

Gallium Lanthanum Sulphide Fibres for Infrared Transmission

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Abstract

Gallium lanthanum sulphide (GLS) glass and fibre have potential for use in both active and passive infrared applications. In this paper the optical, thermal and other key properties, which are essential for understanding the applications and crucial in the quest for practical fibres, are discussed. We describe glass preparation by melt-quenching and subsequent fibre fabrication using both rod-in-tube and extruded preforms. Absorptive and scattering losses are explored as they could represent a fundamental limitation to successful device fabrication. Potential passive and active applications are reported and the prospects for a future generation of sulfide-fibre based devices examined.

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

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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 high pump efficiencies for optical amplification [2]. This led to widespread activity towards the goal of demonstrating a low-loss sulphide glass optical fibre and a 1310 nm optical fibre amplifier [3-7]. A practical amplifier for this transmission window is yet to be realized. However as work on this glass system progressed it became clear that gallium lanthanum sulphide (GLS) glass fibres had considerably more to offer than only an optical amplifier.

There are many candidates for infrared transmitting fibre based typically on halide or chalcogenide glasses. The most successful of the heavy metal fluoride glasses to date is ZBLAN, which has been extensively studied [8]. There are several families of chalcogenide glasses, based on sulphides, selenides and tellurides [1,9-11]. These various glasses each have associated advantages and disadvantages. Typical of all the fluoride glasses, ZBLAN has a transmission window extending from approximately 300 nm to 4.5 microns, can be drawn to fibres with low optical losses and single-mode, doped cores have been achieved. This glass however is hygroscopic, leading to questionable environmental stability for the fibre. Glasses based on arsenic sulphide have, likewise, been drawn to low loss single mode fibre. They have a slightly

shifted transmission window of 600 nm to 8 microns, reflecting a lower phonon or vibrational energy for the glass matrix. Should the fibre burn or degrade however, it will release arsenic into the environment. Moreover it is difficult to dope arsenic based fibres with rare-earth ions to make active devices [10]. Selenide and telluride based glasses can have a very wide transmission window. Different compositions may be used to give a fibre with extended short or long wavelength transmission, typically over the range from 1 to 15 microns. The glass may be drawn into fibres, albeit with relatively high losses. They again use very toxic components, have low dopant solubility, and have high attenuation at visible and near infrared (NIR) wavelengths, which is where the pump wavelengths for many dopants lie.

Gallium lanthanum sulphide based glasses address many of these problems. As a passive waveguide it offers a transmission window from the visible region of the spectrum to about 5 microns. The glass is non-toxic as it does not contain the usual arsenic based glass former. Moreover, its thermal stability is enhanced, with a melt temperature around 1000°C, well above that of other chalcogenides.

GLS also offers promise as an optically active material. With a composition based on lanthanum sulphide, it can be readily doped to high levels of any of the lanthanides ions simply by substitution. Unlike a silica glass host where rare earth ion clustering limits concentrations to a few hundred parts per million, we have prepared glasses with concentrations of hundreds of thousands of parts per million. It is possible to obtain a glass with even 40% by weight erbium sulphide [12]. The ease of doping with rare earth ions combined with its infrared transparency and low phonon energy make this glass an ideal candidate for infrared sources and laser. Researchers are pursuing lasers in the 3-5 micron region for a wide range of applications [13].

Other properties of this glass suggest the possibility of applications in areas which are just emerging. Measurements of the third order non-linear index show that among optical glasses, GLS offers the highest reported nonlinearity reported to date demonstrated in a glass [14]. This index, two order of magnitude stronger than that in silica glass, provides the possibility of shorter, more efficient switching devices. As in all the chalcogenide glasses, GLS shows a number of interesting photoeffects. Its linear index is easily modified, either temporarily with visible light or perhaps permanently with higher intensity illumination [15]. Also, the high index, density and low phonon energy suggest that GLS offers enhanced acousto-optic properties. Measurements which have been performed in bulk glass confirm this possibility [16] but work has not yet progressed to fibre.

