

IR luminescence in bismuth-doped germanate glasses and fibres

A.A. Pynenkov, S.V. Firstov, A.A. Panov, E.G. Firstova, K.N. Nishchev, I.A. Bufetov, E.M. Dianov

Abstract. We have studied the optical properties of lightly bismuth doped (≤ 0.002 mol %) germanate glasses prepared in an alumina crucible. The glasses are shown to contain bismuth-related active centres that have been identified previously only in bismuth-doped fibres produced by MCVD. With increasing bismuth concentration in the glasses, their luminescence spectra change markedly, which is attributable to interaction between individual bismuth centres.

Keywords: optical fibre, bismuth, bismuth centres, luminescence.

1. Introduction

The broad absorption and luminescence bands of bismuth-related active centres (BACs) in bismuth-doped glasses and crystals make them attractive materials for lasing and optical amplification at wavelengths where the rare-earth ions are ineffective [1].

To date, however, bismuth-doped lasers and optical amplifiers have only been made using optical fibres [2, 3], but no gain media based on bismuth-doped bulk glasses (BGs) or crystals have been reported. It should be noted that only on/off gain in bismuth-doped BGs has been demonstrated previously (see e.g. Refs [4, 5]). Comparison of data in the literature shows that, in the vast majority of published reports concerned with bismuth-doped BGs, their optical properties, especially their luminescence behaviour, differ significantly from those of fibres of similar composition. Comparison of available data is however impeded by the fact that different excitation wavelengths, spectral ranges of luminescence detection and Bi concentrations were often used in different studies. It is therefore of interest to compare the properties of BGs and optical fibres within one study. It is reasonable to make such comparison for BGs and fibres of various compositions (pure silica, aluminosilicate, phosphosilicate and other materials). This paper compares the optical properties of crucible-melted bulk bismuth-doped germanate glasses and MCVD germanate-core fibres.

Bismuth-doped germanate glasses (BiGGs) have been the subject of a number of studies [6–13]. An optical fibre with a

silica cladding and bismuth-doped germanate glass core (BiGF) was investigated by Firstov et al. [14]. Spectra of the BiGGs (in particular, their luminescence spectra) in all the above-mentioned studies differ significantly from luminescence spectra of the BiGF. For example, the IR luminescence bands of the BiGF are situated at 940 and 1650 nm, whereas the BGs have at least one peak around 1300 nm.

There are several possible reasons for this. First, when glass is prepared in a crucible, the crucible material can always contaminate the melt. This is particularly so in the case of alumina crucibles (which were used in most of the above-mentioned studies) and leads to additional doping of the germanate glass with up to 10 mol % alumina (as shown by Guo et al. [13]), which cannot but affect the luminescence spectrum of the glass.

Second, the bismuth concentration in the BiGGs was as a rule considerably higher than that in the BiGF. It is known that increasing the doping level may produce extra luminescence bands, which are missing at low dopant concentrations. This is the case, e.g., in ruby crystals at sufficiently high chromium concentrations [15] and in bismuth-doped CsI crystals as the bismuth concentration increases [16]. This class of phenomena includes the formation of $Pb^{+(1)}-Pb^{2+}$ active centres in alkaline-earth fluoride crystals at elevated Pb concentrations [17].

In view of this, to properly compare the luminescence properties of BiGGs and BiGF we prepared and investigated germanate glasses with low bismuth concentration (in the concentration range typical of optical fibres for bismuth lasers and amplifiers) and a considerably higher bismuth concentration, approaching that in the previously studied glasses. Considerable attention was paid to assessing the influence of the glass preparation procedure on the glass composition. Luminescence studies were carried out in the same spectral regions under identical excitation conditions.

2. Preparation of BGs and experimental procedure

The starting chemicals used in the preparation of bismuth-doped germanate glasses were pure-grade germanium dioxide and extrapure-grade bismuth oxide. According to analytical data, the germanium dioxide contained ~ 2 mol % SiO_2 as a major impurity. To obtain a low bismuth content of the glass (comparable to that of the BiGF, ~ 0.1 mol %), the bismuth oxide was sequentially diluted with germanium dioxide. After several dilution steps, we obtained a mixture with the following nominal chemical composition: about 100 mol % $GeO_2-0.002$ mol % Bi_2O_3 (BiGG1). BiGG1 glass was prepared in a loosely covered alumina crucible in air at 1600 °C

