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Near-Infrared Luminescence of Bismuth in Silica-Based Glasses with Different Additives¹

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Abstract—The near-infrared (NIR) luminescence spectra and changes caused in them by an exposure to ArF excimer laser radiation were studied in bismuth-doped silica-based glasses containing Al, P or Ge and B additives. Experiments were conducted using specimens in the form of optical waveguides synthesized by surface plasma chemical vapor deposition (SPCVD), using bismuth-doped glass sample as the light-guiding core. Excited by ~808, ~904, and ~970 nm wavelength laser diodes, the NIR luminescence spectra were recorded in the 700–2000 nm wavelength range at temperatures of 105 and 300 K. The UV laser treatment was found to cause changes in both integrated intensity and spectrum shape of NIR luminescence associated with bismuth impurities. The observed changes are discussed with the assumption of photo-induced reconfiguring of different bismuth inclusions, which might present in the glass network in the form of separate ions and atoms, interstitial molecules, and bulk semiconductor nanoclusters.

Keywords: bismuth, clustering, silica, near-infrared luminescence, SPCVD

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INTRODUCTION

Although the discovery of NIR luminescence in silica based glasses was reported 15 years ago [1], a rigorous, consistent, and comprehensive model of the active bismuth center responsible for the luminescence in the NIR spectral region is still not reported. It is clear that on dissolving of little amount of virtually any activator, it will be present in the glass network mainly as separated atomic-size centers without the formation of larger aggregates. But with an increase in concentration, separate centers have a chance to come together, in other words, to form impurity clusters with the distance between single atoms or ions being in an order of magnitude smaller than the value corresponded to their uniform distribution over sample volume. Hence, under that logic there is a possibility of the co-existence in an activated host impurity defects of the two different types: point and bulk. Surely, impurity defects of an intermediate size in the form of molecular aggregates may also be present as well.

One might divide the publications dedicated to the problem of bismuth NIR luminescence into two big groups. The first one assembles papers, in which experimental data and theoretical calculations are based on the assumption that the NIR-luminescence centers are by nature occur as separate atoms or ions

(Bi⁰ [2], Bi⁺ [3], Bi⁵⁺ [1]), BiO molecules [4] and bismuth dimers (Bi₂⁻, Bi₂²⁻ [5, 6], Bi₂ [7]). These species can be chemically bonded to the centers of the glass network or unbounded interstitials located in the network voids. The second group of papers considers NIR luminescence of Bi-doped glasses associated with the presence of larger aggregates in the form of bismuth clusters [7–9].

Although bulk bismuth crystal is a semimetal, owing to the quantum effects, with the size decrease, bismuth clusters become semiconductors with band gaps dependent on clusters size and shape [10, 11]. In that regard, it is worth noting a set of papers discussing bismuth based quantum dots [12–15]. However, even in these papers the authors could not indicate unambiguously particular electron transitions responsible for the origin of NIR luminescence. It is only known with certainty that the band gap increases with the decrease of nanoparticle volume. Availability of the two extremes (L and T points) in Brillouin zone for containment of excited charge carriers allows for both direct and indirect (intervalley) transitions in such type of a semiconductor.

In bulk crystals, indirect electron transitions are possible solely with the participation of phonons ensuring momentum conservation, whilst in nanocrystals significant function starts to perform surface states [16] that can lead to essential increase of indirect

¹ The article is published in the original.

transition probability as compared to bulk samples. It is worth mentioning that the surface conductivity of bismuth including that of nanocrystals is of the metallic type, [15, 17]. A probable association of bismuth NIR luminescence with indirect electron transitions in semiconductor inclusions might be reasoned by a strong dependence of the transition probability on temperature. This probability might either grow or reduce with the temperature increase depending on whether phonon absorption or emission is necessary in order to satisfy the law of conservation of momentum.

One more attribute of a potential origin of NIR luminescence via recombination through the indirect interband transitions is a greater as compared to the recombination via direct transitions lifetime of the nonequilibrium charge carriers. Decay time of bismuth NIR luminescence measured in different glasses amounts to hundreds of microseconds [1–3, 18, 19], that favor the recombination mechanism of NIR luminescence via indirect transitions as well.

A strong motive to analyze luminescence spectra at different temperatures is brought about by the features of the temperature dependence of energy gaps of interband transitions for both bulk semiconductors and quantum dots. As a rule, band gap energy of non-magnetic semiconductors increases with decrease of temperature, and one might expect a blue shift of the recombination luminescence peak, although the direction of the shift may be different [20–24].

Besides measurements at different temperatures, a practicable way to further find insight into the origin of active bismuth centers responsible for NIR luminescence might be an experiment on the influence of deep UV laser exposure on bismuth containing silica glasses. If bismuth centers responsible for NIR luminescence are associated with some defects of the glass network, which change configuration under the action of intense UV laser irradiation, one might anticipate a change in the NIR luminescence spectrum as well. As a model of such defects in silica can serve neutral oxygen vacancy associated with germanium (V [Ge-T], where T is either Ge or Si) or the Ge lone-pair center (GLPC) in germanosilicate or AlO_4^- in aluminosilicate glasses whose concentrations diminish as the result of exposure of such glasses to hard UV irradiation [25–27].

Significant difficulties with unambiguous specification of a bismuth center contributing into NIR luminescence in silica are due to the fact that optical emission and absorption by bismuth atoms and ions are associated with electron transitions between states within their outermost electron shells. This peculiarity distinguishes bismuth species from the rare earth ions, in which central electron transitions take place between states inside well screened inner f-shells. As a consequence, luminescence and absorption spectra of bismuth species in glass are sensitive to the environ-

ment of the nearest neighbor and is strongly dependent on the host material.

In the present paper we demonstrate and discuss the results of our experimental study aimed at the clarification of the origin of bismuth luminescence centers in silica in the light of the above described separation of the active centers into point-like and bulk quantum dots types.

