

On the nature of near-IR emitting Bi centres in glass

E.M. Dianov

Abstract. Based on analysis of the structure and optical properties of Tl, Pb and Bi centres in crystals and comparison of their spectra with the near-IR luminescence spectra of bismuth-doped glasses, a model is proposed for the near-IR emitting bismuth centres in glass. Experimental evidence is presented in support of the model.

Keywords: optically active bismuth centres in glass, bismuth-doped optical fibres.

The observation of broadband luminescence of bismuth centres in glasses widely used to fabricate optical fibres [1–3] has offered the possibility of producing bismuth-doped fibres suitable as a gain medium in the spectral region 1100–1500 nm, where no efficient fibre lasers and/or optical amplifiers were until recently available.

In 2005, the first bismuth-doped silica glass fibres were fabricated [4, 5] and cw operation of a bismuth-doped fibre laser was demonstrated [6]. These advances have sparked intense interest in bismuth-doped materials. Broadband near-IR luminescence has been found and investigated in many glasses and crystals. The bismuth-doped fibre lasers and amplifiers created to date cover the spectral region 1100–1550 nm (see e.g. Refs [7–9]). However, the nature of the near-IR emitting bismuth centres is not yet clear. The proposed models of the Bi centres consider Bi^{5+} [2] and Bi^+ [10] ions, Bi clusters [11], Bi_2 and Bi_2^- molecules [12–14], BiO radicals [15], Bi-related point defects [16] and other species. Unfortunately, none of these models is supported by any direct, conclusive evidence.

At the same time, the results of extensive research into the luminescence spectra and lasing performance of crystals doped with Tl and Pb – bismuth's neighbours in the sixth period of the Periodic Table, similar in properties – allow more definite conclusions to be drawn as to the origin of the IR Bi luminescence in glasses and glass fibres.

The optical properties of Tl-doped alkali halide crystals (KCl, KBr, RbCl and others) were studied extensively in the 1980s. X-ray and gamma irradiations were shown to produce near-IR emitting defect centres in these materials

(see e.g. [17–20] and references therein). Detailed studies of such centres enabled the structure of at least three of them to be identified. $\text{Tl}^0(1)$ and $\text{Tl}^0(2)$ centres have the form of a Tl^0 neutral atom on the cation site near an anion vacancy and between anion vacancies, respectively. $\text{Tl}^0(1)$ is a lasing centre whose transitions enable laser operation tunable over the range 1400–1700 nm [18, 19]. A Tl dimer centre is composed of Tl^+ and Tl^0 near an anion vacancy [20]. This centre has three absorption bands in the range 635–1110 nm and emits in the range 1450–1505 nm in KCl, RbCl and KBr crystals.

X-ray irradiation of Pb-doped CaF_2 , SrF_2 and BaF_2 crystals was reported to produce similar near-IR emitting centres [21, 22]. These include $\text{Pb}^+(1)$ (a Pb^+ ion near an anion vacancy), a $\text{Pb}^+(1)\text{--Pb}^{2+}$ dimer (Pb^+ and Pb^{2+} near a vacancy) and $\text{Pb}^0(2)$ (Pb^0 between two anion vacancies). The relative amounts of these centres depend on irradiation temperature and initial Pb concentration. The formation of such optical centres is not accidental: Tl^0 and Tl^+ are isoelectronic with Pb^+ and Pb^{2+} , respectively.

Figure 1a shows the emission spectra of the $\text{Pb}^+(1)$ centre (excitation wavelength $\lambda_{\text{ex}} = 660$ nm), $\text{Pb}^+(1)\text{--Pb}^{2+}$ dimer ($\lambda_{\text{ex}} = 740$ nm) and $\text{Pb}^0(2)$ centre ($\lambda_{\text{ex}} = 1020$ nm) in a $\text{SrF}_2:\text{Pb}^{2+}$ crystal gamma-irradiated at 300 K. The spectra were measured at 10 K. The quantum yield of luminescence was close to unity up to room temperature.

