Glass fibers doped with transition elements: V^{5+}, Cr^{3+}, Cu^{+} and Bi^{3+}

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Abstract

With the goal of finding strong broad-band fluorescence we investigate V, Cr, Cu and Bi as dopants in glass fibers (silica or Pyrex). All the fibers are manufactured with the technique of granulated oxides [1]. Spectra and lifetimes are measured. Excitation is performed with a N_2 laser (337 nm), a HeNe laser (633 nm), a Ar^{+} laser (458 nm to 514.5 nm) or a Ti:sapphire laser (808 nm). Lifetimes have been measured with 337 nm excitation. Vanadium in different as yet undetermined valences and Cu^{+} show a broad spectrum with 125 nm FWHM ranging from 475 nm to 600 nm. Cu^{+}:silica glass shows a rather strong fluorescence that can easily be seen with the naked eye. The Bi^{3+} doped fiber shows two broad emission bands, one in the visible range from 600 nm to 800 nm and one in the near IR range from 1250 nm to 1500 nm. No fluorescence could be measured with Cr^{3+}.

Introduction

Broadband light sources are required for applications where low coherence is needed. These are applications where in principle white light interferometry is used. This allows restricting contrast to the very short length corresponding to the temporal coherence length. One example is confocal microscopy where generally broad band light sources such as small arc lamps or strong light emitting diodes are used. Another example is optical coherence tomography OCT. Possible broad band emitters are ions of transition metals in glass fibres.

Although the investigation of transition metals in crystals is well established, there has been up to now only limited interest in studying transition metals in glass hosts. For these elements in fused silica we know of a high non-radiative relaxation rate by the strong electron phonon coupling between chromophore and silica host. Thus we expect low luminescence efficiency. This can possibly be compensated by the strong interaction of the luminescents with the pump over long distances (some meters to several tens of meters).

In our report we describe manufacturing, excitation and emission properties of V^{5+}, Cr^{3+} and Cu^{+} incorporated in pure silica and Bi^{3+} doped in Pyrex glass and in pure silica.

Experimental

For the experiments several fibers are drawn from self prepared performs. For most of the preforms pure silica tubes are used with an outer diameter of about 20 mm and an inner diameter of about 17 mm. A mixture of granulated silica and oxides of the dopant is filled in the tube. The tube becomes to the cladding of the drawn fiber while the mixture in the center builds the core. The tube dimensions lead to fibers with a very large core compared to the cladding diameter. Before drawing the fiber the preform is evacuated and heated for one hour to 1300°C for silica and a few hundred °C for Pyrex respectively. The fibers are then drawn at a temperature of about 1750 °C – 2000 °C for the silica preforms and 1200 °C for the Pyrex preforms. To obtain the best possible vitrification the preform is drawn at high temperature. This high temperature leads to low viscosity of the silica and therefore requires a very small

drop (very small drawing force) at the beginning of the drawing process. A small drop is obtained if the preform is slowly (with 1mm per minute) inserted into the hot zone of the furnace. As soon as the weight of the drop is sufficient to overcome the viscosity of the SiO_2 the drawing process starts. For our experiments only the first few meters of the fiber are used. This includes diameters from the drop with several mm down to the fiber with 100 µm.

Vanadium

A preform is prepared with 1 at % V with respect to Si. Vanadium is added as dry powder of V_2O_5. No additional doping for wave-guiding is used. V_2O_5 is thermally decomposed at 1750°C [2, B-152]. Since fiber drawing is performed at higher temperatures the fiber appears dark black corresponding to V valences of V^{4+} (deep black or blue) and V^{3+} (black) [2, B-152]. No conductive V film is deposited in the fiber core.

