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Spectroscopic study of optical centers formed in Bi-, Pb-, Sb-, Sn-, Te-, and In-doped germanate glasses

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We have shown that the broadband near-IR (NIR) fluorescence recently discovered in Bi-doped glasses is not specific due solely to Bi ions. Glasses doped with different 6*p* (Bi, Pb) and 5*p* (Sn, Sb) ions exhibit very similar behavior characterized by four major spectral peaks observed in two-dimensional excitation–emission plots and the lifetime of metastable level of about 400 μs. Our results challenge the existing models of optical centers in Bi-doped glasses. Point defect optical centers caused by the presence of 6*p* (Bi, Pb) and 5*p* (Sn, Sb) ions are proposed for the explanation of NIR emission in these laser materials. © 2008 Optical Society of America

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The rebirth of the telecommunications industry and increasing demands for broadband optical amplifiers and lasers have stimulated interest for the search of novel materials suitable for wideband operation in the near-IR (NIR) range of 1100–1600 nm [1–4]. Recent discovery of NIR emission from Bi-doped glasses [5,6] and demonstration of laser operation and amplification in the 1150–1300 nm [7–10] range raised overwhelming interest because the broadband emission and the long lifetime of metastable level are very favorable properties for inexpensive fiber-optic laser and amplifier devices. Spectroscopic properties of Bi-doped glasses of different chemical compositions have been studied in numerous publications [10–15], but nature of the optical centers is still controversial. To the best of our knowledge, all considered models involved Bi-levels as a part of the spectroscopic model, because Bi-ion was supposedly an unique ion responsible for IR fluorescence (with the exception of one publication, where Te ion was found to exhibit similar emission [16]).

The present Letter reports on spectroscopic behavior of germanate glasses doped with 6*p* (Bi, Pb) and 5*p* (Sb, Sn, In, Te). In contrast to the majority of published papers, where Bi was considered to be the unique dopant to produce IR fluorescence centers, it is shown that Pb-, Sb-, and Sn-doped glasses exhibit similar properties. These new results show the necessity to revise previously suggested models of optical centers.

GeO_2 glass samples doped with 1 mol.% Bi_2O_3 (or PbO, In_2O_3, SnO_2, Sb_2O_3, TeO_2) and 12 mol.% AlF_3 have been prepared by heating of an appropriate initial charge (Pt crucible, muffle furnace) up 1450°C for 1 h with following quenching onto a copper plate. Melting was carried out in air and nitrogen atmospheres (fluorescence was observed in Bi- and Pb-doped samples synthesized in both air and nitrogen atmospheres; Sb- and Sn- doped samples exhibit fluorescence only if synthesized in nitrogen atmosphere; In- and Te- doped samples show no emission regardless of synthesis atmosphere). Chemical compositions of the samples are shown in Table 1.

We will use the letter M to denote any M $=(\mathrm{Bi}, \mathrm{Pb}, \mathrm{Sn}, \mathrm{Sb}, \mathrm{Te}$ and In)-doped glasses where no exact specification of dopant is needed. The wing of UV high-energy band extending to the visible range of spectrum is responsible for coloration (from yellow to brown) of M-doped and (M and Al)-doped samples (except for In-doped, which is colorless). In addition, weaker bands appear at ~500, ~700, ~800, and ~1000 nm. The ratio of the intensity of strong UV band to the intensities of these weaker bands depends on M and Al contents and synthesis conditions. This indicates that the strong UV band and the above mentioned weak bands are associated with different optical centers. A similar conclusion was made for Bi-doped silica-based glasses [17].

Figure 1 shows fluorescence spectra of Bi-, Pb-, Sn-, and Sb-doped samples taken upon excitation with 514, 680, 810, and 980 nm laser lines. All glasses show similar fluorescence spectra indicating similarity of optical centers. Aluminum codoping significantly enhances fluorescence in Bi-, Pb-, Sb-, and Sn-doped samples. The role of Al is still not understood; it was shown earlier [11–13] that Al (or Ta [13]) codoping is indispensable for broadband IR emission.

The common practice is to use only a few lines of available laser sources for excitation, which have been utilized for fluorescence study of Bi-doped glasses in a number of publications [7–19]. This approach may lead to difficulties of correct interpretation of results especially if material contains different types of optical centers with a strong dependence of fluorescence on excitation wavelengths.