Samples preparation and experimental details on spectral-luminescence measurements are described in Section 1. The results of the conducted experiments are presented in Section 2. Section 3 summarizes the main conclusion of the performed experiments.

1. SAMPLES AND EXPERIMENTAL TECHNIQUE

For the experimental study, we fabricated special samples in the form of cylindrical silica rods of 4 mm outer diameter with a bismuth-doped silica-based core of approximately 700 micrometers in diameter. This was accomplished using surface plasma chemical vapor deposition (SPCVD) [28] on the inner surface of a substrate silica tube of 20 mm outer diameter and 2 mm wall thickness, in which amorphous silicon dioxide layer, containing bismuth and co-dopants was deposited. SiCl_4 , BiCl_3 and O_2 served as starting components in the vapor-gas mixture for the synthesis of the bismuth activated glass layer. Vapors of AlBr_3 , POCl_3 , GeCl_4 and BCl_3 were added to the mixture in the experiments involving glass co-doping by aluminum, phosphorus, germanium and boron respectively. The plasma-chemical synthesis was implemented with the help of a scanning with the frequency of 8 Hz plasma column along the ~25 cm in length section of the substrate tube. The temperature of the substrate tube wall during the deposition process was about 1150°C. The thickness of the deposited glass layer was approximately 150 μm .

The tube with the deposited layer was shaped in the form of a rod by heating it from outside while spinning in the flame of the longitudinally moving hydrogen-oxygen burner. Thus, received preforms were redrawn to create the above-mentioned cylindrical optical waveguides, the research target of which was bismuth activated glass core in the middle. The amount of dopants existing in the synthesized glass of the core was determined using EDX analysis. X-ray microanalysis of the samples were obtained using raster electronic microscope Quanta 200 equipped with the EDAX spectrometer. The results of the X-ray microanalysis of the active core glasses are presented in the Table 1. The luminescence spectra were recorded as follows. A pump radiation from a laser diode was incident on the sample waveguide core via a standard optical fiber with pure silica core of 105 μm in diameter and numerical aperture $\text{NA} = 0.2$. Luminescence was recorded using two different spectrometers depending

Table 1. Concentrations of additives to silica in the specimens under investigation according to energy-dispersive analysis

Specimen	Chemical elements	Concentration, at %
Bi	Bi	0.09 ± 0.01
BiP	Bi	0.015 ± 0.010
	P	2.34 ± 0.04
BiAl1	Bi	0.014 ± 0.010
	Al	2.37 ± 0.04
BiAl2	Bi	0.021 ± 0.010
	Al	3.22 ± 0.04
BiGeB	Bi	<0.01
	Ge	1.53 ± 0.04
	B	<4

on the spectral range. For the registration of luminescence spectra in the region of wavelengths from 1 to 2 μm spectrometric complex DDS-30 (LomoTM) was used, which was accomplished by transferring an image of the lateral surface of the core of the luminescing sample on the input slit of the monochromator with the help of a wide-band mirror condenser. The luminescence radiation was filtered by a monochromator and was recorded using PDA10DT (ThorlabsTM) photoreceiver based on the InGaAs photodiode.

The registration of spectra in the wavelengths range 0.7–1.1 μm was carried out with the help of the AVS-MC2000 spectrometer. For this measurement, the image of the lateral surface of a bismuth-doped core of the waveguide by means of lenses was projected at the end of a standard 200 μm pure silica core optical fiber connected to the entry of the spectrometer. Luminescence was excited by different laser diodes emitting at wavelengths of ~ 904 , ~ 967 , and ~ 808 nm. The first two were capable to render up to 3 W of power, and the latter up to 1.3 W in CW oscillation mode.

To study the possible effect of glass processing by hard, intense UV radiation on the features of bismuth NIR-luminescence, some samples were exposed to ArF excimer laser radiation (193 nm wavelength). The exposure time of each sample amounted to 1000 s, which corresponds to the exposure dose of 5 kJ/cm^2 . The pulse repetition rate in these experiments was 50 Hz, pulse energy density being about 100 mJ/cm^2 . The duration of an individual pulse was ~ 20 ns.

The measurements at low temperatures (~ 105 K) were carried out using a homemade liquid nitrogen flowing optical cryostat fitted with a cold copper finger. To monitor the temperature, a thermocouple junction was set in contact with the cold finger at a distance of a few millimeters and glued to the finger specimen. The pump radiation from diode lasers in this case was delivered to specimens through a side window

of the cryostat with the help of the collimator-lens arrangement.

2. LUMINESCENCE SPECTRA

A. The Dependence on Pump Wavelength

Figures 1 and 2 show normalized to maxima steady state bismuth luminescence spectra obtained for glasses of various compositions recorded in 1–2 μm (Fig. 1) and 0.7–1.1 μm (Fig. 2) wavelength ranges. The spectra are depicted in the logarithmic scale. Pumped at a wavelength of 808 nm, spectra for samples Bi and BiGeB are identical at all wavelengths in the measurement span. The spectra consist of two main shoulders peaking at around 0.88 eV (1420 nm) (Figs. 1a, 1d) and 1.50 eV (826 nm) (Figs. 2a, 2d) accompanied with a duet of the satellite peaks shifted from the main ones to the lower energy side at around 0.13 eV. The shift magnitude is rather close to the value of maximum phonon energy in silica, which is about $1050\text{--}1100\text{ cm}^{-1}$ (0.130–0.136 eV) [29]. This satellite peaks might be associated with the luminescence process comprising simultaneous emission of a photon and absorption of a phonon by the glass host.

