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Advances in Gallium Lanthanum Sulphide Glass for Optical Fibre and Devices

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ABSTRACT

The advantages of gallium lanthanum sulphide (GLS) based glass over other competing glasses for active and infrared applications are evident through its low-phonon energy, high rare-earth solubility, high transition temperature and non-toxicity. However this glass often devitrifies during fibre drawing due to a small separation between the crystallisation and fibre drawing temperatures. Improving GLS fabrication technology may hold the key to achieving practical optical waveguide devices. In this paper, we describe the current GLS research status, methods of improving glass purity and our directions toward alternatives to traditional fibre technology, in particular planar channel waveguides and holey or microstructured fibres.

Keywords: Chalcogenide, Fabrication, Optical Fibre, Planar Channel Waveguides, Holey or Microstructure Fibre

1. INTRODUCTION

Gallium lanthanum sulphide glasses (GLS) have been known for several decades [1,2] although it has only been in the last decade that extensive work on their properties, in particular when doped with the rare earth elements, has been undertaken [3]. In parallel with studies on the optical, thermal and spectroscopic behaviour of the glass, efforts on achieving a low loss optical fibre waveguide have continued. A wide range of applications, which have helped to maintain interest in this challenging material, has motivated this work [4-10].

Raw materials used in various applications, whether for semiconductor or optical use, must be purified in a controlled fashion. In the production of GLS we require high purity gallium sulphide, lanthanum sulphide and lanthanum oxide. Though commercially available, these as-purchased compounds are deemed unsuitable as they contain high levels of contaminants in the form of transition metals and non-metallic impurities. These impurities have a direct effect on the performance of a fibre amplifier. As such, it is vital to have raw materials that are relatively free from transition metals such as iron, chromium, and nickel and from non-metallic impurities such as OH^-, carbon and silica. The ionized impurities have very strong absorption bands in the 1-5µm wavelength region, which is the region of interest targeted for devices based on GLS glass. Acceptable levels of transition metal or OH^- impurities are typically <0.1ppm (parts per million by weight) each [11]. We have developed methods for purification and synthesis of raw materials to levels that are acceptable.

Crystallisation is another key issue that must be investigated in detail before crystal free GLS fibre can be attained. Crystals can form for many reasons; impurities in the glass can seed crystals and tend to grow when the glass is heated. Furthermore, GLS is thermally unstable and is prone to crystallisation during fibre drawing as its crystallisation peak (T_p) indicates a strong exothermic event and T_x-T_g is relatively small ($\cong 110^oC$), making fibre drawing difficult [4].

While trying to study and resolve various fabrication issues we are expanding out to new directions. Two key areas currently under investigation are GLS planar structures and GLS holey fibre [12]. Planar structures based on GLS have been previously investigated by the deposition of thin films [13]. However, we have demonstrated the possibility of creating planar channel waveguides in bulk GLS glass. This opens up many new applications for bulk glass waveguides such as glass waveguide lasers and optical splitters. Silica microstructured or holey optical fibre has recently attracted considerable interest in the

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telecommunications field. Holey fibres (Hfs) are optical fibres in which the cladding region is defined by a number of air holes that run the length of the fibre. These holey regions provide an effective index difference between the core region and the microstructured region surrounding it, dramatically increasing the range of optical properties possible in these fibres. Our first fabrication results from non-silica, GLS holey fibres are described in this paper.

2. PROPERTIES

Understanding the basic properties of GLS is vital in developing and achieving devices and applications. Typically, GLS has a molar composition of $65Ga_2S_3{:}32La_2S_3{:}3La_2O_3$, with the oxide added for improved thermal stability during fibre drawing. Alternatively, in GLS oxide (GLSO) we substitute up to 30mol% of La_2S_3 with La_2O_3. As a passive optical fibre, GLS has a transmission window from the visible to 5µm. Table 1 lists and compares key properties, many of which have been discussed in previous publications [14].

