Spectroscopy of yttria-alumina-silica glass doped with thulium and erbium

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Abstract— Yttria-alumina-silica (YAS) glasses doped with Er^{3+} and Tm^{3+} have been examined spectroscopically for their prospect as fibre amplifier gain media for optical telecommunication systems. Absorption and emission spectra, as well as emission lifetime measurements and Judd-Ofelt calculations are reported. Tm^{3+}:YAS glass has a emission bandwidth of 122nm around 1470nm, making it promising for S^+ band amplification.

Index Terms— Erbium, Glass, Optical materials, Spectroscopy, Thulium

I. INTRODUCTION

Glass formation in the system Y_2O_3, Al_2O_3 and SiO_2 has been observed for Y_2O_3 concentrations in the range 10%-25%(mole) [1]-[3]. These glasses exhibit high transformation temperatures about 900°C, which are virtually independent of the composition. Other remarkable properties of these glasses are the high strength and high refractive index, which increases rapidly with the Y_2O_3 content. The glasses are stable and can easily be prepared in large batches.

The structure of yttria-alumina-silica (YAS) glasses is somewhat unconventional, as it contains a large number of five and sixfold coordinated aluminum ions which charge compensate the yttrium ions and thus reduce the formation of clusters [3], [4]. This structure makes the glasses highly promising as laser gain media for high rare earth dopant concentrations.

Raman measurements [5] show that the maximum vibrational energy in YAS glass is about 950cm^{-1}, which is considerably less than silica glass.

Despite the considerable body of work on the structure and properties of these glasses, no investigation of the spectroscopy of doped YAS glasses has yet been published to our knowledge. In this communication, we focus on the spectroscopy of two rare-earth ions, Er^{3+} and Tm^{3+}, because they both show laser emission in the transmission window of silica glass fibre around 1.5μm.

II. EXPERIMENTAL

The glasses with composition 26.25mole% Al_2O_3 (Alfa Aesar 99.997%), 47.5% SiO_2 (Alfa 99.995%), and 26.25%

Y_2O_3 (ABCR 99.999%) have been melted in 30g batches at 1600°C for 1h in an electric furnace flushed with O_2 using a Pt crucible. The glass was cast onto a steel mould preheated to 350°C, annealed for 1h at 900°C and cooled to room temperature at a rate of 30°C/h. For the Tm^{3+} doping, some of the Y_2O_3 had been replaced with Tm_2O_3 to yield a concentration of 3200ppm Tm_2O_3 (corresponding to $3.8 \cdot 10^{19}$ Tm^{3+} ions/cm^3). Two samples doped with Er^{3+} have been prepared similarly with doping levels of 2600ppm Er_2O_3 ($3 \cdot 10^{19}$ ions/cm^3) and 26000ppm Er_2O_3 ($3 \cdot 10^{20}$ ions/cm^3).

Absorption measurements were done with a Cary 500 spectrophotometer on 2.5mm thick polished slices with 2nm resolution.

A Ti-Sa laser at 794nm and about 200mW power, modulated with an acousto-optic modulator, was used to excite the $^3F_4$ level of Tm^{3+}. The fluorescence spectrum was recorded with an Acton Spectrapro 300i monochromator with 5nm resolution and a New Focus 2034 InGaAs diode as detector. A Stanford SR530 lock-in amplifier was used to improve the signal-to-noise ratio. The lifetime of the $^3F_4$ level was measured by using the monochromator to select a 7nm band centered at 805nm, and a photomultiplier in photon counting mode. The setup has a sub-microsecond time resolution. The lifetime of the $^3H_4$ level was measured with the InGaAs diode with a time resolution of 20μs and a Ge-filter to block any light with wavelengths shorter than 1600nm.

For the Er^{3+} doped samples, the fluorescence spectrum was recorded in a similar setup with the Ti-Sa wavelength 980nm to excite the $^4I_{11/2}$ level of Er^{3+}. The resolution of the spectrum is 2.5nm. All fluorescence spectra have been corrected for the spectral response of the system. The lifetime of the $^4I_{13/2}$ level was measured by blocking the pump light with a Si-filter in front of the InGaAs diode. The time resolution of the system is 20μs. The pump power was kept below 10mW to avoid upconversion processes.

III. RESULTS AND DISCUSSION

A. Er^{3+} doped YAS glass

Fig. 1 shows the absorption spectrum of the 26000ppm Er^{3+}:YAS glass with all transitions expected from the energy level diagram. The background absorption at wavelengths shorter than 450nm has been observed in undoped glasses as a yellow tint [3] and may be due to the onset of the fundamental

absorption of the glass host.