A fiber length of 5 cm with a diameter of 600 µm is excited along the axis with the 337 nm emission of a pulsed nitrogen laser (*Garching Instruments mod. SP1/II*). The emission is coupled into the fiber with a Suprasil lens of 20 mm focal length. The fluorescence generated in the fiber core is measured from the side with a fiber-coupled spectrometer (*AVS-USB2000*). The resulting spectrum is shown in Fig. 1:

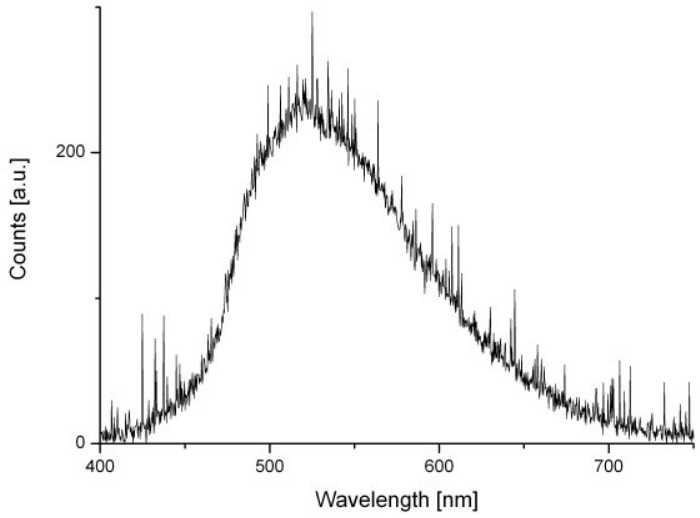

Fig. 1: Fluorescence spectrum of a V^{5+}-doped silica fiber

The width of the fluorescence is about 125 nm at FWHM ranging from 475 nm to 600 nm. These results correspond reasonably well to measurements performed at 77 K [3]. The measured lifetime is about 300 µs, about one order shorter than in experiments performed at 77 K [3].

Chromium

Two different silica preforms doped with Cr^{3+} are prepared, a first one with 1 at % of chromium and a second with 0.1 at %. The result of the first preform is a fiber with an inhomogeneous dark green opaque core, whereas the fiber drawn from the second preform shows a very clear core with a slight green coloring. Fluorescence would be expected around 450 nm [4], 650 nm [5, 6], 800 nm [4, 7], 1 µm [4] and 1.5 µm [6]. Nevertheless, at room temperature no fluorescence is detected by excitation wavelengths of 337 nm (N_2 laser), 458 nm to 514.5 nm (Ar^+-laser, *Spectra Physics 2040E*), 632.8 nm (HeNe-laser, *Melles Griot 05-LHP-991*) and 800 nm (Ti:sapphire, *Spectra Physics mod. 3900*), and 400 nm, frequency doubled Ti:sapphire *(Time-Bandwidth Tiger).*

Copper

A preform is made with 0.1 at % Cu^+ as a dopant. Monovalent copper is introduced as Cu_2O. After drawing the preform the fiber pieces with diameters between 100 µm and a few millimeters show a slight red coloring similar to the Cu_2O used for doping. This allows the assumption that the added copper staid in its valence. CuO would appear black [8] as well as the fine-dispersed metal. The Cu^+ fiber is excited with the 337 nm emission of the N_2 laser. The broad-band fluorescence can easily be seen with the naked eye. The maximum intensity is found around 550 nm with a FWHM of about 150 nm (Fig. 2). According to [9] Cu^+ shows three absorption bands between 250 nm and 350 nm in dependence of the dopant concentration. These absorption bands are assigned to the transitions from singlet $3d^{10}$ to the triplet $3d^94s^1$ [9] and/or to the singlet $3d^94s^1$ [10]. A description of Cu^+:crystal or Cu^+:glass spectroscopy is found in [11, 12].