The presence of such satellite peaks in the luminescence spectrum hypothetically favors the fact that an active center responsible for luminescence is a chemically bonded to the glass network bismuth atom or ion. At the same time such kind of luminescence spectrum is not observed in the samples BiP and BiAl2 pumped at 904 and 970 nm wavelengths (Figs. 1b, 1c). It is difficult to conclude on the presence or absence of the satellite peaks in the luminescence spectra of Bi and BiGeB samples pumped at these wavelengths (Figs. 1a, 1d), because of the availability of several overlapping bands in these spectra. This makes it practically impossible to identify such satellite peaks.

The absence of satellite peaks in the spectra of samples BiP and BiAl2 pumped at 904 nm and 970 nm wavelengths (Figs. 1b, 1c) can be attributed to the fact that unattached to the glass network bismuth interstitials are excited in these samples. In addition, eventual defects of the silicon dioxide network located in the vicinity of bismuth might also influence the presence of satellite peaks. The other reason for the absence of the satellite peaks in the spectrum might be a cluster-like, bulk aggregation rather than a bismuth point center to be responsible for NIR luminescence.

Rather wide bands of the observed spectra might be associated with two different types of bismuth luminescent species. The first are the point defects with a diagram of energy levels strongly dependent on the electrostatic field strength inside the glass network. In this case, the width of the luminescence spectrum governs by a strong non-uniform broadening. The other type are bismuth clusters with properties intrinsic in semiconductors, including the presence of wide-band luminescence.

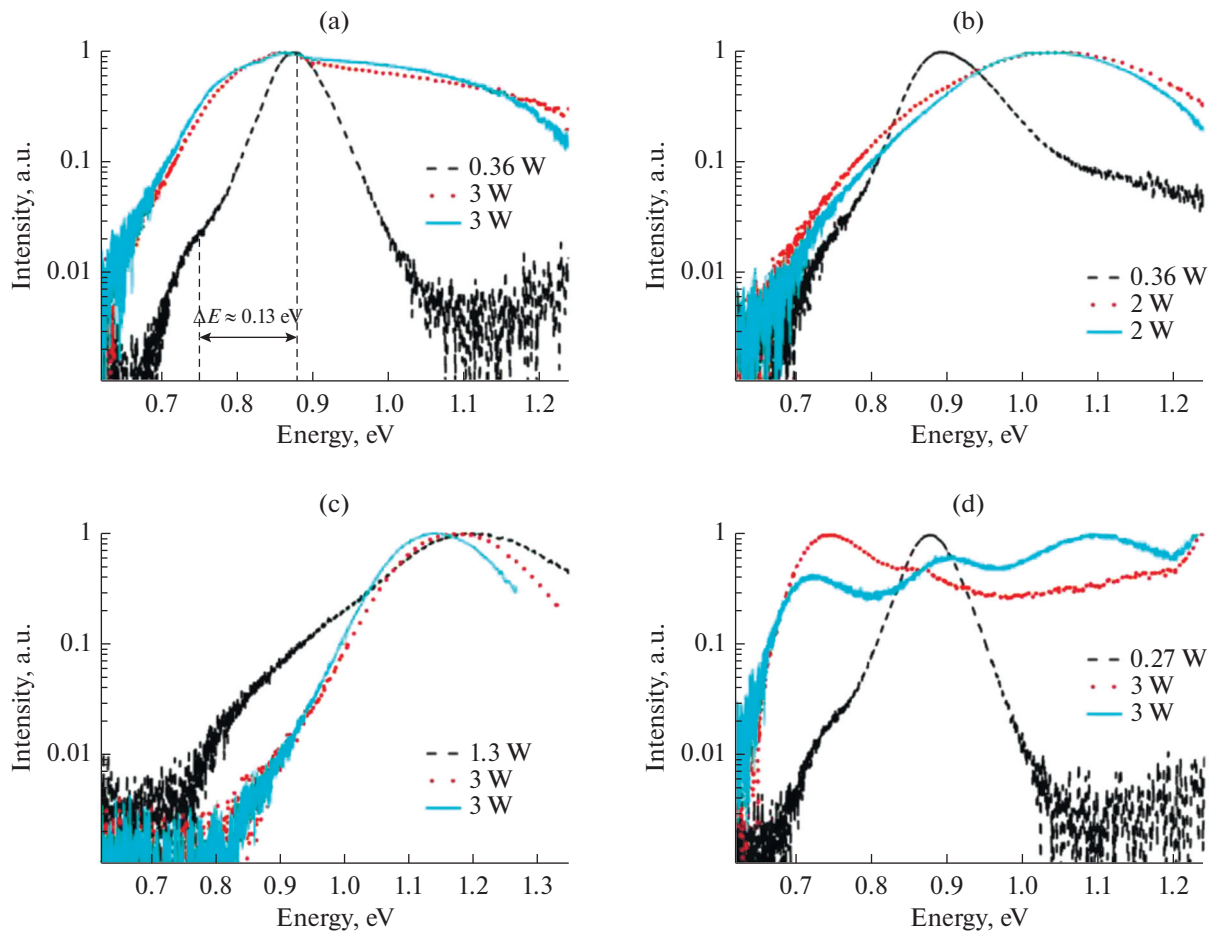


Fig. 1. Normalized to maxima steady-state NIR luminescence spectra obtained in the wavelength range from 1 to 2 μm : (a) Bi, (b) BiP, (c) BiAl₂, (d) BiGeB. The pump wavelength corresponding for dashed curves is 808 nm, for dotted curves is 904 nm, for solid curves is 970 nm. Plot legends indicate pump powers.

