NEAR-IR ABSORPTION OF Ga:La:S AND Ga:La:S:O GLASSES BY FEL-BASED LASER CALORIMETRY.

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ABSTRACT

Optical absorption of Ga:La:S and Ga:La:S:O glasses in the near infrared was investigated by laser calorimetry using the free-electron laser source at the Thomas Jefferson National Accelerator Facility. An absorption coefficient of 1.2 and $2.1 \cdot 10^{-2} \, cm^{-1}$ was measured at $1.55 \mu m$ for Ga:La:S and Ga:La:S:O respectively. Comparing this result with conventional transmission measurements, we conclude that absorption is the prevailing loss mechanism in the near-IR region for these materials.

INTRODUCTION

Glasses based on gallium and lanthanum sulphides (GLS) [1] have attracted considerable interest due to their potential for photonic applications. Their transparency window ranges from about 0.7 to $5 \mu m$, making them suitable for applications both in the telecom window, and in the mid-IR. The presence of lanthanum in the glass network leads to high solubility of rare earth ions. The low phonon energy ($\sim 425 cm^{-1}$) of the sulphide host reduces the non-radiative quenching and the high refractive index (~ 2.35 at $1.5 \mu m$) leads to high radiative transition rates. Thus, optical transitions are available, in rare earth doped GLS glasses, that are commonly not observed in the more conventional glass hosts, enabling new schemes for fibre lasers and optical amplifiers. The high refractive index of GLS glasses also correlates with high third order nonlinearity, which is attractive for all-optical switching. Higher glass transition temperature, chemical stability and non-toxicity represent an advantage over other chalcogenides.

The realisation of practical devices is however a challenging task. While fiberisability of GLS glasses has been demonstrated [2], attenuation in typical fibres is still of the order of dBs per meter. This loss, described as partly absorptive and partly due to light scattering, has until now been assumed to be extrinsic, that is, caused by residual impurities, crystals and other defects introduced during the fabrication. However, the bulk loss of GLS glasses has never been adequately measured neither have the loss mechanisms been fully clarified. Since in other sulphide glass systems the weak absorption tail of the electronic absorption edge determines a fundamental transparency limit, the identification and quantification of the loss mechanisms in GLS glass is desirable.

Laser calorimetry is an established method to measure bulk absorption of optical materials [3]. Compared to transmission measurement, this technique has higher sensitivity and is virtually insensitive to Fresnel losses from the interfaces and scattering; however its application has been restricted to the few wavelengths for which high power laser sources were available. In order to overcome this limitation and investigate the glass properties in the crucial telecommunications window at $1.55 \mu m$, we used a tunable free electron laser (FEL) source. The FEL at the Thomas Jefferson National Accelerator Facility [4] is designed to deliver maximum output power in the infrared (over 2kW at about $3 \mu m$); however, when tuned in its third harmonic, it can also deliver average output powers in excess of 100W in the band from 1 to $2.1 \mu m$. This makes it an ideal light source for near infrared absorption calorimetry.

