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Gallium Lanthanum Sulphide Fibre for Active and Passive Applications

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ABSTRACT

At Southampton, our work has focussed on gallium lanthanum glass and fibre, for both active and passive applications. As part of our ongoing programme, optical, thermal and mechanical properties of these glasses are under study. In parallel with this, fibre drawing is being refined in a quest for practical fibres. Over the past year, improvements have been made in understanding and eliminating the sources of loss in these glasses. In this paper, we describe the current specifications of fibres based on this material group. Recent progress in several applications, in particular those extending into the infrared will be reported and the prospects for a future generation of sulphide-fibre based devices examined.

Keywords: Infrared, Optical Fibre, Chalcogenide, Power Delivery, Laser

1. INTRODUCTION

Optical fibres drawn from sulphide-based glasses have been studied now for almost two decades. Initial work began in the 1970's when fibres from glasses based on arsenic sulphide or germanium sulphide rapidly found application as infrared waveguides, providing transmission to beyond 5 microns[1]. In 1993, the first active application of a sulphide glass was demonstrated and measurements on bulk samples of rare-earth doped gallium lanthanum glass showed the possibility of pump efficiencies of over 60%[2]. This lead to widespread activity with the goal of demonstrating a low-loss sulphide glass optical fibre and an 1310 nm optical fibre amplifier[3-7]. However, application of fibre is critically dependent on the achievement of a low loss single-mode optical fibre.

There are several families of chalcogenide based glasses. Arsenic- based glasses have been drawn to low-loss single mode fibres ($100\mathrm{dBkm}^{-1}$ at $4\mu\mathrm{m}$[8]) and have a transmission window of 600nm to 8μm for passive applications. These glasses however tend to suffer from a strong SH^- absorption band around 4μm, the centre of the important 3-5μm window. Their phonon energy is low, $\sim 400\mathrm{cm}^{-1}$, indicating the possibility of efficient active devices, but rare earth solubility is limited. Also, should the fibre burn or degrade, it will release As into the environment which reduces its attractiveness.

Germanium-based glasses are more attractive for active devices. By modifying the glass structure with Ga or As, rare-earth solubility is improved. Transmission in the visible is slightly restricted compared to As_2S_3 glass which may effect pump absorption or applications at 1310nm however these glasses remain promising and several groups are pursuing fibres in these materials.

Gallium based glasses address many of the problems of those above. The transmission window of 500nm to 6μm is suitable for telecommunications applications as well as in the critical 3-5 micron window of the infrared red. Through modification of these glasses, in particular Ga:La:S glass with oxides or halides, visible transmission can be extended until the glass is virtually transparent[9]. A reasonably low phonon energy of 425cm^{-1} gives high quantum efficiency for radiative transitions of excited dopant ions. For example, although a 1.3μm fibre amplifier using the Pr^{3+} $^1G_4$-$^3H_5$ transition has been demonstrated in ZBLAN, its quantum efficiency is only 4%, whereas in Ga:La:S the same transition has an efficiency of 68%[10]. Furthermore, one group has achieved single mode fibre with losses of 1.2 dBm^{-1} and demonstrated an efficient 1.3μm amplifier with a Ga:Na:S glass[11]. In our own experiments, we have found the higher rare earth dopant levels needed for 3-5μm active devices is again limited by the solubility of Ga:Na:S, which is not the case however for Ga:La:S. This glass is environmentally stable, and non-toxic, giving advantages over the other candidate glasses. Moreover, the glass transition temperatures are greater than 500°C, providing additional stability.

For these reasons, and in particular the high rare-earth solubility, low toxicity and ability to draw into fibre with a wide transmission range unhindered by SH^-, we have concentrated our activity on the Ga:La:S glass family. Fibre losses are currently high, a few dB/m, however it is impurity limited and thus the potential for improvement is real.