A way that could distinguish between the two above-mentioned origins of NIR luminescence is the dependence of the shape and spectral position of the luminescence band on pump wavelength. For the interband electron transitions, position of the luminescence spectrum peak should not change with pump wavelength. On the other hand, for atoms and ions with a luminescence band strongly non-uniformly broadened, this dependence must be essential: with an increase of the pump wavelength (a decrease of pump photon energy), luminescence peak wavelength should shift to the red side. As one can see from Fig. 1b for the specimen BiP, luminescence peak position is situated at 1180 nm or 1.05 eV and does not depend on pump wavelength (904 or 970 nm). Such behavior of the luminescence spectrum shape is more specific to the recombination luminescence in semiconductors. This might be an additional indication to the clusters with semiconductor type band energy diagram, to be responsible for NIR luminescence excited at these wavelengths in the SBiP specimen.

In the case of BiAl₂ sample (Fig. 1c), however, an increase of the pump wavelength (in other words a decrease of the exciting photon energy) leads to a decrease of the energy of radiative transition (luminescence spectrum maximum is shifted towards smaller photon energies). This identifies rather point-like bismuth NIR luminescence centers in silica with aluminum additive.

B. The Dependence on Temperature

Figure 3 shows spectra of steady state luminescence excited at a wavelength of 904 nm at sample temperatures of 300 and 105 K. One can see that cooling did not contribute to an individualization of separate lines in spectrum structures. That testifies non-uniform broadening as the main factor determining the luminescence band shape. At the same time, luminescence spectra of some specimen, for example Bi (Fig. 3a) and GeB (Fig. 3d) significantly change with the temperature reduction. One of the reasons of such changes

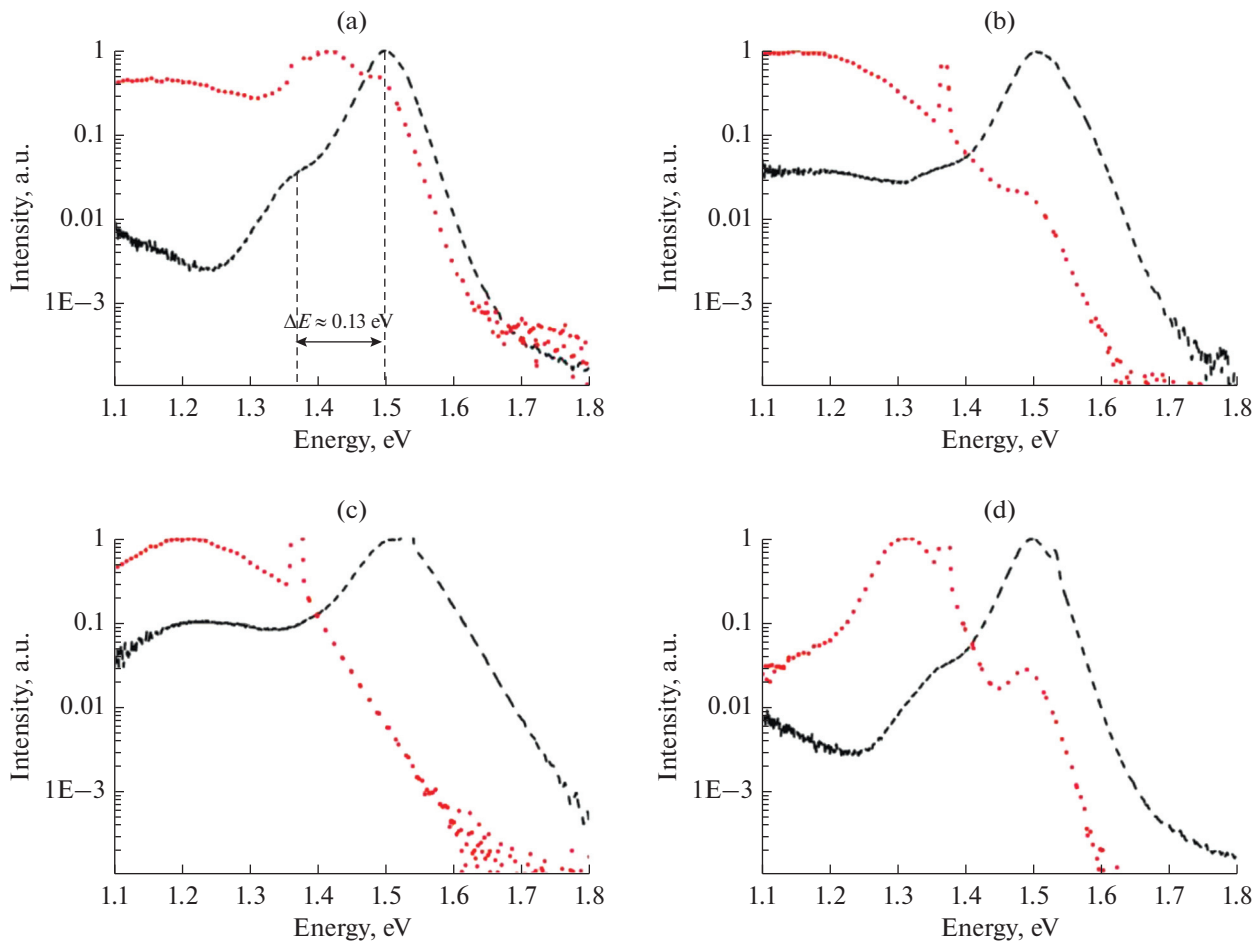


Fig. 2. Normalized to maxima steady-state NIR luminescence spectra obtained in the wavelength range from 0.7 to 1.1 μm : (a) Bi, (b) BiP, (c) BiAl₂, (d) BiGeB. The dashed curves correspond to the pump power 0.36 W and pump wavelength 808 nm; the dotted curves correspond to the pump power 1.3 W and pump wavelength 904 nm. Narrow lines at 1.37 eV (904 nm) and 1.53 eV (808 nm) are associated with the scattered pump laser light.

might be the presence in the glass network of various types of centers simultaneously contributing to NIR luminescence in different parts of the overall spectrum. In particular, a stronger temperature dependence of the luminescence intensity is specific to interstitial centers. In the case of an atom or an ion chemically bonded to the glass network principal factor determining the temperature dependence of the luminescence is the phonon spectrum of the host. However, in the case of interstitial point centers an additional factor of the dependence on temperature is a frequency of the collisions between the point-like center and a boundary of the void, in which such center is located.

