

Bismuth-doped Mg–Al silicate glasses and fibres

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Abstract. This paper compares the optical properties of bulk bismuth-doped Mg–Al silicate glasses prepared in an iridium crucible to those of optical fibres prepared by the powder-in-tube method and having a core identical in composition to the glasses. The bulk glasses and fibres are shown to be similar in luminescence properties. The optical loss in the fibres in their IR luminescence band is about one order of magnitude lower than that in the crucible-melted glasses. The level of losses in the fibres and their luminescence properties suggest that such fibres can be made to lase near 1.15 μm .

Keywords: Bi-doped Mg–Al silicate glasses and fibres, powder-in-tube process, luminescence, optical losses.

1. Introduction

The luminescence properties of bismuth-doped glasses are the subject of intense research aimed at identifying the nature of the emission centres involved, improving the quality of the glasses and extending the range of lasing wavelengths [1]. It is well known that the luminescence and lasing properties of bismuth-doped glasses and fibres strongly depend not only on their composition but also on the conditions under which they were produced. In connection with this, the development of advanced processes for the fabrication of bismuth-containing active materials with reproducible properties is a priority issue. To date, optical gain and lasing have been demonstrated in silica fibres doped with very small amounts of bismuth (~ 0.01 at %) and containing Al, Ge and P or no other dopants. Most of the Bi-doped fibres reported to lase were fabricated by the MCVD process, but recent work [2] has shown that lasing can in principle be achieved in bismuth-doped fibres produced by the powder-in-tube (PIT) process. Note that no lasing of bismuth-doped bulk glasses has been reported to date.

The purpose of this work was to compare the luminescence properties and optical losses of bulk glasses prepared in an iridium crucible to those of optical fibres fabricated by the PIT process using the same glass batch.

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2. Glass composition

The bulk glasses and fibre cores had the composition 60 mol % SiO_2 + 30 mol % MgO + 10 mol % Al_2O_3 (magnesium aluminosilicate ternary eutectic with a melting point of 1355 °C). As shown earlier [3, 4], bismuth-related active centres in glass of this composition are similar in luminescence properties to those in silica glass containing several per cent alumina [5]. The relatively low melting point of this glass composition (compared to silica glass), in combination with the high boiling points of the constituent oxides, suggests that high homogeneity can be achieved in the core of active fibres produced by the PIT method from large-particle materials. Another advantage of this composition is the high bismuth oxide solubility in it (2–3 mol % without formation of light-scattering colloidal Bi). It is also worth noting that the fabrication of optical fibres of this composition (rich in magnesium oxide) through chemical vapour deposition seems to be impossible because there are no suitable volatile Mg precursors.

3. Preparation of the bulk glasses and optical fibres

The starting chemicals used to prepare the glasses and fibre core materials were extrapure-grade MgO , Al_2O_3 , SiO_2 and Bi_2O_3 powders ranging in particle size up to 100 μm . The powders were dry-mixed, with no liquid medium. To obtain identical compositions of the fibre cores and bulk glasses, we used the same glass batches, containing 0, 0.005, 0.025, 0.125 and 0.625 at % Bi.

Bulk glass samples weighing about 100 g were prepared in an induction-heated iridium crucible under dry nitrogen. The melt was homogenised by an iridium stirrer. After holding at about 1800 °C for 30 min, the melt was cooled and solidified in the crucible, which was then turned upside down and again heated. The cylindrical glass ingot thus separated from the crucible was annealed at 750 °C in order to relieve the internal stress.

In the first step of the fibre fabrication process, a powder mixture was placed into a tube of Heraeus Tenevo F300 extrapure silica glass prepared by a chemical process. The tube was 100 mm in length, about 9 mm in outer diameter and 3 mm in inner diameter and was sealed at one end. The tube and powder were consolidated into a fibre preform by heating in the furnace of a drawing tower, and the preform was then drawn into fibre. In this process, the unsealed, upper end of the tube was open to the atmosphere (Fig. 1).

The preform sintering/fibre drawing process involved several steps and was similar to that described elsewhere [6, 7]. First, the preform was lowered through the hot zone

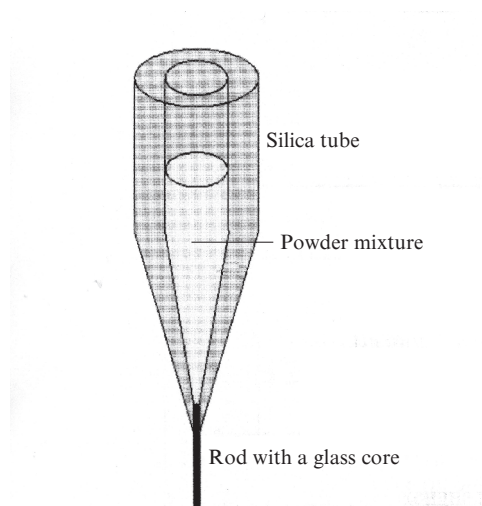


Figure 1. Schematic of the PIT preform fabrication process.