In this paper, we described the preparation of GLS glass, its key optical, thermal and other properties, discuss fibre fabrication along with present and future applications of gallium lanthanum sulphide fibre.

Glass Preparation

Traditionally, the chalcogenide glasses are prepared by melting and compounding the elemental constituents of the glass, for example arsenic sulphide glasses are prepared by melting together elemental arsenic and pure sulphur to form the compound As_2S_3 . Similarly, germanium gallium sulphide glasses are prepared by compounding germanium gallium and sulphur together for several hours or even days [1,9]. The resulting melts are then rapidly cooled to form the glass. However, where other chalcogenides are melted in sealed ampoules

containing the required amounts of elemental precursors, gallium lanthanum sulphides are melted from prepared batches of Ga_2S_3 , La_2S_3 and La_2O_3 . Batches of powders are placed in a vitreous carbon crucible and melted in a tube furnace at 1150°C for typically 24 hrs depending on the batch size. The molten Ga_2S_3 fluxes the lanthanum precursors incorporating them into the liquid at temperatures much lower than their melting point. After quenching the resulting melt the glasses are then annealed near the glass transition temperature.

The binary gallium lanthanum sulphide system has a maximum stability for a gallium to lanthanum ratio 70:30 [17]. It is this composition that has been the focus of our work. Glass formation extends from about 60:40 to 80:20 for this two-component glass. Through the addition of a third or fourth component to the basic GLS glass, a wide range of modified compositions with varying properties can be realized. We have experimented with a wide range of modifiers. This was originally motivated by the quest for a glass stabilizer, an additional component which would improve the thermal characteristics of the glass and thus aid fibre drawing. In this search, other properties were also found to vary sometimes in a useful way. A selection of the compositions studied can be found in table 1.

The majority of attention has focussed on the addition of oxides, in particular lanthanum oxide, to GLS glass. We now believe that a small percentage, typically 1-2 weight percent of lanthanum oxide, is essential for glass stability, although all the La_2S_3 can be incorporated into the glass by substitution for lanthanum sulphide [18]. The addition of oxide radically improves thermal stability of the glass but at the expense of its phonon energy and thus potential for active applications. This increased maximum phonon energy is also mirrored by a slight decrease in the infrared transmission limit. The addition of lanthanum oxide also

provides increased visible transmission with a shift of approximately 40 nm into the blue end of the spectrum.

The substitution of cerium for lanthanum has been studied. Replacement of up to half of the lanthanum was found to improve the stability of the glass against devitrification [19]. The addition of aluminium or indium sulphide [18], as a substitute for gallium sulphides is another alternative. Like oxides, the lighter aluminium ion improves the visible transmission of the glass and shifts the characteristic temperatures. However, the environmental stability of Al modified glass is compromised and this composition is readily attacked by moisture. Conversely, indium considerably darkens the glass and visible transmission is totally lost. The glass becomes black but thermal stability remains enhanced.

The addition of halides to the glass composition has also been extensively examined. Lanthanum fluoride at up to 3 weight percent has been added to the glass [20]. This relatively small addition provided improve visible transmission and thermal stability. There is also some suggestion that the level of OH⁻ impurity decreased. Further improvements in visible transmission and stability were obtained with cesium chloride modification. At levels of 25 weight percent, cesium chloride results in a glass that has full visible transparency and has drawn easily into fibre. The glass however was somewhat prone to attack by moisture [21]. Other modifiers included bismuth [22], germanium [23] and sodium [24], but these have been less studied.

Glass Properties

An understanding of the basic 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.

Optical Properties

The transmission through GLS glass, as in any optical material, is determined by three intrinsic sources of loss; absorption by electronic transitions where a photon has sufficient energy to excite electrons to the conduction band or a defect state, absorption of photons by phonon interaction at the multiphonon edge of the material, and scattering. These electronic and multiphoton absorptions define the limits of the transmission window. The total intrinsic loss is given by the addition of these three main loss components.

