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# Anti-Stokes luminescence in bismuth-doped alumino- and phosphosilicate fibres under two-step IR excitation

S.V. Firstov, K.E. Riumkin, V.F. Khopin, S.V. Alyshev, E.G. Firstova, M.A. Mel'kumov, A.N. Gur'yanov, E.M. Dianov

***Abstract.*** **We have studied the luminescence properties of optical fibres with a bismuth-doped alumino- and phosphosilicate glass core under two-step excitation and obtained new experimental data on the properties of luminescence centres in such fibres.**

***Keywords:*** *bismuth, optical fibre, bismuth centres, two-step excitation.*

## 1. Introduction

Bismuth-doped optical fibres are gain media possessing unique optical and lasing characteristics, which are determined primarily by the physicochemical properties of the dopant. To date, bismuth-doped fibres have been demonstrated that possess gain in the range 1100–1800 nm. Using such fibres, the world's first lasers and amplifiers operating in the range 1140–1775 nm have been made (at the Fiber Optics Research Center, Russian Academy of Sciences) [1–6]. It should be noted that the potentialities of these gain media have not yet been fully explored. The low bismuth concentration in the fibres employed in lasers and the rapid rise in unbleachable losses with increasing bismuth concentration [7, 8] are the main factors that impede many potential applications of such fibres. Such difficulties cannot be overcome without a clear understanding of the physical nature of the bismuth-related active centres (BACs), which remains the subject of discussion. There is no doubt that further research and accumulation of experimental data on such media will provide a more detailed insight into the nature and properties of the bismuth centres, which is important for the ability to create laser media with improved performance parameters.

It is worth noting that a characteristic feature of the bismuth-doped fibres is that their optical properties strongly depend on the chemical composition of the glass. On the one hand, this ensures lasing in a wide spectral range. On the other, this presents serious difficulties in analysis and interpretation of results, including luminescence spectra of fibres, because absorption and luminescence bands of different active centres strongly overlap. Some advances in understanding the luminescence properties of the BACs have been made using fibres with simple compositions: $SiO_2$ + Bi and $GeO_2$ + Bi. It has been shown that such media typically contain only one type of IR centre, responsible for optical gain and lasing in the near-IR spectral region, and energy level diagrams of such centres have been determined. However, even in this case the use of two characterisation techniques was necessary: combined excitation–emission spectroscopy (CEES) (contour plots of luminescence intensity against excitation and emission wavelengths) [9, 10] and two-step excitation spectroscopy (TSES) [11]. TSES allows one to study the properties of BACs having a certain energy level structure, which significantly differentiates it from CEES.

Optical fibres of more complex compositions (bismuth-doped phospho- and aluminosilicate fibres), which typically have inhomogeneously broadened absorption and luminescence bands, have already been studied by CEES. However, in contrast to fibres with simple compositions, the energy level positions of the BACs in such fibres are difficult to determine, especially in the case of aluminosilicate fibres [9].

In this paper, we present our findings on the luminescence properties of bismuth-doped alumino- and phosphosilicate fibres under two-step IR excitation (TSES).

## 2. Experimental

We studied single-mode optical fibres with a second order mode cutoff wavelength near 1 μm. The fibres were drawn out from MCVD preforms. The fibre core was ~6–8 μm in diameter and consisted mostly of bismuth-doped silica glass with small additions (2–4 mol%) of $P_2O_5$ or $Al_2O_3$. The total bismuth concentration in all the fibres was within 0.02 at% (sensitivity limit of our analytical facilities). Note that the aluminosilicate fibres contained different active centre concentrations, which were estimated from the absorption in the fibres. The main characteristics of the fibres are presented in Table 1.

In this study, sequential two-step excitation was used in luminescence measurements. The experimental setup was described in detail elsewhere [11]. Previously, this setup was successfully used to study BACs in optical fibres with simple

**S.V. Firstov** Fiber Optics Research Center, Russian Academy of Sciences, ul. Vavilova 38, 119333 Moscow, Russia; Institute of Physics and Chemistry, N.P. Ogarev Mordovian State University, Bol'shevistkaya ul. 68, 430005 Saransk, Russia; e-mail: fir@fo.gpi.ru;
**K.E. Riumkin, S.V. Alyshev, E.G. Firstova, M.A. Mel'kumov, E.M. Dianov** Fiber Optics Research Center, Russian Academy of Sciences, ul. Vavilova 38, 119333 Moscow, Russia;
**V.F. Khopin, A.N. Gur'yanov** G.G. Devyatykh Institute of Chemistry of High-Purity Substances, Russian Academy of Sciences, ul. Tropinina 49, 603950 Nizhnii Novgorod, Russia