EXPERIMENTAL

Sample preparation. Two glass compositions were considered for this study, namely the $65Ga_2S_3:30La_2S_3:5La_2O_3$ (Ga:La:S) and the $78Ga_2S_3:22La_2O_3$ (Ga:La:S:O) composition. Sulphide precursors are not commercially available with the necessary purity; they were synthesized from electronic-grade gallium metal (7N pure) and purified lanthanum fluoride, respectively. The lanthanum oxide was commercial grade (5N)
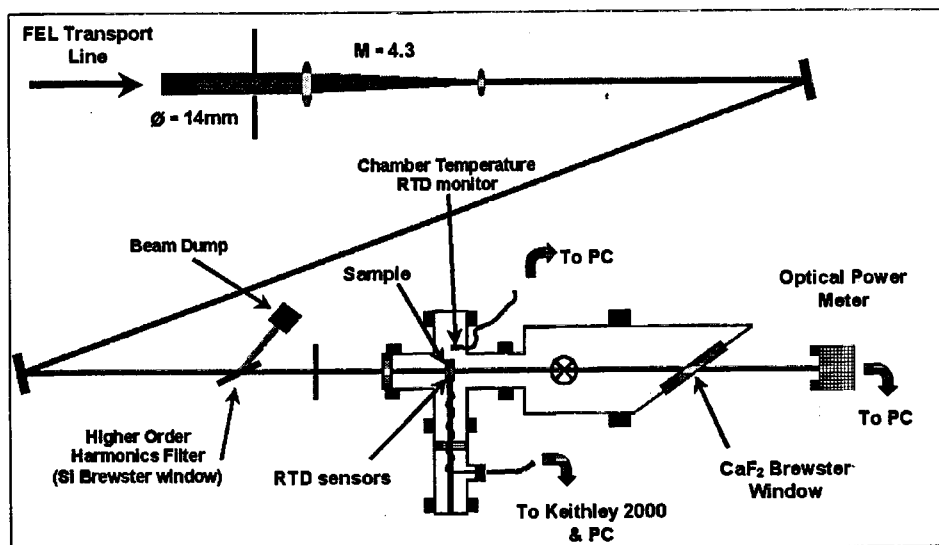
FIGURE 1: Experimental setup: laser beam path and calorimeter.

material, which was baked out at high temperature prior to glass melting to eliminate any absorbed moisture. Batches with the nominal compositions were prepared, thoroughly mixed and then loaded in a silica-lined furnace; glass melting was performed inside vitreous carbon crucibles at 1150°C for about 20hrs; melts were quenched in a water jacket at room temperature. The whole batching and melting process was accomplished under controlled (dry N or Ar) atmosphere. Glass ingots were annealed at 500 °C for several hours and were subsequently cut into 26mm diameter discs with thickness ranging from 2 to 13mm. The flat faces were accurately polished to an optical finish.

Transmission of these samples was measured in the range 400-2000nm by a Cary 500 VIS/NIR spectrophotometer. As thicker GLS samples can easily defocus or steer the analysing beam off the ideal path due to high refractive, a 110mm diameter, PTFE coated integration sphere was used.

Calorimeter. The temperature increase due to laser absorption is typically small; a resolution of a few mK is therefore desirable for the temperature reading. Samples and sensors must be adequately shielded from external temperature fluctuations. To provide the best insulation, we employed a vacuum chamber (kept at 10^{-3} torr); the chamber itself consisted of thick stainless steel flanges and had large thermal capacitance. Additional insulation was placed outside the chamber to minimise thermal disturbances.

The samples were clamped on an aluminium ring holder. Eight resistive temperature sensors (Pt thin film RTD) were permanently attached to the holder. In our design the aluminium body contributed to the effective heat capacity of the system, and the thermal contact between sample and detectors was very reproducible. The sample holder mount was kept in place at the centre of the chamber via a long, thin walled steel tube with very poor thermal conductivity, and exchanged heat with the chamber walls mainly by irradiation.

The RTDs were connected in series and a Keithley 2000 digital multimeter was used to measure their resistance by the 'four wires' method. As the precision of the multimeter is $10m\Omega$, and the RTD resistors are calibrated to the DIN standard ($\alpha_R = 3850 ppm \cdot K^{-1}$), the resolution of our setup was about 3mK.

Laser Source and optical path. The FEL was operated in its third harmonic lasing (THL) at 1.55µm, with sub-ps pulse width and a micropulse repetition rate of 37 and 74MHz. The average power during the measurements was set at about 20W, which produced an excellent signal. Higher power was readily available, but it could have damaged the samples or induced undesired nonlinear effects. The FEL beam was collimated to a diameter of about 3mm using a pair of calcium fluoride lenses [fig1]. A silicon Brewster window was used to filter out a small amount (1-2%) of higher order harmonics contained in the beam; since these are totally absorbed by GLS, they would have been particularly detrimental for our measurement.

