On the Possibility of Excited-State-Absorption from $^5D_4$ in Tb^{3+}:Al^{3+}:SiO_2

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Abstract

A Tb^{3+}:Al^{3+} silica fibre is been manufactured and characterized with respect to scattering losses. The fluorescence from $^5D_4$ is measured. It shows strong saturation with respect to the pump-power. This saturation is explained with saturating ground-state-absorption (GSA) and excited-state-absorption (ESA) of 488 nm pump-light in the $^5D_4$ level. A simulation of the saturation process shows that the cross-section for ESA can be larger than for GSA.

Introduction

When optically pumped at a wavelength of 488 nm, Tb^{3+} doped in silica glass shows strong fluorescence in the $^5D_4$ to ^7F_J transition. For J = 6 blue (485 nm), J = 5 green (542 nm) J = 4 orange (586 nm) and J = 3 red (620 nm) transitions are found that might be very well suited in applications such as RGB colour displays. Tb^{3+} shows laser action in some crystals and in liquids [1], but as yet it has not been possible to achieve laser action in glass with 488 nm pumping [2]. Even the extremely favourable geometry of a doped glass fibre that keeps pump-light confined and therefore at high intensity over large lengths in the fibre core has not allowed the occurrence of laser action. The cross-section for stimulated emission in the $^5D_4 \rightarrow {}^7F_5$ transition has been estimated to be $1.3 \cdot 10^{-21}$ cm^2 [2]. With a reasonable concentration of ions excited to the $^5D_4$ level (e.g. 10^{19} cm^{-3}) and a sufficient fibre length (e.g. 1 m) there should be no problem to achieve laser emission.

Up to now, however, all experiments that should lead to laser action in 488 nm pumped Tb^{3+}:glass failed. It has therefore to be assumed that either a sufficient population of $^5D_4$ cannot be reached or that 542 nm emission is reabsorbed.

In our letter we report on manufacturing of a Tb^{3+}(0.5 at.%):Al^{3+}(3.5 at.%):silica glass fibre. The losses of the fibre are characterized and measurements of $^5D_4 \rightarrow {}^7F_J$ fluorescence (for J = 3, 4 and 5) as a function of 488 nm pump-light intensity are performed. Strong saturation is found for all wavelengths. This strongly suggests that the losses are not induced by reabsorption of the emitted fluorescence but rather to excited state absorption of pump-light in the $^5D_4$ level preventing sufficient population for laser action. Also bleaching of the ground-state cannot be excluded. A numerical simulation of the process well describes the measured data.

Properties of the fibre

The preform is produced with the method of granulated oxides [3]. A mixture is prepared with 35.73 g granulated silica, 1.52 g alumina and 0.6 g terbium oxide. This mixture is filled in a silica glass tube of 5 by 3 mm diameter. The mixture will form the future core and result in Tb^{3+}(0.5 at %): Al^{3+}(3.5 at %): SiO_2. The filled tube is placed in the centre of a larger silica tube with 19 by 16 mm diameter. The remaining free space is filled with granulated SiO_2. The filled preform is mounted in the fibre drawing tower. After preheating to 1400 °C and evacuation for 2 hours the fibre is drawn at a furnace temperature of about 1930 °C. The fibre with a diameter of 100 µm and a core of 16 µm is coated with UV-curing resin (DSM Desotech DS 2055). A length of about 150 m is prepared for the experiments.

The losses of the fibre are determined by a cut-back measurement at 633 nm, a wavelength where scattering, but no absorption occurs. The result is shown in Fig. 1.