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**Table 1.** Characteristics of the bismuth-doped fibres.

| Sample | Composition | Absorption*/dB m$^{-1}$ | Optical gain/dB m$^{-1}$ at 300/77 K |
|---|---|---|---|
| P1 | $P_2O_5-SiO_2-Bi$ | 0.27 | ~0.05/no data |
| A1 | $Al_2O_3-SiO_2-Bi$ | 1.5 | 0.3/0.5 |
| A2 | $Al_2O_3-SiO_2-Bi$ | 8.6 | No gain/2 |
| A3 | $Al_2O_3-SiO_2-Bi$ | 50 | No gain |

*The absorption coefficient at a wavelength of 1000 nm for the aluminosilicate fibres and at $\lambda$ = 1240 nm for the phosphosilicate fibre.

compositions (bismuth-doped silica and germanate glass cores). Two-step luminescence excitation was also used in studies of rare-earth-doped media (see e.g. Arahira et al. [12]). The basic principle of this method is that radiation at two different wavelengths is used to excite a gain medium. One wavelength is fixed and corresponds to a certain transition – ground state absorption (GSA) or excited state absorption (ESA) – and the other is varied with a certain step. Anti-Stokes luminescence is observed when the excitation photon energy coincides with a transition energy (resonant excitation).

In our measurements, excitation was provided by a supercontinuum source (Fianium SC450). From the broad supercontinuum spectrum, two spectral bands around $\lambda_{ex1}$ and $\lambda_{ex2}$ (with a bandwidth $\Delta\lambda$ ~ 5 nm) were cut by an acousto-optic filter. The wavelength $\lambda_{ex1}$ was constant, whereas $\lambda_{ex2}$ was varied from 1100 to 2000 nm in 10-nm steps. The optical power at both excitation wavelengths was 200–700 μW. Luminescence was detected in the range 400–1600 nm on two spectrometers: Ocean Optics QE65000 and NIRQuest. The measurements were performed at room temperature and liquid-nitrogen temperature. In data processing, the luminescence spectra were normalised to the transmission function of the measuring system, the excitation power and the spectral sensitivity of the spectrometer.

## 3. Results and discussion

Figure 1 shows luminescence spectra of the phosphosilicate fibre (P1) under two- and one-step excitation. It is seen that, in both cases, there is luminescence in the range 750–780 nm.

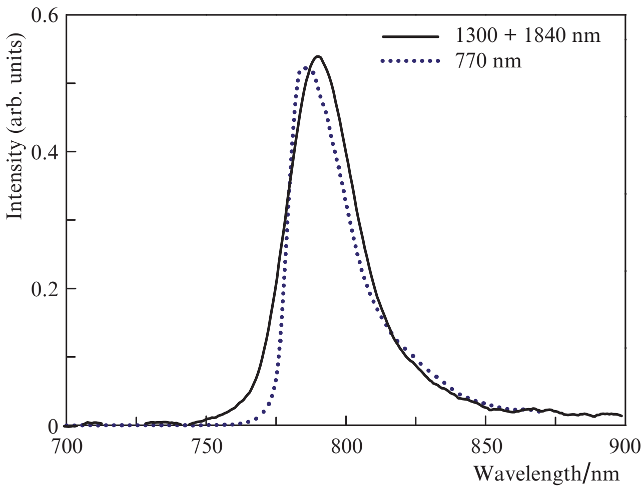


**Figure 1.** Luminescence spectra of sample P1 under one-step (770 nm) and two-step (1300 + 1840 nm) excitation.

The observed similarity between the Stokes and anti-Stokes luminescence spectra obtained with the two excitation schemes suggests that, in both cases, luminescence is due to the same optical transition of the same active centre. A similar situation was observed for the aluminosilicate sample A1, but the luminescence peak was then located at a shorter wavelength (~740 nm) in comparison with sample P1.

