

Near-IR Absorption of Ga:La:S and Ga:La:S:O Glasses by FEL-based Laser Calorimetry.

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Abstract

The optical absorption of bulk 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 $1.2 \cdot 10^{-2} \text{ cm}^{-1}$ and $2.3 \cdot 10^{-2} \text{ cm}^{-1}$ was measured at $1.55 \text{ } \mu\text{m}$ for Ga:La:S and Ga:La:S:O respectively. Comparing this result with conventional transmission measurements, we show that absorption is the prevailing loss mechanism in the near-IR region.

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1. Introduction

Glasses based on gallium and lanthanum sulphides (GLS) have potential for photonic applications [1-3]. Their transparency window range (≈ 0.7 to $5 \mu\text{m}$) makes them suitable both for telecom and mid-IR. High rare-earth solubility, low phonon energy ($\sim 425 \text{ cm}^{-1}$) and high refractive index (~ 2.35 at $1.5 \mu\text{m}$) make them ideal hosts for rare-earth doped devices. Their high refractive index also correlates with high third order nonlinearity [4], which is attractive for all-optical switching. Also, 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 was demonstrated [2], attenuation is still of the order of dB per meter even in unstructured fibres [3]. 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 [5]. However, the bulk loss of GLS glasses has never been adequately measured nor has the loss mechanism been fully clarified. Since in other sulphide glass systems the weak absorption tail of the electronic absorption edge determines a fundamental transparency limit [6], the identification and quantification of the loss mechanisms in GLS glass is desirable.

Laser calorimetry is an established method to measure the bulk absorption of optical materials [7]. Compared to transmission measurements, this technique has higher sensitivity and is virtually insensitive to Fresnel losses from 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 glass properties in the crucial $1.55 \mu\text{m}$ region, we used a tunable free electron laser (FEL) source. The FEL at the Thomas Jefferson National Accelerator Facility is designed to deliver maximum output power in the mid-IR (over 2 kW at about $3 \mu\text{m}$) [8]; however, when tuned in its third harmonic, it can deliver average output powers in excess of 100 W from 1 to $2.1 \mu\text{m}$, making it ideal for near-IR absorption calorimetry.

2 Experimental

Two glass compositions were considered in this study; the Ga:La:S, composed of Ga₂S₃ and La₂S₃, with a few percent of La₂O₃ added to improve the glass formation, and the Ga:La:S:O, where La₂S₃ content is substituted by La₂O₃. Sulphide precursors are not commercially available with the necessary purity, thus they were synthesized in house from high purity precursors. Batches of powders were thoroughly mixed and loaded in a silica-lined furnace; glass melting was performed inside vitreous carbon crucibles at 1150 °C; melts were quenched to room temperature and subsequently annealed at 20 °C below their respective T_g. Trace level analysis of transition metal impurities was performed by glow discharge mass spectroscopy (GDMS); Fe was the main impurity (0.8 ppm), whereas other elements such as Cr, Ni, Ti were all lower than 0.1 ppm. Glass ingots were cut into 26 mm diameter discs with thickness ranging from about 2 to 13 mm. The flat faces were accurately polished to an optical finish.

Transmission of these samples was measured from 0.4 to 2 μm by a Cary 500 UV/VIS/NIR spectrophotometer. As thicker GLS samples can easily defocus or steer the analysing beam off the ideal path due to high refractive index, a 110 mm diameter, PTFE coated integration sphere was used. The sphere was fitted with a PM tube and a PbS detector.

The temperature increase due to laser absorption is typically small; a resolution of a few mK is therefore desirable. Samples and sensors must be adequately shielded from external temperature fluctuations. We employed a vacuum chamber (kept at 10⁻³ torr), which consisted of thick stainless steel flanges with 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 detectors (Pt thin film RTD) were 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, held in place at the centre of the chamber, exchanged heat with the chamber walls mainly by irradiation. The RTD sensors were connected

in series and a Keithley 2000 digital multimeter measured their resistance in a four terminal configuration. The overall resolution was about 3 mK.

The FEL was operated in its third harmonic lasing at 1.55 μm , with sub-ps pulse width and a micropulse repetition rate of 37 and 74 MHz. The average power during the measurements was set at about 15 W, 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 3 mm using a pair of calcium fluoride lenses (fig. 1). A silicon Brewster window filtered out a small amount (1-2 %) of higher order harmonics contained in the beam that would otherwise have caused strong absorption in our samples.

The whole calorimeter was mounted on a micropositioner for accurate alignment. 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. Similarly, the exit port was fitted with a calcium fluoride Brewster window to avoid back-reflections hitting the sample holder or the sensors. The transmitted power was measured with an optical power meter.

3 Results

Transmission of GLS samples is dominated by the Fresnel loss. Repeated measurements showed that transmission was consistent within 0.05 % T in a 10 mm diameter central area for most of the samples; however, GLS samples thicker than ≈ 10 mm showed inhomogeneity even in a ≈ 3 mm diameter central area and were not used for calorimetric analysis. From the differential transmission of homogeneous samples with different thickness, the total attenuation of Ga:La:S and Ga:La:S:O was determined (fig. 4).

