Optical properties of active bismuth centres in silica fibres containing no other dopants

I.A. Bufetov, S.L. Semenov, V.V. Vel'miskin, S.V. Firstov, G.A. Bufetova, E.M. Dianov

Abstract. **Optical fibre preforms and fibres with a bismuth-doped silica core containing no other dopants have been fabricated by the powder-in-tube technique. The optical loss has been measured for the first time in such fibres in a wide spectral range, from 190 to 1700 nm. We have studied the luminescence of active bismuth centres and the luminescence lifetime for some of their bands in both the preforms and the fibres drawn out from them.**

Keywords: *bismuth, broadband IR luminescence, bismuth-doped optical fibre.*

Bismuth-doped optical fibres are potentially attractive as active media of amplifiers for the next generation of broadband optical fibre communication systems, with an optical gain in the range 1300–1500 nm, and as active media of fibre lasers in the range 1150–1550 nm [1]. No model consistent with all experimental data reported for IR-emitting active bismuth centres (ABCs) in bismuth-doped glasses has however been proposed to date despite the intense research in this direction (see, e.g., Dianov [2]), which suggests that the ABCs have a complex structure. The optical properties of bismuth-doped silica fibres are known to be significantly influenced by other dopants present in the glass [1]. The addition of aluminium, phosphorus, germanium, titanium and other elements to bismuth-doped silica glasses modifies their luminescence and absorption spectra, giving rise to a variety of lines due to ABCs coordinated to silicon, aluminium, phosphorus, etc. In this context, there is special interest in the study of the SiO_2–Bi system, with no other dopants, where only ABCs associated with silicon may be present. The first data on the visible and IR luminescence of bismuth-doped pure silica fibres were reported by Neff et al. [3]. The ABCs in such glass were shown to luminesce in the visible and IR spectral regions when pumped at 337 and 488–514 nm at

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room temperature. Very recently, Razdobreev et al. [4] have demonstrated and investigated a low-temperature (10 K) luminescence of sol-gel derived bismuth-doped silica glass.

The objective of this work was to fabricate Bi-doped silica fibres and study their optical properties. Fibre preforms were produced by the powder-in-tube technique as described elsewhere [3, 5]. The raw materials used were SiO_2 (particle size, 50–200 μm) and Bi_2O_3 (1–10 μm) powders. Appropriate amounts of the powders were weighed out on a laboratory balance and thoroughly mixed. The powder mixture composition was adjusted so that the mole fraction of Bi_2O_3 in the glass was 0.03 % to 0.05 %.

The cladding material was Heraeus F300 high-purity silica glass. The outer diameter of the silica tube was 15 mm, and the wall thickness was 1.3 mm. Immediately before the fusion step, the tube was filled with a mixture of the SiO_2 and Bi_2O_3 powders. Next, the tube was placed in a glass-blowing lathe and connected to a vacuum system. The powder mixture was fused under vacuum at a temperature slightly below 1900 °C using an oxygen-propane torch. This process led to complete sintering of the powders and partial bismuth diffusion to the silica glass.

The resultant preform, 300 mm in length and 12 mm in diameter, was deep brown in colour. An outer layer of the pure-silica cladding was removed by dissolving it away in concentrated hydrofluoric acid, so that the preform diameter was reduced to 8 mm. Next, the preform was drawn at 1850 °C into 125-μm-diameter fibre coated with a polymer whose refractive index was smaller than that of silica glass. Subsequently, we studied the optical properties of both the resultant multimode bismuth-doped fibre and the preform it was drawn out from.

The optical loss in the bismuth-doped fibres and preforms was measured between 190 and 1700 nm (Figs 1, 2). In the range 300–1700 nm, the loss was evaluated by comparing the transmittance of different lengths of the fibre (from several centimetres to 10 m). The UV loss was measured on a Shimadzu UV-3101PC spectrophotometer. The polished platelets 1–5 mm in thickness, cut perpendicular to the preform axis, were used in these experiments. Note that, on the whole, the optical loss spectrum of the Bi-doped silica fibre is considerably simpler than the absorption spectra of bismuth-doped fibres studied previously (see, e.g., [1]).