An alternative possible explanation for the observed dependence of luminescence intensity on temperature is the assumption regarding indirect radiative recombination transitions accompanied by phonon excitation in semiconductor inclusions in the glass network. In this case, the absorption of pump light occurs via a direct interband transition weakly

dependent on temperature. Certainly, one would suppose a possibility of the opposite process, when luminescence would be a result of the direct interband recombination and absorption would occur via indirect transitions. In that case, however, it would be difficult to explain such a long lifetime of the observed NIR luminescence.

Figure 4 demonstrates normalized spectra of the steady state luminescence recorded at 300 and 150 K temperatures. Graphs are shown in the logarithmic scale. The spectral pattern of almost all the samples weakly depends on temperature. For the BiP sample pumped at 808 nm, one can find only some increase of the luminescence intensity in the vicinity of 1.1 eV as compared to the other parts of the spectrum. This can indicate a dominating contribution to luminescence from the interstitial centers or clusters with indirect transitions.

Similar behavior, but less pronounced, can be observed for the BiGeB sample. In the case of the BiAl₂ sample excited at 970 nm (Fig. 4c), only some

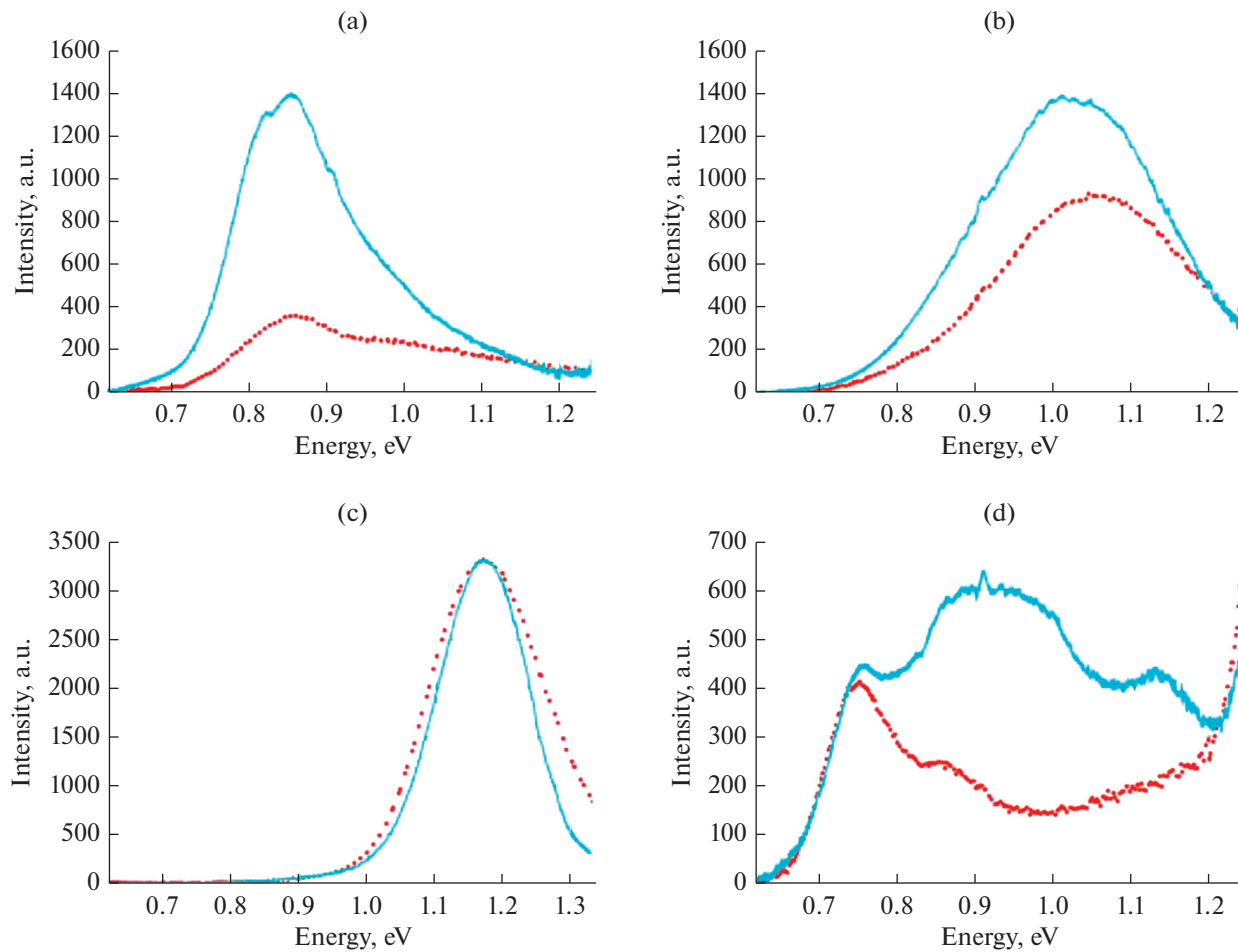


Fig. 3. Steady state NIR luminescence spectra of different samples recorded in the wavelength range of 1–2 μm at 300 and 105 K temperatures: (a) Bi, (b) BiP, (c) BiAl₂, (d) BiGeB. All the measurements were carried out at 904 nm wavelength laser diode pumping, output power being up to 3 W. The sample temperature corresponding for dotted curves is 300 K, for solid curves is 105 K.

narrowing of the spectrum without any shift of the peak wavelength takes place with the decrease of temperature. This favors not only a point-like structure of this center, but testifies the absence or a very small magnitude of the excited level Stark splitting.

