Sn codoping effects on the photoluminescence of SiO_2:Ge

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We present an observation of the photoluminescence features introduced by Sn doping in the SiO_2:Ge core of an optical fiber preform, excited in the vacuum-ultraviolet energy region by synchrotron radiation. Detailed measurements as a function of the excitation energy indicate the presence of two specific emissions around 3.5 and 3.7 eV related to two excitation channels at 5.7 and 5.9 eV, underlying an absorption band centered at about 6 eV. These data put in evidence the capability of Sn to introduce specific optically active defect configurations, contrary to Ge, which mainly introduces perturbations on otherwise intrinsic oxygen-deficient-center sites. [S0163-1829(97)09116-9]

Point defects in amorphous SiO_2 have attracted the interest of many researchers for several decades. Theoretical studies were devoted to the definition of the local structure and of the excitation mechanisms of silica defect sites,[1–5] but several aspects are still controversial and the subject of current investigations. Applicative goals often motivated both theoretical and experimental works owing to the crucial importance of defects in modifying the optical transmission and the electric resistivity of SiO_2-based components for signal communications and electronic devices.[6–8] Indeed, the main evidence investigated in this field include the absorption and emission optical bands introduced by defects in the visible-UV region within the energy gap of the material.[6] In this framework, substitutional impurities in SiO_2 glasses constitute particularly interesting systems. Silicon substitution by other isovalent ions, such as Ge and Sn, gave indications of the possible defect structures (mainly related to oxygen vacancies) through the spectroscopic changes induced by the different ionic parameters (electronegativity, ionic radius, spin-orbit coupling) of the heavier cations.[9] An applicative interest also exists since the cation substitution is currently employed in the optical fibers technology to obtain refractive index profiles. Growing attention was recently given to the role of Sn codoping on the photosensitivity of Ge-doped silica for photoproduction of refractive index gratings;[10,11] the physical process responsible of such an effect is still debated. Only one model, to our knowledge, was proposed for the optical response of possible Sn-related defects embedded in the silica lattice, i.e., a silicon substitutional configuration, similarly to Ge. In accordance with this model, it was proposed that this dopant could be involved in defect sites constituting impurity perturbed variants of typical intrinsic defects mainly connected to oxygen vacancies. In fact, some differences were shown in the photoluminescence (PL) spectra, mainly with near-UV excitation, in Sn-doped silica with respect to pure and Ge-doped SiO_2.[9]

To our knowledge, no spectroscopic data were reported up to now by excitation near the band edge where the most relevant photoinduced changes were suggested to take place. In this paper we report on measurements performed by synchrotron radiation excitation in the 4–8-eV energy range on Sn-codoped SiO_2:Ge fiber preforms.

Samples were preforms of optical fibers produced by the modified chemical vapor deposition method (MCVD) prepared for this investigation by Pirelli Cavi SpA (Milano, Italy). The Ge profile was similar to that of commercial fiber preforms, with a maximum value at about 10 at. %; as for Sn, concentration profile was monitored by scanning electron microscopy analysis, and turned out to be approximately 0.2 at. % with a constant distribution. Measurements were carried out by employing synchrotron radiation at 290 K at the SUPERLUMI experimental station on the *I* beamline of HASYLAB at DESY (Hamburg, Germany) equipped with a 2-m primary monochromator. The excitation spectral bandwidth was 0.33 nm. Photoluminescence excitation (PLE) and PL signals were detected by a CCD camera, while transmission was collected by a photomultiplier. The spectral bandwidth in emission was about 3 nm. Electron paramagnetic resonance (EPR) measurements were carried out at 290 K by using an *X*-band (9.12 GHz) spectrometer in order to reveal possible paramagnetic defects. Different microwave power and field modulation conditions were employed to detect both easily saturable signals (typically E'-like signals) and less saturable ones (arising from coordination defects of oxygen sites).

In Fig. 1 the absorption spectrum of the investigated Sn-doped sample is displayed from 4.5 to 7 eV. Besides the 5.2-eV and high-energy tails of the components already detected in Ge-doped silica above 6.5 eV,[12–14] a further structure around 6 eV is also clearly shown. The presence of this band is accompanied by particular features both in the excitation and emission spectra. Figures 2 and 3 show three dimensional plots obtained by collecting PL emission spectra