2. GLASS PROPERTIES

An understanding of the basic optical and thermal properties of gallium lanthanum sulphide based glasses is essential for understanding the applications and challenges of achieving practical fibre. Here we discuss key results from our ongoing programme of the characterization of these glasses.

2.1 Optical Properties and Intrinsic Loss

The first applications of chalcogenide fibres were to exploit their IR transmission, which far exceeds that of silica and fluoride based fibres. The long and short wavelength edges of the transmission window are limited by the multiphonon and electronic (Urbach) absorption edges respectively. For comparison to other glasses, the absorption edges were measured for the standard compositions, nominally 70:30 Ga:La:S, using thin slices of bulk glass. Transmission spectra of the bulk glasses were measured between 300nm-700nm using a dual beam Perkin-Elmer Lambda 9 spectrophotometer. Infrared measurements were performed using a Fourier transform infrared spectrometer, Perkin-Elmer System 2000 and corrected for interface reflections. The light source was a broadband NiCr wire with a TGS detector. Two thicknesses of bulk samples were polished for each glass, the thickness of each set was measured and found to be nominally 400μm, and 170μm. The limiting factor in measuring attenuation in the FIR region was the intensity of the MIR source used in the FTIR for these measurements. In the short wavelength region the attenuation was no longer dominated by the multiphonon edge, but by a mixture of the edge, impurity absorptions and scattering.

In the limit of low loss, the dominant loss mechanism between these two edges is scattering from small scale fluctuations of the refractive index that are frozen into the lattice upon quenching from the liquid.

There are two main causes of index fluctuations: from density fluctuations and from compositional fluctuations in the glass. We have followed Lines[12] and a thermodynamic approach to finding the fluctuations in the glass composition and converting these into fluctuations in dielectric permittivity, from which the loss coefficient can be evaluated.

In figure 1, the UV and long wavelength edges are plotted together with the calculated attenuation from Rayleigh scattering. It was found that the Rayleigh scattering from compositional fluctuations in the glass was approximately one order of magnitude more significant than Rayleigh scattering from density fluctuations, and this was due to the strong compositional dependence of the refractive index leading to a compositional Rayleigh scattering terms of $5.89\times10^{-18}\lambda^{-4}$. By contrast, the comparable density Rayleigh terms was $2.62\times10^{-19}\lambda^{-4}$ (λ in nm, loss in $\mathrm{dBm^{-1}}$). To the best of our knowledge this is the first time that compositional fluctuations have been included in calculating the minimum material attenuation of a chalcogenide glass.

The Ga:La:S glass has a loss minimum of $0.5\mathrm{dBkm^{-1}}$ at 3.5μm, which is comparable to a theoretical estimate for the minimum loss of $As_{40}S_{55}Se_5$, 0.02 $\mathrm{dBkm^{-1}}$ at 4.8μm[8],and ZBLAN, $0.01\mathrm{dBkm^{-1}}$ at 2.5μm[13]. It is possible that these values obtained were based solely on density scattering calculations and thus may be underestimated.