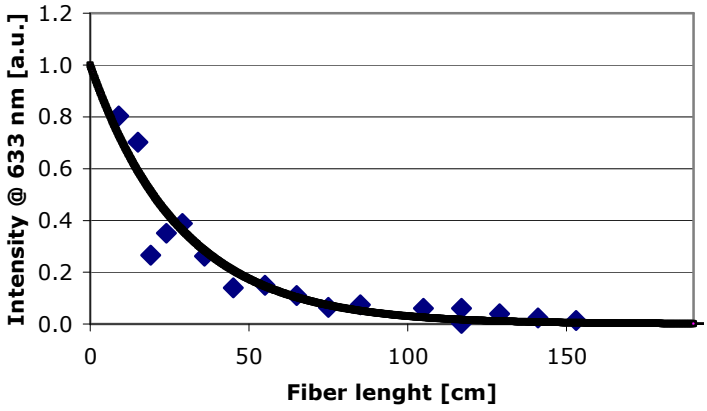

Fig. 1: Result of a cut-back measurement. The transmitted light at 633 nm can be described with an exponential of 28.5 cm extinction length

From Fig. 1 it is seen that scattering losses are considerable. An extinction length of 28.5 cm @ 633 nm corresponds to 15.3 cm @ 542 nm if a λ^{-4} law for scattering is assumed. The fluorescence of the fibre is measured with the arrangement of Fig. 2.

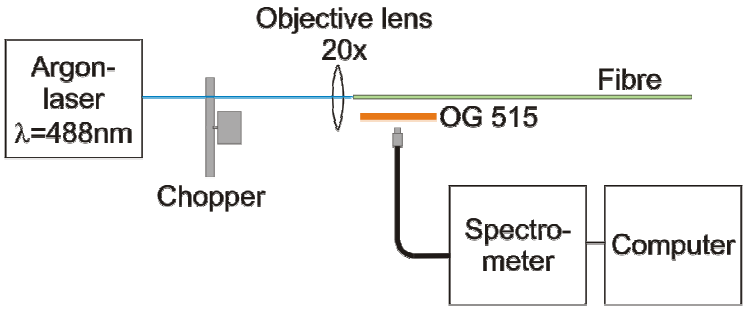

Fig. 2: Experimental arrangement for the measurement of fluorescence decay along the fibre.

The fibre is excited with the 488 nm emission of a single line argon laser allowing a maximum output power of 2.8 W. The beam is chopped with a duty cycle of 0.1 to avoid thermal effects. With a 20 x microscope objective the beam is focused onto the core region of the fibre. 542 nm fluorescence emitted perpendicular to the fibre axis is detected with a fibre-coupled spectrometer (Avantes USB 2000). Scattered pump-light is suppressed with a selective filter (Schott OG 515). Measuring at various positions along the fibre allows determining the extinction length at 542 nm. The result is shown in Fig. 3.

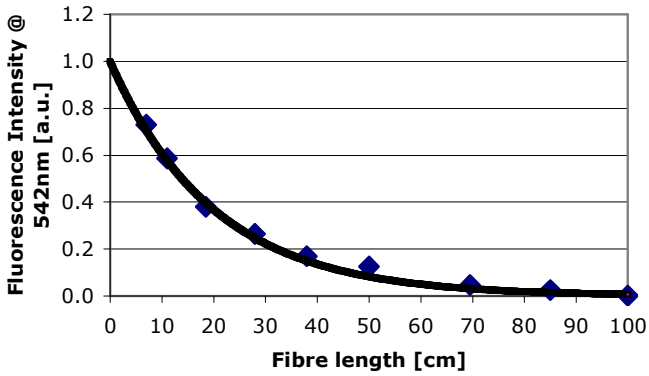

Fig. 3: Extinction measured at 542 nm. The fluorescence decay along the fibre can be described with an exponential of 20 cm extinction length.

Comparison with the extinction due to pure scattering of 15.3 cm shows that the true absorption length must be much longer than shown in the experiment of Fig. 3. This is in agreement with the measurement in Duran-like glass [1]. With the cross-section of $\sigma = 1.23 \cdot 10^{-22}$ cm^2 reported therein, an absorption length of 73 cm would be expected. The energy level scheme of Tb^{3+} [4] is shown in Fig. 4.