	Silica	**Fluoride**	**Sulphide**
Composition	**SiO2**	**ZBLAN**	**Ga:La:S**
Optical			
Refractive index at 0.589µm	1.458	1.499	2.4833
Abbe number	68	76	13.7
Zero material Dispersion wavelength (µm)	1.3	1.6	2.5-3
Nonlinear 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 (^oC)	1175	260	560
Melting Temperature (^oC)	>2200	450	842
Specific Heat (cal/g-^oC))	0.179	0.151	0.109*
Mechanical			
Expansion coefficient ($^oC^{-1}$ 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

Table 1: Comparison of key properties between sulphide, fluoride and silica based devices
*approximated by value for As_2S_3 glass

3. FABRICATION

3.1 Raw Materials

GLS glasses are produced by melting a mixture of gallium sulphide, lanthanum sulphide and lanthanum oxide. Other modifiers can also be added to change the properties of the glass. Commercially available gallium sulphide, lanthanum oxide and lanthanum sulphide are usually specified to no better than 99.999% purity. In some cases this purity is with respect only to metals and other unquantified impurities such as oxides, while water or carbon are also present. In our own experience, many sulphides can contain up to 5% of the oxide from which they were synthesised. Even in the best commercially available materials up to 10ppm of transition metal impurities are commonplace. Such levels of impurity result in extrinsic losses due to absorptions of over 10 dB/m from the raw materials used in the glass. Clearly a method for the purification of commercial starting materials, or a method of synthesising the required materials from high purity precursors, is required. There are many well-developed industrial methods for producing ultra-high purity materials from relatively low grade starting stock. However, these methods tend to be best applied to the production of high purity elemental or single-phase materials with relatively low melting point.

Synthesis of gallium and lanthanum sulphides involves reacting a precursor, metallic gallium for example, with a sulphurising agent, at high temperature. However, bulk sulphur is a difficult material to handle for conversions. Its low boiling point of 444.6°C, would mean a high vapour pressure at the temperatures of synthesis processes which are typically greater than 800°C. Conversion in a sealed ampoule would prevent sulphur loss during the process, but presents significant difficulties such as preventing the ampoule exploding under the vapour pressure of sulphur, making the reaction go to completion, and maintaining purity. If the reactants and products are sealed in an ampoule, any impurities present are also sealed in and are carried into the raw materials. Impurities would not arise from the sulphur, as it can be made to high levels of purity, however the constant contact with the ampoule walls at high temperature could lead to dissolution of the ampoule, and contamination.

Using a flowing gas system eliminates these problems. A flowing system sweeps the by-products of reaction out of the hot zone, preventing them from reacting, and shifts the position of equilibrium by as much as 100% to favour the sulphurised product. Using H_2S, it is possible to convert almost any precursor to a sulphide, depending on the temperatures available. This gives a very wide range of possibilities for potential precursors; and solves the problem of sulphides not lending themselves well to conventional purification techniques. The key then to producing high purity raw material was to convert the high purity precursor materials to the sulphides without introducing any impurities.

Conversions were carried out using a vitreous carbon crucible to hold the material. Gallium (Ga) metal of 99.99999% purity was loaded in a crucible under dry and clean conditions. The material was heated at 20°C min^{-1} to the required temperature, typically 1000°C, and then H_2S was introduced. Lanthanum oxide was converted to lanthanum sulphide using a single step process at 1150°C.

Table 2 shows the impurity levels of a typical Ga to Ga_2S_3 conversion, as measured by glow discharge mass spectroscopy (GDMS). Although certain impurity levels did rise during the conversion process, contamination levels of transition metals were less than 0.1 ppm. Some contamination was likely, particularly of Fe, Ni, and Cr the major constituents of stainless steel.

	Fe	Cr	Ni	V	Mn	Cu	Ti	Co	Al	Mg	Na
Ga Precursor (ppm)	0.0057	0.0018	0.0053	<0.0005	<0.0005	0.039	<0.001	<0.0005	0.009	0.002	0.035
Ga_2S_3 Product (ppm)	0.05	0.04	0.01	<0.05	<0.01	0.02	0.21	<0.01	0.24	0.03	1.7

Table 2: The impurities in 7N gallium (precursor) and the gallium sulphide made from it.