There is another temperature effect observed for the BiP sample, which differs from the one intrinsic in Bi-doped silica with aluminum additive. The NIR luminescence spectrum remains practically unchanged in the shape, but shifts to the blue with temperature increase (see insertion in Fig. 4b). Such behavior of the spectrum is indicative of bismuth bulk semiconductor clusters to be responsible for NIR luminescence. There are two factors which influence a spectral position of the luminescence band in this case. Firstly, it is a change of the bandgap magnitude with temperature. Secondly, it is electrons and holes energy distribution in allowed bands at a finite temperature. The latter obviously leads to a shift of the peak wavelength of recombination luminescence to the blue with an increase in temperature.

C. The Influence of Exposure to UV ArF Excimer Laser Radiation

Figure 5 summarizes normalized NIR luminescence spectra recorded before and after irradiation of samples by UV (193 nm wavelength) laser pulses. One can realize that UV treatment of BiP and BiAl₁ samples had no influence on the spectra of NIR luminescence pumped at 970 nm wavelength (Figs. 5a, 5b). In the sample with phosphorous additive, no changes in the NIR luminescence spectrum excited at wavelengths of 904 and 808 nm were observed as well. However, as the result of the UV laser treatment, the NIR luminescence spectrum shape of SBiAl₁ sample pumped at 808 nm wavelength significantly changed. Because of the UV laser treatment, intensity of the luminescence peak near 1.2 eV decreased, but the one in the neighborhood of 0.9 eV increased. It is known that irradiation of aluminosilicate host with UV light of an ArF excimer laser leads to a decrease in the concentration of charged AlO_4^- defects transforming them

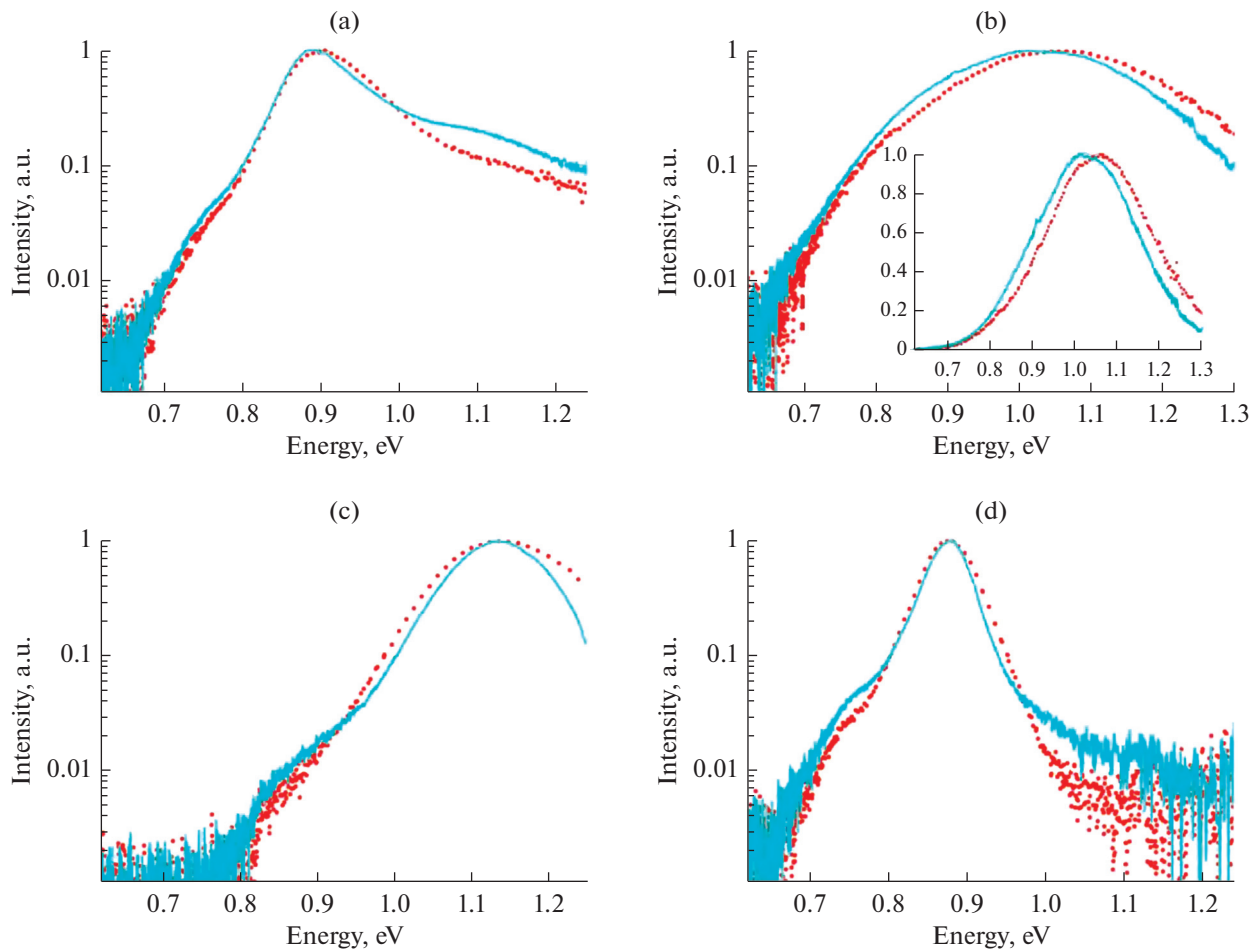


Fig. 4. Normalized steady-state NIR luminescence spectra recorded in 1–2 μm wavelength range at temperatures of 300 and 105 K. The spectra are depicted in the logarithmic scale: (a) BiP, 1.3 W pump power at 808 nm wavelength, (b) BiP, 3 W pump power at 904 nm wavelength (insertion: the spectrum in the linear scale), (c) BiAl₂, 3 W pump power at 904 nm wavelength, (d) BiGeB, 0.52 W pump power at 808 nm wavelength. The sample temperature corresponding for dot curves is 300 K, for solid curves is 105 K.

to neutral AlO_4^- aggregates [27]. This lets one suppose that AlO_4^- aggregates are present in the neighborhood of the bismuth center responsible for NIR luminescence in silica with aluminum additive.

