figure 2. These data show that small positive changes are present below the 4.9 eV band and at the absorption edge tail. The prolonged laser exposure effects are reported in the same figure where the absorption difference between 3×10^4 and 10^4 pulses irradiated samples is also shown: further bleaching at 4.0 and 7.0 eV are observed with a stronger effect on the latter band. Instead, the absorption slightly increases in the 5.9 eV region. Small changes in the shape of the differential spectrum are also observed below 5 eV.

A Kramers-Kronig estimate of the expected refractive index change from the observed absorption changes in the VUV region has been carried out in order to evaluate the extent of other possible photoinduced processes (rather than photoconversion optically active defects) possibly contributing to refraction index changes, e.g. photoactivated compaction. From the Kramers-Kronig relations the refractive index change Δn may be expressed as a function of the integrated change $\Delta\alpha$ of absorption coefficient from 4.1 to 8.1 eV:

$$\Delta n(\lambda) = \frac{1}{\pi^2} P \int_{4.1eV}^{8.1eV} \frac{\Delta\alpha(\lambda)}{1-\left(\frac{\lambda'}{\lambda}\right)^2} d\lambda' \qquad (1)$$

where the symbols have the usual meaning. The estimated value at 1.5 μm is $\Delta n=-3\times10^{-4}$.

Figure 3 shows first derivative EPR spectra of samples exposed to 10^4 and 3×10^4 laser pulses. A narrow line (about 0.2 mT wide) at 343 mT and other broader structures at 343.5, 345 and 347 mT (corresponding to g-values of 2.001, 1.994, 1.986 and 1.976) indicate the presence of Si-E' centres [5] (responsible for the narrow line at 2.001) and of Sn variants of E' centres [6] (axial Sn-E' with $g_{\|}=1.994$ and $g_{\perp}=1.977$ and orthorhombic Sn-E' with

g_1=1.994, g_2=1.985 and g_3=1.975). All these centers consist of sp^3 unpaired electrons in dangling bonds of three-fold coordinated Si or Sn-substituted-Si sites [5,6]. The relative intensity of the structure at g=1.985 - characteristic of the low symmetry variant of Sn-E' center - decreases after prolonged laser exposure, the main contribution arising from axial Sn-E' centers.

4. Discussion

The results just described constitute the first report of the defect-related absorption features in Sn-doped silica, up to the intrinsic absorption edge. These data allow us to clarify at least three facts: i) the VUV absorption spectrum in Sn doped silica shows a pattern similar to that observed in germanosilicates, confirming the substitutional introduction of Sn in optically active defect-structures typical of Ge-doped silica; ii) the photosensitivity of Sn-doped silica, specifically the positive photoinduced change of refractive index observed in Sn-doped silica fibres, cannot be simply ascribed to photoconversion of optically active defects, since the resulting absorption difference from the visible range up to the intrinsic edge in the VUV is negative; iii) the comparison between absorption changes and EPR spectra allows the identification of the possible absorption component related to the E'-Sn centers.

The first consideration is consistent with photoluminescence (PL) results [7,8] where the substitutional role of the dopant has been evidenced through the PL excitation spectra which are similar to that observed in Ge-doped silica. This fact is not trivial since the substitutional introduction of tin is not easily achieved by conventional chemical vapour deposition methods. The absence of Sn-related spurious phases is confirmed by the energy position of the absorption edge, nearly coincident with that of pure silica [5].

As regards the details of the absorption spectrum, the observed pattern shows a red shift with respect to the absorption spectrum of a Ge-doped silica fiber preform. In fact,

equivalents of the 5.1, 6.5 and 7.2-7.4 eV bands of the germanosilicates [9,10] appear at 4.9, 5.8 and 7.0 eV in the Sn-doped silica spectrum. We point out that the 5.8 eV component cannot be ascribed to paramagnetic E'-like centers, despite their absorption in this energy region [5,10], because it is also detected in the virgin sample where no EPR signal was observed.