A.A. Pynenkov, A.A. Panov, K.N. Nishchev, N.P. Ogarev Mordovian State University, Physics and Chemistry Institute, Bol'shevistskaya ul. 68a, 430005 Saransk, Russia; e-mail: alekspyn@yandex.ru; S.V. Firstov, E.G. Firstova, I.A. Bufetov, E.M. Dianov Fiber Optics Research Center, Russian Academy of Sciences, ul. Vavilova 38, 119333 Moscow, Russia; e-mail: fir@fo.gpi.ru

Received 6 November 2012

Kvantovaya Elektronika 43 (2) 174–176 (2013)

Translated by O.M. Tsarev

over a period of 80 min. The melt was slowly cooled to room temperature in air. Note that the bismuth concentration in the glass may differ from the intended one because of the high bismuth volatility in the glass preparation process. Germanate glass with a considerably higher bismuth content (~ 1 mol %) (BiGG2) was prepared under similar conditions (temperature, holding time and atmosphere). For comparison, we used an MCVD fibre preform with a germanate glass core doped with less than 0.1 mol % bismuth: $\sim 100\text{GeO}_2 + \text{Bi}$ (BiGF1). The preform was fabricated using a substrate tube of Heraeus 300 silica glass. The optical properties of a fibre drawn out from such a preform were investigated previously [18, 19].

The luminescence and excitation spectra and IR luminescence decay times of the BiGG1 and BiGG2 glasses (polished samples $10 \times 10 \times 2$ mm in dimensions) and BiGF1 fibre preform were measured with an FLSP 920 fluorescence lifetime and steady-state spectrometer (Edinburgh Instruments). All the measurements were made at room temperature.

3. Results and discussion

All the samples studied showed bright near-IR luminescence. Figure 1a presents their spectra under 460-nm excitation. The luminescence spectrum of the BiGG1 sample contains prominent bands centred near 830, 950, 1150, 1400 and 1630 nm. The spectrum of the BiGF1 preform also contains luminescence bands at 830, 950, 1400 and 1650 nm, but there is no band at 1150 nm. Finally, the luminescence spectrum of the BiGG2 glass has the form of an almost structureless band extending from 900 to 1600 nm.

As shown earlier [14], the luminescence bands at 950 and 1650 nm are due to IR-emitting bismuth centres associated

with Ge atoms (Ge-BACs). Such bands are present in the spectra of the BiGG1 and BiGF1 samples, indicating that they contain Ge-BACs. In addition, the two samples have luminescence bands at 830 and 1400 nm, which are due to IR-emitting bismuth centres associated with Si atoms (Si-BACs) [19]. The formation of such centres in the BiGF1 sample is caused by silicon diffusion from the silica cladding to the germanate core [14], and that in the BiGG1 sample is due to the presence of silica impurities in the starting materials. At the same time, the BiGG1 sample has a luminescence band at 1150 nm, in contrast to BiGF1. This band is similar in position and width to the luminescence bands of bismuth-doped aluminosilicate fibres. In addition, a luminescence band near 1150 nm was observed previously in germanate glasses codoped with bismuth and aluminium at relatively low Bi_2O_3 concentrations (~ 0.01 mol %) [8]. At higher bismuth concentrations, a luminescence line at 1300 nm was observed.

Comparison of the present results and earlier data leads us to assume that bismuth centres associated with aluminium atoms in germanate and silica-based glasses luminesce around 1150 nm. Since the BiGG1 sample was melted in the alumina crucible, it might be contaminated with alumina at the level of several percent through the dissolution of the crucible material, as shown by Guo et al. [13]. In our experiments, this assumption was confirmed by direct determinations of the sample composition. The 1150-nm luminescence band observed in the BiGG1 sample is therefore assignable to bismuth centres associated with aluminium atoms.

