GLASS LUMINESCENCE

PACS numbers: 42.70.Ce; 78.60.Lc; 42.70.Hj; 42.55.Wd
DOI: 10.1070/QE2012v042n10ABEH014891

Effect of variable valence impurities on the formation of bismuth-related optical centres in a silicate glass

B.I. Galagan, B.I. Denker, Lili Hu, S.E. Sverchkov, I.L. Shulman, E.M. Dianov

Abstract. **We have studied the effect of variable valence impurities (cerium and iron) on the formation of bismuth-related IR luminescence centres and the optical loss between 1000 and 1300 nm in a magnesium aluminosilicate glass. The results demonstrate that additional doping of the glass with ceria leads to effective bleaching in a wide spectral range, including the luminescence range of the bismuth centres. At the same time, ceria reduces the concentration of luminescence centres. Gamma irradiation of the glass bleached by cerium restores the luminescence centres but leads to a background loss in a wide spectral range. Iron is shown to be a very harmful impurity in bismuth-doped active media: even trace levels of iron prevent the formation of bismuth-related active centres in the glass and produce a strong, broad absorption band centred near 1 μm.**

Keywords: *bismuth centres, broadband IR luminescence, glass.*

1. Introduction

Bismuth-doped glasses allow one to build tunable fibre lasers and optical amplifiers for a wide spectral range (1100–1550 nm) [1–6]. The bismuth oxide concentration in the fibres used for this purpose is ~0.1%, and their typical length is in the order of several tens of metres.

Despite the significant advances in bismuth fibre laser development, the nature of the bismuth-related IR luminescence centres in glasses is not yet clear. At the same time, there is solid evidence that the generation of bismuth-related active centres is associated with oxygen deficiency in the glass host, i.e., reducing (or even slightly oxidising) conditions are needed for the formation of IR-emitting bismuth centres in molten glass. A wide range of bismuth-containing glasses have been reported to date to exhibit IR luminescence [7–11], but lasing has only been demonstrated in silica-based fibres. One obstacle to lasing in both silica fibres and multicomponent glasses is the optical loss (absorption and scattering) in the luminescence band of the bismuth centres. It is reasonable to assume that the loss is due to uncontrolled impurities introduced into the melt either with starting reagents or (in the case of crucible melting techniques) from the crucible material, as well as to the products of chemical reactions involving bismuth.

The purpose of this work was to study the effect of variable valence impurities (Ce and Fe) on the generation of bismuth-related IR luminescence centres and the optical loss between 1000 and 1300 nm in a silicate glass with the aim of reducing the loss in the lasing range of the bismuth centres.

B.I. Galagan, B.I. Denker, S.E. Sverchkov, I.L. Shulman A.M. Prokhorov General Physics Institute, Russian Academy of Sciences, ul. Vavilova 38, 119991 Moscow, Russia;
e-mail: galagan@ran.gpi.ru, glasser@Lst.gpi.ru;
Lili Hu Shanghai Institute of Optics and Fine Mechanics, Chinese Academy of Sciences, 390 Qinghe Road, Jiading, 201800 Shanghai, People's Republic of China;
E.M. Dianov Fiber Optics Research Center, Russian Academy of Sciences, ul. Vavilova 38, 119333 Moscow, Russia

Received 14 May 2012; revision received 23 August 2012
Kvantovaya Elektronika **42** (10) 940–942 (2012)
Translated by O.M. Tsarev

2. Sample preparation

The glass studied had the ternary eutectic composition $10Al_2O_3-30MgO-60SiO_2$. A bismuth-doped glass of this composition was investigated previously by Denker et al. [12]. In particular, they showed that, when present in low concentrations, the bismuth-related IR luminescence centres in that glass had a high luminescence quantum yield. This suggests that the glass under consideration is a potential lasing medium. Glass samples for this investigation were prepared by two methods. A number of bismuth-doped cerium-containing glasses were prepared through melting in an induction-heated iridium crucible under nitrogen at ~1700 °C for 1 h. Melt homogenisation with an iridium stirrer and subsequent separation of the solid glass ingot from the crucible allowed us to obtain samples of good optical quality up to 5 cm in length and up to 4 cm^2 in cross-sectional area, which ensured relatively high accuracy in our optical-loss measurements. In the case of the iron-containing glasses, glass batches were melted in alumina ceramic crucibles in air. Several corundum crucibles containing 50-g galss batches were placed in a resistance furnace and held at 1550 °C for 2 h. Next, the crucibles were withdrawn from the furnace and cooled in air.

