Fabrication and spectroscopy of erbium doped gallium lanthanum sulphide glass fibres for mid-infrared laser applications

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Gallium lanthanum sulphide based glasses are proposed as high quality hosts for rare-earth doped, mid-infrared fibre lasers, that would offer compact and rugged sources for gas sensing, atmospheric transmission, and medical applications. The infrared emission spectroscopy of erbium doped glasses and fibres shows the potential of this glass host for the above applications. Mid-infrared transitions at 2.0, 2.75, 3.6, and 4.5µm have been detected and characterized.

1. Introduction

There is considerable international interest in developing mid-infrared (MIR) laser sources for gas sensing, atmospheric transmission, and medical applications. Many characteristic absorption 'fingerprints' of gases and vapours lie in the 2-5µm wavelength range, as do the atmospheric transmission windows. Our work targets specific wavelengths for these applications such as 4.3µm emission from Dy^{3+} for CO_2 detection, 4.7µm from Pr^{3+} and 4.8µm from Tb^{3+} for CO and O_3 detection, 3.4µm from Pr^{3+} for CH_4 detection, and 3.9µm emission from Ho^{3+} for atmospheric transmission. Diode pumped rare-earth doped fibre lasers would offer compact and efficient alternatives to the either relatively weak, or very complex MIR sources currently available, such as thermal emitters, gas lasers, OPO's or semiconductor lasers.

A fibre laser geometry is advantageous as the waveguiding gives good overlap of pump and laser modes, and the pump intensity is high, reducing the threshold, and increasing efficiency. A prerequisite for the rare-earth host material is a low phonon energy leading to MIR transparency and low non-radiative decay rates and therefore high quantum efficiency of radiative transitions. Conventional silica fibres do not fulfill these requirements leading to a need for new host materials with lower phonon energies that must also be suitable for fibre drawing. Mid-infrared transmitting fibres are currently either fluorozirconate based, with the disadvantages of being hygroscopic, and having a relatively small transmission window (~1-3µm), or As_2X_3 (X= S, Se etc.) based with the disadvantage of toxicity should the fibre burn or degrade, and low rare-earth solubility. Our approach to MIR lasers is based on stable, non-toxic, and non-hygroscopic chalcogenide glasses based on gallium and lanthanum sulphides with the molar composition $70Ga_2S_3:30La_2S_3$ (GLS), and $70Ga_2S_3:30La_2O_3$ (GLSO), both of which have been drawn into fibre successfully. [1] They have a low phonon energy (425cm^{-1} for GLS) and a wide transmission window that extends to beyond 8µm with an absolute loss minimum around 4µm.

2. Glass properties.

Starting materials of Ga_2S_3, La_2S_3, or La_2O_3 powders are batched and mixed, before transferring to a vitreous carbon crucible in a silica tube. Melting is done at 1150°C for sever- al hours to give a homogenous glass ingot upon quenching. For thermal analysis 30g test melts are produced, which also give enough glass for small bulk glass samples to be cut and polished from. These are used for spectroscopic measurements. Fibre drawing is done by a rod-in-tube method, for which 220g ingots of glass are produced, cut, and optically polished into rods and tubes. Fig. 1 shows a glass ingot, some polished tubes, and a tube that has been stretched into a cane for insertion into a tube.

Fig. 1. A photograph of GLS glass; a 220g ingot, some polished rods (110mm x 8mm), and a drawn 'cane'.

