

# Photoinduced processes in Sn-doped silica fiber-preforms

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Effects induced by ultraviolet excimer laser on Sn-doped silica fiber preforms were analyzed by means of optical and electron paramagnetic resonance (EPR) techniques. Bond breaking in substitutional Sn sites was evidenced by the Sn-E' EPR signal due to  $sp^3$  unpaired electrons in three-fold coordinated Sn sites. Red photoluminescence excited at 633 nm, due to non-bridging-oxygen sites, was also observed after laser exposure. The intensity of this emission did not follow the Sn concentration profile, being observed at the core-cladding interface and in the core center. Birefringence data showed that these effects are accompanied by stress relief in the Sn doped region. Different structural features of core and cladding were evidenced by micro-Raman measurements and related to the observed photosensitivity.

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The generation of spatially modulated refractive index changes in silica-based optical fibers can be obtained by exposure to a periodic pattern of ultraviolet (UV) radiation [1]. In this way, longitudinal gratings can be written and used for optical signal processing in fiber optics. However, the photoactivated mechanisms underlying the refractive index changes are not yet fully understood. Two main processes probably contribute to the final effect: the photoconversion of optically active point defects and the structural densification of the material [1]. Several papers showed that doping with substitutional atoms, such as Ge and Sn, is crucial for the enhancement of photorefractivity. In particular, Sn doping gives enhanced and more stable photosensitivity with respect to Ge doping, although it is more difficult to achieve. Little data is available on Sn-doped silica and the origin of the photorefractivity in this case has never been investigated in detail. In a recent paper, we obtained optical fibers with enhanced photorefractivity by doping silica with 0.15 mol% of tin oxide [2]. Absorption data on preforms of this material in the UV region up to the band-to-band absorption edge [2,3] indicated that the absorption changes due to photoconversion of optically active defects cannot account for the change of refractive index observed in the fibers. This is somewhat different from that observed in normal Ge-doped fibers, and suggests that the photorefractivity of Sn-doped material is a more complex process. In order to clarify the kind of processes which take place in Sn-doped silica fibers when exposed to UV radiation we have carried out in this study a broader analysis of the effects induced in Sn-doped fiber preforms by 248 nm laser exposure by means of electron paramagnetic resonance (EPR) spectroscopy, micro-Raman mapping, photoluminescence (PL) measurements and stress polarimetry.

Slices about 100  $\mu\text{m}$  and 1 mm thick were cut and optically polished from silica optical fiber preforms obtained by the modified-chemical-vapour-deposition method, with a core diameter of about 0.8 mm and an average core doping of 0.15 mol%  $\text{SnO}_2$ . Different samples were exposed to an increasing number of pulses from a KrF excimer laser (emission wavelength

248 nm, pulse fluence  $80 \text{ mJ/cm}^2$ , repetition rate 20 Hz). EPR measurements were carried out at room temperature with an EMX Bruker spectrometer operating at about 9.6 GHz. Micro-Raman and PL mapping were performed by means of a Labram Dilor spectrometer excited by a HeNe laser or Ar laser in backscattering configuration. The excitation spot was about  $3 \mu\text{m}^2$ . Stress birefringence images were collected with a polarimetric microscope working at 633 nm with two crossed polarizers and a quarter-wave plate. The dependence of the transmitted intensity map on the angular position of the quarter-wave plate was analysed by the Jones matrices formalism [4].

In Fig.1 we show the EPR spectrum observed in a sample after exposure to  $3 \times 10^4$  laser pulses. The spectrum shows structures at about 343, 343.5, 345 and 347 mT corresponding to  $g$ -values of 2.001, 1.994, 1.984 and 1.976. Spectral position and linewidth of the signal with  $g=2.001$  are those of the Si-E' center of silica, consisting of a  $\text{sp}^3$  unpaired electron of a three-fold coordinated Si site [5]. The other complex signal resembles that of the Sn-E' center [6], consisting in the Sn variant of Si-E' center with a tin atom substituting for Si. The presence of Sn-E' signal confirms the incorporation of tin in the fiber core and clearly indicates that tin has been accommodated in substitutional position in the Si sites of the silica network. The growth of the Sn-E' signal intensity as a function of the UV exposure time (inset of Fig.1) follows a behaviour similar to the refractive index change in the fiber [3]. The estimated number of UV induced E'-Sn centers after  $3 \times 10^4$  laser pulses corresponds to about 1% of Sn sites within the core. The formation of E' centers (that are coordination defects) may be an indication of a network structural rearrangement which probably starts from bond breaking in the neighbourhood of Sn substituted sites. On the contrary, the contribution of UV-induced E' centers to the optical absorption spectrum has been observed to be negligible [3] and therefore no significant refractive index change can be ascribed to it.