All the glasses were annealed at 750 °C in order to relieve the internal stress, and then glass samples for optical characterisation were prepared.

3. Effect of cerium on the optical properties of bismuth-containing glasses

Ceria is used in glass making as a clarifier of optical glasses. The addition of cerium is thought to contribute to the oxidation of impurities, primarily iron, responsible for parasitic absorption. As shown earlier [13, 14], the addition of ceria to a bismuth-doped glass leads to the dissociation of IR-emitting bismuth centres. This was interpreted as evidence that the bismuth-related IR luminescence centres were reduced forms of originally trivalent bismuth ions in the glass. In this study, the concentration of bismuth-related IR luminescence centres, that of red luminescence centres, and the near-IR optical loss were determined as functions of cerium content in the glass.

As an example, Fig. 1 shows absorption spectra of the glasses prepared in an iridium crucible at ~1700 °C. It is seen that increasing the percentage of CeO_2 in the Mg–Al–Si glass at constant bismuth content leads to overall bleaching in a wide spectral range. For example, at a CeO_2 content of 0.3 mol % the absorption coefficient at a wavelength of 1000 nm dropped from 0.09 to 0.01 cm^{-1}. It is worth noting that a loss of ~0.01 cm^{-1} appears appreciable, whereas the luminescence features characteristic of bismuth centres are extremely weak in this sample.

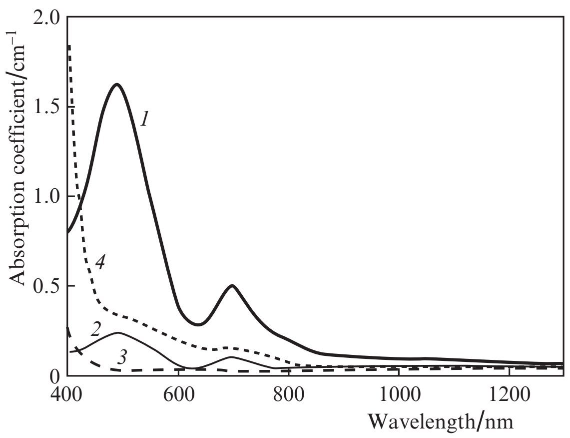

Figure 1. Absorption spectra of the glasses containing 0.25 mol % Bi_2O_3 and (*1*) 0, (*2*) 0.16 and (*3*, *4*) 0.3 mol % CeO_2; (*4*) after gamma irradiation.

Denker et al. [15] considered an alternative approach to producing bismuth-related IR luminescence centres in glass, with the use of ionising radiation. In this study, we examined the effect of gamma irradiation on the bismuth-doped cerium-containing glasses. To this end, we used the nonluminescing sample containing 0.3 mol % CeO_2 and 0.25 mol % Bi_2O_3, which initially had high transmission in a wide spectral region [Fig. 1, spectrum (*3*)]. After exposure to ionising radiation (^{60}Co gamma source, dose of ~500 kGy), it contained bismuth-related IR luminescence centres identical to those forming in cerium-free melts. Its absorption spectrum [Fig. 1, spectrum (*4*)] showed characteristic bands at λ = 500 and 700 nm. Optical excitation in these bands resulted in IR luminescence with a spectrum characteristic of the cerium-free glass. At the same time, because of the irradiation-induced gray absorption, the optical loss in the range 1 – 1.3 μm increased to 0.05 cm^{-1}.