The luminescence spectrum shape of BiGeB sample has also been significantly changed as a result of the irradiation by excimer laser light. Luminescence intensity decreased approximately twice in the vicinity of 0.74 eV (1.7 μm) and 1.34 eV (0.95 μm) and increased near 0.88 and 1.1 eV. These changes can be associated with a UV induced destroy of the GLPC and/or the $\text{V}[\text{Ge}-\text{Ge}]$ neutral oxygen vacancies which are supposed to be present in the nearest neighbor environments of the bismuth centers yielding luminescence near 0.74 and 1.34 eV [30]. The other feature confirming the above hypothesis is a twofold drop of these bands luminescence intensity caused by the ArF excimer laser radiation exposure (see the inset in Fig. 5d), which is a signature of the GLPCs [31].

3. DISCUSSION

The obtained experimental results let us make following assumptions on the origin of the active bismuth centers responsible for NIR luminescence in silica glasses with several additives.

A. No Additives Except Bismuth

The most probable candidate to function as an active center excited by light at a wavelength of 808 nm is atomic bismuth with a neutral oxygen vacancy $\text{V}[\text{Si}-\text{Si}]$ in the nearest neighbor environment [30]. Although the interstitial BiO molecule possesses similar to atomic bismuth luminescence bands (in the wavelength range 800–2000 nm, both the centers have only two luminescence bands centered at 830 and 1420 nm [32]). BiO molecule is weakly connected with host vibrations so that the presence of satellite peaks in its luminescence spectrum is hardly real. Nevertheless, wide bands, which can be excited in this

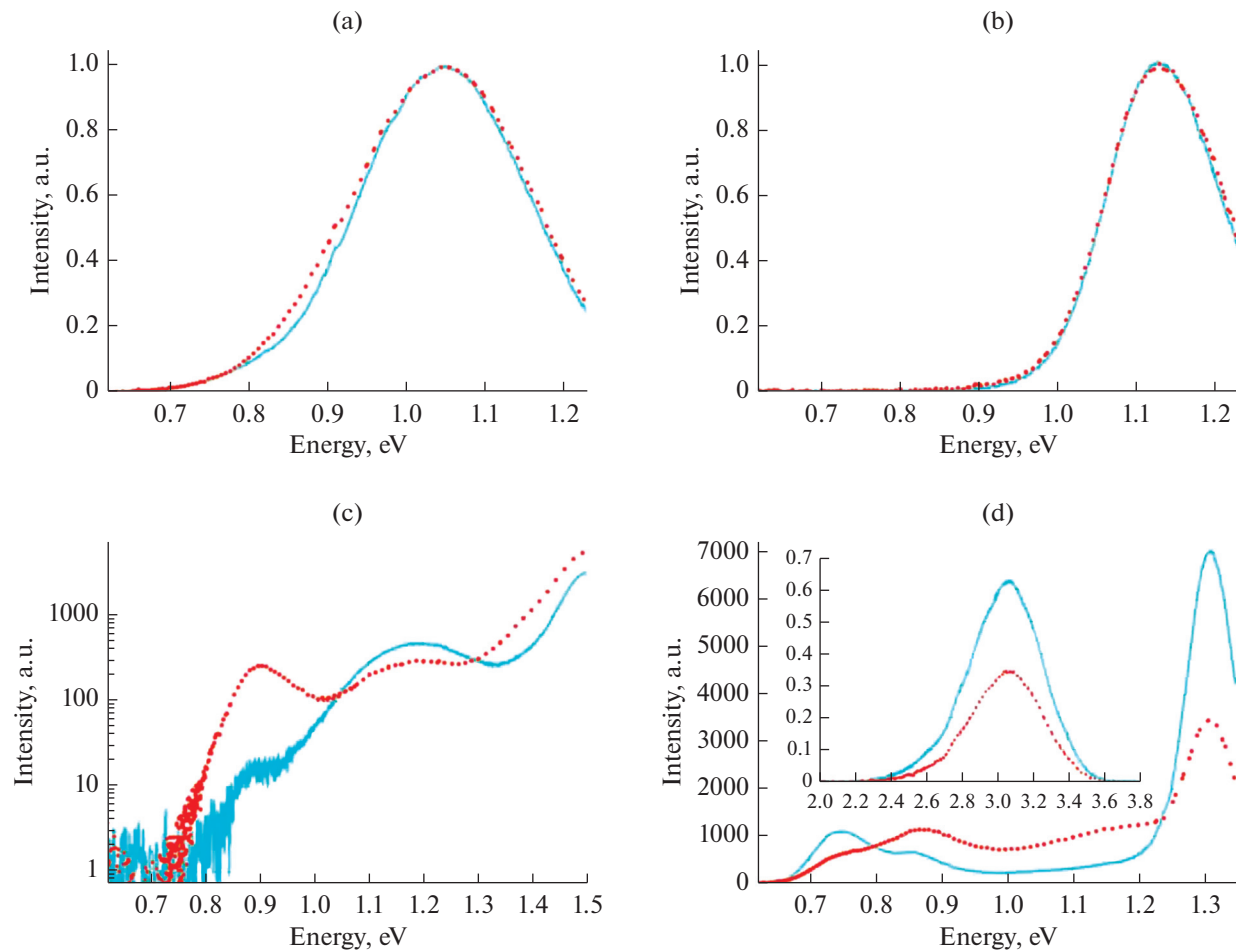


Fig. 5. Steady state NIR luminescence spectra recorded in 1–2 μm wavelength range before and after the irradiation process: (a) BiP, 2W pump at 970 nm wavelength, normalized per unity; (b) BiAl1, 2.3 W pump at 970 nm wavelength, normalized per unity; (c) BiAl1, 1.3 W pump at 808 nm wavelength (graphs are plotted in the logarithmic scale); (d) BiGeB, 3 W pump at 904 nm wavelength. The solid curves correspond to the non-irradiated samples; the dotted curves correspond to the irradiated samples. As for insertion for Fig. 5d, the curves correspond irradiation time 6 s (solid) and 1000 s (dotted).