Raman spectra inside the core and in the cladding are compared in Fig.2. The spectra show the typical pattern of the  $\text{SiO}_2$  Raman spectrum [7] with rather broad bands peaked at

$\omega_1=430\text{ cm}^{-1}$ ,  $\omega_2=800\text{ cm}^{-1}$ ,  $\omega_3(\text{TO})=1100\text{ cm}^{-1}$  and  $\omega_4(\text{LO})=1200\text{ cm}^{-1}$  and two narrow peaks  $D_1$  and  $D_2$  at  $490$  and  $610\text{ cm}^{-1}$ , less intense in the core. These latter peaks are due, respectively, to four-fold and three-fold planar rings of  $\text{SiO}_4$  tetrahedra which give rise to vibrational modes quite decoupled from the other network vibrations [8].  $D_1$  and  $D_2$  peaks are representative of the coordination properties of pure silica and their intensities were observed to increase in densified silica [9]. On the contrary, a decrease was observed in  $\text{GeO}_2$ -doped silica by increasing the doping level [10]. This fact suggests that Sr substitutional doping, as well as Ge doping, probably inhibits an optimum packing of the network and decreases the statistics of low order tetrahedra rings. After laser exposure, no detectable change appears in the Raman spectra, except for specific portions of the preforms where a strong red luminescence, not observed in unexposed samples, dominates the collected spectra when excited by HeNe laser at  $633\text{ nm}$ . This luminescence was attributed to non-bridging-oxygen centers (NBO) [11].

Maps of spectrally integrated scattered and emitted light excited at  $633\text{ nm}$  have been collected and, through the huge difference between the weak Raman scattered light and the intense red emission, the spatial distribution of PL in the preforms has been determined. A section of PL map across the diameter (after 300 laser pulses) is shown in Fig.3 and compared with the refractive index profile. The UV induced PL does not follow the Sn concentration profile, and PL centers are mainly distributed at the cladding-core interface and in the core center.

Results of the polarimetric analysis are reported in Fig.4, showing specific stress-induced birefringence data. Stresses are evidenced in most doped regions. In fact, tensile stresses arise during the production process as a result of the different expansion coefficient and melting temperatures of the cladding and core materials. From the data in Fig.4 (assuming for simplicity the stress-optic constants of pure silica) the largest stress value may be estimated to be approximately  $400\text{ MPa}$ . A easily detectable decrease of specific birefringence is observed as a result of UV exposure, with the largest effect slightly shifted towards the core-cladding interface

with respect to the maximum value of the pre-existing birefringence profile.

The results just described suggest the following mechanism. The introduction of Sn in substitutional positions in the preform core (proved by the observation of 'Sn-E' centers) forces the network into a less compact medium range structure with respect to pure silica, as shown by the lower statistics of threefold and fourfold tetrahedra rings reflected in the lower intensity of  $D_1$  and  $D_2$  Raman modes. Coexisting with the peculiar structural features of the Sn-doped core, there are strong tensile stresses. Starting from this structural and morphological situation, two kinds of processes are induced by UV laser. Bond breaking occurs at the boarderline of the Sn-doped region (that is at the core-cladding interface and in the undoped center of the core) giving rise to an undercoordinated network. This process is evidenced by the formation of photoluminescent NBO. As a result of this process, there is a softening of the morphological constraints at the core boundary. At the same time, a structural reorganization of the Sn-doped network is promoted by coordination changes at Sn defect sites, consistently with the observed creation of E'-Sn centers and the conversion of optically active Sn sites into different defect structures, shown by the bleaching of the defect-related optical absorption [2,3]. The structural reorganization finally results in a stress relief in the strongly stressed Sn-doped region, as shown by the decrease of birefringence.