Figure 2 shows the anti-Stokes luminescence intensity as a function of excitation wavelength $\lambda_{ex2}$ for fibres A1 and P1. It is seen that both fibres have two excitation bands, in the short- and long-wavelength regions. The position of the former band corresponds to the energy of the transition between the ground and first excited (metastable) state, whereas the position of the latter corresponds to the transition between the first excited (metastable) and second excited states. Also shown in Fig. 2 are the optical gain spectra of the fibres. That the shapes and spectral positions of the shorter wavelength bands in the spectra of both the alumino- and phosphosilicate fibres are similar to those of the optical gain bands suggests that the anti-Stokes luminescence results from a transition between energy levels of the active centre responsible for the optical gain.

Figure 3 presents data obtained for different types of optical fibre (including pure silica and germanate glass fibres described elsewhere [11]). In the spectral region under consideration, all the fibres have two characteristic bands, whose position depends on the dopant in the silica glass. It is seen

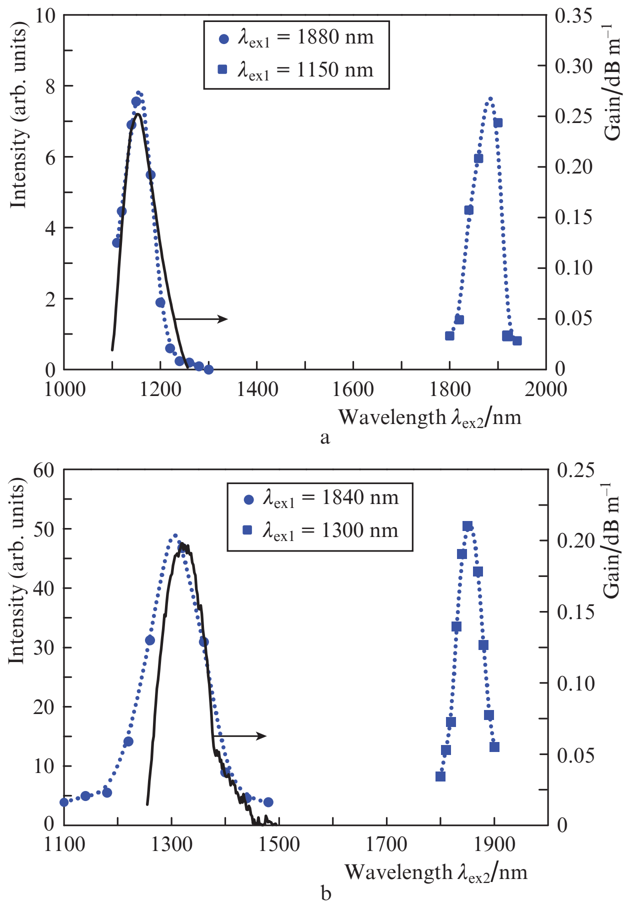


**Figure 2.** Anti-Stokes luminescence excitation spectra under two-step excitation (dotted lines) and optical gain spectra (solid lines) for the bismuth-doped (a) aluminosilicate and (b) phosphosilicate fibres.

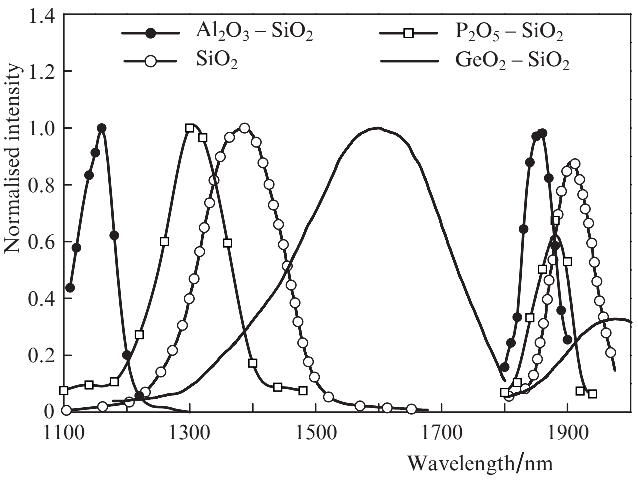


**Figure 3.** Anti-Stokes luminescence intensity as a function of excitation wavelength (under two-step excitation) for different types of optical fibre.