The OH^- absorption peak, at ~2.9 μm, was a substantial feature in the transmission spectrum of GLS based glasses and was used to determine the OH^- content of the glasses and raw materials. In bulk glass samples the size of the OH^- peak can be determined by using a Fourier Transform Spectrometer (Perkin Elmer system 2000). The powdered raw materials had to be incorporated into a KBr binder and then pressed into a transparent pellet before the transmission spectrum could be taken. A background of an undoped KBr pellet was used to correct the spectrum for interface reflections and any OH^- absorption from the KBr itself. In a typical pellet the material of interest was diluted approximately fifty times to give a transparent sample. Samples were normalised for thickness and dopant concentration. The KBr used was spectroscopic (FTIR) grade and was kept and pressed in a nitrogen-purged glovebox. Although this method was not quantitative, it could determine the relative level of OH^- impurity in the raw materials as a function of processing conditions. We typically observe less than 1ppm of OH^- present in our glass.

3.2 Glass Melting

Most gallium sulphide glasses are made in a similar fashion, by quenching from a melt. However, where other chalcogenides are melted in sealed ampoules containing the required amounts of elemental precursors [2], these glasses are melted from prepared batches of Ga_2S_3, La_2S_3, and La_2O_3. Since these precursors are non volatile (the melting points are: ~1125°C for Ga_2S_3, ~2100°C for La_2S_3 and ~2300°C for La_2O_3), melting in an open (argon purged) atmosphere facilitates the removal of volatile impurities particularly OH^-. Batches of powders are placed in a vitreous carbon crucible and melted in a tube furnace at 1150°C for up to 24hrs, 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. Typical batch sizes for test samples (suitable for thermal analysis or spectroscopy) are 20g, while for fibre production, ~170g samples are used from which rods or tubes of glass can be cut and polished.

3.3 Fibre Drawing

Glass ingots (typically weighing 250g) are used to cut and polish rods & tubes measuring 10mm in diameter by 100mm in length. One of the main limitations in 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 outer diameter 10mm, and internal diameter of 3.5mm, a single collapse would give a core-clad ratio of 0.35. Therefore 2 collapses are required to give core diameters of 15μm, and three are needed to achieve smaller core diameters (based on a 125μm outer fibre diameter). The fabrication of such fibres in GLS glasses is possible, although repeated heating leads to crystallisation in the core and results in fibres with 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 uses extrusion for manufacturing fibre preforms. In recent experiments, extrusion was performed through stainless steel dies, under constant pressure and with the temperature adjusted to give a glass viscosity of ~10^8 poise [15].

Core-clad structures are extruded from two discs, arranged such that the core disc initially rests on the cladding disc. Through this disc geometry it can be seen that the core-clad ratio can be altered to some degree by changing the thickness of the respective discs. By making the core disc thin, the core size in the preform is reduced, but the same general shape is 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 1 shows a cross section of a small core GLS fibre produced by this method.

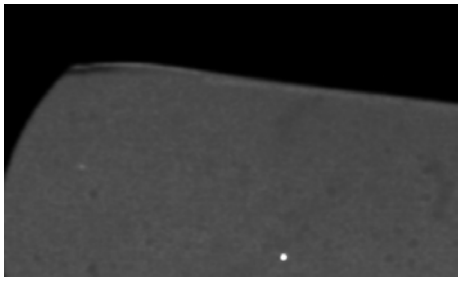

Figure 1: Cross-section of small core GLS fibre single-mode at 1.5μm.