As regards the point defect photoconvertion, the UV-induced bleaching of the defect-related absorption underlines the difference between our Sn-doped SiO_2 preforms and the typical Ge-doped SiO_2 photosensitive fibers. This fact indicates that the role of point defect optical activity in the photosensitivity of tin doped fiber preforms may be not so relevant as in germanosilicates. Keeping that in mind, different mechanisms (e.g. compaction) are to be considered in order to explain the positive refractive index change observed in tin doped fibers. Taking into account the higher photosensitivity observed in Sn-doped samples [4] these mechanisms are expected to be stronger than in Ge-doped silica fibres. In fact, our results suggest an even stronger contribution of such an effect in order to compensate the negative refractive index change corresponding to the UV-induced bleaching of the absorption spectrum.

After prolonged laser exposure a different kind of effect appears, resulting in a deviation from a linear correlation between irradiation and absorption bleaching. The decrease of the high energy range of the spectrum is larger than the bleaching of the 4.9 eV band, whereas the reduction of the two structures are similar after the first steps of irradiation. Absorption components in the 5 and 7-8 eV regions in pure and Ge-doped silica were assigned in the literature to transitions of the same kind of oxygen deficient centre (ODC) defect, although other ODC structures were recognized to contribute to the high-energy absorption alone [8-10]. Our data are indeed in agreement with the presence of more than one optically active defect contributing to the observed absorption pattern. Furthermore, the

differential spectrum shows a minor component with an opposite behaviour, growing with increasing UV exposure. The newly observed band (peaked at about 5.9 eV) may be related to the optical activity of the paramagnetic centres detected in the EPR spectra. After prolonged UV exposure the axial variant of Sn-E' signal dominates the EPR spectrum. In particular, between 10^4 and 3×10^4 pulses the EPR spectrum reveals a modification of the spectrum shape indicating an increasing contribution from E'-Si and axial E'-Sn signals. Contemporary, a decrease of the optical absorption is observed at about 4.5 eV which might be related to the decrease of orthorhombic E'-Sn centres. In fact, similar absorption was observed in germanosilicates due to orthorhombic E'-Ge centres [11]. Incidentally, we cannot exclude that the observed variation of absorption at 4.4-4.8 eV may be related to non bridging oxygen hole centre created at the core cladding interface and not completely filtered by the sample mask. A deeper investigation on bulk material is required in order to achieve a precise identification of the optical activity of the two variants of tin-E' centres.

5. Conclusions

The analysis of the VUV absorption spectrum of Sn-doped silica fiber preforms have shown that the variations of the refractive index induced by UV irradiation cannot be solely explained by a photoconversion of optically active defects which induces VUV absorption changes. In fact, the sign of the latter is negative whereas the observed Δn is positive. Several components contribute to the absorption spectrum, showing some similarities with the absorption pattern observed in Ge-doped silica and different changes as a function of the irradiation. Moreover, a minor component at about 5.9 eV arises at prolonged UV exposure, and can be tentatively attributed to the axial variant of E'-Sn centre.

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References

[1] B. Poumellec, and F. Kherbouche, J. Phys. III France 6 (1996) 1595.

[2] J. Albert, Mat. Res. Soc. Bull. 23 (1998) 36.

[3] N.F. Borrelli, C. Smith, D.C. Allan, T.P. Seward III, J. Opt. Soc. Am. B 14 (1997) 1606.

[4] G. Brambilla, V. Pruneri, and L. Reekie, Appl. Phys. Lett. 76 (2000) 807.

[5] D.L. Griscom, J. Ceram. Soc. Japan 99 (1991) 899.

[6] N. Chiodini, F. Meinardi, F. Morazzoni, A. Paleari, R. Scotti, G. Spinolo, Phys. Rev. B 58 (1998) 9615.

[7] N. Chiodini, F. Meinardi, F. Morazzoni, A. Paleari, R. Scotti, D. Di Martino, J. Non-Cryst. Sol. 261 (2000) 1.

[8] L. Skuja, J. Non-Cryst. Sol. 149 (1992) 77.