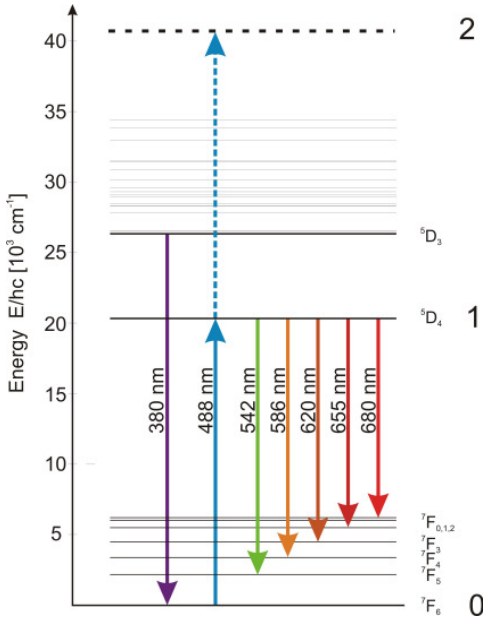

Fig. 4:
Energy level scheme of Tb^{3+}:silica glass

Despite of the strong scattering the fluorescence is clearly visible and the lifetime of the $^5D_4$ level exceeds 2 ms as shown in Fig. 5.

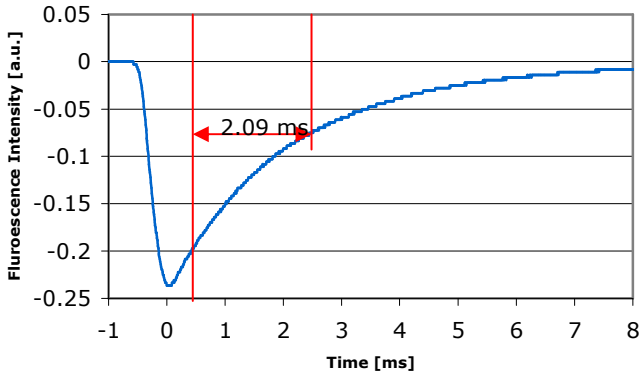

Fig. 5:
Temporal relaxation of fluorescence from $^5D_4$

Also fluorescence from $^5D_3$ is relatively long with 0.8 ms (cf. Fig. 6). Lifetimes have been measured with a chopped excitation. The chopper was operated at 23 Hz. At the position of the beam the velocity of the chopper wheel is 5.8 m/s. With 1 mm beam diameter this leads to a rise time of about 170 µs at the edge of the chopper. The fluorescence signal is filtered with a 20 cm grating monochromator and a selective filter (Schott OG 515) and then detected with a photomultiplier (Hamamatsu R955) terminated with 4.7 kΩ in connection with a digital storage oscilloscope (LeCroy LT374L). The measurements shown in Figs. 5 and 6 are averaged over 1000 pulses.

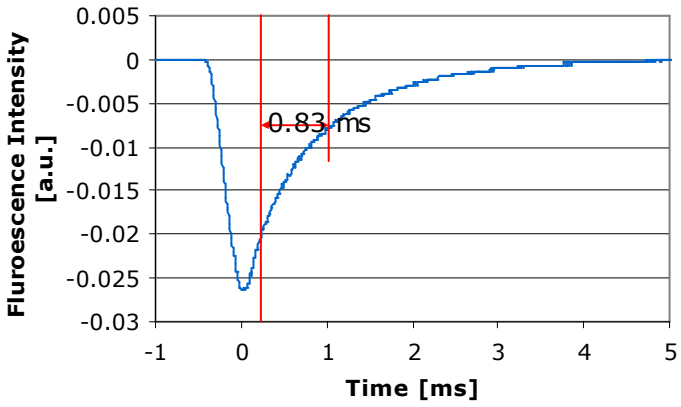

Fig. 6: Temporal relaxation of fluorescence from $^5D_3$

The measured lifetimes of about 2 ms and 0.8 ms are comparable with those measured in a sol-gel based fibre (2.01 ms and 0.98 ms respectively) [2].