Between the transmission window edges, and in the limit of low loss, the dominant loss mechanism 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 these index variations, from density and compositional fluctuations in the glass. We have used the method of Lines [25] to find the fluctuations in the glass density and composition before converting these into permittivity fluctuations from which the total scattering loss coefficient could be evaluated.

Transmission spectra of the glasses were measured between 300 nm-700 nm using a dual beam spectrophotometer (Perkin-Elmer Lambda 9). 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 Tri-glycine sulphate (TGS) detector. Two thicknesses of glass samples were prepared, the thickness of

each was measured and found to be nominally 170 and 450 microns. These relatively thin samples allowed the outer limits of the transmission window to be probed. Figures 1 and 2 show these transmission limits for both GLS glass and GLS modified with oxide.

Figure 3 shows the Urbach and multiphonon absorption edges plotted together with the calculated attenuation from Rayleigh scattering for GLS glasses. The total of the density and compositional scattering is shown. 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 [26].

In figure 3, the lines fitted to the electronic and multiphonon edges are shown along with 99% confidence intervals for the fit. The GLS glass has a loss minimum of 0.5 dB/km at 3.5 microns. The GLS glass estimate is comparable to a theoretical estimate for the minimum loss of arsenic sulphur selenide glass, 0.02 dB/km at 4.8 microns [9] and ZBLAN glass, 0.01 dB/km at 2.5 microns [8]. To the best of our knowledge, these values obtained were based solely on density scattering calculations whereas we have included compositional scattering. As the shape of the GLS fibre loss curves between the electronic and multiphonon edges do not follow the intrinsic loss curve, extrinsic loss sources currently limit the fibre loss. The loss in the 1 - 4 micron region of the spectrum has a complex dependence on wavelength that is predominately from a combination of various transition metal and OH⁻ absorptions.

Accurate refractive index measurements have been made for several GLS compositions using a precision spectrometer (Model GMR-1, Kalnew, Nagano, Japan) at 23°C in the wavelength range of 0.48 and 1.71 microns using Hg, Cd, H₂ and He lamps as spectral sources [27]. The

measurements were analysed using the Wemple equation based on the single electronic oscillator method to determine the average electronic energy gap, E_0 , and the electronic oscillator strength, E_d . The refractive index was measured to be $n_d=2.493$ at the sodium d-line. This value is higher than most oxide and halide glasses and is comparable with other chalcogenides and some heavy metal gallate glasses. Such high refractive indices can be attributed to the incorporation of La_2X_3 ($\text{X}=\text{S},\text{O}$) with a high X coordination number. Consequently, the refractive index increases with rising La_2X_3 content. The substitution of S by O reduces the refractive index. These compositional modifications provide a convenient method of altering the refractive index in order to achieve a core-clad optical fibre.

In general for chalcogenide, oxide and fluoride glasses, a high refractive index corresponds to a low electronic energy gap (E_0) due to the longer resonance wavelengths of the electronic transitions and this results in a higher dispersion all through the glass system [28]. However for GLS, the glass has both a high E_0 and high oscillator strength (E_d). The latter can be explained by the large number of S^{2-} ions in a unit volume with a large oscillator strength. These values reflect the relatively low dispersion characteristics in the GLS glasses as indicated by the low Abbe number.

As mentioned earlier, GLS glasses are promising candidates for optical fibre amplifiers operating in the 2nd telecommunications window. Any nonlinear optical process is undesirable in these optical devices because it would represent a source of nonlinear loss and noise. However, there is further interest in the non-linearity of this glass as it could be a good candidate for all-optical switching devices or other non-linear devices.