The whole calorimeter was mounted on a micropositioner, and was carefully aligned to the optical beam. The entrance port was fitted with a silica window (Spectrosil WF grade). The sample orientation could be adjusted in order to ensure that the reflected beam ($\approx$30% of the incident power) was exiting the chamber without disturbing the measurement. For the same reason, the exit port had a calcium fluoride Brewster window to avoid backreflections hitting the sample holder or the sensors. The transmitted power was measu-
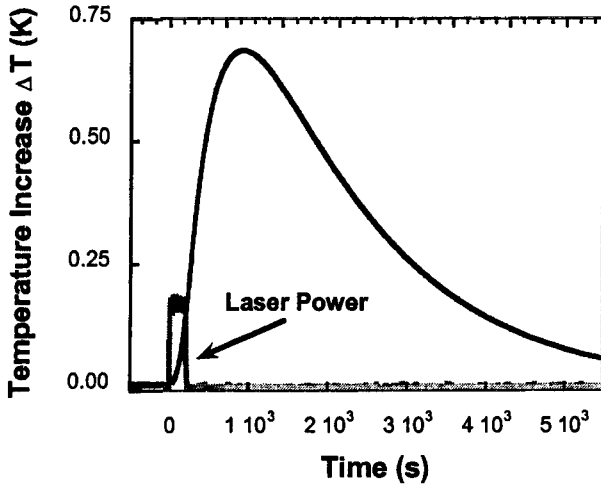
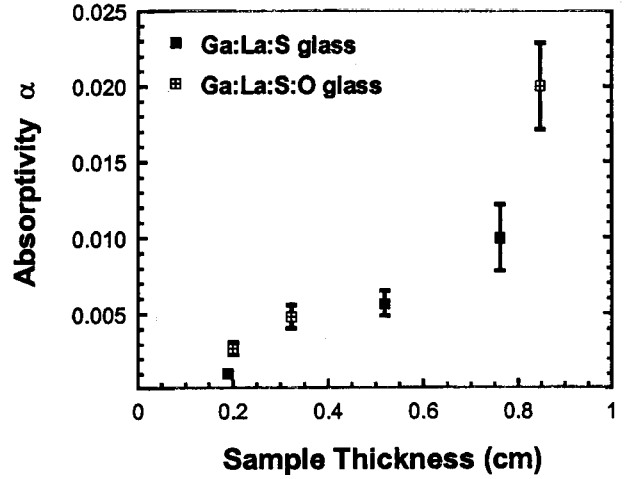FIGURE 2: Typical heating curve. Average power: 12±1W. Heating time: 210s. Sample: Ga:La:S; thickness 7.62mm

FIGURE 3: Plot of the absorbance as a function of the sample thickness for Ga:La:S and Ga:La:S:O samples.

red with a water cooled Molectron PM5K optical power meter, which also served as beam dump.

RESULTS

Transmission Measurements. Transmission of GLS samples is dominated by the Fresnel loss. Repeated measurements showed that transmission was consistent within 0.1% in a 10mm diameter central area for most of the samples; however, GLS samples thicker than $\approx$10mm also showed inhomogeneity even in a $\approx$3mm diameter central area and were not used for calorimetric analysis. From the differential transmission of homogeneous samples with different thickness, the total loss of Ga:La:S and Ga:La:S:O was determined [Fig. 4].

Laser Calorimetry. Figure 2 show a typical heating curve. As the laser power was turned on, heating occurred in the sample; a delay was observed, which was partly due to the poor thermal conductivity of GLS glass, and to the contact thermal resistance between sample and holder. A full measurement run, typically 90min long, included recording the background, heating the sample for about 300s and then monitoring the cooling. Three samples with different thickness were measured for each composition: 2, 5.2, 7.6mm for Ga:La:S and 2, 3.2, 8.5mm for Ga:La:S:O.

As GLS has strong nonlinear properties, it was necessary to ensure that this was not affecting the measurement. The absorption of the same sample was measured twice, keeping the average power constant while switching the micropulse repetition rate from 37 to 74MHz; hence the peak power of every micropulse was varied by a factor of two. If there was a nonlinear component contributing to the total absorption, this should have caused a noticeable effect. As this was not the case in GLS and GLSO samples, we concluded that nonlinear absorption was in fact negligible at the optical power density used.