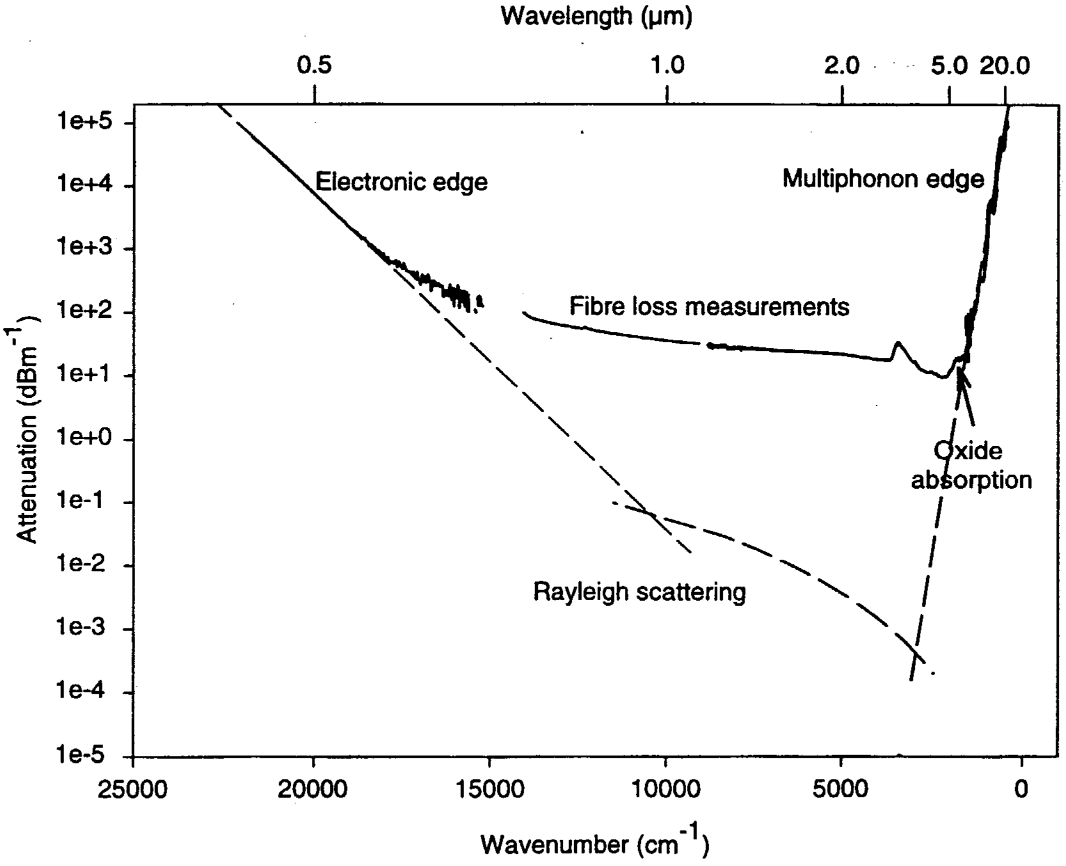

Figure 1. Intrinsic loss curve for Ga:La:S glass based on measured absorption edges and calculated scattering.

2.2 Thermal Properties and Viscosity

The thermal properties and in particular the characteristic temperatures: glass transition temperature, denoted Tg, the onset of crystallisation, T_x, and the peak crystallisation temperature, T_p and convey important information for the drawing of glasses such as Ga:La:S which is prone to crystallization. There are also three defined temperatures in terms of the viscosity of the glass. They are the strain point at which temperature the viscosity of the glass is approximately $10^{14.6}$ poise. At this viscosity the glass will tend to flow rather than fracture, and stresses in the glass will be relieved in hours. The annealing point is the temperature at which the viscosity is approximately $10^{13.4}$ poise, and stresses in a glass at this temperature will be relieved in minutes. The final temperature is the softening point, where the glass has a viscosity of approximately $10^{7.6}$ poise. At or above this temperature the glass can be worked and drawn into fibre.

We use differential thermal analysis (DTA) to determine T_g, T_x, T_p and the melting point T_m and results are summarized in table 1. In Ga:La:S, T_g~560°C, a clear advantage over some As-based glasses. The simple criterion for a good glass for fibre drawing are that the separation of T_g and T_x along with the width of the crystallisation peak T_p-T_x should be large, and the separation of T_m and T_p should be small. If T_x-T_g is small, the material will tend to crystallize at or before drawing, and may not draw at all. It may also be used as a guide to the maximum working temperature of the glass as ant glass held above T_g will eventually crystallise. If the width of the crystallisation peak is large, then some crystallisation may take place, but it will continue slowly, and not complete unless the temperature increases, whereas a small T_p-T_x means that crystallisation completes very quickly once started potentially making fibre very difficult to draw, particularly if T_x-T_g is also small.