Experiments and results

Green, orange and red fluorescence is measured as a function of pump intensity. The experimental arrangement is as shown in Fig. 2 but with the detection at the rear end of the 80 cm long fibre. As a function of pump-power a strong saturation occurs (Fig. 7).

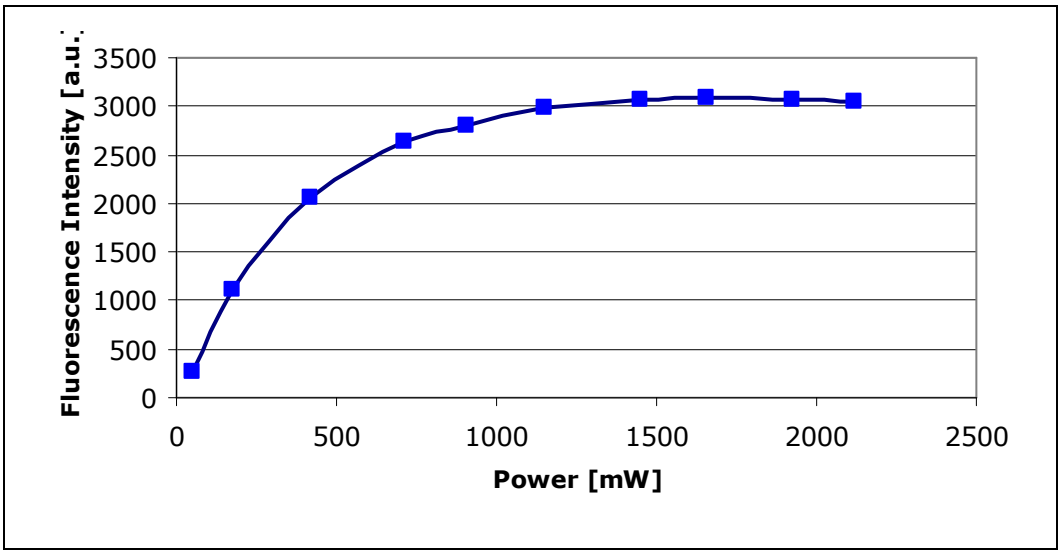

Fig. 7: 542 nm fluorescence intensity as a function of 488 nm pump-power. The same behaviour is also seen when fluorescence at 586 nm and 620 nm is detected.

The linearity of the detector is tested with calibrated neutral density filters. The characteristic is shown in Fig. 8. The deviations from linearity are by far too small to explain the saturation of the emission from $^5D_4$. The saturation is partly due to bleaching of the ground state. Due to the strong scattering losses only a short fibre length receives the full pump-power and leads to fluorescence signal. This short length may suffer bleaching of the ground-state and lead to saturation independent on further fibre length. Experiments with a fibre length of 3.8 m instead of 0.8 m gave the same results.

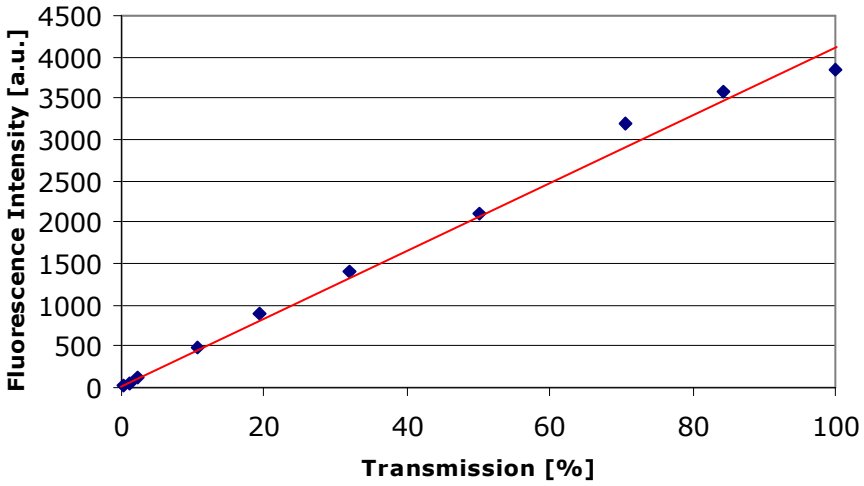

Fig. 8: Linearity test of 542 nm detection in the fluorescence intensity range of Fig. 7.