Glass is a centro-symmetric material and would not normally exhibit second order nonlinearity. However, certain treatments, such as poling using high electric fields ($1\text{kV}/\mu\text{m}$) at relatively high temperatures (eg. 270°C), can be used to induce second order nonlinearity and second harmonic generation (SHG) [29,30]. We have shown that microcrystals are responsible for the frequency doubling process [29]. In the absence of microcrystals there is no SHG signal. For low densities of microcrystals, there is a preferential sample direction for the SHG interaction and the signal is polarisation dependent. The SHG signal remains but these dependencies are lost for higher densities of microcrystals. SHG conversion efficiencies as high as 0.02% have been achieved for GLS.

Sulfide glasses have a large third order nonlinear response ($\chi^{(3)}$) under a strong electromagnetic field because of the high hyperpolarisability of the sulfide ion [14,31]. Nonresonant $\chi^{(3)}$ of binary GLS glasses have been measured as high as 2.8×10^{-12} esu which is about 100 times as large as that of silica glass. The $\chi^{(3)}$ value decreases monotonically with increasing wavelength, whilst increasing monotonically with shrinking optical band gap and rising linear refractive index.

The nonlinear optical response of GLS has been measured by a number of different techniques. Direct measurement of third harmonic generation, using fundamental radiation from a Nd:YAG operated at 1.319 or 1.064 microns, gives the absolute value of the third order nonlinear susceptibility, $\chi^{(3)}$. Alternatively, the Z-scan method allows measurement of the real (nonlinear refraction) and imaginary (nonlinear absorption) components of $\chi^{(3)}$.

A two photon absorption process is thought to be responsible for non linear absorption.

Nonlinear absorption and nonlinear refraction always coexist and both are large for GLS. The two photon absorption coefficient, β , which is proportional to the imaginary part of $\chi^{(3)}$ does not change with increasing La_2S_3 content and has a value of $\sim 40 \text{ cmG/W}$. However, the nonlinear refractive index, γ , which is proportional to the real part of $\chi^{(3)}$, increases with increasing La_2S_3 content. Values of γ lie in the range $30\text{--}45 \times 10^{-18} \text{ m}^2/\text{W}$ corresponding to 30–45% La_2S_3 content. These values represent the largest measured non-resonant non linearity in a glass, thus GLS offers great promise for all optical switching devices [32].

Thermal Properties

The thermal properties and in particular the characteristic temperatures: glass transition temperature, denoted T_g , the onset of crystallisation, T_x , and the peak crystallisation temperature, T_p , convey important information for the drawing of glasses such as GLS which are prone to crystallization. Also important is the softening point, where the glass has a viscosity of approximately $10^{7.6}$ poise (1 poise=0.1 Pa.sec). At or above this temperature the glass can be worked and drawn into fibre.

We used differential thermal analysis (DTA) to determine T_g , T_x , T_p and the melting point T_m and results are summarized in table 2. A typical DTA trace for GLS glass is shown in figure 4. This was recorded on a Perkin-Elmer DTA7 machine using a heating rate of $20^\circ\text{C}/\text{min}$ and a 40 mg sample. In the DTA method the sample and an inert reference material are held together in a furnace that is uniform in temperature over both the sample and reference cups. The temperature difference between sample and reference is measured as a function of temperature. The transition points are measured by the intersection of the tangent to the curve before and after an event. This method will also detect crystallisation and melting

events in the glass.

In GLS glass, the glass transition is about 560°C, a clear advantage over some As-based glasses where it is several hundred degrees lower. The simple criteria for a good glass for fibre drawing are that the separation of T_g and T_x should be large, the crystallisation peak should also be wide and weak and the separation of T_m and T_p should be small. The glass transition temperature T_g determines the intersection of the glass solid and glass liquid phases, so any fibre drawing needs to be at temperatures above T_g . If $T_x - T_g$ is small, the material will tend to crystallise 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 any glass held above T_g will eventually crystallise. Crystallization kinetics and phases in GLS have been analyzed by x-ray diffraction and electron microscopy [33].