To obtain a full picture we have measured a whole set of fluorescence spectra taken at continuously tunable wavelengths from 400 to 1000 nm with the step of 20 nm. The data were then compiled into two-dimentional contour plots in which in-plane axes rep-

Table 1. Positions (Excitation, Emission) and Relative Intensities of A, B, C, and D Peaks (Fig. 2)

Sample		A		B		C		D	
M oxide	AlF_3 mol.%	Position	Ratio to B	Position	Ratio to B	Position	Ratio to B	Position	Ratio to B
Bi	0.75	(560, 1170)	0.45	(710,1140)	1	(800, 1280)	0.18	(1000,1140)	0.08
	3		0.62		1		0.37		0.14
	12		0.80		1		0.62		0.17
	24		0.53		1		0.37		0.16
Pb	12	(540,1120)	0.85	(710,1110)	1	(820,1260)	0.12	(1000,1120)	0.16
Sb	12	(550,1110)	0.62	(700,1110)	1	(800,1270)	0.32	(1000,1110)	0.06
Sn	12	(540,1120)	0.42	(710,1105)	1	(800,1260)	0.25	(1000,1110)	0.11
Te, In	12				no emission				

resent excitation wavelength (vertical) and fluorescence wavelength (horizontal).

Two-dimensional contour line plots are shown in Figs. 2(a) and 2(b) for Bi-doped glass and Pb-doped glass, correspondingly. Plots for Sb- and Sn-doped glasses are similar to the plots shown in Fig. 2. There are four major peaks (denoted as A, B, C, and D); their positions as (excitation, emission) coordinates are listed in Table 1. In contrast to simple fluorescence spectra, these plots take into account both excitation and fluorescence. In spite of the complex shape of the bands and strong dependence of the fluorescence spectra on excitation wavelength, optical centers in all glasses studied have the similar "fingerprints" and can be characterized by A, B, C, and D peaks.

Relative intensities of A, B, C, and D peaks depend strongly on the type of M dopant ion and concentration of both M and Al ions. Table 1 summarizes positions of A, B, C, and D peaks and their relative intensities (normalized to the strongest B peak) for Bi-doped samples with different Al content and for Pb-, Sn-, and Sb-doped samples with 12% of AlF_3. We did not find a straightforward correlation between relative intensities of the peaks and Al content and the type of M ion. It means that some of the A, B, C, and D peaks most probably belong to different optical centers, and they cannot be assigned to the energy levels of a single optical center (either type) as it was considered in numerous publications before.

All samples for M=Bi, Pb, Sb and Sn show similar decay of fluorescence on excitation into the B band at 680 nm. At the first stage of the decays there are short-lived components, while at later stages the decay is close to a single exponential with the lifetime of ~400 μs. The decays are similar to ones observed in [20]. Our preliminary data show that there are several components with the lifetimes in the nanosecond to microsecond range. These measurements show that these fast components are not the initial stage of the long-lived decay discussed above, but they most probably they originate from different optical centers (with similar excitation and emission wavelengths).

For the explanation of IR fluorescence in Bi-doped glasses, several models of optical centers have been

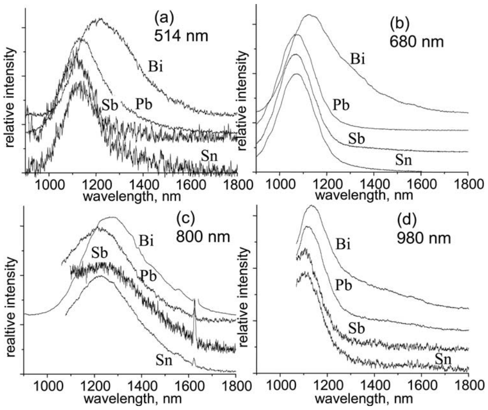

Fig. 1. Fluorescence spectra of germanate glasses doped with 1 mol.% of Bi_2O_3, PbO, SnO_2, and Sb_2O_3 and codoped with 12 mol.% of AlF_3 on excitation at (a) 514, (b) 680, (c) 800, and (d) 980 nm. The plots are vertically shifted for clarity; fluorescence intensity is about zero at 1800 nm for all samples.