Figure 2 shows the peak absorption coefficient of the 500-nm band and the luminescence intensity at 700 nm and 1.15 μm as functions of cerium concentration for the glasses containing 0.25 mol % bismuth oxide. The absorption correlates well with the IR luminescence intensity. With increasing cerium concentration, the bismuth centres responsible for the 700-nm luminescence, which are commonly believed to be single Bi^{2+} ions (see e.g. Ref. [16]), disappear more slowly than the IR-emitting centres. The higher stability of the red luminescence centres to oxidation with cerium correlates with their higher thermal stability reported by Denker et al. [15]. Nevertheless, it is seen in Fig. 2 that both the red and IR luminescence centres completely disappear at the same percentage of cerium (0.3 mol % under the experimental conditions of this study). This gives grounds to believe that the two types of centres oxidise, that is, pass into the most stable state of bismuth, Bi^{3+}, losing the same number of electrons. Taking the red luminescence centres to be single Bi^{2+} ions and assuming, like in an earlier study [17], that the IR luminescence is due to complex bismuth-containing clusters, we are led to conclude that these latter contain Bi^{2+}. This conclusion is consistent with the inference drawn earlier [18] that the IR luminescence centre contains two bismuth ions with a total charge of +5.

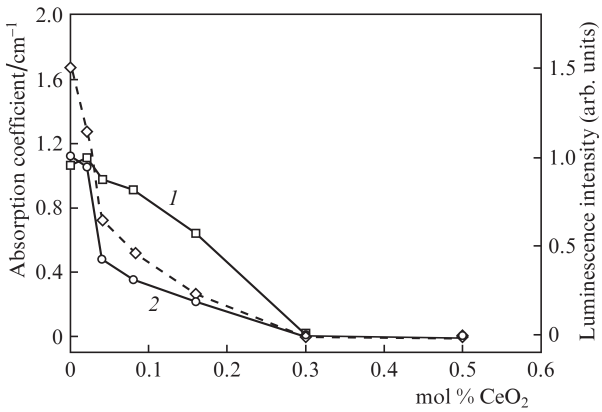

Figure 2. Peak absorption coefficient of the 500-nm band (dashed curve) and luminescence intensity of the bismuth-related optical centres in the (*1*) red and (*2*) IR spectral regions as functions of CeO_2 content for the glasses containing 0.25 mol % Bi_2O_3.

Thus, our data demonstrate that the addition of ceria as an oxidiser leads to a gradual decrease in the concentration of luminescence centres (emitting in both the IR and visible spectral regions), to the extent that no such centres form at a critical ceria concentration (near 0.3 mol % CeO_2 under the conditions of our experiments). The addition of cerium reduces the weak IR absorption as well, but we failed to radically change the situation in favour of the IR luminescence centres by doping with cerium (at least under the conditions of our experiments).

4. Effect of iron on the optical properties of bismuth-containing glasses

Figure 3 shows absorption spectra of a glass sample doped with 1.0 mol % Bi_2O_3 [spectrum (*1*)] and a sample additionally doped with iron to 2×10^{19} cm^{-3} [spectrum (*2*)]. The samples were prepared together in a resistance furnace. The absorption spectra demonstrate that iron is an effective oxidiser of bismuth centres even when present in concentrations much lower than those in the case of cerium. In this process, the iron passes into a divalent state, with a characteristic strong, broad absorption band near 1 μm. No luminescence was detected in the glass codoped with bismuth and iron. Bismuth-related luminescence centres also were not detected at dopant concentrations lower by a factor of 4 (0.25 mol % Bi_2O_3, 5.0×10^{18} cm^{-3} iron atoms). Thus, we are led to conclude that, with decreasing bismuth concentration, the role of iron and similar impurities increases and, accordingly, the purity of the starting reagents for glass production must meet more stringent requirements.

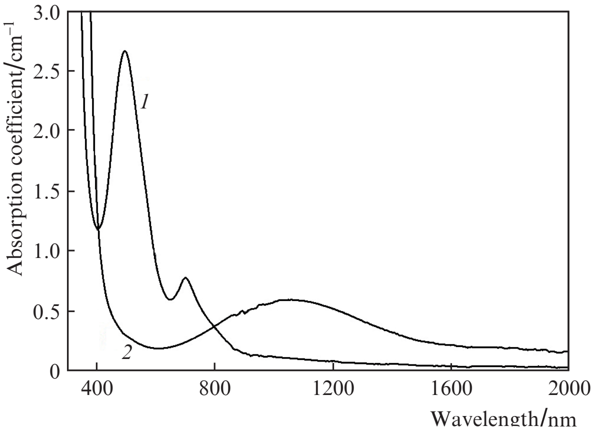

Figure 3. Absorption spectra of glasses doped with 1.0 mol % Bi_2O_3 (5.15×10^{20} bismuth ions per cubic centimetre) and (*1*) containing no other dopants or (*2*) additionally doped with iron to 2×10^{19} cm^{-3}.