The viscosity of glass in the range 10^5 to 10^{11} poise may be determined using the technique of parallel plate rheometry. A commercial Perkin-Elmer TMA7 thermo-mechanical analyser with a displacement sensitivity up to 50 nm and temperature range up to 1000°C was used for both viscosity and expansion coefficient measurements. A glass sample was prepared by cutting and polishing to a cylindrical shape, typically of dimensions 5 mm in both thickness and diameter. For viscosity measurements the sample was held between two parallel plates of Inconel, 0.1 mm thickness and 8 mm diameter. The sample chamber was purged with helium to ensure rapid temperature equilibrium. The compression as a function of time and temperature was recorded as the temperature was increased under a constant force. Recording was stopped once the diameter of the sample approached that of the plates. The viscosity was calculated using the procedure described in reference [34]. The expansion

coefficient was given directly from the TMA software as the slope of the line. The thermal expansion coefficient is relatively low which offers advantages in glass preparation and fibre drawing of core-clad structures.

Several other properties of interest have been measured in GLS glass. These, along with the key optical and thermal properties, are summarized in table 3. The mechanical properties compare favourable with silica and fluoride glasses, both of which have been drawn into practical commercial fibre. The hardness indicates that like most non-oxide glasses, GLS is a soft glass.

Fibre Fabrication and Properties

There are two basic methods of drawing fibre: from a pre-prepared preform or from a melt, termed rod and crucible drawing respectively [35]. We have only used rod drawing to prepare GLS fibres. Core-clad fibres by this method were prepared by stretching (canning) 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.

From 250 g ingots of glass, we could cut and polish several rods or tubes of typically 10 mm diameter by 100 mm long. One of the main limitations of using the rod-in-tube method for producing core-clad fibres is the difficulty in making fibres with small core sizes. With a tube of outside diameter 10 mm, and internal diameter of 3.5 mm, a single collapse would give a core-clad ratio of 0.35. Therefore 2 collapses were required to give a core diameters of 15 micron, and three were needed to achieve smaller core diameters, based on a 125 micron outer fibre diameter. The fabrication of such fibres in GLS glasses, although possible, proved

difficult due to the thermal characteristics of the glass. Repeated heating led to crystallization in the core, resulting in high losses. Two alternative methods to the rod in tube technique were investigated: bulk glass fabrication techniques such as extrusion, and vapour phase techniques similar to those used for silica. The latter proved impractical for implementation in GLS.

The most effective fabrication technique used a combination of extrusion, and the rod-in-tube method for manufacturing fibre preforms. The advantages in using extrusion to do this were that comparatively low temperatures (high viscosities) could be used to fabricate the glass which allowed fabrication without crystallisation, and the cross section of the extruded preform could potentially be defined almost arbitrarily. Extrusion was performed through stainless steel dies, under constant pressure and with the temperature adjusted to give a glass viscosity of $\sim 10^8$ poise [36].

Core-clad structures could be extruded by using two discs, the core disc initially resting on the cladding disc as shown in figure 5. It can be seen from the geometry in figure 5 that the core-clad ratio can be altered to some degree by changing the thickness of the respective discs. The cross section of a typical preform is shown in figure 6. Except for the first 30 mm of preform, the majority of the preform cross section is the core glass, with the cladding as a thin over-layer. Both discs in the extrusion shown had the same thickness. By making the core disc thin, the core size in the preform is reduced, but the same general shape applied for all extrusions using two discs. Using the combined extrusion and rod-in-tube method losses in the cores of GLS fibres dropped by approximately one order of magnitude. Figure 7 shows a cross section of a small core GLS fibre.

The fibre loss was measured using a standard cutback method with a double monochromator (Bentham), lock in amplifier and silicon detector for 0.5 - 1.1 microns, and the FTIR with a HgCdTe detector for the range 1 to 10 microns. The tested fibre lengths were of the order of two metres with one metre cutbacks, and measurements were done on unclad and uncoated fibre to eliminate sources of loss such as core-clad interface scattering. The nominal fibre diameter was 200 microns. The length of the cutback ensured that the dominant effect measured was due to the removal of this length of fibre over variability of the fibre cleaves. The fibre ends were cleaved a minimum of six times to ensure reproducibility. Measurements were repeated a minimum of four times to reduce random errors.