Fibre loss was measured using a standard cutback method with a double monochromator (Bentham), lock in amplifier, silicon detector for 0.5 - 1.1μm and the FTIR with a HgCdTe detector for the range 1 - 10μm. Tested fibre were approximately, two metres long with one-metre cutbacks, and the nominal fibre diameter was 200μm. Measurements were done on unclad and uncoated fibre to eliminate sources of loss such as core-clad interface scattering and 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, with measurements repeated a minimum of four times to reduce random errors.

Figure 2 shows the lowest loss GLS fibre drawn to date, from a polished rod. Absorptive losses arise from infrared-absorbing impurities in the starting materials and glass; the main contaminants being OH^- and transition metals. The OH^- infrared absorption peak at 2.9μm has a magnitude of 10 dB/m and covers a substantial part of the spectrum stretching between 2.8 to 3.4μm. The tail of the absorption will extend further as the background loss of the fibre is reduced. The peak OH^- absorption height measured confirms there is typically less than 1ppm of OH^-, although there is some evidence that OH^- impurity can lead to scattering losses in the fibre. Little SH^- impurity, characterized by a peak at 4μm, can be seen in our glasses compared to other chalcogenides [11,16].

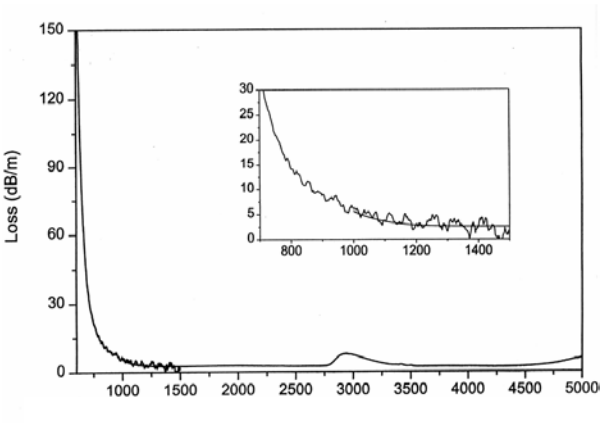

Figure 2: Lowest GLS fibre loss to date

3.4 Planar Channel Waveguides

Various methods are available for fabricating planar channel waveguides in glass. These include; ion exchange [17], chemical vapour deposition techniques (such as PECVD [18] and FHD [19]), ion beam machining [20] and direct UV writing of waveguides [21]. We have been investigating direct UV writing with a CW frequency doubled argon-ion laser operating at

244nm. Previous work on thin-film GLS show that the films grown were sensitive to argon-ion laser emissions at 488nm, resulting in a negative refractive index change ($\triangle$n) of ~ -1% [22]. An alternative approach using 20keV e-beams to write gratings in the material gives a positive index change of ~ 0.015 (less than 1%) [23].

There are several advantages of using bulk glasses in the production of channel waveguides, such as the flexibility of adjusting the composition of the glass material and the relative ease of producing multiple samples. The glass samples used in these experiments were based on the standard GLS composition (65:32:3) mol%, with a UV absorbance of 90dB/cm at 244nm. Samples of dimensions (20x15x6) mm and were optically polished and cleansed with methanol before any UV writing was performed, providing a smooth clean surface to prevent scattering of any propagating light. Each sample is then set on a computer controlled 2D translation stage and exposed to a UV beam with varying powers and scan rates. The laser setup is capable of delivering between 20-200mW of UV power and able to accelerate to scan rates of up to 5000mm/min. The typical laser flux was $\geq$ 500mW/cm^2, while the laser spot size applied to the sample surface ranged between 10-50μm, yielding different results. With the UV beam focused on the surface using a smaller laser spot size, the sample surface was ablated at even the lowest powers. To avoid this effect, UV writing was subsequently performed with the focal plane slightly above the sample surface, yielding well-formed channel structures. It was also observed that writing with beam powers above 100mW completely ablated the sample surface regardless of spot size.