In summary, our data supports a model of photosensitivity in  $\text{SnO}_2$ -doped silica preforms mainly due to structural rearrangement. This is mediated by modifications of the morphological constraints due to the composite preform features and related to the frozen stress reservoir in the core.

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## References

- [1] B. Pournellec, and F. Kherbouche, J. Phys. III France **6**, 1595 (1996).
- [2] G. Brambilla, V. Pruneri, and L. Riekse, Appl. Phys. Lett. **76**, 807 (2000).
- [3] A. Anedda, C.M. Carbonaro, A. Berpi, N. Chiodini, A. Paleari, R. Scotti, G. Spinolo, G. Brambilla, and V. Pruneri, J. Non-Cryst. Sol in press.
- [4] P.S. Thecaris and E.E. Gdoutos, *Matrix Theory of Photoelasticity*, Springer-Verlag, Berlin 1979.
- [5] D.L. Griscom, J. Ceram. Soc. Jpn. **99**, 899 (1991).
- [6] N. Chiodini, F. Meinardi, F. Morazzoni, A. Paleari, R. Scotti and G. Spinolo, Phys. Rev. B **58**, 9615 (1998).
- [7] F.L. Galeener, Phys. Rev. B **19**, 4292 (1978).
- [8] A. Pasquarello, and R. Car, Phys. Rev. Lett. **80**, 5145 (1998).
- [9] A.E. Geissberger, and F.L. Galeener Phys. Rev. B **28**, 3266 (1983).
- [10] S.P. Mukherjee, and S.K. Sharma, J. Non-Cryst. Sol. **71**, 317 (1985).
- [11] L. Skuja, J. Non-Cryst Sol. **179**, 51 (1994).

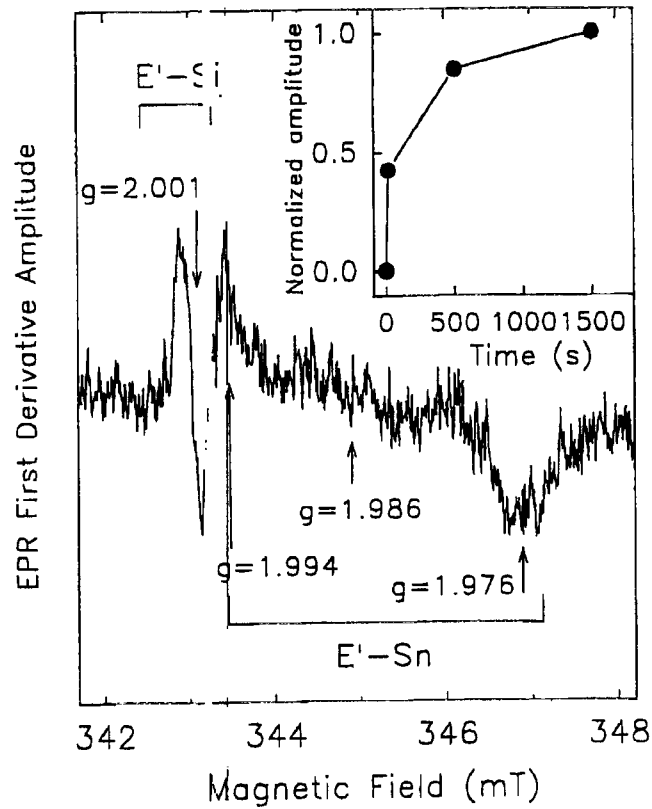


Figure 1. Representative first derivative EPR spectrum in X-band at 300 K of 0.15% SnO<sub>2</sub>-doped silica fiber preforms after  $3 \times 10^4$  pulses from KrF excimer laser. Inset: normalized EPR amplitude vs. UV laser pulses.