Thus, the BiGG1 sample has three luminescence bands at wavelengths above $1 \mu\text{m}$, which are assignable to Al-BACs, Si-BACs and Ge-BACs, respectively. To obtain more detailed information about these bands, we measured their excitation spectra in the range 250–850 nm (limited by the sensitivity of the FLSP 920's photodetector), which are presented in Fig. 1b. The excitation spectrum of the 1630-nm luminescence comprises a band centred at 460 nm, consistent with the energy level diagram of the Ge-BAC in the fibre produced from the BiGF1 preform [14], and a band centred at 395 nm, which indicates the position of the next higher energy level of the Ge-BAC. The excitation spectrum of the 1400-nm luminescence consists of two bands, centred at 460 and 370 nm. Consequently, in contrast to the excitation spectrum of the Ge-BAC, the excitation spectrum of the Si-BAC in the BiGG1 glass at 1400 nm differs somewhat from that of the Si-BAC in bismuth-doped pure SiO_2 , which comprises excitation bands at 420 and 375 nm [20]. The main distinctions between the observed excitation bands of the 1400-nm luminescence in the BiGG1 glass and pure SiO_2 glass were their broadening and shift to longer wavelengths. These distinctions may be caused by the fact that, as a result of the substantial overlap between the 1400- and 1630-nm luminescence bands, the observed excitation spectrum of either band is a combination of the excitation spectra of the 1400- and 1630-nm bands.

At wavelengths longer than 400 nm, the excitation spectrum of the 1170-nm luminescence is identical to a typical excitation spectrum of the IR luminescence of bismuth-doped aluminosilicate glasses [21]. In the UV spectral region, the spectrum has a previously unreported, strong excitation band centred at 330 nm.

From measured luminescence decay curves, we evaluated the lifetimes of the main IR luminescence bands in the BiGG1 sample. According to our results, the decay of the three main luminescence bands at wavelengths above $1 \mu\text{m}$ can be repre-

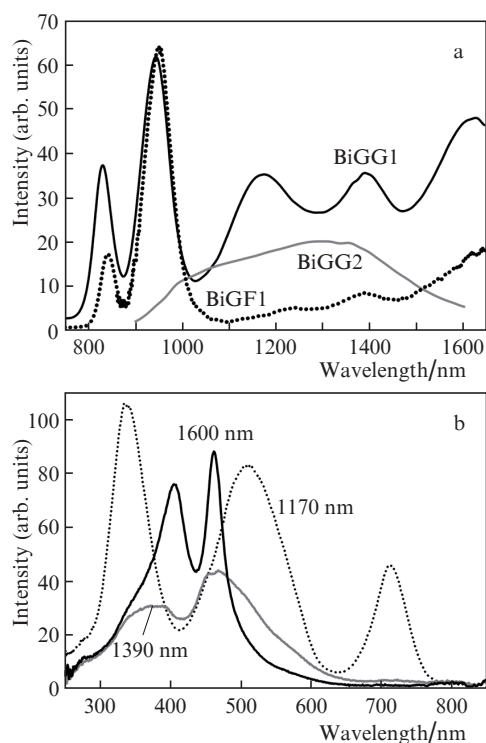


Figure 1. (a) IR luminescence spectra of the BiGG1, BiGG2 and BiGF1 samples at an excitation wavelength of 460 nm. (b) Luminescence excitation spectra of the BiGG1 glass.

sented by a single exponential. The lifetimes of the luminescence bands centred at 1150, 1400 and 1630 nm were determined to be about 750, 600 and 500 μ s, respectively. The first value agrees well with earlier data for BACs in aluminosilicate fibres [22], and the second, with the luminescence decay time of BACs in silica fibres [19].

In the BiGG2 sample, with an increased bismuth content, the luminescence decay in different spectral regions cannot be represented by a single exponential. Satisfactory agreement with experimental data can only be achieved by using a combination of several exponentials with characteristic times from 10 to 200 μ s.

4. Conclusions

The present results indicate that, at low bismuth concentrations, crucible-melted bismuth-doped germanate glasses may contain bismuth-related active centres similar to those identified previously in bismuth-doped fibres [14]. Germanate glass doped with $\sim 10^{-3}$ mol % Bi was shown to contain Al-BACs, Si-BACs and Ge-BACs. The diversity of active centres in the germanate glass was due to the presence of appropriate impurities, introduced in different glass preparation steps. Simultaneous excitation of these centres produces a very broad luminescence band, extending from 1100 to above 1650 nm (Fig. 1a). Increasing the bismuth content to ~ 1 mol % seems to cause interaction between individual bismuth centres (and formation of Bi clusters, including dimers), which adds much complexity to the luminescence spectrum of the glass and reduces the luminescence decay time. It is worth emphasising here that lasing in bismuth-doped active glass elements (optical fibres) has so far been achieved only in the presence of BACs that form in glass at low bismuth concentrations.

This study demonstrates that active centres similar in luminescence properties to centres present in bismuth-doped fibres can be produced in bulk germanate glasses.