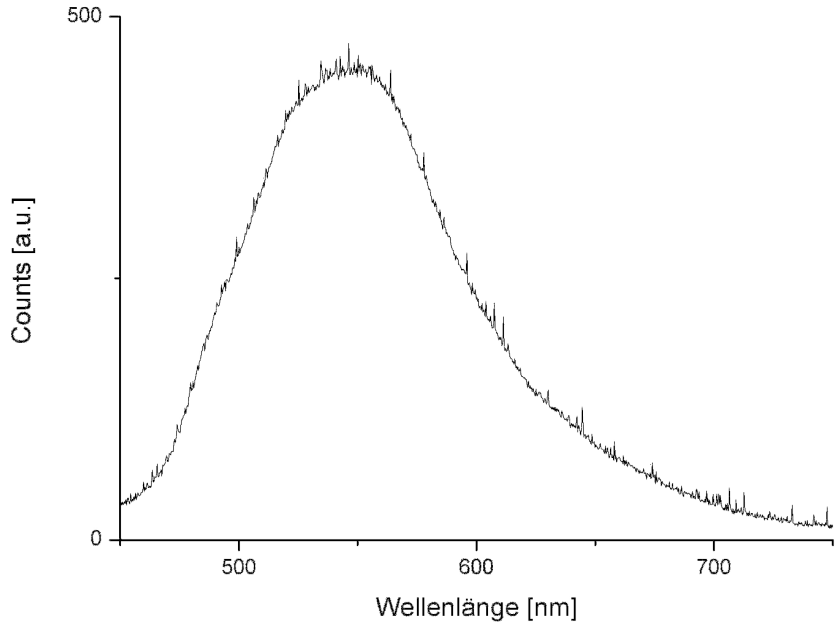

Fig. 2: Fluorescence spectrum of a Cu^+ doped silica fiber

To measure the lifetime of the fluorescence, the laterally emitted light is collimated and dispersed in a prism. The short-wavelength part of the spectrum is blocked with an edge to eliminate pump-light. The long-wavelength part is detected with a photomultiplier *(Hamamatsu R955)* in connection with a digital oscilloscope (LeCroy 9310) terminated with 50 Ω. The temporal characteristic of the emission is shown in Fig. 3.

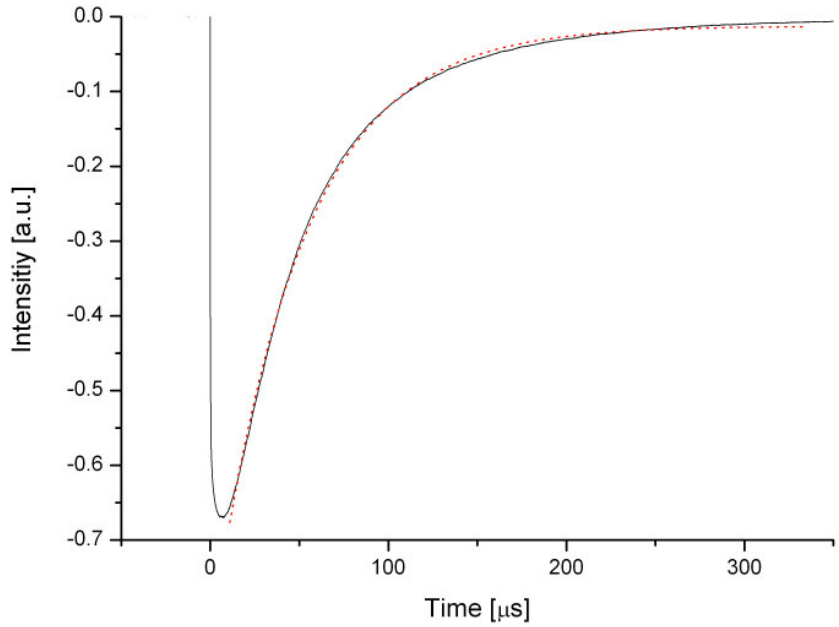

Fig. 3: Fluorescence emission of a Cu^+ doped silica fiber after ns excitation at 337 nm. The fluorescence curve is accumulated from 200 measurements.

Upon excitation with ns-pulses at 337 nm, the long wavelength part of the emission reaches its maximum about 8 µs after excitation. This delayed rise of the fluorescence is characteristic for a three-level-system [9, 10]. The relaxation of the second level occurs with a lifetime of about 50 µs (cf. Fig. 3) In contrast to [10] no dual exponential characteristic is detected. The exponential fit with 50 µs decay time cannot be distinguished from the measured curve. The fluorescence of the Cu^+ doped fiber lies in the region between 500 nm and 600 nm at FWHM similar to the fluorescence of the V^{5+} doped fiber. Because of this very wide spectrum, the good efficiency and the long lifetime, copper is a very promising candidate to obtain a broadband emitter.

