Glass fibres doped with the transition elements Ti^{3+}, Co^{2+}, Zn^{2+}, Ni^{2+}, Mn^{2+} and with Bi^{3+} and Bi^{3+}-Al^{3+}

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Abstract

With the goal of finding strong broadband fluorescence we investigate Ti^{3+}, Co^{2+}, Zn^{2+}, Ni^{2+}, Mn^{2+}, Bi^{3+} and Bi^{3+}-Al^{3+} as a dopant in optical SiO_2 glass fibres. Preforms are manufactured with the technique of granulated oxides and drawn to fibres. The produced fibres are optically excited with either a N_2 laser (337 nm), a HeNe laser (633 nm), a Ar^+ laser (458 nm to 514.5 nm), a laser diode (980 nm), a sodium vapour lamp or a mercury vapour lamp. While Ti^{3+}, Co^{2+}, Zn^{2+} and Ni^{2+} show no noteworthy fluorescence, Mn^{2+} emits at 590 nm with a FWHM of about 100 nm. A very bright emission is found in Bi^{3+}-doped glass. In the visible a band is centred at 600 nm with a width of 154 nm FWHM (with Al^{3+}). In the infrared region a second band is centred at 1400 nm with a width of 235 nm FWHM. With addition of Al^{3+} this band can be shifted to a centre wavelength of 1150 nm.

Introduction

Broadband light sources are required for many applications where white light interferometry is used [1]. Possible broad band emitters are metal ions in a glass host. A very promising host is a silica fibre. With a small core the fibre allows restricting guided light to a fundamental transversal mode and therefore promises to reach high brilliance. Broadband emitters based on rare earths have already been described [2]. Since the 4f electrons in rare earths are well shielded by a Neon L-shell with respect to the surrounding host, their spectra are not particularly narrow. In transition metals the 3d electrons with their He shield have a much closer interaction with the host. Therefore they also have broader fluorescence spectra than rare earths. Even broader spectra are expected from metals that have no shielding of the involved electrons.
As yet, however, the interest in transition elements or metals incorporated in a silica fibre for the generation of broadband luminescence was rather limited. It is therefore interesting to investigate transition-element-doped silica fibres with respect to their spectral properties. Using the method of dry granulated oxides for manufacturing the preforms allows performing such an investigation rapidly and at low cost [3].

In this report we describe manufacturing, excitation and emission properties of Ti^{3+}, Co^{2+}, Zn^{2+}, Ni^{2+}, Mn^{2+}, Bi^{3+} and Bi^{3+}-Al^{3+} doped silica glass fibres. Excitation is performed with N_2 laser (337 nm, *Garching Instruments mod. SP1/II*), a HeNe laser (633 nm, *Melles Griot 05-LHP-991*), an Ar^+ laser (458 nm to 514.5 nm, *Spectra Physics 2040E*), a laser diode (980 nm, *Nortel 15122B-W1002*), a sodium vapour lamp (*Osram Na/10*) and a mercury vapour lamp (*Osram Hg/10*).

Experimental

All investigated fibres are produced in the same way: A silica glass tube with an outer diameter of 20 mm and an inner diameter of 17 mm is filled with a mixture of granulated silica and metal oxide. The preforms are then drawn at a temperature of about 2000 °C into fibres with diameters ranging from several millimetres close behind the drop to typically 100 µm. A more detailed description of the manufacturing process can be found in [3].

Titanium

A first fibre doped with 1 at % Ti_2O_3 is drawn. The drop and even the thinner fibre pieces are black coloured and completely opaque. A considerable amount of Ti_2O_3 is not solved in the glass host. This material is visible as a black granulated inclusion leading to very strong absorption and scattering of the pump laser light (Ar^+ laser 458 nm to 514.5 nm). When the fibre is observed through a straight vision prism from the side, the laser line at 514.5 nm is extinct after a bare 1 mm of propagation in the fibre. This shows that the dopant concentration is too high. Consequently, a second fibre doped with only 0.1 at % Ti_2O_3 is drawn. In this fibre upon visual inspection the drop contains only a very small amount of undissolved Ti_2O_3. But due to refractive index variations the transmitted light is strongly scattered.

In literature spectroscopic properties of titanium-doped glasses are reported. The production methods of the glasses, however, are completely different. A similar glass is described in [4]. It was manufactured with sol-gel technology. When excited at 380 nm it showed fluorescence at 460 nm and 560 nm. Other absorption and emission bands are described in [5] and [6]. But the manufacturing technique using a chemical reaction in a steady state laser torch is possibly not suitable for a comparison. Nevertheless, in our experiments pumping both samples with 253.7 nm, 337 nm, 457 nm-514 nm, 589 nm and 633 nm did not result in measurable fluorescence.