Depopulation of $^5D_4$ is either by an up-conversion process such as excited state absorption ESA or energy exchange up-conversion. In view of the dopant concentration of only 0.5 at % energy exchange up-conversion is not very probable. The probability for direct dipole-dipole interaction is inversely proportional to the 6^{th} power of the distance between interacting ions [5]. It can therefore be assumed that ESA and saturation of GSA is responsible for the behaviour of Fig. 7.

In this case, a simplified set of rate equations of the system can be calculated. Denoting $^7F_6$ as level 0, $^5D_4$ as level 1 and level 2 as the high level after ESA has occurred (cf. Fig. 4) leads to

$$\frac{dN_1}{dt} = W_p - \frac{N_1}{\tau_1} - W_p' \tag{1}$$

With

$$W_P = \frac{\lambda_P \cdot P_P}{h \cdot c \cdot L \cdot A_P} \cdot \left(1 - e^{-(\{N_0 - (1+\frac{\sigma_1}{\sigma_0}) \cdot N_1\} \cdot L \cdot \sigma_0)} \right) \tag{2}$$

and

$$W_P' = \frac{\lambda_P \cdot P_P}{h \cdot c \cdot L \cdot A_P} \cdot \left(1 - e^{-N_1 \cdot L \cdot \sigma_1} \right) \tag{3}$$

With

P_P, the pump power at λ_p = 488 nm,

h, Planck's constant,

c, the vacuum speed of light,

L, the fibre length,

A_P, the pumped core area,

σ_0, the cross-section for ground-state absorption,

σ_1, the cross-section for ESA,

N_0, the number of Tb^{3+} ions in the ground state,

N_1, the number of exited Tb^{3+} ions in $^5D_4$,

τ_1, the lifetime in $^5D_4$.

Neglecting scattering losses and assuming population only in the levels 0, 1 and 2 and identical lifetimes in 2 and 1, then the term $(1+\frac{\sigma_1}{\sigma_0}) \cdot N_1$ in the exponent of (2) holds for the depopulation of the ground state.

With Equations (1)-(3) the density of ions in the $^5D_4$ level can be calculated (Fig. 9).

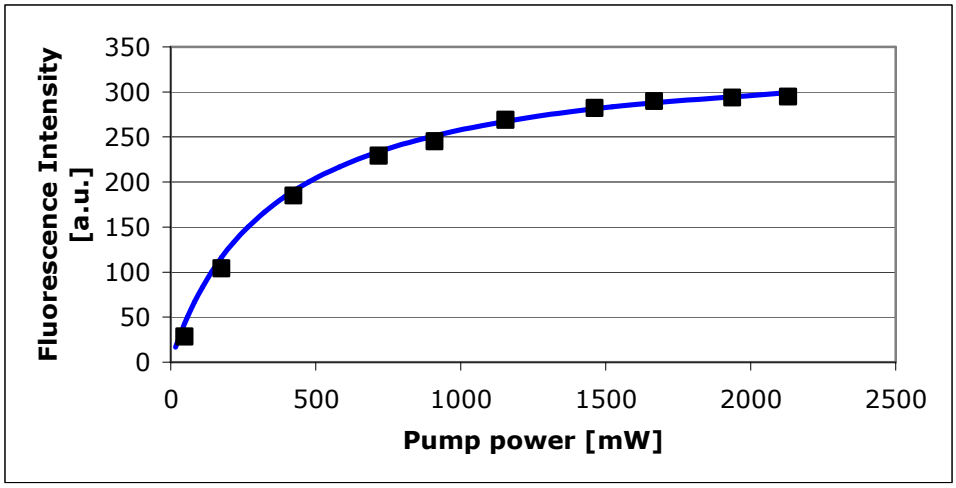

Fig. 9: *Measured points: Fluorescence intensity at 586 nm as a function of pump power. Solid line: Calculated density of excited ions in the $^5D_4$ level as a function of pump power. This density is proportional to the measured transitions from $^5D_4$ to ^7F_J. The fit is obtained with $\sigma_1 = 1.15 \cdot 10^{-21}$ cm^2 and $\sigma_0 = 1.9 \cdot 10^{-22}$ cm^2 [1] leading to a ratio of about $\sigma_1/\sigma_0 = 6$.*