5. Conclusions

The addition of ceria to a bismuth-doped glass leads to effective bleaching in a wide spectral range, including the luminescence range of bismuth centres. At the same time, ceria reduces the concentration of both IR- and red-emitting bismuth centres. Gamma irradiation of the glass bleached by cerium restores the luminescence centres but leads to a background loss in a wide spectral region.

Trace levels of iron prevent the formation of bismuth-related luminescence centres and produce a strong, broad absorption band centred near 1 μm.

Acknowledgements. This work was supported by the Presidium of the Russian Academy of Sciences (basic research programme No. P24) and in part by the Russian Foundation for Basic Research (Grant Nos 11-02-01065-a and 11-02-9161-GFEN_a).

References

1. 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)].
2. Dianov E., Shubin A., Melkumov M., Medvedkov O., Bufetov I. *J. Opt. Soc. Am. B*, **24**, 1749 (2007).
3. Razdobreev I., Bigot L., Pureur V., Favre A., Bouwmans G., Douay M. *Appl. Phys. Lett.*, **90**, 031103 (2007).
4. Bufetov I.A., Firstov S.V., Khopin V.F., Medvedkov O.I., Guryanov A.N., Dianov E.M. *Opt. Lett.*, **33**, 2227 (2008).
5. Dianov E.M., Firstov S.V., Khopin V.F., Medvedkov O.I., Gur'yanov A.N., Bufetov I.A. *Kvantovaya Elektron.*, **39**, 299 (2009) [*Quantum Electron.*, **39**, 299 (2009)].
6. Dvoyrin V.V., Medvedkov O.I., Mashinsky V.M., Umnikov A.A., Guryanov A. N., Dianov E.M. *Opt. Express*, **16**, 16971 (2008).
7. Mingying Peng, Jianrong Qiu, Danping Chen, Xiangeng Meng, Congshan Zhu. *Opt. Express*, **13**, 6892 (2005).
8. Xian-geng Meng, Jian-rong Qiu, Ming-ying Peng, Danping Chen, Quan-zhong Zhao, Xiong-wei Jiang, Cong-shan Zhu. *Opt. Express*, **13**, 1628 (2005).
9. Xian-geng Meng, Jian-rong Qiu, Ming-ying Peng, Danping Chen, Quan-zhong Zhao, Xiong-wei Jiang, Cong-shan Zhu. *Opt. Express*, **13**, 1635 (2005).
10. Mingying Peng, Jianrong Qiu, Danping Chen, Xiangeng Meng, Ivyun Yang, Xiong-wei Jiang, Cong-shan Zhu. *Opt. Lett.*, **29**, 1998 (2004).
11. Ren Jing, Chen Dan-Ping, Yang Guang, Xu Yin-Sheng, Zeng Hui-Dan, Chen Guo-Rong. *Chin. Phys. Lett.*, **24**, 1958 (2007).
12. Denker B., Galagan B., Osiko V., Shulman I., Sverchkov S., Dianov E. *Appl. Phys. B*, **95**, 1105 (2009).
13. Shifeng Zhou, Gaofeng Feng, Jiaxing Bao, Hucheng Yang, Jianrong Qiu. *J. Mater. Res.*, **22**, 1435 (2007).
14. Denker B., Galagan B., Osiko V., Sverchkov S., Dianov E. *Appl. Phys. B*, **87**, 135 (2007).
15. Denker B.I., Galagan B.I., Musalitin A.M., Shulman I.L., Sverchkov S.E., Dianov E.M. *Laser Phys.*, **21**, 746(2011).
16. Liangbi Su, Peng Zhou, Jun Yu, Hongjun Li, Lihe Zheng, Feng Wu, Yan Yang, Qiuhong Yang, Jun Xu. *Opt. Express*, **17**, 13554 (2009).
17. Dianov E.M. *Kvantovaya Elektron.*, **40**, 283 (2010) [*Quantum Electron.*, **40**, 283 (2010)].
18. Denker B.I., Galagan B.I., Osiko V.V., Shulman I.L., Sverchkov S.E., Dianov E.M. *Appl. Phys. B*, **98**, 455 (2010).