[9] M.J. Yuen, Appl. Optics 21 (1982) 136.

[10] V.B. Neustruev, J. Phys.: Condens. Matter 6 (1994) 6901.

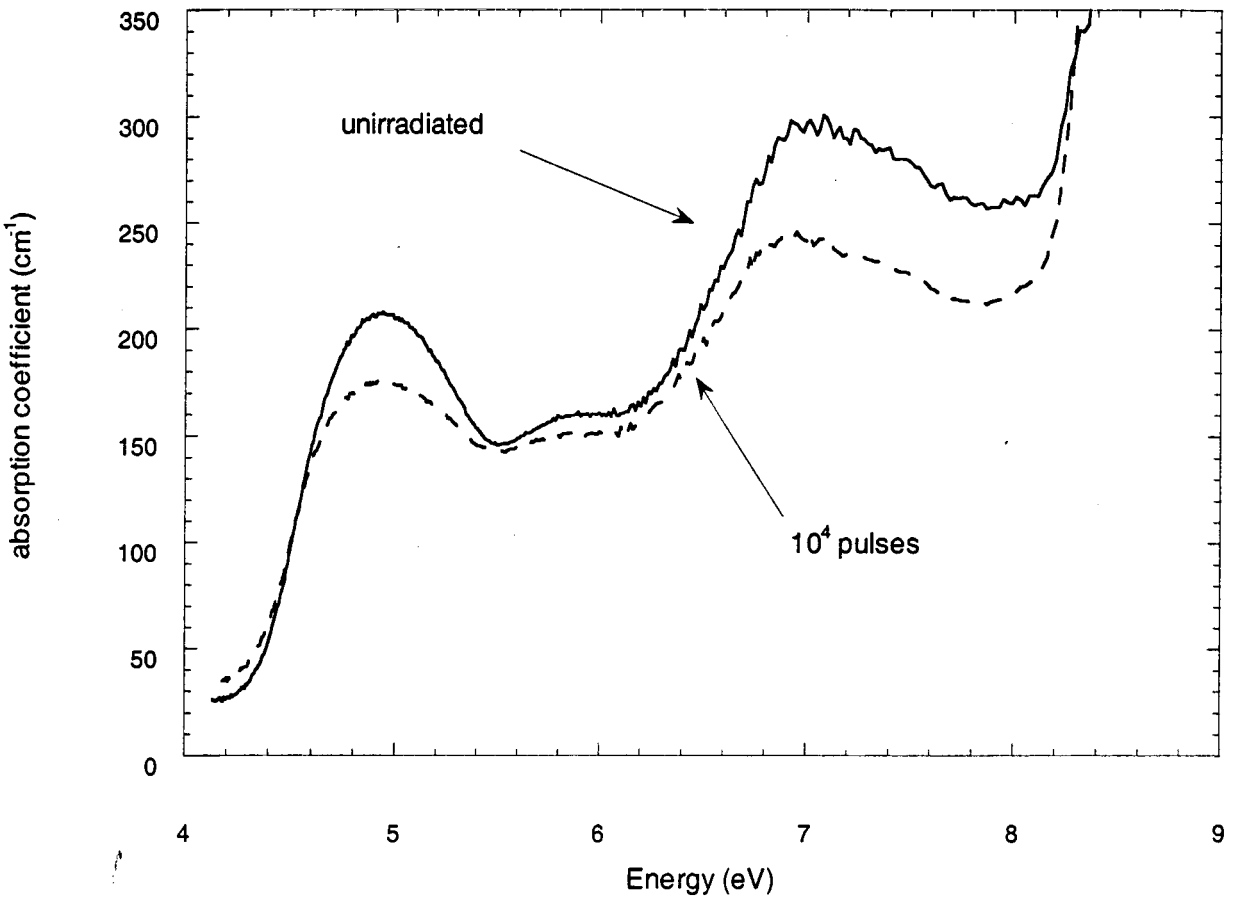
[11] N. Chiodini, F. Meinardi, F. Morazzoni, A. Paleari, R. Scotti, Phys. Rev. B 60 (1999) 2429.

