

# Use of nanoporous glass for the fabrication of heavily bismuth-doped active optical fibres

E.M. Dianov, L. Yang, L.D. Iskhakova, V.V. Vel'miskin, E.A. Plastinin, F.O. Milovich, V.M. Mashinsky, S.V. Firstov

**Abstract.** We report on the fabrication of bismuth-doped active optical fibres using porous glass as a fibre core material. The fabrication of bismuth-doped porous-glass-based fibres is a technologically complex process that includes several high-temperature processing steps. Carefully adjusting conditions of all process steps, we have produced the first optical fibres with a rather high bismuth concentration (up to 0.5 at% and above) and necessary luminescence characteristics. Luminescence spectra of the materials produced in this study are presented.

**Keywords:** optical fibre, bismuth doping, porous glass, lasing.

## 1. Introduction

In the last decade, a great deal of attention has been paid to bismuth-doped optical fibres as a new gain medium. The reason for this is that they can be used for lasing in a wide spectral range of the near-IR region, including the ranges 1250–1500 and 1625–1775 nm, where there are no efficient rare-earth-doped fibre lasers. The first bismuth-doped fibres were made in 2005. In the same year, they were demonstrated to lase [1]. In the next decade, the use of bismuth-doped fibres with various core glass compositions enabled lasing in the spectral range 1140–1775 nm. Moreover, bismuth-doped fibre amplifiers were demonstrated with peak gain wavelengths of 1320, 1430 and 1700 nm [2–7].

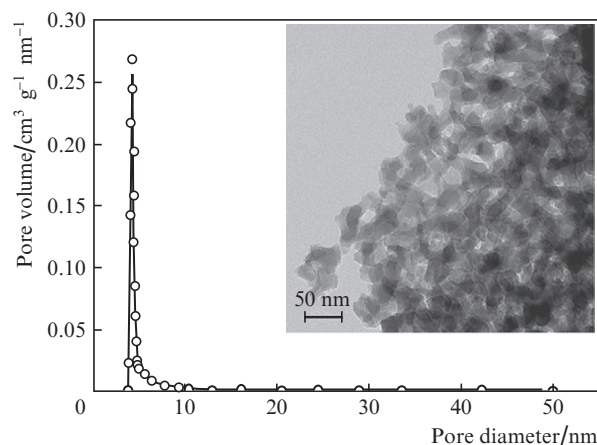
Despite the great advances in bismuth-doped fibre lasers and amplifiers, there is a serious issue to be addressed: bismuth-doped fibre lasers and amplifiers have high efficiency only at very low bismuth concentrations (0.01 at% or lower). As a result, long lengths (50 to 100 m) of active fibre have to be used, which is undesirable in a number of applications. Raising bismuth concentration leads to bismuth clustering, accompanied by an increase in optical loss and decrease in luminescence intensity, which in turn leads to a reduction in the efficiency of lasers and optical amplifiers. One way to solve this problem is to use porous glass (PG) for producing

gain media. PG is typically prepared through the phase separation of two-phase alkali borosilicate glasses. The resultant porous structure has approximately the following composition: SiO<sub>2</sub>, 96.4%; B<sub>2</sub>O<sub>3</sub>, 2.9%; Al<sub>2</sub>O<sub>3</sub>, 0.2%; and Na<sub>2</sub>O, 0.02% [8]. The use of PG for the fabrication of various light sources, primarily luminescent sources emitting at various wavelengths, dates back to the 1980s (see e.g. Anpo et al. [9] and Mack et al. [10]), but efficient rare-earth-doped fibres utilising PG and efficient PG-based fibre lasers have been demonstrated only recently [11, 12]. Several studies concerned with the incorporation of bismuth into PGs and their luminescence properties have been reported to date [13–17].

In this paper, we report the fabrication of the first bismuth-doped PG-based optical fibres.