Thermal analysis is performed using a Perkin-Elmer DTA7 for transition temperatures, and for viscosity measurements a Perkin Elmer TMA7 is used, which has been adapted for parallel plate rheometry. It is best to perform fibre drawing at temperatures well below the crystallisation temperature of the glass. To this end a simple test of the thermal quality of a glass with respect to fibre drawing may be measured by the separation of the drawing temperature (T_η; the temperature at which the viscosity ~10^6 poise) and the peak crystallisation temperature (T_p). A large value for T_p- T_η would give a glass that is more suitable for fibre drawing. For GLS T_p- T_η=46°C, and for GLSO T_p-T_η=130°C. This makes GLSO an easier glass to draw into fibre without crystallisation. A typical cross section of a double clad uncoated GLSO fibre is shown in Fig. 2.
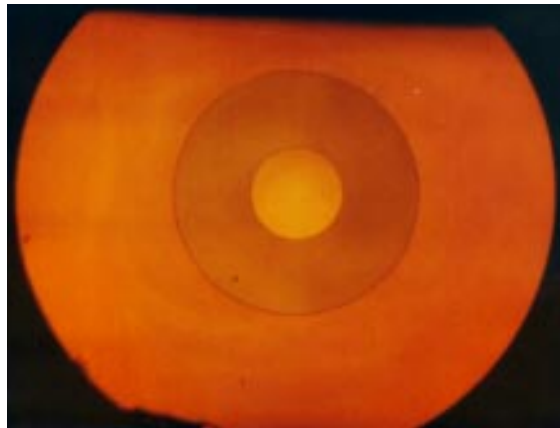

Fig. 2. Cross section of a double clad uncoated GLSO fibre.

Minimum losses of about 4dBm^{-1} at 4µm have been achieved in unclad GLSO fibres. The attenuation spectrum is largely flat over a wide wavelength range. The loss in the 1-3µm region of the spectrum has a complex dependence on wavelength that is a combination of absorptions from transition metal impurities and scattering effects. Transition metal absorptions in GLS based glasses have been measured by intentionally doping the glass with transistion metals, to identify individual contributions of transition metal ions to the materials loss. In the 3-5µm region the absorption comes primarily from scattering from inclusions, crystallites and bubbles, and from OH$^-$ impurity introduced by the La_2O_3. It is anticipated that purification of the starting materials will improve the loss considerably by removing the absorptions from transition metals, and also reducing the number of nucleation sites for crystallization, and hence the scattering loss. [2]

These glasses have several advantages over other glass materials as rare-earth hosts. The solubility of rare-earth ions is extremely high due to the presence of lanthanum as a glass former, and the emission cross sections of rare-earth levels are enhanced by the high refractive index (n=2.4 for GLS, 2.2 for GLSO). Combined with the low phonon energy, this potentially gives access to MIR transitions for lasers. We have chosen the erbium ion as an example to show the effect of the glass host on the spectroscopy of the incorporated rare-earth ions.

3. Mid-infrared spectroscopy of erbium doped GLS glasses and fibres

The trivalent erbium ion (Er^{3+}) is probably the most widely studied rare-earth dopant in glass fibres due to the success of the EDFA (Erbium Doped Fibre Amplifier) in silica based glasses. [3] EDFA's make use of the 1.55µm transition from the $^4I_{13/2}$ level to the ground state (Fig. 3). In silica glasses the $^4I_{13/2}$ level is the only metastable level with a typical lifetime of 10ms whereas all the higher lying levels show lifetimes shorter than 10µs. The high phonon energy of the glass host causes large non-radiative decay rates for levels with small energy gaps to the next lower level and quenches emission from these levels. Changing the host material from silica to a material with lower phonon energies considerably changes the spectroscopic properties of the embedded Er^{3+} ions.
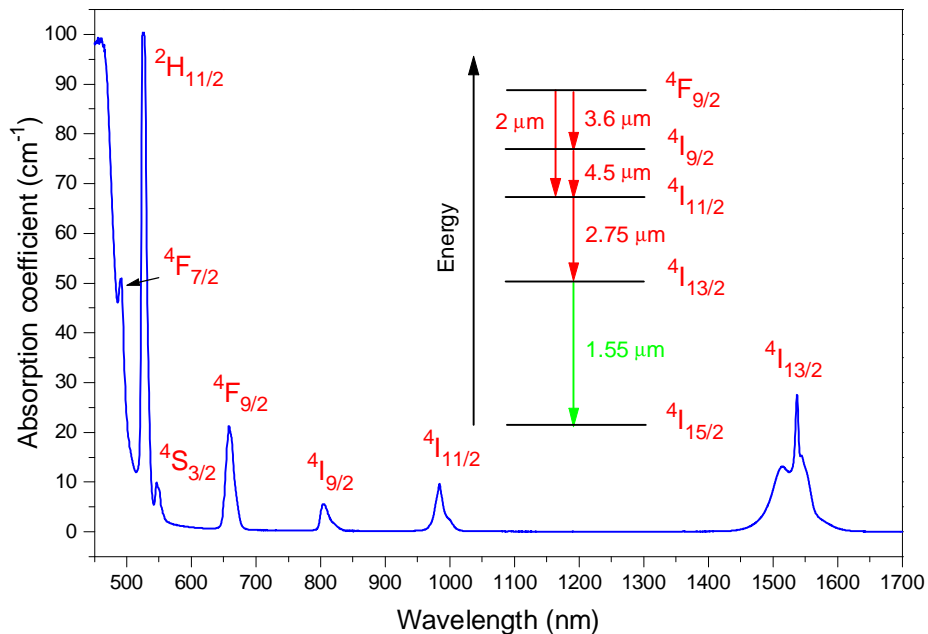