Observation of the UV written regions was performed with an optical microscope, the resulting channel structure of which is shown in figure 3. A Tencor Instruments Alpha-Step profiler was used to profile peaks and surface ridges and a He-Ne laser operating at 633nm was used to confirm guidance of a channel as shown in figure 4. It was observed that the most promising channels were written at powers between 30-60mW and scan rates between 2000-4000mm/min. Channels are indicated as peaks on the alpha-step profiler and evidence of extreme stress in some channels is apparent in the form of stress fractures propagating down the length of the channel. Formation of these peaks is attributed to photothermal expansion when local melting is followed by expansion and quick cooling as the laser beam traverses the surface of the glass. Dimensions of the channel waveguides above the glass substrate vary between 10-40μm in width and 30-100nm in height. Mode profiling of these channels was performed with a He-Ne laser at 633nm with several channels showing single mode properties (figure 5). Beam widths of less than 8μm (at 1/e^2 intensity diameter, figure 6) with positive refractive index changes as high as 10^{-3} was measured. Loss measurements are in progress, however preliminary measurements indicate low loss waveguides are possible as no visible scattering is observed in the channels. Loss measurements in the bulk glass before laser exposure is less than 0.1dB/cm (at 1 μm).

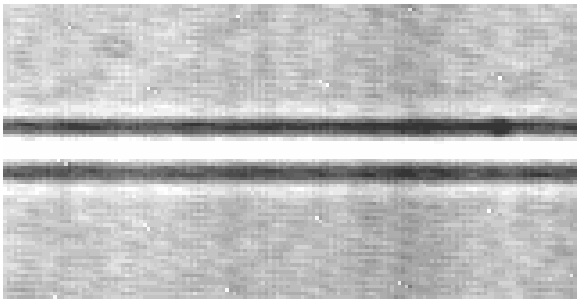

Figure 3: Top View of Channel Waveguide measuring 12μm in width and 40nm in height

Figure 4: Output Spot from channel waveguide with light coupled in from a 633nm He-Ne laser

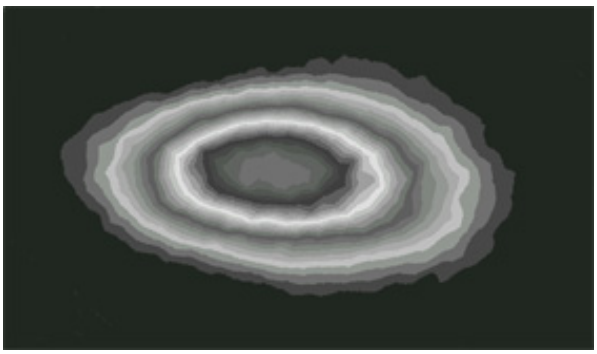

Figure 5: GLS channel waveguide single-mode intensity distribution, measured at 633nm

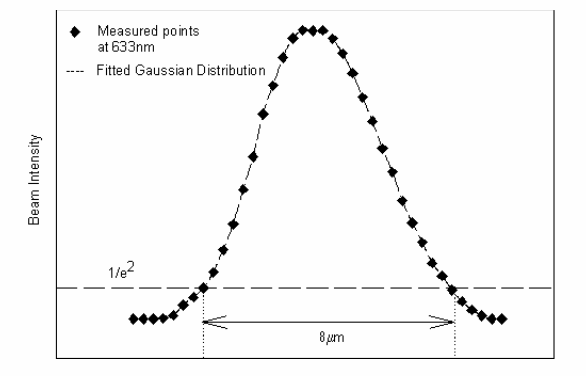

Figure 6: Beam Width at $1/e^2 \sim 8\mu m$

3.5 Holey Fibre

In recent years, great interest has been generated by the development of holey or microstructured optical fibres. The large and controllable variations of transverse refractive index offered by these fibres provide new opportunities for the control and guidance of light [24, 25]. To date, holey fibres are usually made from conventional silica glasses, although this technology provides a powerful new technique for producing glass fibres in other materials. The significant advantage for novel glasses is that different core and cladding glass compositions are no longer required. This relaxes the fabrication difficulties associated with core and cladding glasses with differing thermal properties. Holey fibre geometry, also increases the range of possible optical properties of the resulting fibre.