Ruan et al. [24] studied optically active Bi centres in a BaF_2 crystal and observed luminescence bands centred at 1070 and 1500 nm when the crystal was pumped at 500 and 700 nm. Given that Bi^{2+} and Bi^+ are isoelectronic with Pb^+ and Pb, respectively, the bands were assigned to $\text{Bi}^{2+}(1)$ and $\text{Bi}^+(2)$ centres, analogous to the $\text{Pb}^+(1)$ and $\text{Pb}^0(2)$ centres. No luminescence of any dimer centre was detected, which was attributed to the low Bi concentration (1 at %) in the BaF_2 .

Thus, at excitation wavelengths from 400 to 1000 nm, the optically active Tl, Pb and Bi centres in crystals have near-IR luminescence bands in the range 900–1700 nm.

Given that the IR bismuth luminescence bands in almost all the bismuth-doped glasses and glass fibres studied to date are also located in this spectral region (Figs 1b, 1c) and that Tl^0 , Pb^+ and Bi^{2+} are isoelectronic with each other ($6s^2 6p^1$), there are substantial grounds to believe that the near-IR emitting bismuth centres in glasses are optical defect centres similar to the Tl, Pb and Bi centres in crystals. Because Bi and Pb are similar in many properties, and also because Pb^0 , Pb^+ and Pb^{2+} are isoelectronic with Bi^+ , Bi^{2+} and Bi^{3+} , respectively, it is reasonable to assume that Bi-doped glasses may contain the following optical defect

E.M. Dianov Fiber Optics Research Center, Russian Academy of Sciences, ul. Vavilova 38, 119333 Moscow, Russia;
e-mail: dianov@fo.gpi.ru

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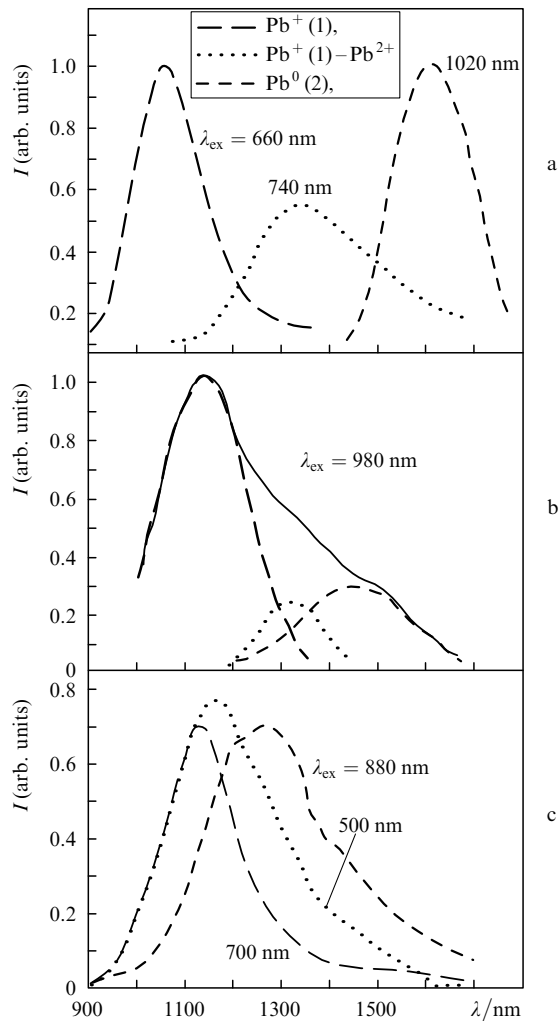


Figure 1. Luminescence spectra of (a) optically active Pb centres in a SrF_2 crystal [21], (b) bismuth-doped germanosilicate glass [23] (the solid line shows the measured spectrum and the broken lines represent Gaussian components) and (c) bismuth-doped $\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ glass excited at different wavelengths [14].