Acknowledgements. This work was supported by the Russian Foundation for Basic Research (Grant No. 11-02-01318a), the RF Ministry of Education and Science (Project No. 2.6247.2011) and the RF President's Grants Council (Support to Young Scientists of Russia Programme, Grant No. MK-2380.2012.2).

References

1. Bufetov I.A., Dianov E.M. *Laser Phys. Lett.*, **6** (7), 487 (2009).
2. Dianov E.M., Dvoyrin V.V., Mashinsky V.M., Umnikov A.A., Yashkov M.V., Gur'yanov A.N. *Kvantovaya Elektron.*, **35**, 1083 (2005) [*Quantum Electron.*, **35**, 1083 (2005)].
3. Shubin A.V., Bufetov I.A., Melkumov M.A., Firstov S.V., Medvedkov O.I., Khopin V.F., Guryanov A.N., Dianov E.M. *Opt. Lett.*, **37** (13), 2589 (2012).
4. Fujimoto Y., Nakatsuka M. *Appl. Phys. Lett.*, **82**, 3325 (2003).
5. Zhou S., Dong H., Zeng H., Feng G., Yang H., Zhu B., Qiu J. *Appl. Phys. Lett.*, **91**, 061919 (2007).
6. Peng M., Qiu J., Chen D., Meng X., Yang I., Jiang X., Zhu C. *Opt. Lett.*, **29**, 1998 (2004).
7. Peng M., Meng X., Qiu J., Zhao Q., Zhu C. *Chem. Phys. Lett.*, **403**, 410 (2005).
8. Peng M., Wang C., Chen D., Qiu J., Jiang X., Zhu C. *J. Non-Cryst. Solids*, **351**, 2388 (2005).
9. Sharonov M.Yu., Bykov A.B., Petricevic V., Alfano R.R. *Opt. Lett.*, **33**, 2131 (2008).
10. Jiang X., Lousteau J., Richards B., Jha A. *Opt. Mater.*, **31**, 1701 (2009).
11. Jiang X., Jha A. *Opt. Mater.*, **33**, 14 (2010).
12. Guo X., Li H.J., Su L.B., Yu P.S., Zhao H.Y., Liu J.F., Xu J. *Laser Phys.*, **21**, 901 (2011).
13. Guo X., Li H., Su L., Yu P., Zhao H., Wang Q., Liu J., Xu J. *Opt. Mater.*, **34**, 675 (2012).
14. Firstov S.V., Khopin V.F., Bufetov I.A., Firstova E.G., Guryanov A.N., Dianov E.M. *Opt. Express*, **19** (20), 19551 (2011).
15. Shawlow A.L., Devlin G.E. *Phys. Rev. Lett.*, **6**, 96 (1961).
16. Su L., Zhao H., Li H., Zheng L., Fan X., Jiang X., Tang H., Ren G., Xu J., et al. *Opt. Mater. Express*, **2**, 757 (2012).
17. Focke M., Lohse F., Spaeth J.M., Bartram R.H. *J. Phys.: Condens. Matter*, **1**, 13 (1989).
18. Bufetov I.A., Semenov S.L., Vel'miskin V.V., Firstov S.V., Bufetova G.A., Dianov E.M. *Kvantovaya Elektron.*, **40**, 639 (2010) [*Quantum Electron.*, **40**, 639 (2010)].
19. Bufetov I.A., Melkumov M.A., Firstov S.V., Shubin A.V., Semenov S.L., Vel'miskin V.V., Levchenko A.E., Firstova E.G., Dianov E.M. *Opt. Lett.*, **36** (2), 166 (2011).
20. Bufetov I.A., Firstova E.G., Khopin V.F., Vel'miskin V.V., Firstov S.V., Nischev K.N., Guryanov A.N., Dianov E.M. *Proc. 5th Europhoton Conf.* (Sweden, Stockholm, 2012) paper ThP. 25.
21. Denker B.I., Galagan B.I., Musalitin A.M., Shulman I.L., Sverchkov S.E., Dianov E.M. *Laser Phys.*, **21** (4), 746 (2011).
22. Dvoyrin V.V., Kir'yanov A.V., Mashinsky V.M., Medvedkov O.I., Umnikov A.A., Guryanov A.N., Dianov E.M. *IEEE J. Quantum Electron.*, **46** (2), 182 (2010).