Figure 8 shows the lowest loss fibre drawn to date, drawn from a polished GLS glass rod. Absorptive losses arise from infrared-absorbing impurities in the starting materials and glass; the main contaminants are OH⁻ and transition metals. The OH⁻ infrared absorption peak at 3 microns has a magnitude of 10 dB/m and covers a substantial part of the spectrum stretching from 2.8 to 3.4 microns, and the tail of the absorption will extend further as the background loss of the fibre is reduced. The peak height we have measured indicates there is less typically than 1 ppm of OH⁻. There is some evidence that OH⁻ impurity can lead to scattering losses in the fibre. Little SH⁻ impurity, characterized by a peak at 4 microns, can be seen in our glasses compared to other chalcogenides [1.9].

The first row transition metals are the main metallic impurities which have absorptions in the IR. In chalcogenide glasses, the high refractive index enhances the absorption (and emission) cross sections of ions in the matrix, so the absorptions are strong. Analysis by glow discharge mass spectroscopy (GDMS) revealed typical impurity levels in the Ga₂S₃ we synthesized of

the order of 50 ppb for Fe, Co and Ni, while in the La_2S_3 higher levels were found, approaching 1 ppm Fe. The impact that trace amounts of these impurities would have on the glass was assessed by melting glasses containing an intentionally added, known amount of transition metal sulphide and measuring the absorption spectra.

Peak absorptions for the transition metals are given in table 4. Some ions such as V or Ti have absorptions confined to shorter wavelengths, whereas the absorption from Fe extends out beyond 5 microns, as shown in figure 9. However, all absorptions will generate problems for pumping the fibres. Copper, a major concern in fluoride glasses, showed no absorption peak in GLS suggesting a Cu^+ oxidation state. Combining the GDMS and absorption results to calculate the expected loss from included transition metals show they currently dominate GLS losses.

Although the unclad GLS fibre loss is not dominated by scattering losses, as the core size decreases scattering becomes much more significant. The strength of a scattering centre may be measured simply by the relative refractive index difference of the centre and glass. However only small numbers of bubbles, carbon particles, silicon particles, alumina particles and SiO_2 particles will give high loss, depending on the particle size.

Scattering will become a very significant source of loss for single mode fibres. A single 2 micron particle is calculated to give scattering of greater than 1dB. Hence with a particle density of 2 or 3 per metre of fibre the losses begin to rival those of transition metal absorptions. SEM analysis and GDMS 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.

Applications

The original application of our work in GLS glass was a practical and efficient 1.3 micron optical fibre amplifier. While this device still remains of interest, attention has expanded in both the telecommunication field, where other active devices now appear possible and also further into the infrared. Here, the 3-5 micron window has numerous potential applications in the sensing, medical, aerospace and industrial fields. In general, applications of this glass can be categorized as passive and active. Passive applications encompass any which use the fibre only as a waveguide, to transmit radiation from one point to another. Active applications process light in some way, through amplification, lasing or switching, or exploit some active or changeable property of the glass.

Passive transmission

The ability to move and manipulate the light around without using costly and delicate articulated arms and mirrors is a common requirement for several applications. The material that is most widely used in fibre optics is currently silica which provides a transmission window that extends only to about 2 microns.

Power handling of GLS fibres has been assessed by coupling to a Nd:YAG laser operating at 1064 nm. A total of 5 W of power was guided through a core of about 150 microns with no decrease in transmission and no apparent laser damage. With their high glass transition temperature these glasses offer the potential for greater power handling capacity and also reduced toxicity due to elimination of arsenic-containing compounds. This opens the range

of applications of this glass to a variety of fields.

Lasers with emission wavelengths around 2.9 microns are widely used in surgery. This radiation corresponds to the strongest absorption band of water and thus biotissues, allowing a host of medical applications [37]. 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, remote spectroscopy and targeting systems. The other significant application is in high energy delivery systems, for example CO lasers at 5 microns used for cutting and welding [9,38-39]. In all of these applications a flexible fibre has a very significant advantage. Several passive applications of chalcogenide fibre are described in references 1 and 9.