Cobalt, zinc and nickel

Similar results without noticeable fluorescence have been obtained with three different preforms doped with 0.1 at % CoO, 0.1 at % ZnO, or 0.1 at % NiO. It is reported that Co^{2+} (695 nm, [7]) and Ni^{2+} (1250 nm, [8]) showed fluorescence in glass-ceramics, but no report about fluorescence of these ions in a silica glass host was found. For ZnO doped SiO_2 fluorescence is reported in the UV to visible region (350 nm-490 nm) and also around 550 nm [9]. The samples in the mentioned report were made with sol-gel technique. All three samples were excited with the N_2-laser, the Ar^+-laser, the HeNe-laser, a laser diode at 980 nm, a sodium vapour lamp and a mercury vapour lamp. Neither in the visible nor in the near infrared any fluorescence was detected from these samples within the detection limit of our fibre-coupled spectrometers (Avantes *AVS-USB2000 and AvaSpec-NIR256-1.7).*

The absence of fluorescence in the fibre doped with ZnO may possibly be explained by the different manufacturing process. Our preforms are all heated up to about

2000 °C. It is reported [10] that ZnO dissociates very fast above temperatures of 1950 °C. In [9] the temperature was kept below 1100 °C. Therefore it is possible that heating to 2000 °C under evacuation leads to complete loss of ZnO.

Manganese

Four silica fibres with different dopant concentrations have been drawn: 0.1 at % Mn^{2+}, 1 at % Mn^{2+}, 2 at % Mn^{2+} and 5 at % Mn^{2+}. The 2 % and the 5 % doped fibres show cracks in the silica cladding. It further seems that the cores of these two fibres are not completely vitrified; most of the dopant is still visible as a fine powder. Two 15 cm long fibres from the 0.1 at % Mn^{2+} and the 1 at % Mn^{2+} samples and a 5 cm sample with 2 at % Mn^{2+} are excited along the axis with an Ar^{+} laser. A broad fluorescence could be detected with a fibre coupled spectrometer (*AVS-USB2000)* from the side of the fibre and also at the rear end of the sample. The measured fluorescence has a FWHM of about 100 nm and is centred at 590 nm (Fig. 1). This is similar with the fluorescence of Mn^{2+} in Zn $(PO_3)_2$ glass [11]. In contrast to this report, however, no shift of the luminescence maximum has been measured as a function of the dopant level. From Fig. 2 in [11] it can be seen that in zinc metaphosphate glass the fluorescence maximum shifts from about 550 nm to 575 nm and then to 655 nm when the dopant concentration is 1 %, 2.5 % and 10 % respectively.

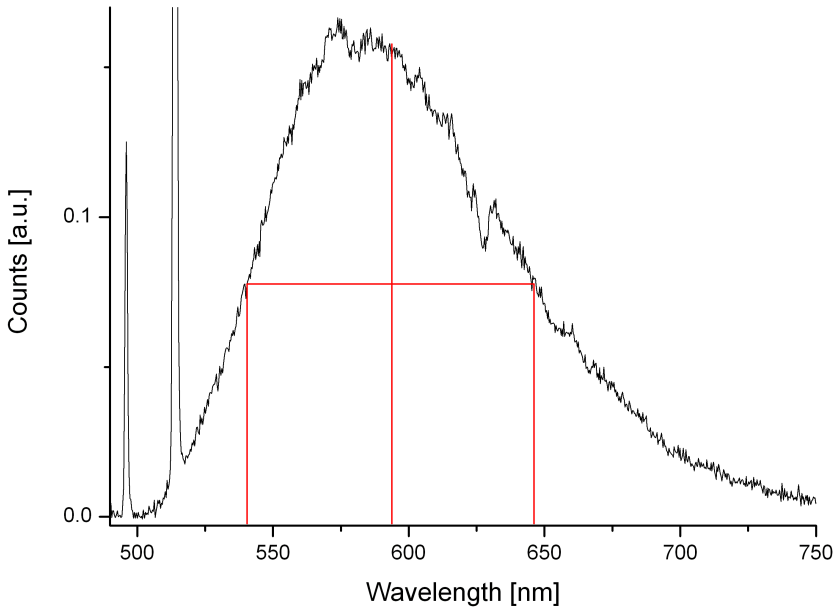

Fig.1: Fluorescence spectrum of an optical fibre doped with 1 at % Mn^{2+}.