DISCUSSION

The time dependence of the temperature increase of a sample undergoing irradiation from t=0 to t=t_0 is [3]:

$$\Delta T(\rho,t) = \frac{\alpha P}{\left(mc_p\right)^{eff}} \cdot \begin{cases} \sum_i \frac{g_i(\rho)}{\gamma_i} \cdot \left(1 - e^{\gamma_i t}\right) & 0 \le t \le t_0 \\ \sum_i \frac{g_i(\rho)}{\gamma_i} \cdot \left(1 - e^{\gamma_i t_0}\right) \cdot e^{\gamma_i(t-t_0)} & t_0 \le t \end{cases}$$

where ρ is the radial coordinate, α is the absorptivity, P is the incident power, $(mc_p)^{eff}$ is the effective heat capacity (sample plus holder), and the g_i coefficients can be calculated from the beam profile and material properties of the sample.
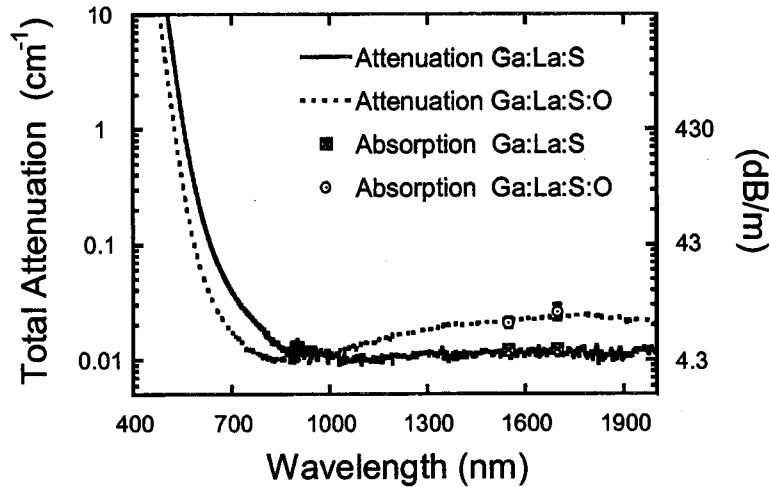
FIGURE 4: Total attenuation of Ga:La:S samples (thickness: 2 & 7.6mm) and Ga:La:S:O (thickness: 2 & 8.4mm), measured by differential transmission spectroscopy. The data points at 1.55μm and 1.7μm show the absorption, as measured by calorimetry.

The total absorptivity of a sample of thickness L is the sum of a surface and a bulk term, and in the limit of low absorption can be written as: $\alpha = \alpha_S + \alpha_B \approx \beta L + 2\sigma$, where σ is the surface absorptivity and β is the absorption coefficient that appears in the Lambert-Beer law. From measurements made on samples with different thickness, it is then possible to determine the two values of β and σ. Figure 3 presents a plot of α versus the sample thickness for the two sets of Ga:La:S and Ga:La:S:O samples. It is clear from the plot that the surface absorption has a negligible contribution. The calculated absorption coefficients are: $(1.2 \pm 0.1) \cdot 10^{-2} \, \text{cm}^{-1}$ for Ga:La:S and $(2.1 \pm 0.1) \cdot 10^{-2} \, \text{cm}^{-1}$ for Ga:La:S:O.

Comparing these values with those shown in Figure 4 for the total attenuation, we conclude that absorption accounts for most of the bulk optical loss in both Ga:La:S and Ga:La:S:O in the wavelength region around 1.55μm. Additional calorimetry measurements at 1.7μm (also shown on Figure 4) confirm the absorptive nature of optical loss and a flat dependence on the wavelength, which is also seen in the transmission measurements. From our measurements it is not possible to draw a definitive conclusion as to whether the absorption is caused by a weak absorption tail or is the sum of broad absorption bands from residual metal impurities.

SUMMARY

Optical loss mechanisms in GLS glasses were investigated at 1.55μm by measuring separately the total attenuation by differential transmission measurements and the optical absorption by FEL laser calorimetry. We found very close agreement in both the low oxide (Ga:La:S) and the high oxide (Ga:La:S:O) compositions, indicating that the loss is mainly absorptive at these wavelengths.

ACKNOWLEDGEMENTS

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