type of glass by 904 and 970 nm wavelength diode lasers, suggest the presence of other different bismuth defects. Most likely pretenders to these defects are Bi^{2-} and Bi_2^{2-} dimers, exhibiting luminescence bands near 1050, 1300, 1450 nm wavelengths for the first and 1000, 1275, 1420 nm wavelengths for the second ones correspondingly [33]. Note that the both centers possess absorption bands near 860 and 880 nm wavelengths correspondingly that made it possible luminescence excitation by the 904 nm wavelength laser diode.

B. Silica with Phosphorous Additive

The most likely candidate to a NIR luminescent center excited at 904 and 970 nm wavelengths in the Bi-doped silica with phosphorous additive is a subvalent bismuth aggregates in the form of Bi_8^{2+} . There are

several features favoring this assumption. In the first instance, all our results indicate a cluster origin of the center responsible for NIR luminescence. The absence of satellite peaks, independent of luminescence peak spectral position on pump wavelength and its shifting with temperature signify this assumption.

In the second instance, Bi_8^{2+} center yields luminescence with a peak wavelength of 1180 nm [34], which remains unchanged with pump wavelength variation from 290 nm to 830 nm. In the third instance, it is the additive of phosphorous—an element which is reported as being coupled with oxygen possesses more acidity in comparison with silicon dioxide [35, 36]. The latter is known to be one of the necessary conditions of holding a subvalent state of bismuth inclusions in glass, both in the form of separate ions and clusters. It is a consequence of the fact that aggregations with a higher acidity would more likely accept an electron pair thus forming around a stable positively charged

bismuth cluster [37]. A similarity of NIR luminescence spectra excited at a wavelength of 808 nm obtained for this type of glass and for Bi-doped silica without additives (Figs. 1a, 1b, 2a, 2b) expects the presence of a similar type of bismuth centers in these glasses.

C. Silica with Aluminum Additive

For the silica host containing both bismuth and aluminum the NIR luminescence center is most likely an interstitial Bi⁺ ion with AlO₄⁻ in the neighborhood environment. Following arguments explains this supposition.

Firstly, it is a weak dependence of the spectral position of luminescence peak on temperature. This fact indicates that electron transitions responsible for NIR luminescence occur between two unsplit energy levels or sub-levels, resulting in a lack of the possibility for electrons in the excited state of an ion to be distributed with respect to energy according to Boltzmann equilibrium at a given temperature. Ion Bi⁺ (transition ³P₁ → ³P₀) [2, 3] fully complies with current requirement.

Secondly, it is a shift of the peak wavelength of luminescence caused by a change in the excitation radiation wavelength, that indicates a point-like nature of the center possessing essential non-uniform broadening.

Thirdly, it is a decrease of the luminescence intensity of this center as the result of glass exposure to the UV ArF laser radiation, that is known, to reduce the concentration of AlO₄⁻ [27]. This process leads to the formation of a center, which is likely associated with either interstitial bismuth atom and oxygen vacancy or interstitial BiO molecule. In doing so, due to some differences in the nearest neighborhood environment the spectrum of NIR luminescence is still slightly shifted away from the characteristic for the pure silica specimen peak in the vicinity of 0.88 eV.

D. Silica with Ge and B Additive

When pumped at 808 nm wavelength in this sample are excited bismuth centers, similar to the ones characteristic for pure silica without additives (that is, most likely, interstitial bismuth atom with a neutral oxygen vacancy V [Si–Si] [38] in the nearest neighbor environment, or, less likely, a molecule BiO). Under the excitation at 904 and 970 nm wavelengths, one of the excited centers is, apparently, interstitial bismuth atom with a GLPC or a germanium neutral oxygen vacancy V [Ge–Ge] in the environment, possessing luminescence bands centered at 1650 and 950 nm wavelengths [30]. As is known, exposure to the ArF excimer laser radiation destroys defects such as V [Ge–Ge] and GLPC in glass [25, 26] leading to a decrease of the luminescence intensity associated with this center.

Other peaks, appeared to be associated with either dimers Bi₂⁻, Bi₂²⁻, or cluster aggregates like Bi₈²⁺ and Bi₅³⁺. The latter can also contribute to the NIR luminescence spectrum, while its main maximum lies in longer wavelengths part of the spectrum [39]. However, an increase of luminescence peaks centered at 1400 and 1100 nm wavelengths caused by specimen exposure to UV laser radiation reflects in favor of negatively charged interstitial dimers, as this deep UV irradiation causes the formation of free electrons in a glass matrix, which may favor the formation of negatively charged defects.

CONCLUSIONS

We performed a study of Bi-doped silica based glasses of various compositions synthesized via SPCVD. It was demonstrated that the presence of aluminum in silica can lead to equilibrium shifting towards the formation of interstitial Bi⁺ ions rounded with AlO₄⁻, while phosphorous additive favored the formation of bismuth clusters such as Bi₈²⁺. Additional evidence was found that it is an interstitial bismuth atom with a neutral germanium oxygen vacancy V [Ge–Ge] or GLPC in the neighboring environment responsible for luminescence peaks centered at 1650 and 950 nm wavelengths excited by pumping at 904 nm wavelength.

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