Judd-Ofelt analysis has been done as described elsewhere [6]. The J-O parameters obtained are: $\Omega_2 = (6.04\pm0.09)\cdot 10^{-20}$ cm^2, $\Omega_4 = (1.85\pm0.12)\cdot 10^{-20}$cm^2, and $\Omega_6 = (1.34\pm0.05)\cdot 10^{-20}$ cm^2 with a rms error of 1.7%. For the lower doped sample the values are the same within the error margins. They are close to values reported for sodium aluminosilicate glasses with similar alumina content [7].

From the absorption band of the lowest excited level $^4I_{13/2}$ (inset in Fig. 1), the emission cross section of the 1.5μm band has been calculated as described in [8]. The result is compared with the measured emission spectrum, scaled by λ^5 and a constant factor, in Fig. 2. The peak emission cross section is 0.7$\cdot$ 10^{-20}cm^2 at 1534nm, which is similar to other silicate glasses [9]-[10]. The width of the emission band is 46nm, which also is comparable to other silica-based glasses [9].

The fluorescence of the $^4I_{13/2}$ level at 1.5μm has a single exponential decay characteristic for both samples, as shown in Fig. 3. The lifetimes are 7.5ms for the highly doped sample and 7.0ms for the lower dopant concentration, respectively. From the Judd-Ofelt parameters the radiative lifetime, 6.8ms, has been calculated. This is, within experimental errors, the same as the measured lifetime of the sample with low Er^{3+} concentration. This indicates that the radiative quantum efficiency is close to unity.

The apparent increase in lifetime for the highly doped sample may be a result of radiation trapping due to re-absorption of fluorescence light.

The fluorescence lifetime of Er^{3+} ions doped into alumino-phosphosilicate glass has been shown [11] to decrease for concentrations exceeding 0.1wt%. No similar effect can be found from our data for yttria-alumina-silica glass, even though we used concentrations up to 2.5wt%. This proves it is possible to use high Er^{3+} concentrations without any detrimental effect on the quantum efficiency. Potential applications for this material are short active devices. Also, the absence of any measurable concentration effects confirms there is no clustering of the rare earth compound in these glasses. This agrees well with the structural model suggested by Shelby [3].

B. Tm^{3+} doped YAS glass

The absorption spectrum of Tm^{3+}:YAS glass in Fig. 4 shows all the absorption peaks expected from the energy level diagram. The $^3H_4$ and $^3F_4$ levels are labeled according to the dominant wavefunction contributing. There is some broad background absorption in the 600nm – 800nm region, which may be caused by transition metal impurities in the sample and is subject to further investigation.

Best results for the Judd-Ofelt calculations were obtained by omitting the $^1D_2$ level and by merging the overlapping $^3F_2$ and $^3F_3$ levels. The J-O parameters, $\Omega_2 = (6.98\pm0.66)\cdot 10^{-20}$cm^2, $\Omega_4 = (0.17\pm0.53)\cdot 10^{-20}$cm^2, and $\Omega_6 = (1.65\pm0.17)\cdot 10^{-20}$cm^2, agree with values published [12], [13] in that Ω_2 is the largest parameter. A more detailed comparison is not appropriate, because three ($^3F_4$, $^3H_4$, and $^1G_4$) out of the six transitions used

are hypersensitive [12].

The fluorescence spectrum of the $^3F_4$ — $^3H_4$ transition around 1470nm, relevant for telecommunications amplifiers has been converted into absolute emission cross sections using the Füchtbauer-Ladenburg equation [14]:

$$\sigma_{em}(\lambda) = \frac{A\lambda^5 I(\lambda)}{8\pi n^2 c \int I(\lambda)d\lambda} \qquad (1)$$

The radiative rate for the transition (144s^{-1}) has been calculated from the Judd-Ofelt parameters. Fig. 5 shows that the peak emission cross section is about 0.24$\cdot$ 10^{-20}cm^2 at 1460nm, comparable to tellurite glasses [15]. However, due to the errors of the Judd-Ofelt parameters and the overlap between the 1.4μm and the 1.8μm band, this value is likely to have an error of about 15%.

The more important information in Fig. 5 is, however, that the emission band has a full width at half maximum of 122nm and is thus far broader than in other glasses, such as tellurite or fluoride glasses [15]. This makes the Tm^{3+}:YAS glass system extremely interesting for broadband amplification in the telecommunications S$^+$ band.

The fluorescence decay of the $^3H_4$ level, the lower level of the 1470nm transition, is single exponential with a lifetime of 1.2ms, compared with 0.2ms – 0.5ms reported in silica glass [16]. This indicates that the nonradiative decay rates in YAS glass are considerably reduced compared with other silicate glasses, as expected from the lower maximum phonon energy.