Traditionally, it has been difficult to fabricate low-loss single-mode compound glass fibres due to problems arising from the different physical properties of the core and cladding materials. The varied heating steps required to fabricate single-mode compound glass fibre tends to promote crystallisation, thus inducing losses. Holey fibres can be made from a single-material, eliminating the problems induced by the core/cladding interface. They can also be made using a single heating step, reducing crystallisation problems, and significantly reducing the fibre loss. In this way, holey fibres provide a new route towards the successful development of low-loss single-mode compound glass optical fibres.

Figure 7 shows a cross-section of a GLS holey fibre. The preform was constructed in a manner analogous to silica HF preforms [26] and this fibre was drawn from the preform in a single step. A solid rod was used to form the core of the fibre, surrounded by six capillaries surrounding this rod; the final structure was placed inside a larger capillary both for structural support and to increase the preform dimensions. The preform was then drawn into a fibre with an outer diameter of approximately 100μm, and a core diameter of 10μm. The holes in the cladding capillaries range in diameter from 1.5 to 4.0 μm, and in this case the inner capillaries did not fit tightly in the supporting capillary, resulting in the core being loosely attached to the cladding. We have for the first time, shown that it is possible to retain the complex transverse structure during fibre drawing, indicating that the viscosity/temperature relationship in GLS glass is well suited to holey fibre fabrication.

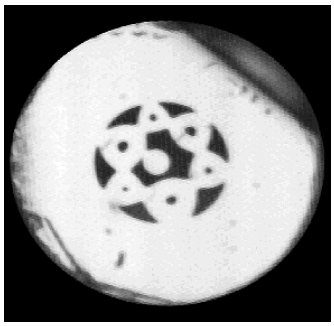

Figure 7: Cross-section of GLS holey fibre

4. APPLICATIONS

We can classify applications based on the GLS glass host in two categories; active and passive. Passive applications would encompass devices that simply act as fibre waveguide, a simple case of transmission of electromagnetic radiation from source to destination. Active applications manipulate the light either by lasing, switching or amplification during its path along the waveguide medium.

Applications of such passive single-mode fibres are far-reaching, including medical, aerospace, sensing, laser and telecommunications. Power handling of GLS has been demonstrated by coupling 5W of 1064nm radiation from a Nd:YAG laser into a 150μm fibre core, with no decrease in transmission or apparent laser damage. With the high glass transition temperature, these glasses offer the potential for greater handling capacity and also the reduced toxicity due to elimination of arsenic-containing compounds. The high refractive index and low phonon energy of GLS make this an ideal glass for a fibre amplifier operating at the 1300nm region [27, 28]. Our previous results also show that GLS based fibres can provide a new route towards infrared lasers in the 3-5μm region, in particular for gas sensing applications [29]. Additionally, the nonlinear, acousto-optic, and photosensitivity properties of GLS glass are all significantly greater than those compared to traditional optical fibre materials.

Planar channel waveguide devices based on the GLS glass system have the potential for use in glass waveguide lasers, wavelength multiplexers and optical switching/splitting in the IR. Further potential for optical couplers (such as directional couplers) in the IR would allow the important applications of power division and wavelength demultiplexing to be realised.

Further devices can be derived from the higher index contrast possible with GLS holey fibres allowing for fibres with very high NA (well in excess of unity). The resulting improvement possible in pump confinement implies tighter focusing, shorter devices and lower thresholds. The unusual properties of holey fibres result from the fact that the structure in the cladding can be on the same physical scale as the wavelength of light. If the fibre is designed appropriately, the guided mode can be made to have significant overlap with any material (gas or liquid) in the holes, which suggests using these fibres to measure gas concentrations.

5. CONCLUSIONS

This paper describes our investigations into the improvement of GLS fibre fabrication techniques. We have shown the possibility of creating low loss channel structures in GLS as well as GLS holey fibre. The potential for exploitation of new applications and devices is promising.

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