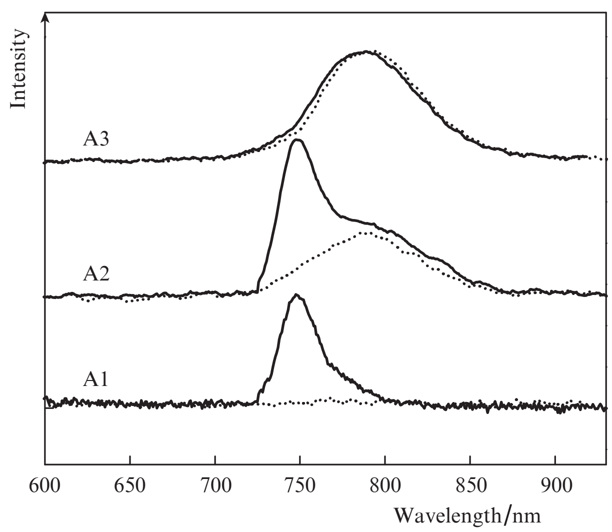


**Figure 4.** 77-K anti-Stokes luminescence spectra of the aluminosilicate fibres A1–A3, differing in absorption, under one-step (1150 nm) (dotted lines) and two-step (1150 + 1880 nm) (solid lines) excitation.

that, in the case of the BACs in the alumino- and phosphosilicate fibres, the bands are located at shorter wavelengths, i.e. the transition energies of the BACs in these fibres are higher than those in the pure silica fibre.

The opposite situation is observed for the BACs in the germanosilicate glass, where transition energies are lower than those of the BACs in silica glass. The experimentally determined energy level positions of the BACs in the aluminosilicate fibres are about 8770 and 13 510 $cm^{-1}$. On the whole, the results obtained for the spectral range 1100–2000 nm suggest that the active centres in the glasses under consideration have similar energy level diagrams.

It is worth noting that the above results on two-step excitation refer to laser fibres with low bismuth concentrations. It is known that increasing the total bismuth concentration may have a negative effect on the optical and lasing characteristics of the fibres (especially in the case of aluminosilicate fibres) because it leads to a considerable increase in unbleachable losses [13, 14] and a decrease in optical gain [7]. For this reason, we used TSES to study aluminosilicate fibres differing in absorption. In addition to sample A1, we used fibres A2 and A3, with a stronger absorption. The main distinction between these samples was that sample A2 showed optical gain only at a temperature of 77 K, whereas sample A3 had zero gain at both 300 and 77 K (Table 1).

Figure 4 shows the 77-K anti-Stokes luminescence spectra of the fibres under one-step and two-step excitation. It is seen that the samples have different anti-Stokes luminescence spectra. In particular, sample A1 has a narrow anti-Stokes luminescence band at a wavelength of 750 nm only under two-step excitation (1150 + 1880 nm), whereas fibre A2 has an additional, broader luminescence band around 780 nm, which can be excited at one wavelength (in particular, at 1150 nm). The narrow band at 750 nm is only observed under concurrent excitation at both wavelengths. Fibre A3 has only a broad anti-Stokes luminescence band. We failed to detect a narrow luminescence band around 750 nm. Thus, the present results indicate, first, that the anti-Stokes luminescence band around 750 nm is due to bismuth-related active centres responsible for optical gain and lasing and, second, that increasing the percentage of bismuth leads to the formation of additional emission centres with broader luminescence bands, whereas the laser active centres disappear.

For sample A3, with a large absorption coefficient, we also obtained the spectral dependence of intensity for the broad anti-Stokes luminescence band centred at 780 nm (one-step excitation) and that of excited state absorption (ESA) at a wavelength of 1100 nm under excitation at $\lambda_{ex}$ = 975, 1060, 1240 and 1460 nm (the ESA measurement scheme was described in detail elsewhere [15]). The results are presented in Fig. 5. It is worth noting that ESA was observed at all the wavelengths used and that the absorption coefficient was found to decrease monotonically with increasing $\lambda_{ex}$ (as was the observed anti-Stokes luminescence intensity). The maximum induced absorption (~80 dB $m^{-1}$) was obtained at $\lambda_{ex}$ = 975 nm.

In addition to the ESA, we measured the IR Stokes luminescence due to the transition of the BACs from the first

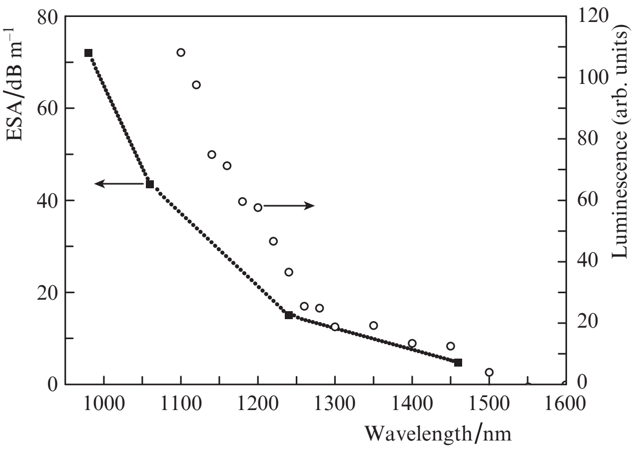


**Figure 5.** 780-nm anti-Stokes luminescence intensity and 1100-nm excited state absorption (ESA) as functions of excitation wavelength for sample A3.