(1500–1600 °C) of the induction furnace at $\sim 10 \text{ mm min}^{-1}$ (which took 10 min). This resulted in complete melting of the oxide mixture. The molten glass accumulated in the lower part of the cladding tube, which remained sufficiently strong and retained its shape. In addition, this step included gas release from the powder.

In the second step, the glass preform was drawn into rods at a temperature of 1850–1900 °C and drawing rates from 1.5 to 2 m s^{-1} . The three-component melt formed the core of the rods, and the silica tube formed a cladding. The core to cladding diameter ratio in the rods was typically the same as that in the preforms. Because of the increased brittleness of the rods, due to the considerable thermal expansion mismatch between silica and magnesium aluminosilicate glasses, the length of the drawn rods did not exceed 0.4–0.5 m. The diameter of rods produced from one preform varied from 0.1 to 1.5 mm, and their cores contained various defects (Figs 2, 3).

To obtain fibre preforms, the most perfect portions of the rods were jacketed in an extra, undoped silica cladding of desired thickness. The preforms thus produced were drawn at 1850–1900 °C into fibres with a standard polymer coating,

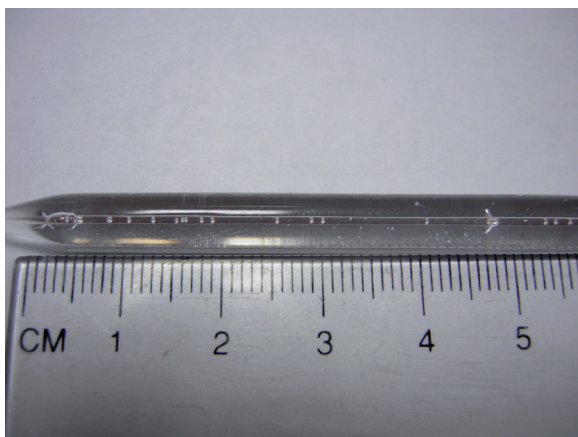


Figure 2. Appearance of a rod (enclosed in a silica sheath to improve its strength).

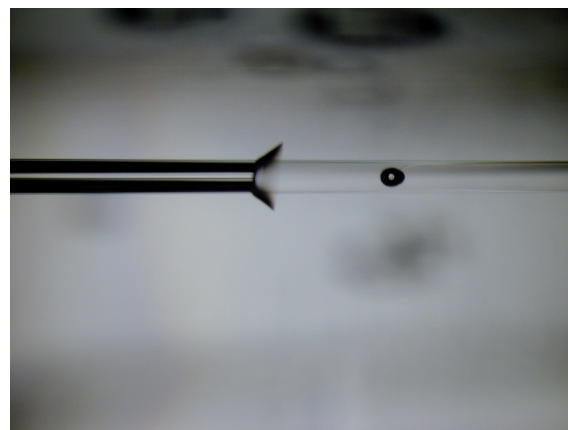


Figure 3. Photograph of the core of a fibre preform. The core is seen to contain different defects: cracking at the channel–core interface and a gas bubble.

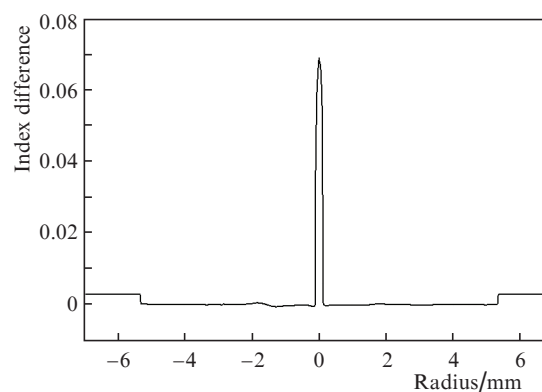


Figure 4. Typical refractive index profile of a silica fibre preform with a Mg–Al–Si oxide glass core.

outer cladding diameter of 125 μm , and core diameter of 7–10 μm . At this core diameter and the core–cladding index difference used (Fig. 4), the fibres were multimode.

4. Luminescence properties of the samples

Figure 5 shows examples of the absorption spectra of the fibres and bulk glasses. Comparison of the spectra indicates the following:

1. The absorption spectra of the Bi-doped fibre and bulk glass contain bands at 500 and 700 nm, characteristic of IR luminescence centres in aluminium-containing glasses (see, e.g., Ref. [5]). At a given bismuth concentration, the absorption bands of the bulk glasses and fibres differ little in strength. The presence of magnesium produces no additional absorption bands relative to aluminosilicate glasses.

Both the glass and fibre have prominent absorption bands superimposed over a structureless (wavelength-independent) loss background. In the spectral range 800–1700 nm, the background loss in the bulk glass is significantly (one order of magnitude) higher than that in the fibre.