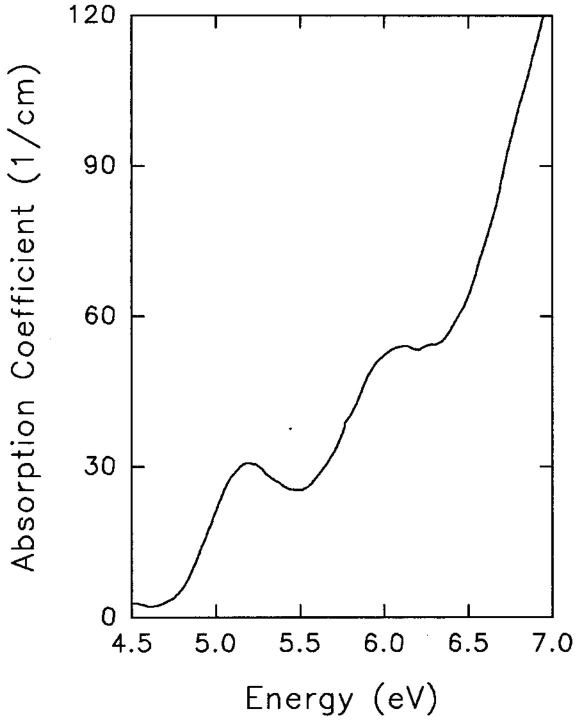

FIG. 1. Optical-absorption spectrum of the Sn-codoped SiO_2:Ge sample performed at 290 K.

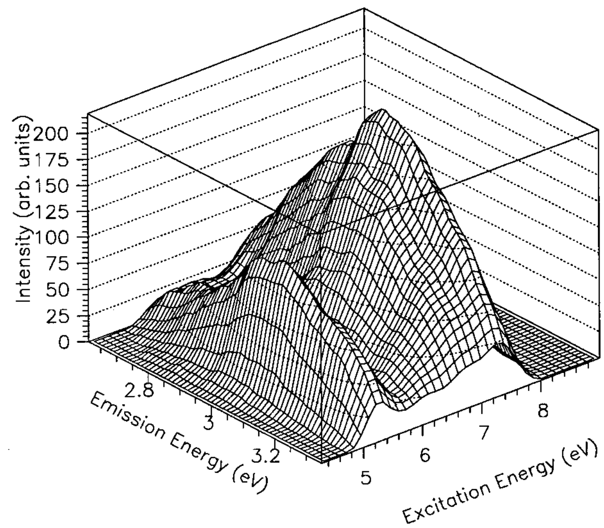

FIG. 3. Three-dimensional view of PL spectra in the β region (around 3 eV) as a function of the excitation energy, in the Sn-codoped SiO_2:Ge sample at 290 K. Data are smoothed by a bidimensional fast-Fourier-transform algorithm.

as a function of the excitation energy. Figure 2 refers to the emission range centered around 4.2 eV (α region), while Fig. 3 covers the spectral interval centered at 3.0 eV (β region). Two specific emissions are excited at about 6 eV (Fig. 2): a first excited at 5.9 eV, whose presence is observable at approximately 3.5 eV; and a second at slightly higher energy (about 3.7 eV), with excitation around 5.7 eV. These emissions are distinct from those characteristic of standard Ge-doped silica, i.e., the α band detected around 4.3 eV and the β band at 3.1 eV, both excited in two excitation regions, at 5.3 eV and around 6.5–7.5 eV. The excitations at 5.3 and 7.2 eV in the low-emission-energy side of Fig. 2 are the high-energy tails of the two excitation channels of the β emission. The composite character of the α emission (giving the low-energy shift by increasing excitation energy) is also typical of Ge-doped materials,[15] as well as the low-energy tail of the β band in the high-energy excitation region.[16]

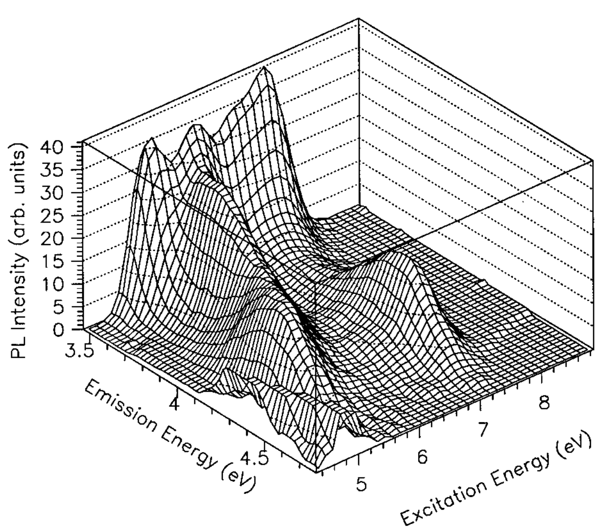

FIG. 2. Three-dimensional view of PL spectra in the α region (around 4 eV) as a function of the excitation energy, in the Sn-codoped SiO_2:Ge sample at 290 K. (The feature at high emission energy, linearly drifting from 4.4 to 4.8 eV, is due to reflected excitation light, only partially suppressed to clarify the figure.) Data are smoothed by a bidimensional fast-Fourier-transform algorithm.

The features of the composite structure at 6 eV are better depicted in Fig. 4, where the PLE spectra taken at the emission energies of 4.3, 3.7, and 3.5 eV are displayed [curves (A), (B), and (C), respectively], showing the excitation peaks at 5.7 and 5.9 eV clearly distinct from the typical PLE bands of Ge-doped silica [see, for example, curve (A) concerning the α PL band]. Contributions from α and β excitations are also evident as peaks around 5.3, 6.7, and 7.2 eV in curves (B) and (C).