In this fit the cross-section of ESA is considerably larger than that for GSA. In view of the quadratic behaviour of the losses by ESA as a function of pump-power, there is not much hope to reach threshold for laser activity by harder pumping. In this case excitation with a different wavelength has to be considered. Nevertheless, these results are but preliminary. For a more precise measurement and calculation of ESA fibres with considerably lower scattering losses have to be manufactured.

With the quadratic characteristic of the transitions by ESA, fluorescence with quadratic characteristic is expected from the ESA target level. This fluorescence expected at 244 nm has not been found. After relaxation, emission from $^5D_3$ has overall a rather linear behavior with some saturation at higher pump power (Fig. 10).

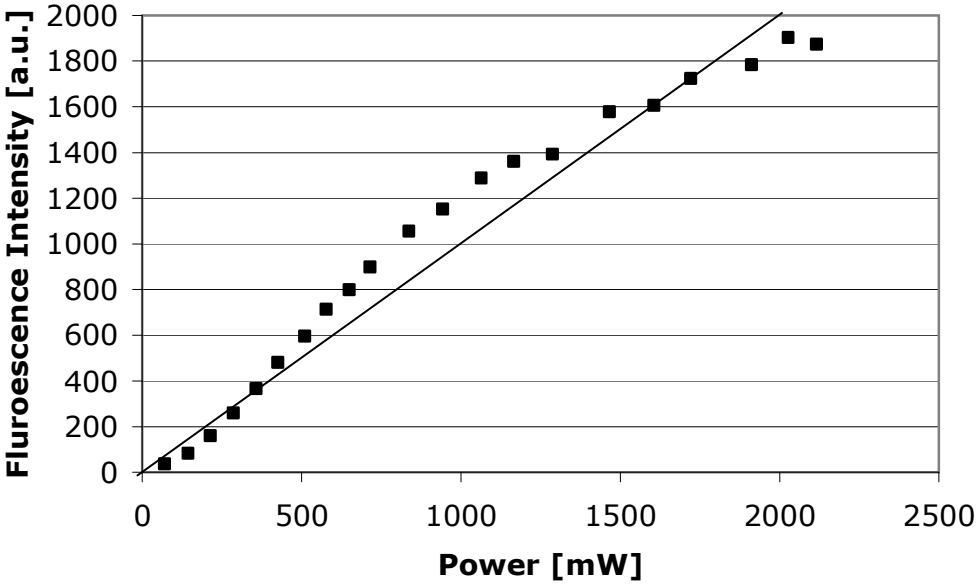

Fig. 10: Fluorescence from $^5D_3$ to $^7F_6$ as a function of pump-power

According to [6] it is assumed that the ESA from $^5D_4$ with a pump wavelength of 488 nm ends in an excited state of the type $4f^7 5d^1$ that is higher than all $4f^8$ levels. In [6] this level is measured to have its maximum at 231 nm and the width is sufficient also to strongly absorb a wavelength of 244 nm. The $4f^7 5d^1$ levels partly overlap with the glass matrix band [7]. It has to be assumed that part of the excitation induced by ESA is non-radiative.

Conclusion

In conclusion a Tb^{3+}:Al^{3+} silica fibre has been manufactured and characterized with respect to scattering losses. The measurement of fluorescence from $^5D_4$ shows strong saturation with respect to the pump-power. This saturation is explained with ground-state bleaching and with ESA of 488 nm pump light in the $^5D_4$ level. A simulation of the ESA process shows that the cross-section for ESA can be larger than for GSA.

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