Figure 2 shows a typical calorimetric heating curve. As the laser power was turned on, heating occurred due to a fraction of the beam being absorbed by the sample. A delay was observed, which was because of the low thermal conductivity of GLS glass and the contact thermal resistance between sample and holder. A full measurement run, typically 90 minutes long, included recording the background, heating the sample for about 300 s and then monitoring the

cooling. Three samples with different thickness were measured for each composition: 1.96, 5.19, 7.62 (± 0.02) mm for Ga:La:S and 2.00, 3.23, 8.48 (± 0.02) mm 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 74 MHz; hence the peak power of every micropulse was varied by $\approx 50\%$. If there were 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.

4 Discussion

Assuming a disc-shaped sample of radius R and a gaussian beam, the time dependence of the temperature increase of a sample undergoing irradiation from $t = 0$ to $t = t_0$ is [7]:

$$\Delta T_R(t) = \frac{\alpha P}{(mc_p)^{eff}} \begin{cases} \sum_i \frac{g_i(R)}{\gamma_i} \cdot (1 - e^{-\gamma_i t}) & 0 \leq t \leq t_0 \\ \sum_i \frac{g_i(R)}{\gamma_i} \cdot (1 - e^{-\gamma_i t_0}) \cdot e^{-\gamma_i(t-t_0)} & t_0 \leq t \end{cases}$$

where α is the absorptivity, P is the incident power, $(mc_p)^{eff}$ is the heat capacity of sample and holder, and the $g_i(R)$ coefficients can be calculated from the beam profile and material properties (see ref. [7] for details).

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. By measuring samples with different thickness β and σ can be determined. 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 is negligible. The calculated absorption coefficient β is $(1.2 \pm 0.1) \cdot 10^{-2} \text{ cm}^{-1}$ for Ga:La:S and $(2.3 \pm 0.2) \cdot 10^{-2} \text{ cm}^{-1}$ 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 1.55 μm wavelength region. Additional calorimetry measurements at 1.7 μm (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. However, according to ref. [5], the specific absorption coefficient of Fe ion in GLS is $0.6 \cdot 10^{-2} \text{ cm}^{-1} \text{ ppm}^{-1}$, hence impurity absorption alone cannot entirely account for the absorption measured in our samples.

5 Conclusions

We have investigated the mechanisms of near-IR optical loss in GLS glasses. The optical absorption in the telecommunication window at 1.55 μm was measured by laser calorimetry using a FEL source. The values found are in very close agreement with transmission measurements of the total attenuation, in both the low oxide (Ga:La:S) and the high oxide (Ga:La:S:O) compositions, giving a strong indication that the optical loss at these wavelengths is mainly absorptive.

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Figure Captions

FIGURE 1: Experimental set-up: laser beam path and calorimeter.

FIGURE 2: Typical heating curve. Average power on the sample: 12 ± 1 W. Heating time: 210 s. Sample: Ga:La:S; thickness 7.62 mm.

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

FIGURE 4: Total attenuation of Ga:La:S samples [thickness: 1.96 & 7.62 (± 0.02) mm] and Ga:La:S:O [thickness: 2.00 & 8.48 (± 0.02) mm], measured by differential transmission spectroscopy. The data points at 1.55 μm and 1.7 μm show the absorption, as measured by calorimetry.