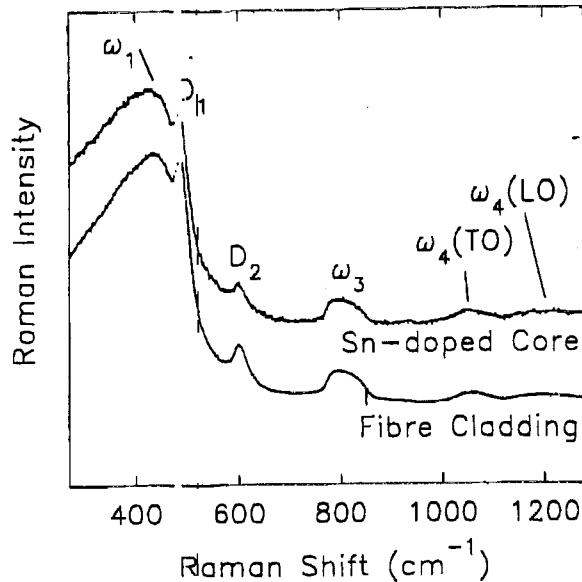


Figure 2. Micro-Raman spectra (2  $\mu$ m diameter of excited area) excited at 514 nm inside the core and in the cladding. Inset: photoluminescence spectrum of the red emission observed by exciting at 633 nm at the core-cladding interface and in the core center of UV irradiated SnO<sub>2</sub>-doped preforms.

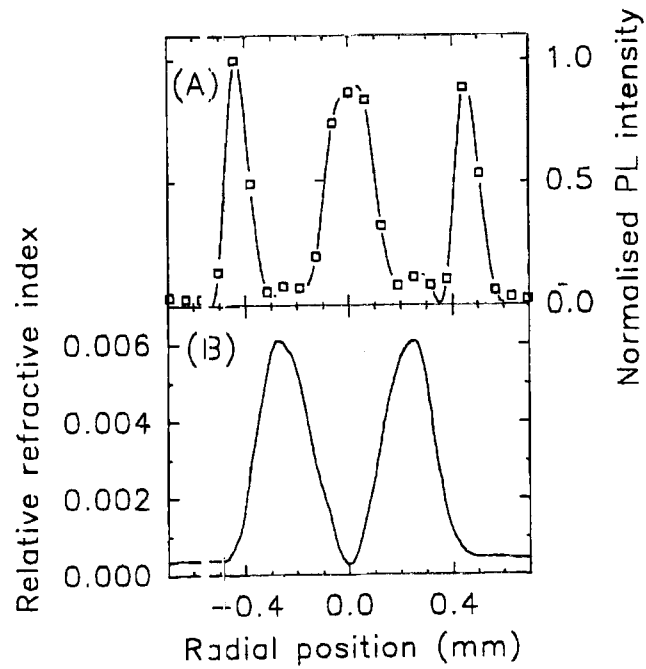


Figure 3. A) Profile of integrated red luminescence along a diameter of Sn-doped silica preforms after 300 pulses of excimer laser; B.) refractive index profile of the same preform.

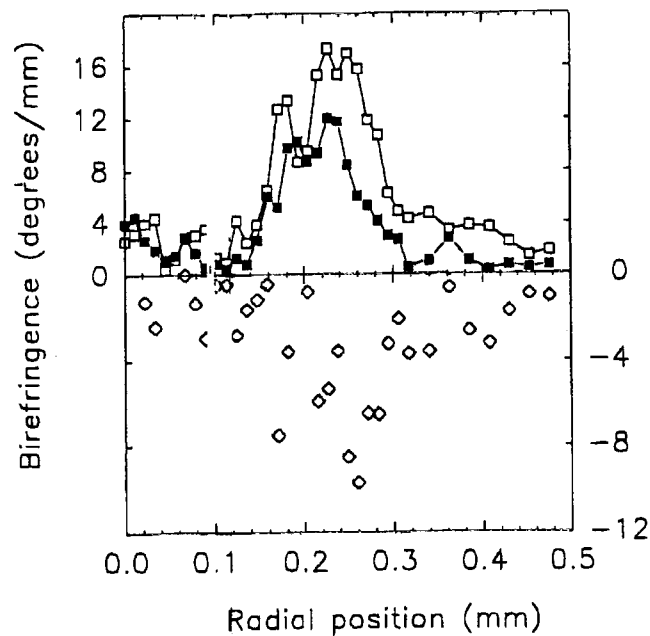


Figure 4. Profile of specific birefringence inside the preform (origin in the core center) before (open circles) and after (filled circles)  $3 \times 10^4$  pulses from KrF excimer laser. The UV-induced change is reported in the lower part of the figure with enlarged vertical axis.