Figures 3 and 8 show GLS has promising potential as the ideal MIR transmitting fibre which can be fully exploited as extrinsic sources of loss are eliminated.

Active Applications

The investigation of mid-infrared sources based on GLS glass is motivated by the lack of powerful, coherent, compact, robust, reliable, and inexpensive devices operating in the infrared. Sources for mid-infrared radiation range from simple heated tungsten wires and black-body sources to more sophisticated and bulky gas lasers, optical parametric oscillators, and difference frequency generation diodes. The strongest competitors for mid-infrared fibre lasers are semiconductor lasers, in particular the new quantum cascade structures. Work is also ongoing on other rare-earth-doped crystals and glasses for mid-infrared lasers.

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, optical parametric oscillators 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.

Over the past four years, detailed spectroscopic measurements have been performed on rare-earth-doped GLS glasses. This has been fully described in reference [13]. Absorption, fluorescence, and lifetime measurements have been performed for eleven lanthanide ions for wavelengths ranging from the visible to the mid-infrared and on mid-infrared transitions in the 3 to 5 micron transmission window. The results of the measurements were used to study the multiphonon decay in GLS glass and to obtain important laser parameters such as the absorption and emission cross sections, branching ratios, and quantum efficiencies from the Judd-Ofelt theory, the Füchtbauer-Ladenburg equation, and the McCumber theory. Twenty-one transitions with peak emission wavelengths longer than 2 microns were identified, seven of which have not been reported in a glass before. Several key wavelengths are now fully characterized [40-45] and are summarized in table 5.

Co-doping schemes such as thulium/terbium, praseodymium/ytterbium,

praseodymium/erbium, and dysprosium/erbium which offer more favourable absorption bands for diode laser pumping have also been investigated with respect to ion-ion energy transfer [40]. By co-doping, improved pump absorption and more convenient pump wavelengths can be obtained.

Lasing has been demonstrated in neodymium-doped GLS glass and glass fibre at 1.08 microns, representing the first reported laser action in a rare-earth-doped chalcogenide bulk glass and glass fibre, respectively [44-45]. The strong thermal lensing in the bulk glass rules out the use of GLS glass as a bulk laser material. The effect was eliminated by using a fibre geometry showing the advantages and necessity of GLS glass fibre. Work continues on developing new lasers at longer wavelengths [46].

Several transitions measured in rare-earth doped GLS glass overlap with the fundamental absorption bands of common gases. In the MIR, 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. Examples include methane and other hydrocarbons which absorb at 3.4 microns; carbon monoxide at 4.7 microns and carbon dioxide at 4.3 microns. GLS provides the possibility of very high sensitivity detectors for these gases. Figure 10 shows an example of the fluorescence achieved and the sensitivity of this wavelength range to gas absorptions.

The high refractive index and low phonon energy of GLS glass combine to make this glass an ideal candidate for an amplifier operating at 1.3 microns. Unlike the erbium-doped silica amplifier operating at 1.55 microns, there is no efficient amplifier for the telecommunications

window around 1.3 microns. No rare-earth dopants in a silica host provide measurable 1.3 micron emission. An amplifier made by doping with praseodymium has been demonstrated in ZBLAN glass, however its quantum efficiency is only 4% [47]. In GLS the same transition has an efficiency of 68% [2-3]. The promise of an amplifier in a gallium sodium glass reveals the potential for a practical device [24]. Furthermore, dysprosium doping in GLS also provides 1.3 microns emission through a transition that is totally quenched in all glasses other than sulphides [48].

Finally, the high index, density, absorption characteristics and low phonon energy of Ga:La:S makes this material a candidate for emerging applications which exploit its high nonlinearity, photorefractivity and acousto-optic merit [14-16, 49-50]

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Table 1. The addition of modifiers to the base gallium lanthanum sulphide composition.