excited state level to the ground level and the anti-Stokes luminescence due to the transition of the BACs from the second excited state level to the ground level. The excitation source used was a 1240-nm semiconductor laser diode with an output power of ~300 mW. The results are presented in Fig. 6. It is seen that the Stokes luminescence intensity is a linear function of excitation power up to 10 mW, whereas the anti-Stokes luminescence intensity increases quadratically. At higher excitation powers, the IR luminescence intensity increases more gradually (with a slope of ~0.5 on the log–log graph), as does the anti-Stokes luminescence intensity (a slope of ~1). At the same time, no IR luminescence saturation was observed even at an excitation power of ~300 mW (intensity of ~1 MW $cm^{-2}$), which is several times the saturation power for the IR luminescence of the BACs in fibres used for lasing [16, 17].

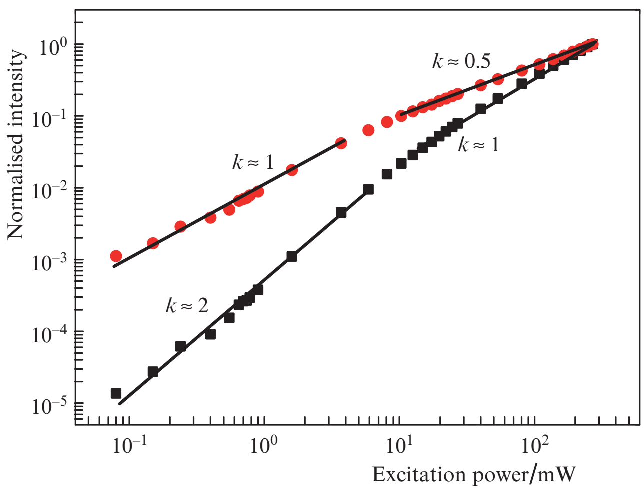


**Figure 6.** Log–log graphs of the Stokes (●) and anti-Stokes (■) luminescence intensity against excitation power for fibre A3.

The luminescence saturation vs. excitation power data obtained here are typical of optical media in which there is energy transfer between active centres, which results in a transition from an excited state to a higher energy level, i.e. an upconversion process. It seems likely that it is upconversion that determines the effect of excitation power on luminescence saturation. Detailed calculations using rate equations for such systems have been the subject of a number of studies (see e.g. Pollnau et al. [18]). Their results are not inconsistent with the possibility that not only upconversion but also excited state absorption may occur in such a system. Upconversion processes in bismuth-doped fibres were assumed previously [17, 19].

Thus, in the fibres with a strong absorption, anti-Stokes luminescence may result from two processes: ESA and upconversion. The data presented in Fig. 4 demonstrates that the broad anti-Stokes luminescence band around 780 nm has a high intensity in the fibres with a strong absorption and is undetectable in the fibres with a weak absorption. Thus, the broad anti-Stokes luminescence band observed in the fibres with a 1000-nm absorption of 10 dB $m^{-1}$ or higher is probably due to the upconversion process in new centres, distinct from the laser active centres in the fibres with low bismuth concentration.

## 4. Conclusions

We have studied the luminescence properties of bismuth-doped optical fibres under two-step IR excitation and obtained excitation spectra for anti-Stokes luminescence at 750 nm in an aluminosilicate fibre and at 770 nm in a phosphosilicate fibre. The observed emission bands and the corresponding transitions between energy levels have been shown to be due to centres responsible for optical gain.

We have observed a new, broad anti-Stokes luminescence band centred at a wavelength near 780 nm in aluminosilicate fibres with a strong absorption (above 10 dB $m^{-1}$ at 1000 nm). The present results obtained for such fibres indicate that they contain no BACs responsible for optical gain and suggest the formation of new bismuth centres, other than BACs, which exhibit an upconversion process, leading to the formation of the new, broad anti-Stokes luminescence band.

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