	T_g (°C)	T_x (°C)	T_p (°C)	T_m (°C)	T_η (°C)
70:30	544	659	816	816	619
67.5:27.5	561	668	695	806	654
65:35	567	688	710	816	664

Table 1. Characteristic temperatures of Ga:La:S glass as a function of composition (T_η= temperature of viscosity 10^6 poise)

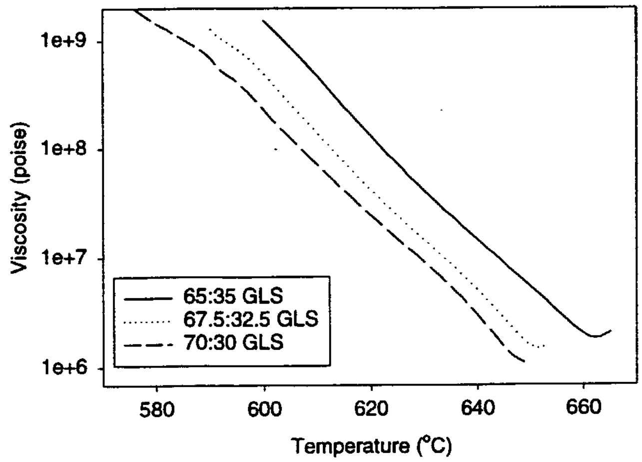

Figure 2. Viscosity as a function of composition for Ga:La:S

The viscosity of glass in the range 10^5 to 10^{11} poise (1poise=0.1Pa.sec) has been determined using the technique of parallel plate rheometry. A commercial thermo- mechanical analyser (Perkin-Elmer TMA7) with a high displacement sensitivity (up to 50nm) and temperature range up to 1000°C was used for both viscosity and expansion coefficient measurements. The sample was cylindrical in shape, typically of dimensions 5mm in both thickness and diameter. We followed the procedure of Wang[14] to determine the viscosity from the thermo-mechanical data. The viscosity of Ga:La:S as a function of composition is shown in figure 2. The limit of the viscosity measurements was around 10^6 poise or the viscosity required for fibre drawing, and the slight curve at the end of each measurement was due to the width of the sample approaching that of the plates, with sample compression becoming correspondingly more difficult.

3. FIBRE DRAWING

There are two basic methods of drawing fibre, from a preform, or from a melt, termed rod drawing, and (double) crucible drawing respectively. We have only explored rod drawing of these glasses however the technique of crucible drawing has never been ruled out as a possible alternative. In rod drawing, a glass preform is suspended in a short furnace, designed to heat a specific region. The temperature of the furnace is raised until the rod softens and begins to neck down and drop. If the conditions are correct then a fibre of glass will be drawn down with the drop to be wrapped around a drum which controls the rate at which fibre is taken from the neck of the preform. The diameter of the fibre is controlled by the furnace temperature, draw speed and the rate at which the preform is fed into the furnace. Core-clad fibres by this method are usually made by stretching (or caning) a rod of glass to a smaller diameter in the drawing tower, then inserting the cane into a tube of cladding glass before pulling to fibre. The core to clad diameter ratio is then equivalent to the ratio of the inner and outer diameters of the tube. It is found that to produce high strength fibres the softening temperature of the cladding should be 20-30°C lower than the core, and the expansion coefficient matched.

From 250g ingots of glass, we could cut and polish several rods or tubes of 10mm diameter and 110mm long. However one of the main limitations by using rod-in-tube for core-clad fibres is the difficulty in making small cores. With an OD of 10mm and ID of ~3.5mm the core-clad ratio was 0.35 (125µm fibre gives a 44µm core). With 2 draws the core could get to ~15µm. Therefore 3 draws were required to get the core size to the order of magnitude required for single mode fibres. This has been achieved, but core/clad fibre losses are typically an order of magnitude higher that unclad fibres. Alternatives to this rod-in-tube approach are now being explored.