The decay of the upper laser level, $^3F_4$, in Fig. 6 is clearly not single exponential. This has been explained by the width of the $^3F_4$ level [17] leading to a distribution of non-radiative decay rates. For comparison with published data, it has been fitted with a single exponential decay function. The lifetime of 100μs is almost three times longer than in aluminosilicate glasses [17]. The radiative lifetime of this level, calculated from the Judd-Ofelt parameters, is 470μs, equivalent to a radiative quantum efficiency of about 20%. The calculated radiative lifetime depends critically on the Judd-Ofelt Ω_4 parameter, which in our analysis has a fairly large error. More work is thus needed to determine the quantum efficiency of the $^3F_4$ level of Tm^{3+} in this material more accurately.

IV. CONCLUSION

We present results of spectroscopy on Er^{3+} and Tm^{3+}-doped yttria-alumina-silica glass for the first time. The absorption spectra and Judd-Ofelt parameters for both ions agree well with data for other rare-earth doped glasses.

Er^{3+}:YAS glass shows emission from the $^4I_{13/2}$ level centered at 1534nm with a width of 46nm. The emission lifetime is 7.0ms, indicating effectively unity quantum efficiency. The fluorescence decay is single exponential in the Er^{3+} concentration range used (up to 2.5wt%, equivalent to 3$\cdot$ 10^{20} ions/cm^3). These results make YAS glass an interesting host material for high dopant concentrations, thus enabling short device lengths. Further work on Er^{3+}:YAS should determine the upper Er^{3+} concentration limit.

Tm^{3+}:YAS glass has an outstandingly broad $^3F_4$ → $^3H_4$ emission band centered at 1460nm with a width of 120nm. The lifetime of the lower level, $^3H_4$, is 1.2ms, whereas the upper level lifetime is about 100µs. The quantum efficiency of the upper level to be about 20% has been calculated from the Judd-Ofelt parameters. Both these features make Tm^{3+}:YAS an interesting candidate for an optical S^+ band amplifier. Also, this system may be suitable for lasing on the $^3F_4$ → $^3H_5$ transition around 2.3µm. Future work will include an investigation into the composition dependence of the emission characteristics as well as co-doping to reduce the lifetime of the lower level.

V. REFERENCES

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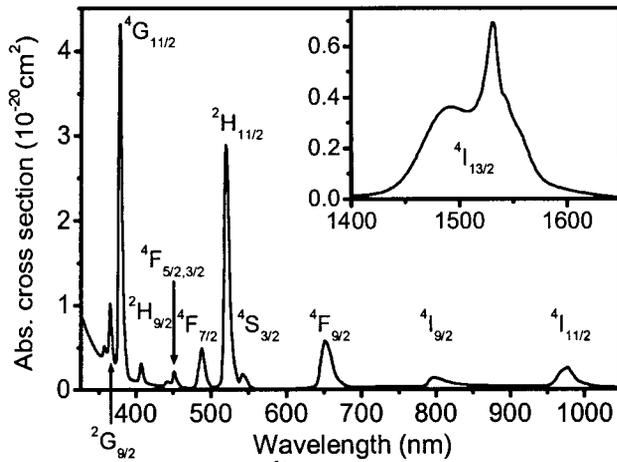
Fig.1. Absorption spectrum of Er³⁺:YAS glass. The axes of the inset are in the same units as the main graph.

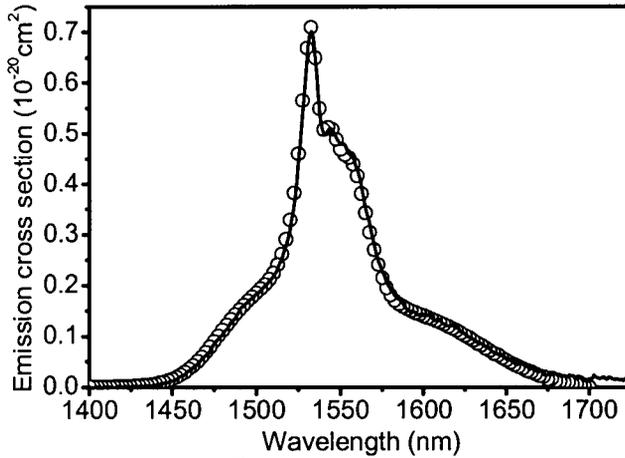Fig. 2. Fluorescence of Er³⁺:YAS glass (line) compared with McCumber calculations (symbols). The peak emission cross section is $0.7 \cdot 10^{-20} cm^2$ and the width of the band about 43nm.
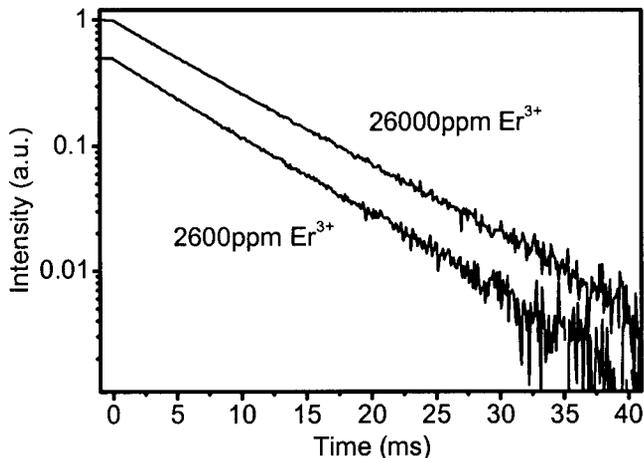