## 2. Experimental results

The starting material for the fabrication of bismuth-doped fibre preforms had the form of cylindrical PG samples about 3 mm in diameter. The samples were prepared through the phase separation of an alkali borosilicate glass at Wuhan National Laboratory for Optoelectronics, Huazhong University of Science and Technology (Wuhan, People's Republic of China). Figure 1 shows the pore size distribution in the samples. It is seen that the average pore diameter is 4–5 nm. The inset in Fig. 1 shows a transmission electron microscope (TEM) image of the as-prepared porous glass.



**Figure 1.** Pore size distribution in the PG. Inset: TEM image of the as-prepared PG.

E.M. Dianov, L.D. Iskhakova, V.V. Vel'miskin, E.A. Plastinin, V.M. Mashinsky, S.V. Firstov Fiber Optics Research Center, Russian Academy of Sciences, ul. Vavilova 38, 119333 Moscow, Russia; e-mail: dianov@fo.gpi.ru;

L. Yang Wuhan National Laboratory for Optoelectronics, Huazhong University of Science and Technology, 430074 Wuhan, China;

F.O. Milovich Moscow Institute of Steel and Alloys (National University of Science and Technology), Leninsky prosp. 4, 119049 Moscow, Russia

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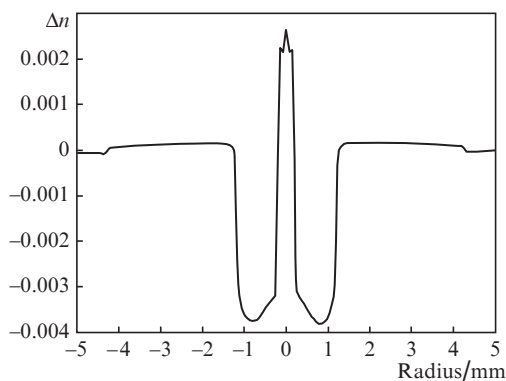
Impurity concentrations in the porous material were determined by ICP-AES\* (Table 1).

**Table 1.** Impurities in the PG samples.

Chemical element	Weight percent
B	1.33
Al	0.19
Fe	$1.4 \times 10^{-4}$
Cu	$1.4 \times 10^{-4}$
Cr	$< 1 \times 10^{-4}$
Ni, V, Co, Mo	$< 5 \times 10^{-5}$
Na	0.05
Ca, K	0.0017
Mn	$1 \times 10^{-5}$

To dope the porous glass samples with bismuth, they were saturated with a bismuth nitrate solution. Before saturation, the porous samples were heat-treated at a temperature of 500°C to remove adsorbed organic impurities and water. The cylindrical samples were impregnated with an aqueous solution of bismuth nitrate [ $\text{Bi}(\text{NO}_3)_3$ ] and 2M  $\text{HNO}_3$  for 15 h at a temperature of 70°C. The  $\text{Bi}(\text{NO}_3)_3$  concentration in the solution was 0.0075, 0.01, 0.05, 0.25, 0.5 or 1.0 M. To sinter the samples impregnated with the bismuth nitrate solution, they were placed in a tube furnace with a controlled helium atmosphere and held at a temperature of 1150°C for 1 h. The samples were heated to 1150°C at a rate of  $\sim 20^\circ\text{C min}^{-1}$ . The heating caused nanopores to collapse, resulting in the formation of transparent glasses containing  $< 0.02$ , 0.05, 0.127, 0.55 or 0.8 at% bismuth.

Since the refractive index of the glasses approached that of silica glass, fibre preforms were fabricated by jacketing the samples in a fluorine-doped silica tube with a lower refractive index. Next, to ensure the desired core to cladding diameter ratio, necessary for obtaining single-mode fibres, the samples were again jacketed, in a pure silica tube. These steps involve additional high-temperature processing of the bismuth-containing samples, which may have an uncontrolled effect on the  $\text{Bi}^{3+}$  reduction process. Figure 2 shows a typical refractive