2. At wavelengths near 1 μm , the optical loss in the fibre is substantially lower than that in the bulk samples of the same composition. This refers to both the doped and, especially,

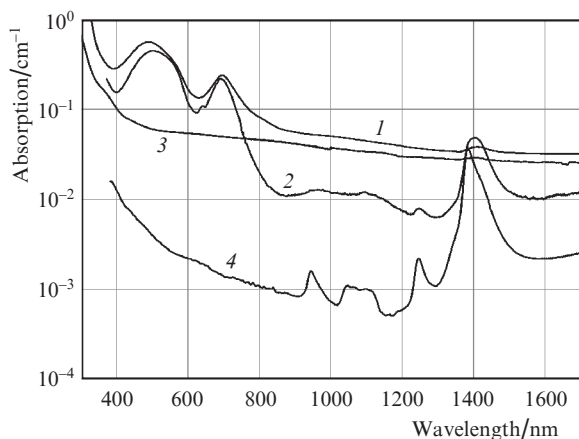


Figure 5. Absorption spectra of (1, 2) 0.125 at % Bi doped and (3, 4) undoped (1, 3) bulk glass samples and (2, 4) fibres.

undoped samples, which differ in loss by more than one and half orders of magnitude. The optical loss in the undoped fibre has a minimum, $5 \times 10^{-4} \text{ cm}^{-1}$, at a wavelength of 1.15 μm , which differs little from the peak emission wavelength of bismuth centres. The high optical loss in the bulk samples (both doped and undoped) seems to result from contamination with trace levels of transition metals from the crucible material. Another possible cause of the high background loss in these samples is defects forming in during glass preparation under reducing conditions (nitrogen atmosphere over the melt). In any case, such losses prevent lasing of the bulk glasses throughout the IR luminescence range of the bismuth centres (1.1–1.3 μm).

3. The absorption spectrum of the bismuth-containing fibres shows an absorption band due to bismuth centres (0.9–1.1 μm), which is also characteristic of bismuth-doped aluminosilicate fibres produced by MCVD. The optical loss in the crucible-melted bulk glasses at these wavelengths is above 0.03 cm^{-1} and obscures the absorption band of the bismuth centres.

4. All of our samples have absorption bands at 1.4 μm , due to OH groups. In the bulk glasses, these absorptions are rather weak and difficult to distinguish from the background loss. In the fibres, the absorptions around 1.4 μm are slightly stronger (about 0.04 cm^{-1}) and markedly exceed (by an order of magnitude) the background loss. These absorptions in the undoped and doped fibres differ somewhat in shape and width. The above spectral differences lead us to conclude that the absorption in question in the bismuth-doped fibre is due not only to OH groups (absorption centred at 1.38 μm) but also to Bi-related luminescence centres associated with silicon. Such absorption was observed earlier in bismuth-doped germanosilicate [8], pure silica [9] and aluminosilicate [10] fibres. Thus, the Bi-doped fibres under consideration have absorption bands due to Bi-related luminescence centres associated with both aluminium (500, 700 and 900–1100 nm) and silicon (1400 nm). The absorption bands at 1.24 and 0.95 μm in the spectrum of the undoped fibre arise from OH groups. The origin of the composite band around 1.1 μm is not yet clear, and several hypotheses can be put proposed. It may be that it indicates the position of the cutoff wavelength in the fibre or arises from unidentified impurities.

The fibres were found to be similar in luminescence properties to the bulk glasses, as evidenced by Fig. 6, which shows

the luminescence spectra of a bulk glass and fibre at an excitation wavelength of 532 nm. The spectra consist of two peaks (in the visible and near-IR spectral regions), which correspond to two distinct types of emission centres, characteristic of bismuth-doped aluminium-containing glasses [5].

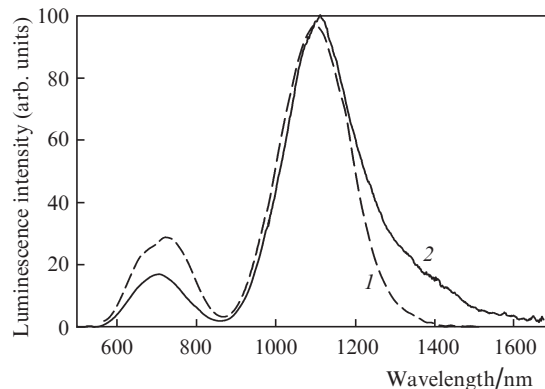


Figure 6. Luminescence spectra of the (1) optical fibre and (2) bulk glass containing 0.125 at % Bi.

The relatively low level of losses in the fibres fabricated as described above and their luminescence properties suggest that, by optimising the Bi concentration, they can be made to lase at $\sim 1.15 \mu\text{m}$.

5. Conclusions

Bismuth-doped fibres consisting of a silica cladding and multicomponent glass core with a relatively low melting point have been fabricated for the first time using the PIT method. The optical properties of the fibres were compared to those of bulk glasses of the same composition prepared in an iridium crucible. The luminescence spectra of the bulk glasses and fibres are shown to differ little. The crucible-melted bulk glasses show about one order of magnitude higher level of background losses in comparison with the fibres. The relatively low level of losses in the fibres and their luminescence properties suggest that, by optimising the Bi concentration and fabrication process, such fibres can be made to lase near 1.15 μm .

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