Figure 3 shows the loss of a typical unclad fibre. The fibre loss was measured using a standard cutback method with an adapted FTIR spectrometer and a HgCdTe detector for 1µm-10µm

4. SOURCES OF LOSS

While the minimum predicted loss is of interest for looking at the ultimate material limits, the fibre loss is of more interest for at the present time. Fibre loss measurements are several orders of magnitude higher than the minimum theoretical loss and thus identifying the causes of loss is a significant part of the process of eliminating them. We now have details of absorption and scattering from impurities. The weak tail is as yet an unquantified source of loss in Ga:La:S glasses. There is however no reason to suggest that it will not behave as it does in other chalcogenides, so will not be discussed here.

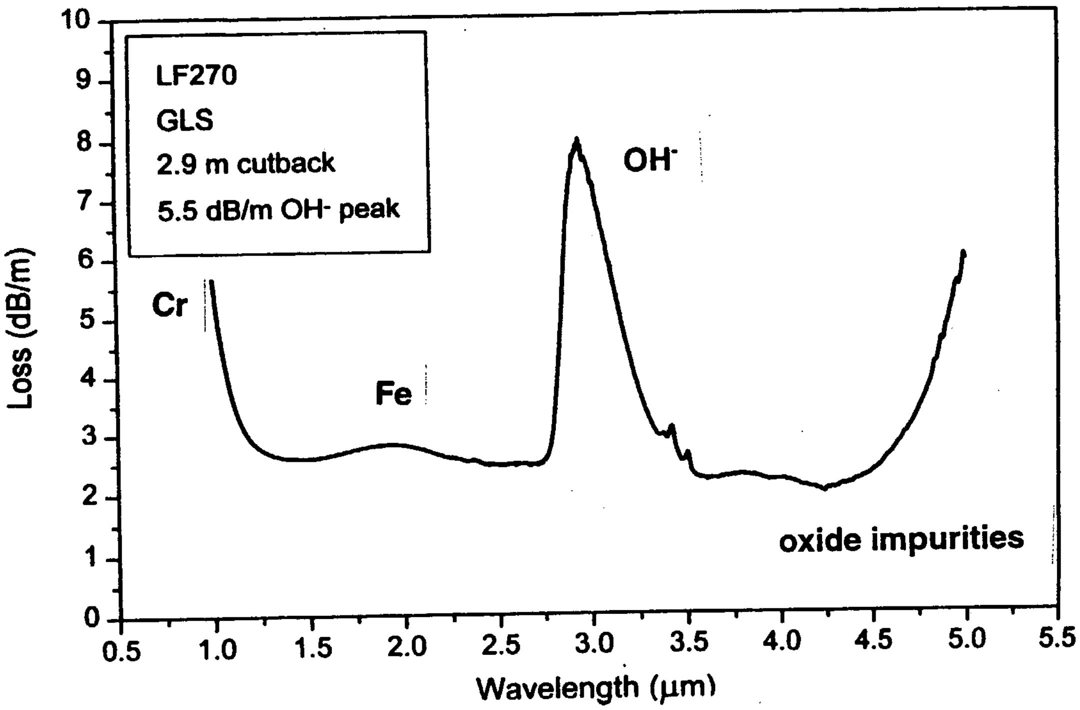

Figure 3. Attenuation measured in an unclad Ga:La:S fibre

4.1 Absorptive Losses

With reference to figure 3, the OH^- absorption peak around 3μm is obvious. The height of the peak indicates less than 1 ppm of OH^-. The width of the peak, stretching from 2.8μm to 3.4μm covers a substantial part of the spectrum, and the tail of the absorption will extend further as the background loss of the fibre is reduced. There is some evidence that OH^- impurity can lead to scattering losses in the fibre.