Bismuth

According to experiments with Bi-doped fibers [13] also bismuth shows strong broad-band emission even leading to laser emission. It is, however, not clear from which valence the emission originates. In a first experiment we test Bi^{3+}. A fiber doped with 0.1 at % Bi^{3+} is drawn. Pyrex is used for the preform because of the low boiling point of 1890°C [2, B-73] of Bi_2O_3. A very strong fluorescence at 1100 nm and 1400 nm would be expected [13] while exciting with 800-900 nm. But no fluorescence could

be seen at this excitation range. Only with an argon ion laser at 458 nm, 477 nm, 488 nm, 496 nm and 514.5 nm as pump source two fluorescence bands in the visible and in the infrared region can be observed. The band centered at 625 nm has a full width at half maximum of about 175 nm, the one at 1300 nm has a width of about 200 nm. (Fig. 4)

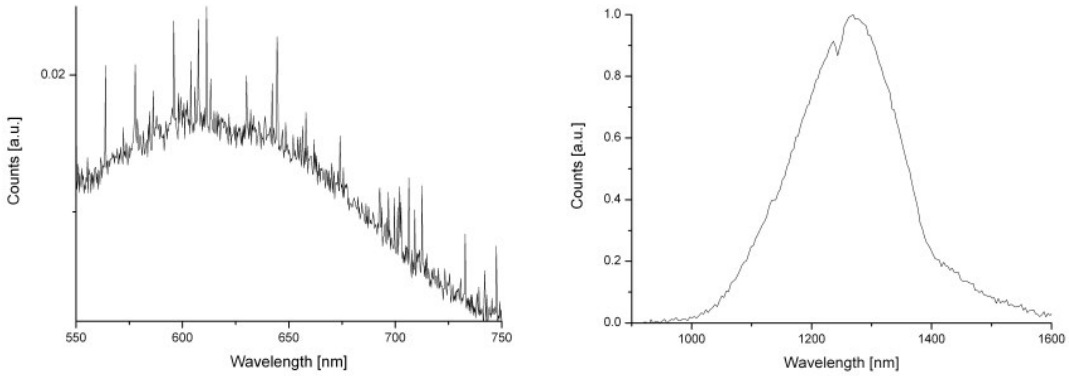

Fig. 4: Fluorescence spectrum of a Bi^{3+} doped Pyrex fiber

Another fiber doped with 0.1 at % Bi^{3+} is drawn. For this fiber pure silica glass is used as host material. This fiber is drawn at a temperature of about 2050°C. The maxima of the two fluorescence bands are shifted to shorter wavelengths in the visible (595 nm) and to longer wavelengths in the infrared region (1380 nm). The FWHM of the visible band is about 100 nm the one of the IR band 200 nm. (Fig. 5)