Modifier	Change to Glass	Reference
lanthanum oxide	improved stability, visible transmission	18
cerium sulphide	improved stability	19
aluminium sulphide	improved stability, visible transmission	20
indium sulphide	improved stability, loose visible transmission	21
lanthanum fluoride	improved stability, visible transmission, purification	22
cesium chloride	improved stability, visible transmission	23
bismuth sulphide	raise refractive index	24
germanium	no obvious improvement	25
sodium	improved low loss fibre	26

Table 2. Characteristic temperatures of GLS glass as a function of composition

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

a. T_η = temperature of viscosity 10⁶ poise

Table 3: Key Properties of Sulphide Glasses and Comparison with Silica and Fluoride Glass

	Silica	Fluoride	Sulphide
Composition	SiO ₂	ZBLAN	GLS
Optical			
Refractive Index at 0.589 μm	1.458	1.499	2.4833
Abbe Number	68	76	13.7
Zero Material Dispersion Wavelength	1.3	1.6	See a.
Non-linear index (esu x 10 ⁻¹³)	1	0.85	300
Approximate transmission range (μm)	0.16 - 2.0	0.22 - 4.0	0.53 - 5.0
Thermal			
Glass Transition (°C)	1175	260	560
Melting Temperature (°C)	>2200	450	842
Specific Heat (cal/g-°C)	0.179	0.151	0.109 ^b
Mechanical			
Expansion Coefficient (°C ⁻¹ x 10 ⁻⁶)	0.55	17.2	10.6
Density (g/cm ³)	2.2	4.33	4.04
Poisson's Ratio	0.17	0.3	0.24
Elastic moduli (Gpa): Youngs	73.1	58.3	59
Shear	31.2	20.5	23
Bulk	36.7	47.7	24.5
Knoop Hardness (kg/mm ²)	600	225	206

a. not available

b. approximated by value for As₂S₃ glass

Table 4. Absorptions due to transition metals

Ion	dB/m per ppm	λ_{peak}
Ti	0.25	1
V	1.2	1.2
Cr	9	1
Fe	3.5	2
Co	3.5	1.6
Ni	2.5	1.9

Table 5. MIR transitions observed in rare-earth doped GLS

Rare Earth Ion	Pump Wavelengths (microns)	Emission Wavelength (microns)
Praseodymium	1.02, 1.57, 2.0	3.4, 4.7
Neodymium	0.815, 0.89, 1.65	5.1
Terbium	0.8, 2.0	4.8
Dysprosium	0.81, 0.91, 1.1, 1.3, 1.7	4.3
Holmium	0.65, 0.76, 0.9	3.9, 4.9
Erbium	0.66, 0.805	3.6, 4.5
Thulium	0.7, 0.8, 1.22	3.8

Figure Captions

Figure 1. Electronic absorptions which define the short wavelength transmission limit for GLS and oxide modified esGLS glass.

Figure 2. Multiphonon absorptions which define the long wavelength transmission limit for GLS and oxide modified GLS glass.

Figure 3. Intrinsic loss curve for GLS glass with a typical fibre loss measurement superimposed.

Figure 4. Typical thermal analysis curve for GLS glass

Figure 5. Schematic of the extrusion process for producing a simple core-clad structure.

Figure 6. The distribution of core and clad diameters along the preform for a double disc extrusion.

Figure 7. Cross section of a single mode GLS fibre with $NA=0.22$ and core diameter of 1.8 microns.

Figure 8. Attenuation of lowest loss GLS fibre to date showing losses approaching 1 dB/m at 4 microns.

Figure 9. Absorption spectrum of iron impurity in GLS glass

Figure 10. Fluorescence spectrum of Dy^{3+} -doped GLS glass (a) uncorrected spectrum showing absorption due to atmospheric CO_2 , (b) CO_2 absorption measured using infrared spectroscopy and (c) corrected Dy^{3+} -fluorescence.

