Metallic impurities also introduce absorptions in the IR. The first row transition metals have caused difficulties with other materials systems, ZBLAN and silica in particular, and are also extremely common, so are likely impurities. In chalcogenide glasses, the high refractive index enhances the absorption (and emission) cross sections of ions in the matrix, so the absorptions are expected to be strong. However, in contrast to ZBLAN and silica, chalcogenide glasses are reducing in nature, which may alter the oxidation state of some transition ions in the glass from what would be expected in an 'oxidising' glass host. Glow discharge mass spectroscopy (GDMS) was used to analyse the impurity content of the raw materials and glasses. Typical impurity levels in the Ga_2S_3 were on the order of 50 ppb for Fe, Co and Ni, while in the La_2S_3, we measured higher levels, approaching 1 ppm Fe.

A study into the absorptions of transition metal ions in Ga:La:S was carried out to assess the impact that trace amounts of these impurities would have on the glass. Glasses were melted that contained an intentionally added, known amount of transition metal sulphide (in its 3+ form if possible, if not then its 2+ or 4+) and melted in the usual way, for 24 hours. This gave the impurity time to reach its stable oxidation state in glass. The absorption spectra was measured using the FTIR, with an undoped sample as a background to account for interface reflections.

Ion	dB/m per ppm	λ_{peak}
Ti	0.25	1.0
V	1.2	1.2
Cr	9	1.0
Fe	3.5	2
Co	3.5	1.6
Ni	2.5	1.9

Table 2. Absorptions due to transition metals

Peak absorptions for the transition metals are given in Table 2. The absorptions from these impurities are extremely strong. Some ions such as V or Ti have absorptions confined to shorter wavelengths, whereas the absorption from Fe extends out beyond 5μm, with obvious consequences for entire 3-5μm window. Even so, all absorptions will generate problems for pumping the fibres. For example the peak absorption of Cr in Ga:La:S reaches 9dBm^{-1}ppm^{-1} at 1μm, exactly where the pump wavelength for Pr^{3+} is. One surprising result is that copper, a significant problem in fluoride glasses showed no absorption peak in Ga:La:S, which is perhaps indicative of an altered oxidation state to Cu^{+} rather than Cu^{2+}.

The concentration of impurities measured by GDMS can be used together with these plots to calculate the expected loss from included transition metals. The result is shown in figure 4, together with a measured loss plot from an earlier fibre. The shape of the two plots can be seen to be of the same form. The peak at 2.8μm on the top (fibre) plot is the onset of the OH^{-} absorption, and the spike at 1.4μm is from the beamsplitter in the FTIR.

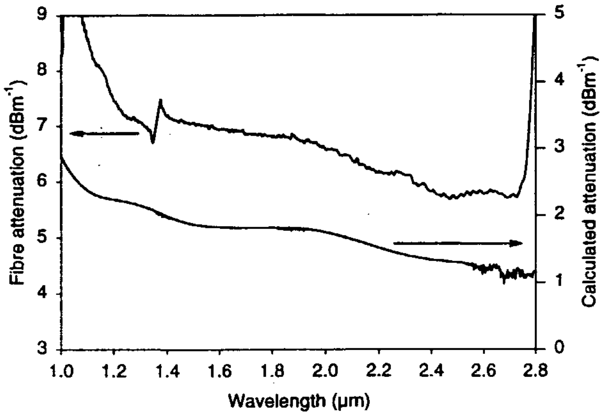

Figure 4. Fibre Absorption in 1-3 micron region comparing fibre attenuation with calculated combined absorption of transition metals.

Given the measured level of transition metal impurities, the strength of their absorptions, and the similarity of the measured and calculated loss plots, it can be claimed with some certainty that the loss in Ga:La:S based glass fibres is currently limited to a significant extent by the absorption from transition metal impurities.