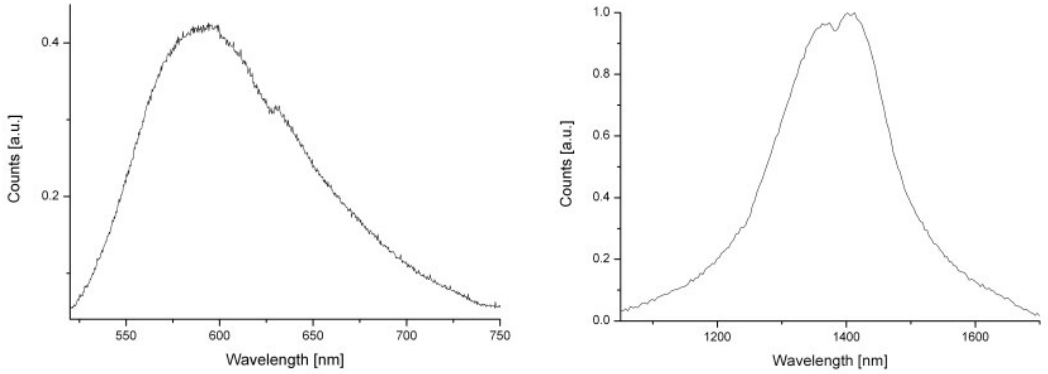

Fig. 5: Fluorescence spectrum of a Bi^{3+} doped silica fiber

The visible fluorescence of the Bi^{3+}:silica fiber became so strong that it can also be observed with the naked eye or easily be photographed through a straight vision prism (Fig. 6).

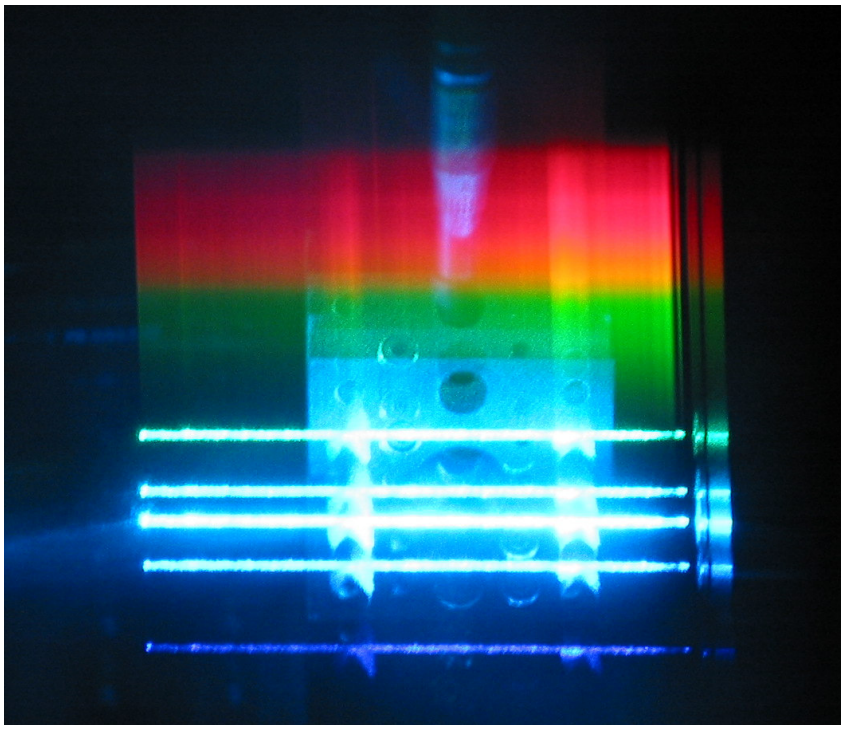

Fig. 6: The fluorescence of a Bi^{3+}:silica fiber. The picture is taken through a straight vision prism. In the bottom part of the picture the five lines of the argon laser can be seen, above the wide fluorescence band.

Summary

With the goal of finding strong broad-band fluorescence we have investigated V, Cr, Cu and Bi as dopants in glass fibers (silica or Pyrex). Spectra and lifetimes have been measured. Excitation is performed with 337 nm (V, Cr, Cu), 458 nm to 514.5 nm (Cr, Bi), 633 nm (Cr), 808 nm (Bi, Cr). Lifetimes have been measured with 337 nm excitation. V^{5+} (and/or vanadium in other valences) shows a broad spectrum with 125 nm FWHM ranging from 475 nm to 600 nm. Also Cu^{+} shows a broad spectrum around 550 nm with a FWHM of about 150 nm. Bi^{3+} shows two fluorescence bands in the visible and in the infrared region, centered at about 600 nm and 1350 nm depending on the drawing temperature. No fluorescence could be measured with Cr^{3+} doped fibers. The lifetimes of V:silica glass and Cu^{+}:silica glass were measured

as 300 μs and 50 μs respectively. Cu^{+}:silica glass showed a rather strong fluorescence that could easily be seen with the naked eye.

Acknowledgments

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