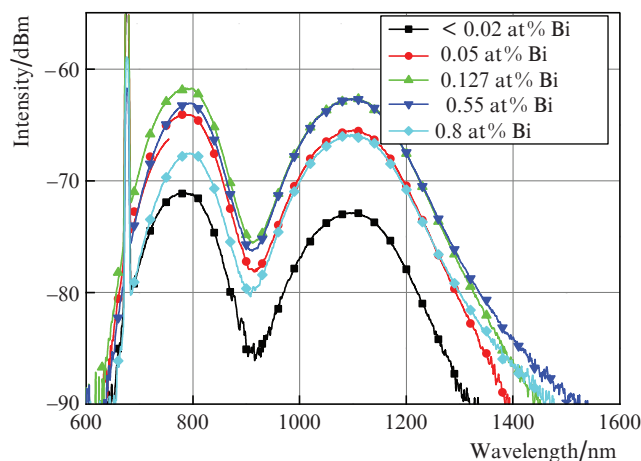


**Figure 2.** Typical refractive index profile of the fibre preforms.

\*The analyses were performed on an iCAP 6300 Duo inductively coupled plasma optical emission spectrometer at the Shared Research Facilities Center, Kurchatov Institute National Research Center/State Scientific-Research Institute of Chemical Reagents and High Purity Chemical Substances.

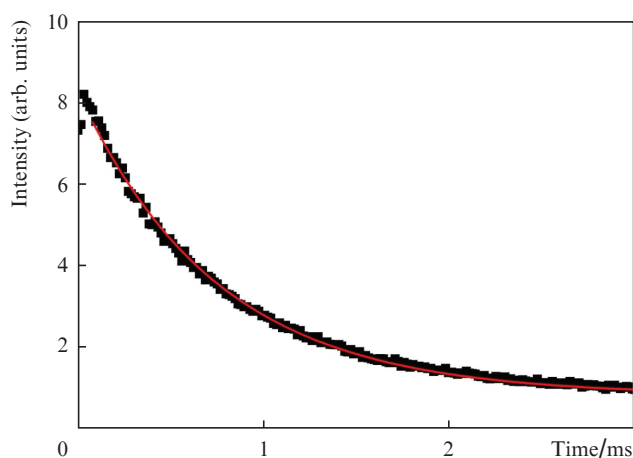
index profile of the preforms. The preforms thus produced were drawn into single-mode optical fibres and their luminescence spectra were then measured.

Figure 3 shows luminescence spectra of the glass samples differing in bismuth concentration. The luminescence spectra each contain two bands, peaking at 800 and 1100 nm, and are typical of bismuth in aluminosilicate glasses. In our case, the formation of such luminescence centres was due to the presence of residual Al in the porous material. It is seen that the shape of the spectra on the whole remains unchanged over the entire range of Bi concentrations studied (0.02–0.8 at%), whereas the intensity of the emission bands varies by about one order of magnitude.



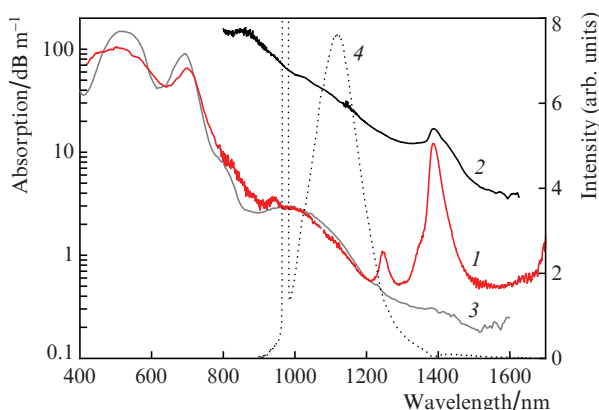
**Figure 3.** Luminescence spectra of the glass rods differing in bismuth concentration. The excitation wavelength is  $\lambda_{\text{ex}} = 676$  nm.

Figure 4 shows the luminescence decay curve of the sample containing 0.55 at% bismuth. The luminescence lifetime is 750  $\mu\text{s}$  in the 1100-nm range and 3 to 10  $\mu\text{s}$  around 800 nm. The values obtained in this study agree well with previously reported characteristic luminescence lifetimes in Bi-doped aluminosilicate fibres and preforms produced by MCVD.