4.2 Scattering Loss

Although the unclad fibre loss is not dominated by scattering losses, as the core size decreases, using the rod-in-tube technique, scattering becomes much more significant. The strength of a scattering centre may be simply measured by the relative refractive index difference of the centre and glass. Crystals therefore are not the strongest scattering centres as the refractive index of the crystals are usually similar to the glass matrix. A large number of crystals will obviously give a high loss, however only small numbers of bubbles (refractive index (N) ~ 1), carbon particles (N ~ 3.05 +1.3j at 5μm), silicon particles (N ~ 3.42 at 5μm), Alumina particles (N ~1.62 at 5μm) and SiO_2 particles (N ~ 1.35 at 5μm) will give high loss, depending on the particle size[8]. It is always true that the larger the particles or crystals the larger the loss per centre. However in the limit when all particles give wavelength independent scattering, particles of the same size introduce the same optical loss independent of the relative refractive index of the centre and glass. The stronger the scattering centre the smaller the particles need to be to reach this limit.

It is clear that scattering will become a very significant source of loss for single mode fibres. A single 2μm particle, of any of the above impurities, is calculated to give scattering of greater than 1dB. Hence with a particle density of two or three per metre the losses begin to rival those of transition metal absorptions. Through SEM analysis and GDMS we have identified particles of silica and alumina in our glasses. These have been traced to the raw materials. Current purification plans aim to reduce these impurities to tolerable levels.

5. APPLICATIONS

The original application of our work in Ga:La:S glass was a practical and efficient 1310nm optical fibre amplifier. While this device still remains of interest, attention has expanded, in particular further into the infrared. The 3-5μm window has numerous applications in the sensing, medical, aerospace and industrial fields. Many industrially and environmentally important gases and chemicals have characteristic absorption fingerprints in the IR. These absorption features are at their fundamental wavelengths and are several orders of magnitude stronger than the higher order modes that can be detected at shorter wavelengths. This gives the possibility of very high sensitivity detectors for gases such as CO_2, NO_x, SO_x, H_2O, and CH_4 to mention a few. Access to the water fundamental at 2.9μm gives rise to a host of medical applications such as tissue cutting. In the IR there are several regions where the atmospheric attenuation is very low, which gives several possible applications, such as free space communications operating in the transmission window, thermal imaging, and targeting systems. The other significant application is in high energy delivery systems (for example CO lasers at 5μm) for cutting and welding. In all of these applications the ability to move and manipulate the light around with a flexible fibre is a very significant advantage.

Unlike most other chalcogenides, Ga:La:S materials need not be used only for passive wave-guiding. The very property of low phonon energy that gives transparency in the infra-red, may make them suitable as hosts for rare-earth or other dopants. A low phonon energy reduces the non-radiative decay rate of excited dopant levels, which could potentially be used to generate efficient MIR fluorescent, super-fluorescent, and laser sources; Laser action has been demonstrated at many wavelengths, the longest to date is at 3.9μm in a Ho^{3+} doped ZBLAN fibre[15]. Longer wavelength lasing has been demonstrated in non-fibre solid state devices but a fibre geometry has several advantages for such devices over solid state devices: The guiding gives good overlap of pump and output laser modes, and the pump intensity is high, reducing threshold, and increasing slope efficiency. Fibre systems tend to be easy to fabricate, are very rugged, and have good beam quality. We have now demonstrated and fully characterized the absorption, fluorescence and lifetime of eleven rare-earth ions doped in Ga:La:S glass. Twenty-one transitions with peak emission wavelengths greater than 2μm were identified, seven of which have not been reported in a glass before. Lasing was demonstrated in neodymium doped Ga:La:S fibre at 1.08μm represented the first reported laser action in a chalcogenide[16]. Laser action at other wavelengths is actively being pursued.

Finally, the high index, density and low phonon energy of Ga:La:S makes this material a candidate for emerging applications which exploit its high nonlinearity and acousto-optic merit.

6. CONCLUSIONS

The advantages, and potential of working with Ga:La:S, currently outweigh the difficulties in fibre drawing. The causes of loss are now well known, and steps can now be taken to remove them. This will involve a purification scheme which will have a twofold effect: firstly it will remove the absorption losses from transition metals, and secondly it will go some way to eliminating scattering from impurities. Ga:La:S glass is therefore the material of choice for several emerging applications.

7. ACKNOWLEDGEMENTS

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