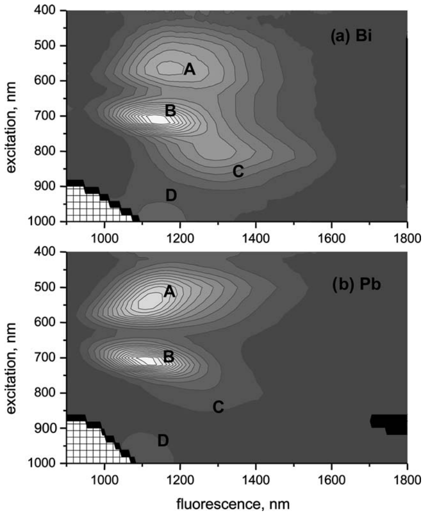

Fig. 2. Contour plots of fluorescence intensity for (a) Bi- and (b) Pb-doped (AlF_3 co-doped) germanate glasses. Sn and Sb plots are similar; for details see Table 1.

proposed in the previous literature. They include: (i) models based on splitting of energy levels of Bi ion of different valence states from Bi^{5+} to Bi^{+} [6,12]; (ii) cluster models $(Bi\text{ or }Te)_2$, $(Bi\text{ or }Te)_2^-$ [16]; and (iii) models of BiO radicals [15]. These models are based on the following assumptions: (i) Excitation bands belong to the same optical center and/or excitation is terminating on the same metastable level; (ii) free Bi ion wave functions are included in the models, and therefore strong spin-orbit interaction of Bi is to be a significant part of these considerations.

The similarity in optical properties can be expected only for the ions belonging to the same row in the periodic table (Bi and Pb) or (Sb and Sn) because 6*p* and 5*p* ions are known to easily change valence state, particularly under high temperature and reducing atmosphere conditions during glass synthesis. It is hard to expect similarity of spectra for the elements belonging to the different rows of the periodic table (Bi and Sb) or (Pb and Sn) because of very different spin-orbit constants. Spin-orbit constants for lighter 5*p* elements are about as twice as smaller than for 6*p* elements; at the same time spin-orbit constants are large for both 6*p* and 5*p* elements (several thousands inverse centimeters) [18]. The models of optical centers in Bi-doped glasses proposed in the literature are based on the electronic states of an M dopant ions; all these models should be significantly affected by spin-orbit splitting. Strong dependence of energy levels on spin-orbit constants should exist in both the models where electronic states of a free ion are considered [8,14] and for the models with molecular orbitals [15,19] and Bi clusters [15,21]. Lack of significant shift in the positions of fluorescence and excitation bands in 5*p* elements compared with 6*p* elements observed in our work raise a question about the applicability of the existing models of optical centers for explanation of the optical behavior of glasses doped with 6*p* (Bi, Pb) and 5*p* (Sb, Sn) elements.

In our opinion, the search for and development of possible models of optical centers in glasses with NIR fluorescence should be extended to point defects and localized states in glasses. It was shown that color centers related to the point defects in glasses (oxygen vacancies, bridges, unterminated bonds) might be formed under high-temperature heat treatment [22]. This assumption may also be confirmed by our experiments on Bi- and Pb-doped glass preparation at different temperatures that revealed obvious increase of optical density of the glasses with increasing temperature of synthesis.

In summary, we have shown that NIR emission that was considered to be specific only to Bi-doped (and Te-doped [16]) glasses also exists in other 6*p*-elements (Pb)- and 5*p*-elements (Sb, Sn)-doped glasses. Optical centers in these glasses are essentially the same and can be characterized by four peaks in the excitation–emission plot. In accordance with new data, the models of optical center suggested earlier should be revised to satisfy the following conditions: (i) *p* orbitals of the dopants should not be considered as a major part of the energy level model, and (ii) four bands observed in the absorption and excitation spectra are most likely to be assigned to different centers. We propose to consider point defects in glasses caused by dopants and heat treatment as possible candidates for optical centers responsible for NIR fluorescence. These 6*p* and 5*p*-elements-doped glasses offer new tunable glass lasers in the NIR (1100–1600 nm) for cw and femtosecond operation.

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