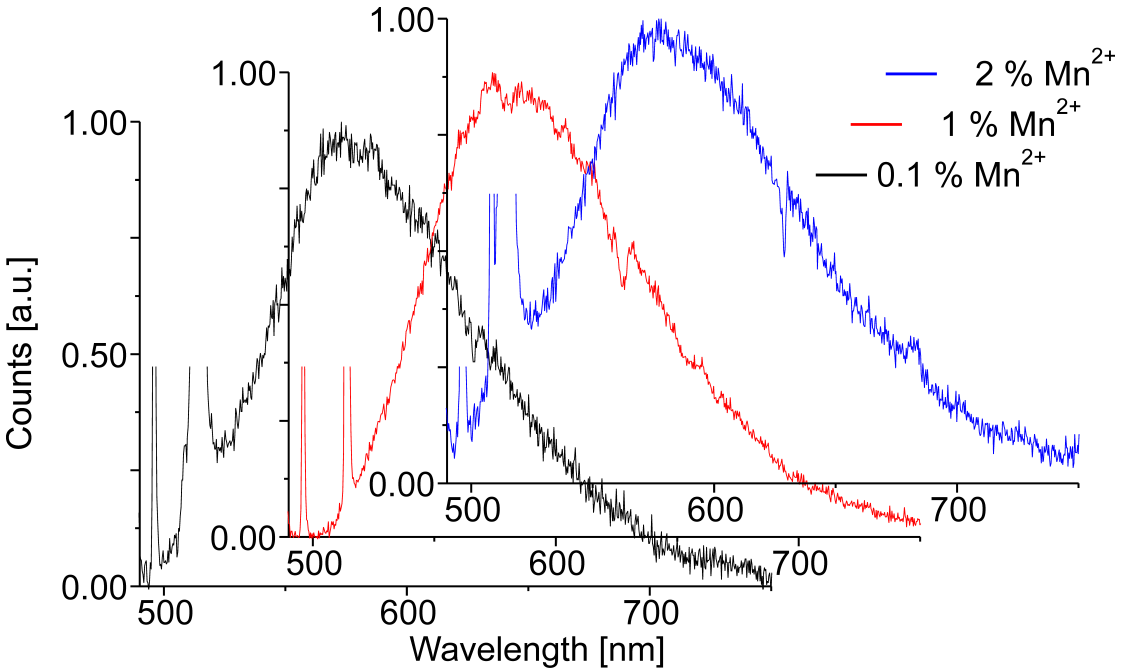

Fig. 2: Fluorescence spectra of Mn^{2+} doped optical fibres with different dopant levels.

The fluorescence spectrum of Mn^{2+} is very similar to those of V^{5+} Cu^{+} or Bi^{3+} as shown in [1]. They all have a maximum in the vicinity of 600 nm and a width of about 100 nm FWHM.

Bismuth / Bismuth-Aluminium

Comparing the results of [1] with [12] or [13] revealed different results in the NIR emission band. In [1] only one band was measured with a peak at 1400 nm. In [12] and [13] double-peaked emission at 1100 nm and at 1400 nm was measured. Since only the fibre described in [1] was free of Al^{3+}, the content of Al^{3+} could be a possible reason for a two-peaked fluorescence.

To test this assumption, two fibres are drawn from two different preforms: preform a) doped with 0.1 at % Bi_2O_3 and 1 at % Al_2O_3, and preform b) doped with 0.1 at % Bi_2O_3 and no aluminium. Both samples are excited along the axis with an Ar^{+} laser. The fluorescence is detected with fibre coupled spectrometers (visible: *AVS-USB2000*, near infrared: *AvaSpec-NIR256-1.7*) at the rear end of the fibre. The result is shown in Fig. 3.