**Figure 4.** IR luminescence decay kinetics at a wavelength  $\lambda_{\text{lum}} = 1150$  nm in the preform containing 0.55 at% bismuth. The filled squares represent the experimental data and the solid line is a fit to  $y = y_0 + A \exp(-t/\tau)$  with  $\tau = 751 \mu\text{s}$ .

Figure 5 presents absorption and luminescence spectra of the fibres containing 0.05 and 0.55 at% bismuth. Also shown for comparison is the absorption spectrum of an MCVD aluminosilicate fibre containing less than 0.02 at% bismuth. It is seen that, at the low bismuth concentrations, the absorption spectra of the fibres produced by different processes (spectra 1 and 3) are qualitatively and quantitatively similar. In both cases, the spectra contain absorption bands at wavelengths of 500, 700 and 1000 nm, due to bismuth-related active centres (BACs) associated with aluminium. Note that, in the wavelength range 400–1200 nm, the absorption spectrum of the fibre produced using porous glass and containing 0.05 at% bismuth is essentially identical to that of the MCVD fibre, doped with a much smaller amount of bismuth (under 0.02 at%). This strongly suggests that these fibres are similar in both the BAC concentration and background loss level. Therefore, the PG-based process has greater potential from the viewpoint of raising BAC concentration without drastically increasing the background loss. The effect of such loss can be illustrated by the example of the fibre containing 0.55 at% bismuth: the loss in it is substantially higher and the relative intensity of the bands due to active centres is lower. One possible cause of the increase in optical loss is a nonuniform bismuth distribution and bismuth clustering, but further, more detailed studies are needed to resolve this issue. The strong absorption at wavelengths above 1200 nm in the spectra of the PG-based fibres is due to residual OH groups (bands near 1240 and 1380 nm).



**Figure 5.** Absorption spectra of the fibres containing (1) 0.05 and (2) 0.55 at% bismuth. Also shown for comparison are (3) the absorption spectrum of an MCVD aluminosilicate fibre doped with less than 0.02 at% bismuth and (4) the IR luminescence spectrum obtained under excitation at a wavelength  $\lambda_{\text{ex}} = 975$  nm for the sample containing 0.05 at% bismuth.

### 3. Conclusions

In this study, bismuth-doped optical fibres have been fabricated for the first time using porous glass as a fibre core material. The fibre fabrication process comprises the following steps:

1. Determination of the parameters of the as-prepared porous glass (structure, chemical composition, impurity concentrations and optical loss).
2. Impregnation of porous glass samples with a bismuth nitrate solution.
3. High-temperature sintering of the samples, formation of bismuth oxide and collapse of the nanoporous structure into a transparent, homogeneous bismuth-doped glass.

4. Fabrication of fibre preforms by jacketing the core in a silica tube.

5. Fibre drawing.

Bismuth-doped PG-based fibres are more technologically difficult to fabricate than rare-earth-doped active optical fibres. The point is that, to obtain near-IR luminescence,  $\text{Bi}^{3+}$  should be reduced to a lower valency state. However, since the reduction of bismuth is strongly influenced by the temperature and composition of the ambient atmosphere, the reduction of bismuth in the described process, which includes several high-temperature processing steps, is difficult to control. In particular, excessive reduction of bismuth leads even to the formation of metallic bismuth nanoparticles, accompanied by disappearance of luminescence and a considerable rise in optical loss and inhomogeneity in the glass [18].

We were able to obviate the main technological difficulties and obtain bismuth-doped optical fibres with a sufficiently high bismuth concentration and necessary luminescence characteristics.

Nevertheless, two more issues should be resolved: reducing the concentration of OH groups and other impurities and improving the uniformity of the bismuth distribution over the fibre core. These issues can be resolved by optimising parameters of the third processing step: sintering of porous glass samples impregnated with a bismuth nitrate solution. The third step is very important for the ability to obtain high-quality gain media and, as shown earlier [16], requires that the process atmosphere and temperature program be carefully adjusted. Samples should be heated rather slowly, with intermediate isothermal holds during this multistep process [16], which involves bismuth nitrate decomposition within the nanoporous matrix and the formation of bismuth oxides [19], followed by pore collapse as a result of viscous flow in the skeleton of the nanoporous structure [20].

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