Fig. 3. Absorption spectrum of 9.7mol% Er^{3+} doped GLS glass
and Er^{3+} energy levels indicating the infrared transitions

For spectroscopic measurements the Er^{3+} ions were excited at 660nm ($^4F_{9/2}$) with a DCM dye laser and at 810nm ($^4I_{9/2}$) with a Ti:sapphire laser. Fluorescence spectra were measured with a 300mm monochromator and a liquid nitrogen cooled InSb detector. The fluorescence was collected from the end of the fibres and from the side of the bulk sample, both doped with 1.57mol% Er^{3+}. Spectra were corrected for system response and atmospheric gas absorptions using a black body source. Fig. 4 shows four infrared Er^{3+} emission bands at 2.0, 2.75, 3.6, and 4.5µm. The inhomogeneously broadened emission line shapes, typical for glass hosts, offer the possibility of wide wavelengths tunability. None of these would be observed in silica glasses or other high phonon energy host materials.
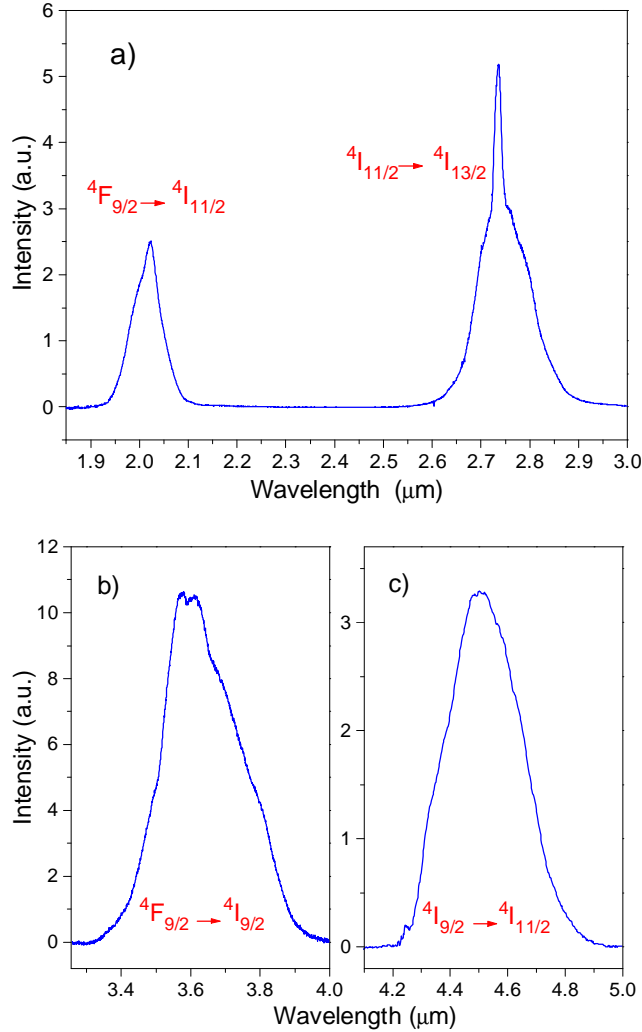