The optical loss spectrum of the fibre (Fig. 1) shows a broad IR absorption band centred at 1400 nm, which consists of two components, one due to ABCs and the other to OH groups. The presence of OH groups is

evidenced by the facts that the top part of the band is asymmetric and that the peak absorption wavelength is 1380 nm. The absorption coefficient at 1380 nm (OH groups) was estimated to be several dB m^{-1}. At wavelengths under 1100 nm, the optical loss rises rapidly with decreasing wavelength, and there is a prominent absorption peak at 820 nm, with a full width at half maximum (FWHM) of 33 nm. On the whole, the spectrum can be decomposed into a number of elementary components, the most prominent of which are the sharp features at 377 (*1*) and 422 nm (*2*) and the broader feature at 470 nm (*3*). It is also worth noting the dip in the optical loss spectrum between features (*1*) and (*2*), centred at 400 nm (Fig. 1, inset).
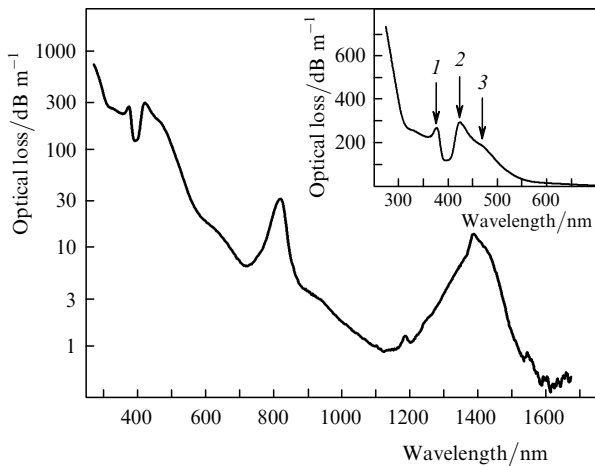

Figure 1. Optical loss spectrum of the fibre. Inset: portion of the spectrum with a linear vertical axis.

In the UV spectral region, the optical loss rises further with decreasing wavelength (Fig. 2). At 190 nm, the loss reaches $\sim 8 \times 10^3$ dB m^{-1}. On the long-wavelength side of the strong absorption band with a centre wavelength under 190 nm, there is an absorption peak at 227 nm, which has FWHM = 30 nm and a height of about 3×10^3 dB m^{-1} (Fig. 2, inset). This peak seems to be due to Bi^{3+} [6, 7]. For comparison, Fig. 2 shows the absorption spectrum of
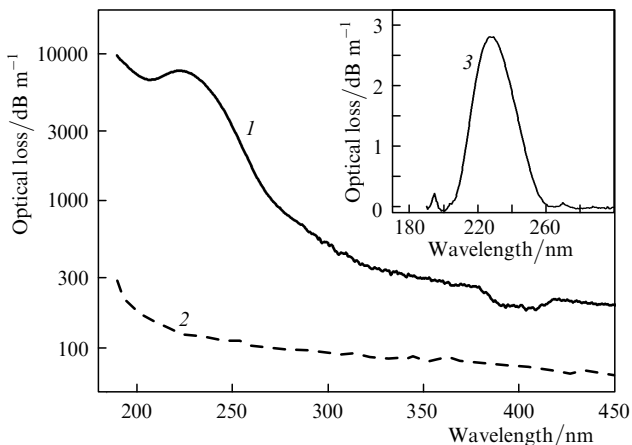

Figure 2. Optical loss spectrum of the fibre preform (*1*). Shown for comparison is the spectrum of pure SiO$_2$ (substrate tube) (*2*). Inset: absorption band centred at 227 nm (*3*).

bismuth-free silica glass. The optical loss spectrum of the fibre preform also has a dip near 400 nm (Fig. 2), which is, however, weaker than that in the loss spectrum of the fibre (Fig. 1).

The luminescence spectra of the bismuth-doped silica fibres and preforms were measured using excitation sources with different wavelengths: a frequency-doubled (244 nm) argon laser, frequency-doubled (457 nm) neodymium solid-state laser operated at 914 nm, frequency-doubled (532 nm) neodymium laser operated at 1064 nm, single-mode laser diode (808 nm), ytterbium fibre laser (1058 nm) and Raman fibre laser (1230 nm).

The excitation light was launched into the fibre (or into the preform core at an excitation wavelength of 244 nm) along its axis, and the luminescence spectrum was obtained in a 90° geometry using an HP70950B spectrum analyser in the IR and an Ocean Optics USB 2000 spectrograph in the range 200–800 nm. All the spectra in Fig. 3 are corrected for the spectral response of the instrument and normalised to the maximum luminescence intensity (except for the luminescence spectrum in Fig. 3a in the range 190–400 nm, where the unprocessed signal from the linear photodiode array of the spectrograph is given).
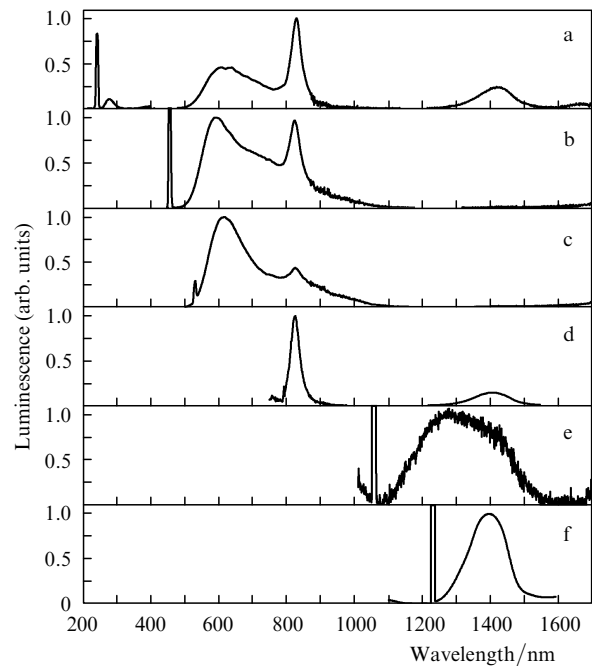