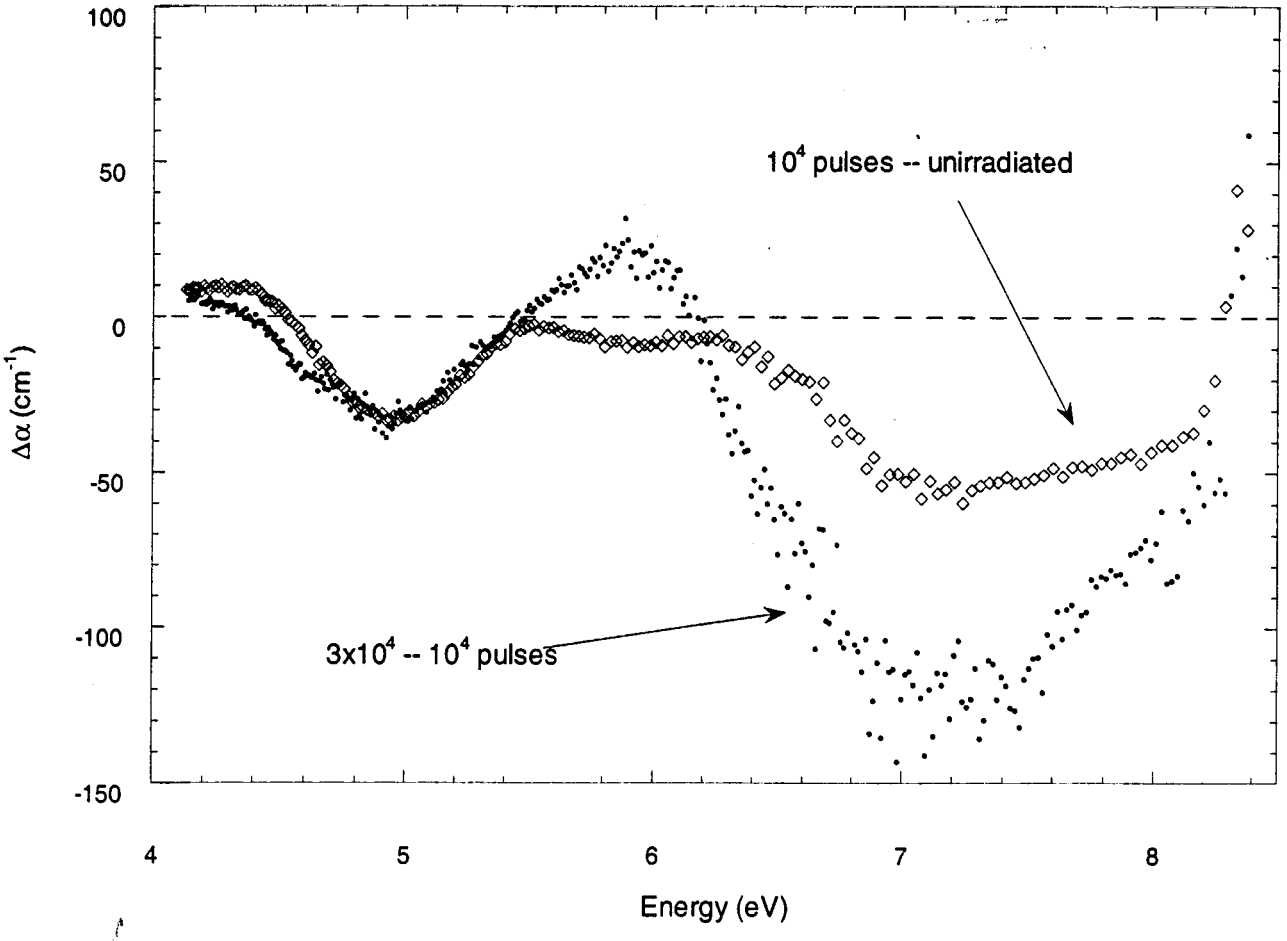
Figure Captions

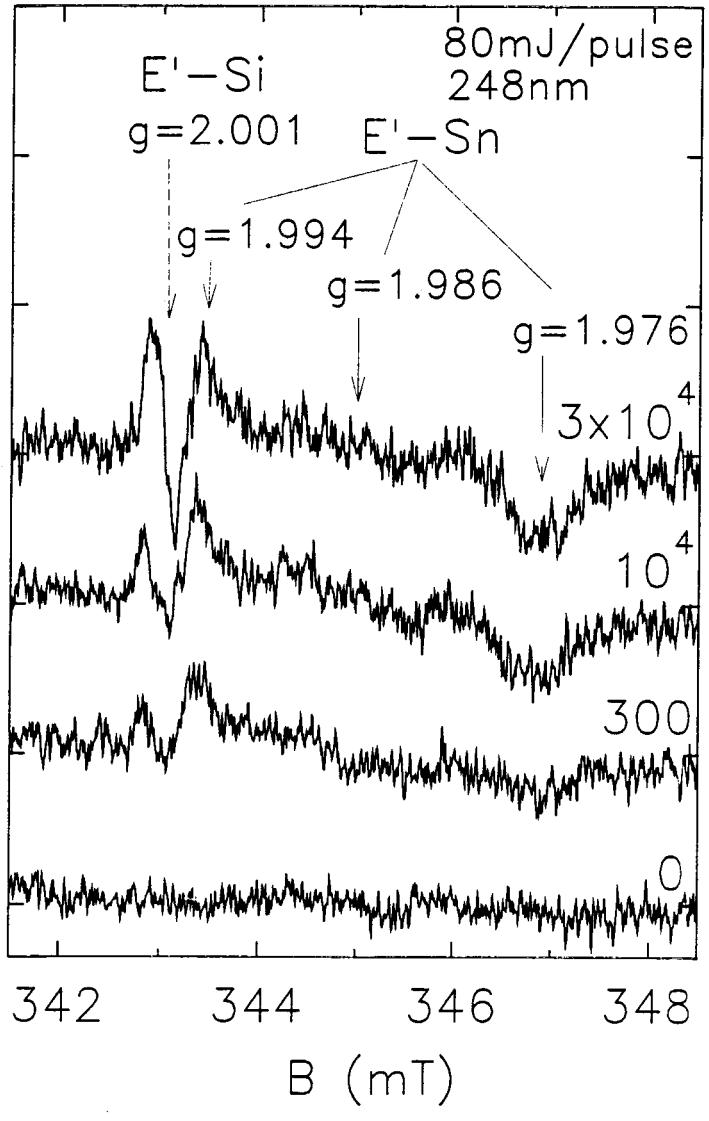
Figure 1. Ultraviolet absorption spectrum of Sn-doped silica fibre preform before and after 10^4 pulses from excimer laser (wavelength 248 nm, pulse duration 20 ns, pulse fluence 80 mJ/cm^2).

Figure 2. UV induced absorption changes after the first 10^4 laser pulses and after prolonged laser exposure (changes after 3×10^4 pulses with respect to the samples exposed to 10^4 pulses).

Figure 3. First derivative EPR spectra of samples exposed to 300, 10^4 and 3×10^4 laser pulses. The features due to E'-Si and E'-Sn centers (axial and orthorhombic variants) are indicated.


absorption coefficient (cm-1)
350
300
250
200
150
100
50
0
4
5
6
7
8
9
Energy (eV)
unirradiated
10^4 pulses


100
50
0
-50
-100
-150
Δα (cm-1)
4
5
6
7
8
Energy (eV)
10^4 pulses -- unirradiated
3x10^4 -- 10^4 pulses


80mJ/pulse
248nm
E'−Si
g=2.001
E'−Sn
g=1.994
g=1.986
g=1.976
3x10^4
10^4
300
0
342
344
346
348
B (mT)