CHANGE OF SPECTROSCOPIC AND STRUCTURAL PROPERTIES OF GERMANOSILICATE GLASS UNDER MECHANICAL COMPRESSION AND UV IRRADIATION

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Optical absorption, luminescence, electron spin resonance, and Raman scattering spectroscopic studies of Ge-related defects in as-made, γ- and UV-irradiated, and pressure-densified germanosilicate glass have been made. On the basis of results obtained, bistable oxygen vacancy is argued to be an adequate model for germanium oxygen-deficient centre with absorption band centred at 5.12 eV. Photobleaching of this defect is presumably accompanied by breaking of sixfold tetrahedra rings in the structure of germanosilicate glass and by creation of threefold rings.

1. Introduction

In modern fibre optics, germanium dioxide GeO_2 is the main dopant of silica glass (glassy SiO_2), which is used to increase the silica refractive index and to form a waveguide structure of an optical fibre. The structural similarity of tetrahedra M0_4 (M is Si or Ge), allows addition of significant amount of GeO_2 to silica glass in the fibre core (typically 3 to 10 mol.% but more than 30 mol.% is technically possible). It is well known that (unlike silica glass) many optical properties of germanosilicate glass and fibres are highly dependent on the technological conditions and on irradiation conditions. This is due to the fact that various germanium-related defects occur in germanosilicate glass in significant concentration, their models being still under investigation.

Initial (intrinsic) germanium oxygen-deficient centres (GODC’s) are known to transform into other (induced) germanium-related defects under exposure to photons of various energies. This transformation determines the properties of germanosilicate fibres, such as radiation resistance, second harmonic generation, excess optical loss in high-Ge-doped fibres, etc.

Very much attention is being paid to the study of the mechanisms of the photorefractive effect in germanosilicate glass, which reveals itself in the process of UV writing of refractive index gratings in optical fibres. Research is focused on photosensitive GODC’s, which are considered to be responsible for the refractive
index change. Some of the suggested mechanisms for this phenomenon deal with glass network rearrangement around UV-destroyed irregular bonds (GODC); these mechanisms involve densification of germanosilicate glass [1] and stress relief [2]. The first effect seems to be stronger and deserves, in our opinion, particular attention.

It is very likely that transformation of point defects can trigger the densification of the surrounding glass network. In turn, the remaining defects can change their spectroscopic properties, owing to the network rearrangement. To exclude a combined effect of UV irradiation both on the defect transformations [3] and on the glass density, we examined the influence of mechanical pressure treatment of germanosilicate glass on the spectroscopic properties of GODC’s and on the glass network [4,5].

2. Intrinsic Defects in Germanosilicate Glass

Figure 1 [3] shows a survey optical loss spectrum stretching over 8 orders of magnitude in spectral range 190-1900 nm (6.5-0.65 eV). It was measured in as-made germanosilicate fibres and preforms (bulk samples) prepared by chemical vapour deposition. For comparison, a pure silica glass loss spectrum is given. One can see that in these glasses optical losses are low and very close in the near infrared region, whereas the intensities of the ultraviolet (UV) absorption bands in germanosilicate glass are much greater (2 to 4 orders of magnitude) than those in silica glass. This fact makes germanosilicate glass and fibres an attractive object for studying the photoinduced effects and for photo-creation of various fibre devices.

Of all the absorption bands observed, the band centred at 5.12 eV (242 nm) is studied most. It is observed even in silica glass containing trace amounts of germanium. This band is always accompanied by a weak band at 3.76 eV (330 nm). Under photoexcitation in the 5.12 eV band, UV and blue luminescence is observed, 4.3 eV (292 nm) and 3.15 eV (390 nm) bands, respectively. The blue luminescence is also excited in 3.76 eV absorption band. There is much evidence that these absorption and luminescence bands belong to the same diamagnetic defect of the glass structure, which is 1) related to a germanium atom and 2) correlates with oxygen deficiency in the glass.

Several models have been put forward to explain this defect. These are Ge$^{2+}$ ion [6], GeO molecule [7], antistructural defect Ge-Ge-Si= [8], two-coordinated neutral germanium atom Ge$_2^0$ (-O-Ge-O-) [9], and, at last, the model of oxygen vacancy neighbouring a Ge atom [10].

On the basis of computer modelling, it was shown recently that the neutral oxygen vacancy (NOV) can exist in two different configurations [11,12]. Figure 2 presents schematically a configuration diagram of bistable NOV. One of them is normal (NOV$_n$) (the distance between the central silicon atoms in the vacancy $R_n=0.23$ nm) and the other is anomalous (NOV$_a$) or so-called 'puckered' ($R_a=0.4$ nm). This modelling gives an acceptable fit to the absorption and luminescence bands mentioned above and photoinduced transition from one state to the other that results