Figure 3. Luminescence spectra of Bi-doped silica fibres and their preforms at excitation wavelengths of (a) 244, (b) 457, (c) 532, (d) 808, (e) 1058 and (f) 1230 nm.

The luminescence band at $\lambda_{max} \approx 280$ nm, present in Fig. 3a (excitation at 244 nm) and in the emission spectra of many bismuth-free fibres, is due to the luminescence of an oxygen-deficient silicon defect centre [8]. The red luminescence band centred at $\lambda_{max} \approx 600$ nm (Figs 3a–3c) is only observed for the bismuth-doped fibres and is attributable to Bi^{2+} luminescence, as suggested by data for crystals [9, 10].

The narrow luminescence band centred at $\lambda_{max} \approx$ 825 nm (as well as the related absorption band at 820 nm) is no doubt due to ABCs and emerges at excitation wavelengths of 244, 457, 532 and 808 nm (resonance excitation). A similar band was observed in a bismuth-

doped germanosilicate glass fibre under 457-nm excitation [11]. The 935-nm luminescence band that was observed in the germanosilicate fibre and had roughly the same width is missing in the spectra of the Bi-doped silica fibres and is, therefore, assignable to germanium-modified ABCs. That the 825-nm band is due to ABCs is evidenced by the fact that, when pumped in this band (at 808 nm), bismuth-doped fibres show lasing at 1320 nm [12]. The luminescence band centred at $\lambda_{max} \approx 1400$ nm is well seen at excitation wavelengths of 244, 808 and 1230 nm. It is due to ABCs associated directly with silicon. Bismuth-doped phosphosilicate glass fibres have luminescence bands at $\lambda_{max} \approx 1300$ nm (phosphorus-related ABCs) and $\lambda_{max} \approx 1400$ nm (ABCs associated with silicon) [13]. Germanosilicate fibres have only one luminescence band in this range, at $\lambda_{max} \approx 1400$ nm, which can be interpreted as evidence that the ABC luminescence bands related to the presence of silicon and germanium are close in position. The fact that, in our experiments, excitation in an absorption band of Bi^{3+} (244 nm) leads to ABC luminescence at 825 and 1400 nm suggests that this ion is directly involved in the formation of IR-emitting Bi centres (or that there is an effective mechanism of excitation energy transfer from Bi^{3+} to active bismuth centres). At an excitation wavelength of 1058 nm, we observe weak luminescence (as evidenced by the high noise level) in the range $1200-1450$ nm (Fig. 3e). The excitation wavelength here falls on the tails of several absorption bands.

We measured the luminescence decay time for the bands at $\lambda_{max} \approx 825$ and 1400 nm under pulsed 808-nm excitation. In both cases, the luminescence decay is well represented by a single exponential, with a characteristic time $\tau = 40$ μs (825-nm band) and $\tau = 640$ μs (1400-nm band). The long 1400-nm luminescence lifetime suggests that silicon-related ABCs might be used for lasing and amplification at this wavelength, which seems to have been achieved in experiments with aluminosilicate fibre containing ABCs coordinated to both aluminium and silicon [14].

The present results are similar in a number of aspects to the data reported by Razdobreev et al. [4], but they are difficult to directly compare because different samples were used: Razdobreev et al. [4] studied monolithic fibre preforms produced by fusion at $\sim 1300\,°C$, whereas we studied fibres drawn out at $\sim 2000\,°C$. Moreover, all our measurements were made at room temperature, whereas Razdobreev et al. [4] reported only 10-K luminescence measurements.

Thus, we have measured the optical loss in bismuth-doped silica fibres in the range $190-1700$ nm and the luminescence spectra of the fibres and preforms in the range $244-1700$ nm. The results lead us to conclude that the samples studied contain both Bi^{3+} and Bi^{2+} ions, which may participate in the formation of near-IR emitting bismuth defect centres according to the model of ABCs proposed by Dianov [2]. The IR luminescence of Bi^{3+} may also originate from its ability to effectively transfer excitation energy to active bismuth centres.

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