Fig. 4. Fluorescence spectra of 1.57mol% Er^{3+} doped GLS glasses and fibres
a) 2.0µm and 2.75µm emission from 3.9cm of 270µm diameter fibre pumped with 60mW at 660nm
b) 3.6µm emission from 8.6cm of 270µm diameter fibre pumped with 70mW at 660nm
c) 4.5µm emission from a bulk glass sample pumped with 570mW at 810nm

Judd-Ofelt calculations and lifetime measurements for Er^{3+} doped GLS glass are given in Ref. 4. We used the given electric and magnetic dipole contributions, A_{ed} and A_{md}, of the radiative transition rate $A = A_{ed} + A_{md}$ and the radiative and measured lifetimes τ_r and τ_m to calculate the branching ratios $\beta = A \times \tau_r$ and the quantum efficiencies $\eta = \beta \times \tau_m/\tau_r$ for the above transitions (Table 1). The emission cross sections σ_{em} were calculated from the

radiative rates A and the measured intensity spectra I(λ) using the Füchtbauer-Ladenburg equation as given in Ref. 5:

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

The refractive index n is 2.36 for all four transitions. Table 1 summarises the radiative properties of the four infrared transitions.

Table 1. Radiative properties of mid-infrared transitions in Er^{3+} doped GLS glass
(A_{ed}, A_{md}, τ_r, and τ_m from Ref. 4)

Transition	λ (μm)	A_{ed} (s^{-1})	A_{md} (s^{-1})	β (%)	τ_r (μs)	τ_m (μs)	η (%)	σ_{em} (10^{-20} cm^2)
$^4F_{9/2} \rightarrow {}^4I_{11/2}$	2.02	249	18	3.7	140	100	2.6	1.52
$^4F_{9/2} \rightarrow {}^4I_{9/2}$	3.62	21	8	0.4	140	100	0.3	0.43
$^4I_{9/2} \rightarrow {}^4I_{11/2}$	4.53	4	4	1.0	1200	590	0.5	0.25
$^4I_{11/2} \rightarrow {}^4I_{13/2}$	2.74	70	26	14.7	1530	1230	11.8	1.10

The values in the second and third rows are in good agreement with the results reported recently by L.B. Shaw et. al who obtained branching ratios of 1% both for the 3.6μm and 4.5μm transitions with measured lifetimes of 100μs and 500μs and cross sections of 0.45×10^{-20}cm^2 and 0.25×10^{-20}cm^2, respectively, in an Er^{3+} doped barium indium gallium germanium sulphide glass. [6]

The measured lifetimes for the 0.0158mol% Er^{3+} doped samples from Ref. 4 do not correspond to the size of the energy gaps to the next lower lying level, i.e. the lifetime of the $^4I_{9/2}$ level is longer than the lifetime of the $^4F_{9/2}$ level although the energy gap is smaller. This clearly indicates that the decay rates are dominated by the radiative decay and that non-radiative rates are very low in GLS glasses.

Nevertheless, quantum efficiencies are relatively low due to the low branching ratios, i.e. strong competing visible and near-infrared transitions from the same levels. However, the demonstration of lasing on the 3.6μm transition in an Er^{3+} doped fibre based on a fluorozirconate glass with less favourable spectroscopic properties (lower radiative rates and higher non-radiative rates) shows the potential for mid-infrared fibre lasers based on GLS glass. [7] A first step towards the realisation of these devices was the recent demonstration of the first rare-earth doped chalcogenide glass fibre laser in a Nd^{3+} doped GLS glass fibre at 1.08μm. [8]

Radiation at 2μm finds application in LIDAR systems, radiation at 2.75μm coincides with a strong water absorption in tissue and is used for medical applications, the 3.6μm transition could be useful for H_2S, NO, and SO_2 sensing or remote sensing depending on the wavelengths it is tuned to, and the 4.5μm transition could find use as CO and O_3 gas sensors when tuned to 4.7μm.

In conclusion we present the fabrication and spectroscopy of Er^{3+} doped gallium lanthanum sulphide based glasses and fibres showing the suitability of this glass host for rare-earth doped mid-infrared fibre lasers.

Acknowledgments

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