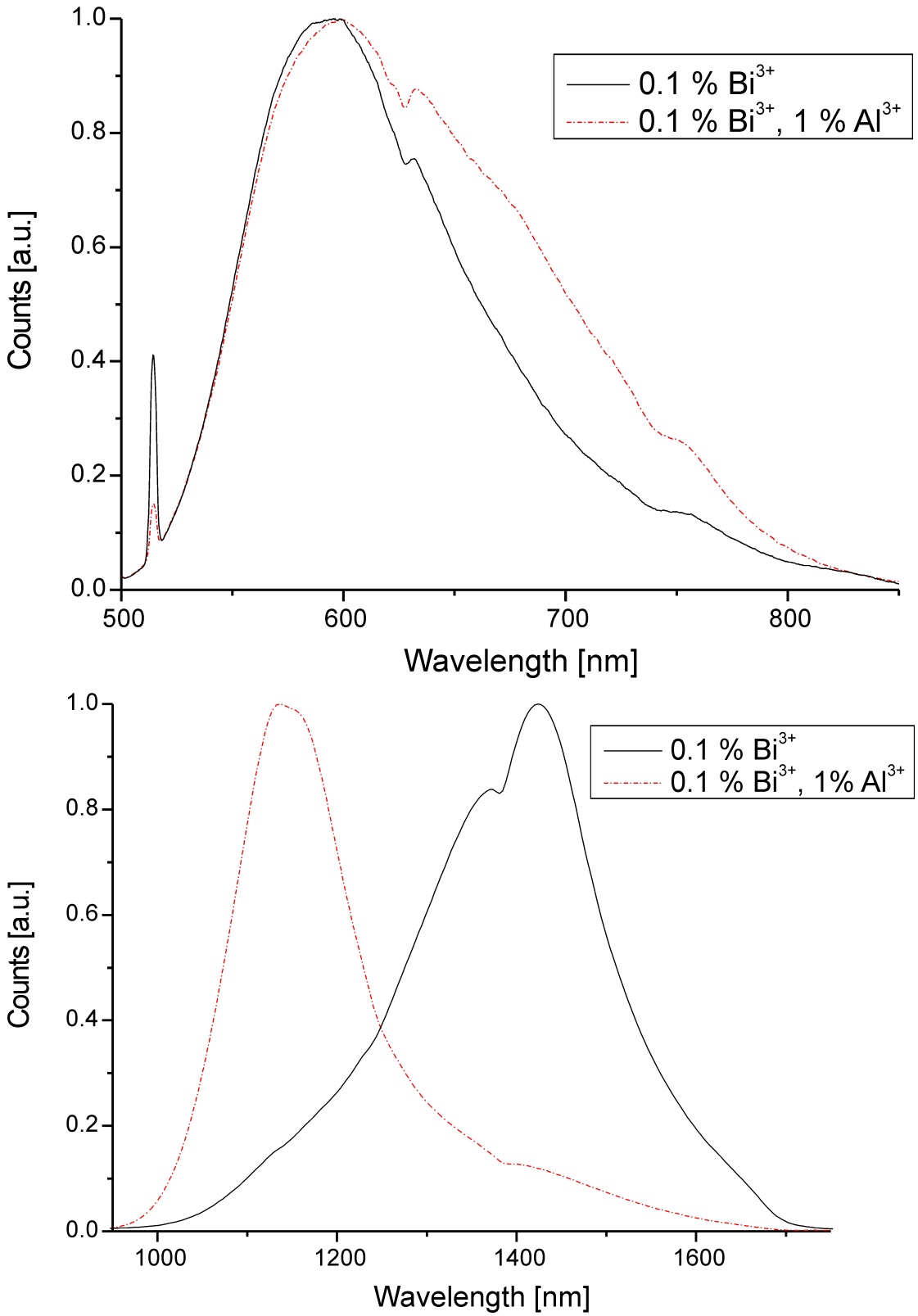

Fig. 3: Fluorescence spectra of two optical fibres in the visible and the near infrared region. The dip at 1400 nm in both curves is assigned to the first harmonic of the O-H stretching vibration.

For the sample b) the same spectra are measured as in [1]. In sample a) the near infrared spectra change (cf. Fig 3 lower picture). The admixture of aluminium produces two effects: the central wavelength of the fluorescence is shifted from 1400 nm to 1150 nm by 250 nm and the FWHM is narrowed by 79 nm. It is assumed that Al^{3+} with 10-times the concentration of Bi^{3+} is sufficient to completely remove the sites responsible for 1400 nm emission. A lower Al^{3+} concentration is expected to allow both emissions: SiO_2 sites leading to 1400 nm emission and Al-sites leading to 1150 nm emission.

Differences are also seen in the visible part of the spectrum. Already with the naked eye it is seen that the fibre doped only with Bi^{3+} appears amber while the one co-doped with aluminium shimmers in a slight rose. In the visible part (cf. Fig. 3 upper picture) the aluminium causes no shift of the spectrum but the width is increased by about 40 nm.

