The influence of co-doping agents on bismuth clustering in silica synthesized by SPCVD

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Abstract. We investigated the variation of near-infrared (NIR) luminescence spectra of bismuth-doped silica-based glasses caused by exposure to intense deep UV (193 nm wavelength) laser radiation. Bismuth-doped optical waveguides consisting of silica with additives of Al and P as the light-guiding core, synthesized via surface-plasma chemical vapour deposition (SPCVD) technology, served as the samples in our experiments. Spectra of steady-state NIR luminescence excited by 808, 904, and 970 nm wavelength laser diodes were measured in a wavelength band of 1-2 µm at temperatures of 105 and 300 K. We found that exposing the glass to intense ArF excimer laser radiation leads to NIR luminescence integral intensity and spectrum profile changes. The observed changes are discussed in the assumption that the UV laser exposure causes photoinduced rearrangement of the glass network in the vicinity of bismuth inclusions. It is expected that the latter are present in the glass network in the nature of separate ions, atoms, as well as 3D clusters.

1. Introduction
Currently, a complete example of the active centre responsible for near-infrared (NIR) luminescence of bismuth [1] is absent. The majority of relevant papers consider the origin of this luminescence in terms of the presence of bismuth ions, molecules, dimers and nano-clusters (Bi⁢⁰, Bi⁺, Bi³⁺, BiO, Bi²⁻, Bi₂²⁻, Bi₃) in the host glass [1–5]. Therein bismuth clusters can be semiconductors with a bandgap depending on their size and shape [6].

A stronger acidity of phosphorus oxide (P₂O₅) as compared to silicon dioxide [7] leads to a stabilization in the P-doped silica subvalent states of bismuth, including the clusters [8]. From this point of view, aluminium additive to the silica has to prevent the formation of clusters due to the amphoteric nature of this metal. In such a way, phosphorus and aluminium dopants have to act in all the contrary way with regard to the probability of the formation of bismuth clusters in silica.

As a rule, the bandgap value of a nonmagnetic semiconductor decreases with respect to temperature leading to a redshift of the recombination luminescence spectrum, although there are instances where a blueshift can occur [9]. For this reason, the recording of the luminescence spectra at different temperatures could give additional information about the origin of the active bismuth centres.

Another way to gain further insight on the origin of NIR luminescence in Bi-doped silica-based glasses could be to examine the dependence of the luminescence spectrum on the excitation wavelength. For interband transitions, the spectral position of the luminescence emission peak weakly depends on the excitation wavelength, whereas for atoms and ions with strong non-uniform
broadening in the luminescence spectrum, the emission peak must blueshift with an increase of the pump photon energy. In addition to identifying the size of the active bismuth centres, there is an important problem on how to recognize their neighbours in silica with variations in co-doping. If the bismuth NIR-luminescence centres are linked to inherent silica defects, an external impact that destroys or forms these defects would change the intensity and the fine structure of bismuth luminescence as well. Deep UV laser radiation is one such impact, which destroys a variety of defects in silica that contain different dopants.

2. Samples and experimental technique
We prepared individual samples constituting cylindrical silica rods of about 4 mm in diameter. Each rod contained a doped silica core of approximately 700 µm in diameter activated by bismuth. For this purpose, we synthesized a layer of amorphous silicon dioxide containing bismuth and other co-dopants via surface-plasma chemical vapour deposition (SPCVD) on the inner surface of a reference silica tube 20 mm in diameter and 2 mm wall thickness. The tube with the deposited layer was consolidated in a rod by means of profusion rotation in a flame of the moving oxygen-hydrogen burner.

These cylindrical optical waveguides with bismuth–doped cores as the experimental units were pulled out from thus obtained rods. We have investigated the following three Bi-doped P or Al co-doped silica samples: S.BiP (phosphorous content of about 2.5 at.%), S.BiAl1 (aluminium content of about 2.4 at.%) and S.BiAl2 (aluminium content of about 3.2 at.%). NIR luminescence was excited by means of three different laser diodes at wavelengths of 808, 904, and 967 nm.

Pump radiation from laser diodes was delivered to a flat end of the sample core with the help of a pure silica core multimode fibre. Luminescence light through the lateral surface of the sample via the other multimode fibre was delivered to the DDS-30 (Lomo™) spectrometer equipped with the PDA10DT (Thorlabs™) InGaAs photoreceiver.

A portion of samples was irradiated by the ArF excimer laser radiation (193 nm wavelength). The exposure dose was as high as 5 kJ/cm² for each sample.

Measurements at a low (~105 K) temperature were carried out with the help of a homemade optical cryostat. In this case, pump light from the diode lasers was delivered to the active core of the sample by means of a collimator-lens assembly.

3. Results and discussion
We found that the NIR luminescence band for the S.BiP sample is centred at the wavelength of 1180 nm (1.05 eV) for both 904 and 970 nm pumping. Such a performance of the luminescence spectrum is inherent to the recombination luminescence of semiconductors. However, in the case of the S.BiAl2 sample, the peak position redshifts with an increase of the pump wavelength. This suggests a rather point-like nature of the active bismuth centres intrinsic in the silica sample with an aluminium additive.

Fig.1 depicts steady-state luminescence spectra obtained at temperatures of 300 K and 105 K. One can see that the cooling influences the NIR luminescence spectra of active bismuth centres in an unexpected way. The temperature reduction of the S. BiP sample pumped at the wavelength of 904 nm leads to an increase of luminescence intensity in the neighbourhood of 1.1 eV (Fig. 1b). This indicates that 3D bismuth clusters are the centres responsible for NIR luminescence. This luminescence is a consequence of the indirect radiative recombination process accompanied by phonon excitation. Pump absorption in this process takes place via a direct electron transition and weakly depends on the temperature. Conversely, with the S.BiAl2 sample, one can observe only a narrowing of the luminescence spectrum and no shifting in the position of the spectral peak (Figs. 1a and 1c). This suggests not only a point-like nature of this type of bismuth centre, but a lack of or an extremely small magnitude of the Stark splitting of the excited state energy level as well. The 3P₁→ 3P₀ transition observed for Bi⁺ ions [3] fully fits these requirements.
Fig. 2 illustrates the impact of the UV laser exposure on the spectra of NIR luminescence. The most significant observable changes are in the spectra of the sample S.BiAl1 excited at a wavelength of 808 nm. These changes can be explained by the recharging of AlO$_4^-$ defects followed by the formation of neutral AlO$_4$ aggregates [10]. Therefore, one can suggest the presence of AlO$_4^-$ in the neighbouring environment of the bismuth centre responsible for NIR luminescence in silica glass with aluminium additives.

Fig.2. Changes in the steady-state NIR-luminescence spectra, as the result of glass exposure to the intense UV laser radiation; a) - S.BiAl1 excited at the wavelength of 808 nm, b) - S.BiP excited at the wavelength of 970 nm.

Fig.1. Steady-state NIR luminescence spectra of different samples (S.BiAl2 - a), c); S.BiP - b), d)) at temperatures of 300K and 105K excited by laser diodes at wavelengths of 904 nm - a), b), d) and of 970 nm - c).
4. Conclusions
The results of our experiments with bismuth-doped silica glasses manufactured by the surface-plasma chemical vapour deposition technology are as follows. The addition of aluminium in the glass network shifts the equilibrium towards the formation of interstitial \( \text{Bi}^+ \) ions environed by \( \text{AlO}_4^- \). Meanwhile, the addition of phosphorus most likely favours the formation of 3D bismuth clusters. These two interstitials contribute to the NIR luminescence observed in these glasses.

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