The obtained results can now be discussed by considering separately the features due to the already observed α and β bands and those of the structures excited in the 6-eV region. Concerning the 5.3-, 6.7-, and 7.2-eV excitation channels, the dominant features observed are the α and β emissions. The 6.7-eV band is characteristic of Ge-doped silicas (appearing at slightly lower energy in some cases[15,17]), but no definite attribution to a specific defect structure was suggested up to now.[15] As regards the 5.3- and 7.2-eV bands, these are usually observed both in undoped and Ge-doped silica,[13,15,18] and attributed to oxygen-deficient centers (ODC's). In a recent study, Skuja[9] proposed the existence of an isoelectronic series of twofold coordinated cation defect sites (Si, Ge, Sn). So the existence of Sn variants of ODC's should be taken into account. These could give rise to spectral contribution in the α and β regions as well as Ge, since our sample presents both Ge and Sn doping. However, composite structures in our spectra should be hardly detectable

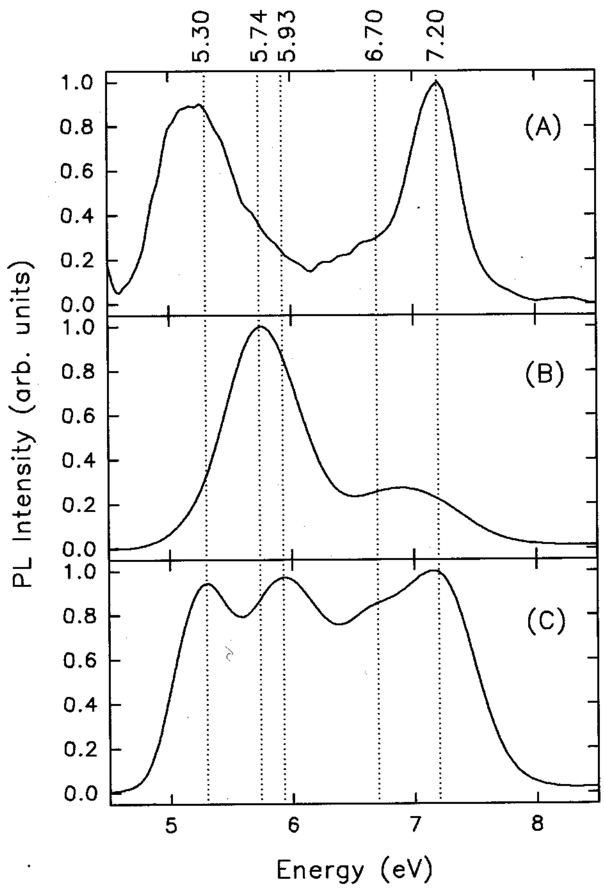

FIG. 4. Room-temperature PL excitation spectra of the Sn-codoped SiO_2:Ge sample at selected emission energies: 4.3 eV (*A*), 3.7 eV (*B*), and 3.5 eV (*C*).

owing to the slight energy shifts expected.[9] So, the existence of Sn variants of ODC defect sites cannot be here confirmed.

The other two structures in the 6-eV region were never previously observed nor in pure or in doped silica. Some variants of E' centers are known to have optical absorption in the same energy region:[6] for this reason, the origin of the composite structure in the 6-eV region was further investigated by EPR measurements, to check possible correlation with paramagnetic centers. The lack of any detectable EPR signal rules out any possible attribution of the 6-eV structure to E'-like defects or other paramagnetic centers. So diamagnetic defect species should be taken into consideration, similarly to ODC's responsible for α and β bands. Nevertheless, the responsible defect cannot be bare variants of ODC's. In fact, (i) the existence of an isoelectronic ODC series is expected to give rather slight PLE energy shifts (approximately 0.1–0.2 eV) from Ge- to Sn-doped silica,[9] which do not match the observed energy differences; (ii) at variance with the well-known ODC-related excitation channels emitting in the α and β bands, the two excitation channels underlying the 6-eV absorption are characterized by different and previously unobserved emissions. The latter point calls for an attribution to localized intracenter transitions, with no energy-transfer processes. The overall phenomenology leads us to suggest a different origin of the excitation and emission features with respect to ODC defects: additional defect bands in Sn-codoped SiO_2:Ge could arise from defect structures directly involving Sn ions. Thus an interesting result arises from our data, suggesting that Sn can also introduce specific optically active defect configurations, contrary to Ge, which mainly introduces perturbations on otherwise intrinsic ODC sites.

In summary, by performing a detailed analysis of the PLE and PL responses on Sn-codoped SiO_2:Ge preforms of optical fibers, we demonstrated the existence of two excitation channels centered at 5.7 and 5.9 eV and characterized by two specific emissions observed at about 3.7 and 3.5 eV, respectively, probably related to the presence of Sn dopant.

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