The lifetimes of the fluorescence have been measured. The visible fluorescence band is excited with a N_2 laser (337 nm), the band in the near infrared region is excited with the Ar^+ laser (458 nm to 514.5 nm). The fluorescence is measured with a photomultiplier (Hamamatsu R955). The decay time of the visible fluorescence for Bi^{3+} is 4 µs. The fluorescence of the Bi^{3+}-Al^{3+} doped fibre shows a double exponential characteristic with decay times of 3 µs and 13 µs (Fig. 4).

The lifetimes of the infrared bands show also a double exponential characteristic: for Bi^{3+} the decay times are 310 µs and 20 µs, for Bi^{3+}-Al^{3+} 740 µs and 180 µs (Fig. 5).

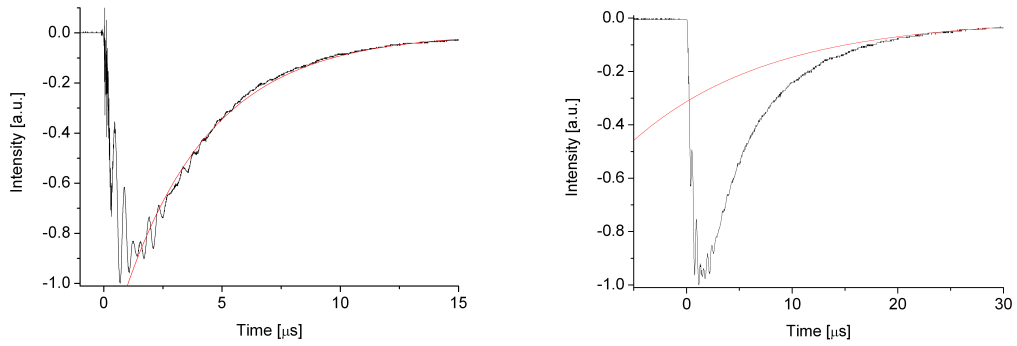

Fig. 4: Measured lifetime of the fluorescence in the VIS. Left: Bi^{3+}. Right: Bi^{3+}-Al^{3+}. The fit in the right figure shows the slow part of the fluorescence decay.

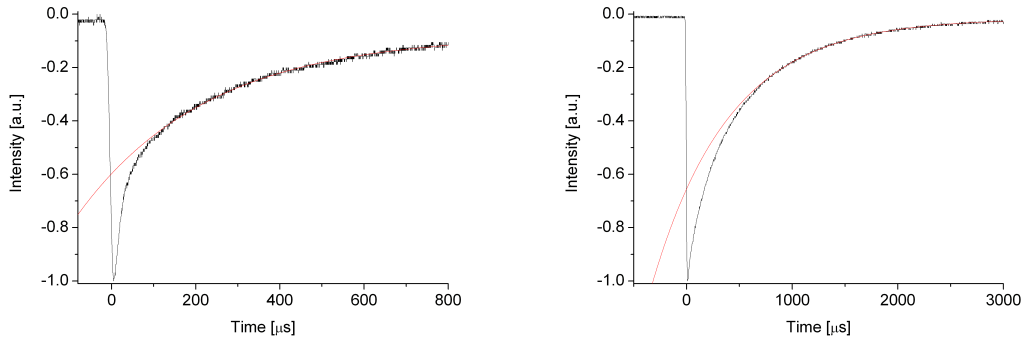

Fig. 5: Measured lifetime of the fluorescence in the NIR. Left: Bi^{3+}. Right: Bi^{3+}-Al^{3+}. The fits show the slow part of the fluorescence decay.

Summary

With the goal of finding strong broadband fluorescence we investigated Ti^{3+}, Co^{2+}, Zn^{2+}, Ni^{2+}, Mn^{2+}, Bi^{3+} and Bi^{3+}-Al^{3+} as a dopant in optical SiO_2 glass fibres. Preforms have been manufactured with the technique of granulated oxides and drawn to fibres. The produced fibres have been optically excited with a N_2 laser (337 nm), a HeNe laser (633 nm), an Ar^+ laser (458 nm to 514.5 nm), a laser diode (980 nm), a sodium vapour lamp or a mercury vapour lamp. While Ti^{3+}, Co^{2+}, Zn^{2+} and Ni^{2+} showed no noticeable fluorescence, Mn^{2+} emits at 590 nm with a FWHM of about 100 nm. A very bright emission is found in Bi^{3+}-doped glass. In the visible a band is centred at 600 nm with a width of 154 nm FWHM (with Al^{3+}). In the infrared region a second band is centred at 1400 nm with a width of 235 nm FWHM. With addition of Al^{3+} this band can be shifted to a centre wavelength of 1150 nm.

Acknowledgments

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