Fig. 3. Fluorescence decay of Er³⁺:YAS glass at 1.5µm. The decays are single exponential with lifetime of 7.0ms (2600ppm Er³⁺) and 7.5ms (26000ppm Er³⁺), indicating that no concentration quenching occurs.
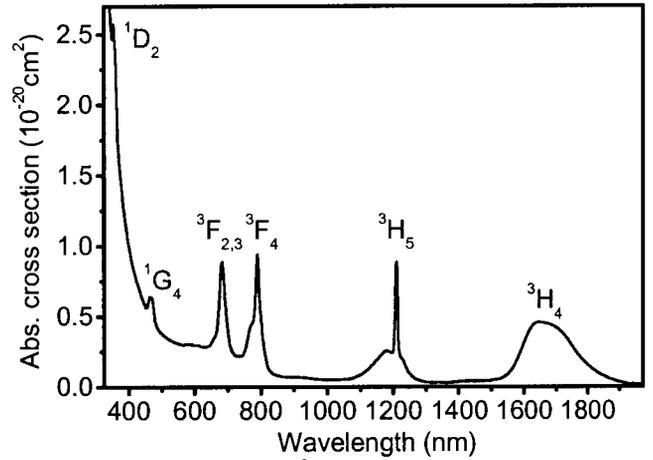

Fig. 4. Absorption spectrum of Tm³⁺:YAS glass.
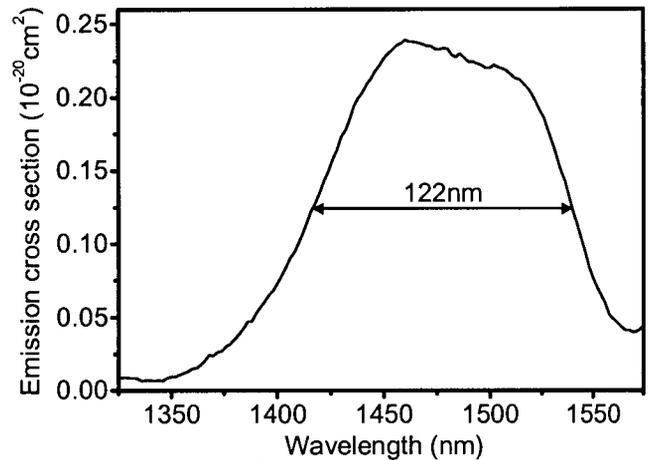

Fig. 5. Fluorescence of Tm³⁺: YAS glass under excitation at 794nm. The emission band is more than 120nm wide, considerably more than in other glasses.
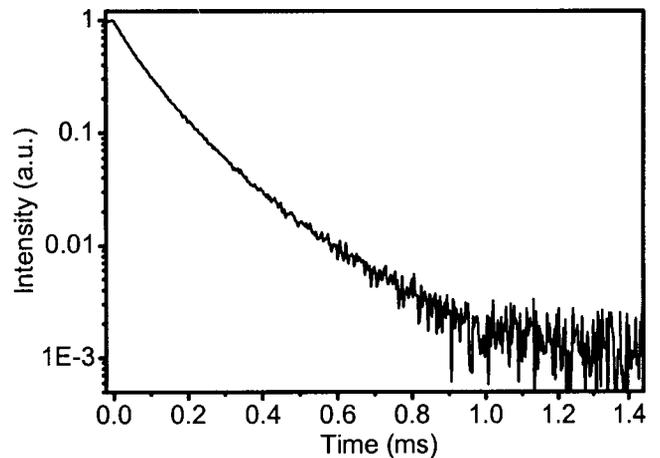

Fig. 6. Fluorescence decay of the ³F₄ level of Tm³⁺: YAS glass. The lifetime of this level is about 100µs, corresponding to a quantum efficiency of about 20%.