centres: $\text{Bi}^{2+}(1)$ (Bi^{2+} + an oxygen vacancy or another anion vacancy), $\text{Bi}^{2+}(1)-\text{Bi}^{3+}$ dimer (Bi^{2+} and Bi^{3+} separated by a vacancy) and $\text{Bi}^+(2)$ (Bi^+ between two vacancies). If this is so, it can be inferred from the luminescence spectra of Bi in various glasses with Bi concentrations high enough (at least 1 mol %) for dimer formation and from comparison with the spectra of Pb in crystals (Fig. 1) that the luminescence bands near 1100 and 1300 nm in bismuth-doped glasses are due to the $\text{Bi}^{2+}(1)$ and dimer centres, respectively.

Given that the glass network has a disordered structure and contains a variety of defects, it seems likely that optical defect centres may contain not only anion vacancies but also other defects of the glass network, which may modify the defect centres, causing a slight shift of the luminescence bands. Depending on glass composition and preparation conditions, only some of the above defect centres may form.

The proposed configurations of optically active bismuth centres are supported by the following experimental evidence:

(i) Near-IR luminescence is observed in Pb-doped germanosilicate fibres [25] and germanate glasses [16].

The luminescence bands are located around 1100 and 1260 nm, which suggests that they are due to the $\text{Pb}^+(1)$ and dimer centres, respectively (Fig. 1a). On the other hand, almost all Bi-doped glasses have luminescence bands around 1100 and 1300 nm. One very important conclusion from the above is that the position of the luminescence bands of the optically active Pb and Bi centres depends little on host composition and structure (glass or crystal).

(ii) Experimental data [14] demonstrates that the 500-nm absorption coefficient of bismuth centres in Bi-doped glasses varies quadratically with bismuth concentration (Fig. 2), which can be interpreted as evidence of Bi dimer formation. Moreover, the net charge on the dimer was determined to be $5+$ [26], which coincides with the charge on the proposed dimer $\text{Bi}^{2+}(1)-\text{Bi}^{3+}$.

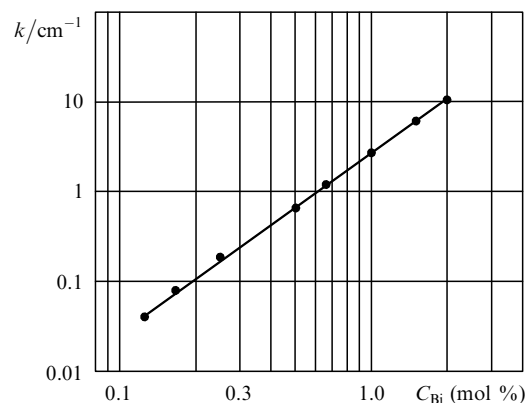


Figure 2. 500-nm absorption coefficient of bismuth centres in glass as a function of bismuth content.

(iii) Bi-, Pb-, Sn- and Sb-doped germanate glasses have very similar near-IR luminescence spectra at various excitation wavelengths [16]. Sharonov et al. [16] believe that the observed luminescence is due to point defects or local states produced in the glass by the dopants. They, however, did not propose any structure of the optical centres. The above experimental data and their interpretation strongly suggest that the Bi-, Pb-, Sn- and Sb-doped glasses contain similar optical defect centres and, hence, have similar luminescence spectra. This can be inferred by examining the following series of elements with the isoelectronic structure ns^2np^1 : Tl^0 , Pb^+ , Bi^{2+} , Sn^+ and Sb^{2+} . It then becomes clear why glasses doped with Sn and Sb luminesce only when prepared in a nitrogen atmosphere [16], in contrast to those doped with Pb and Bi. It is well known that Pb^{2+} and Bi^{3+} can easily be reduced at high temperatures, whereas the reduction of Sb^{3+} and Sn^{4+} requires a nitrogen atmosphere.

Finally, the structure of the proposed defect centres is consistent with ample experimental evidence that the near-IR luminescence is due to bismuth in a low valence state.

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