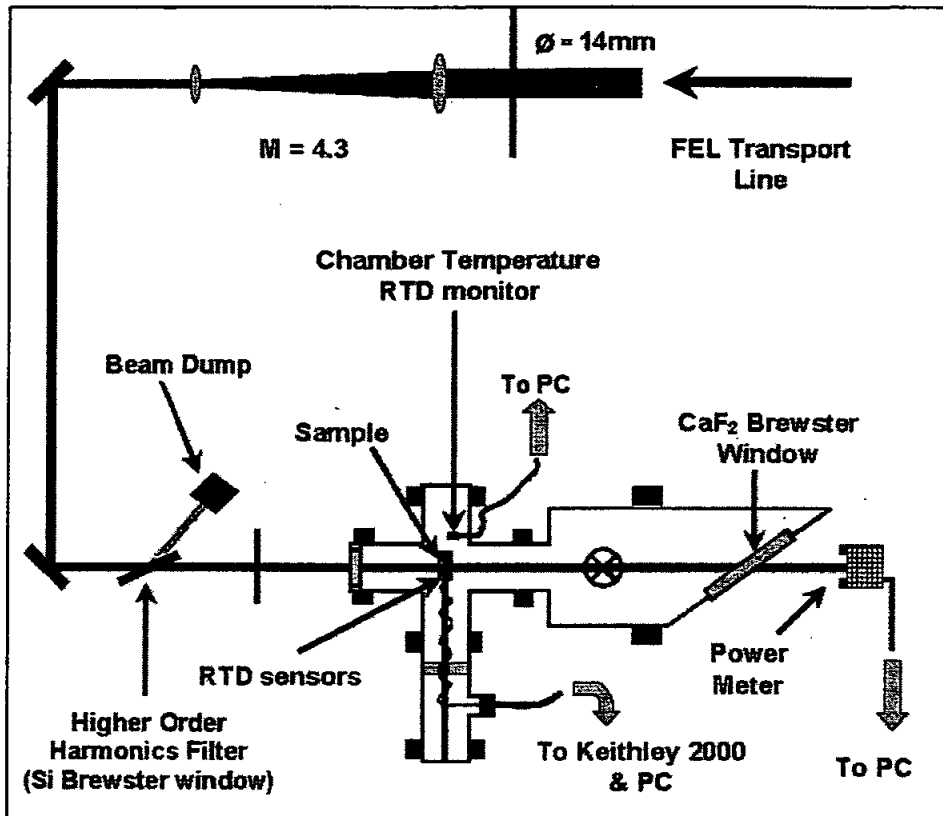


FIGURE 1

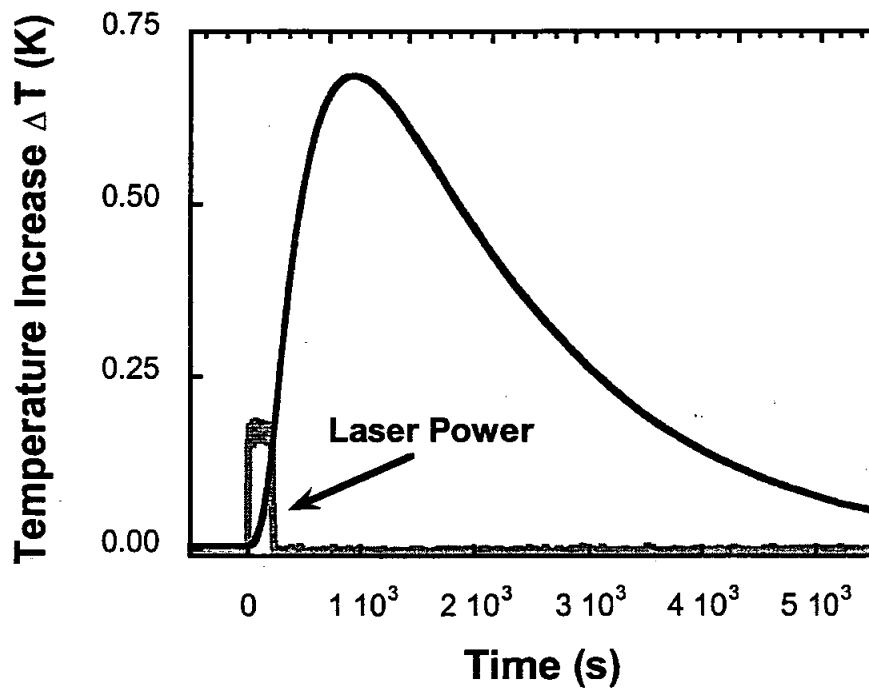


FIGURE 2

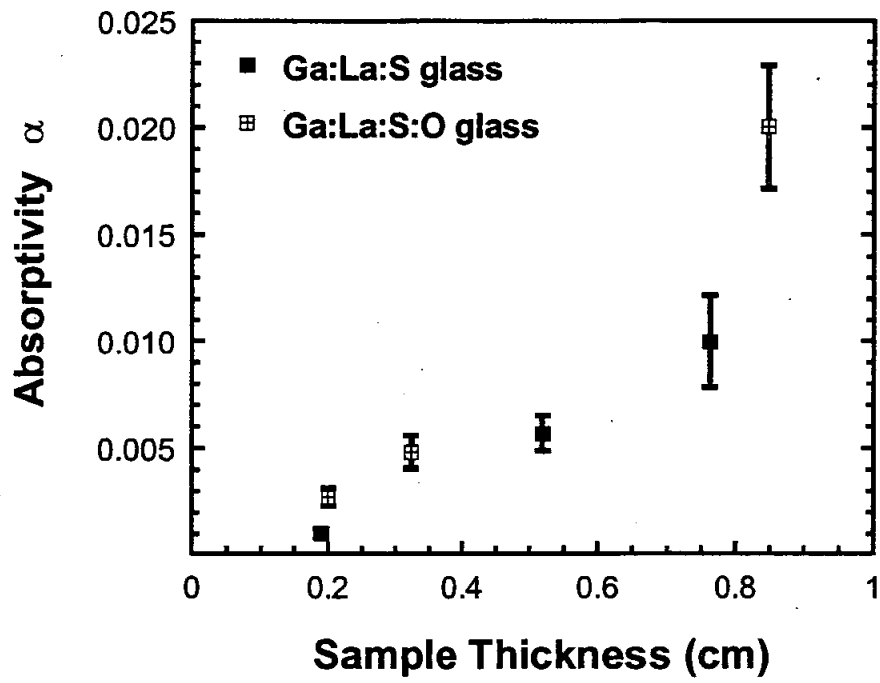


FIGURE 3

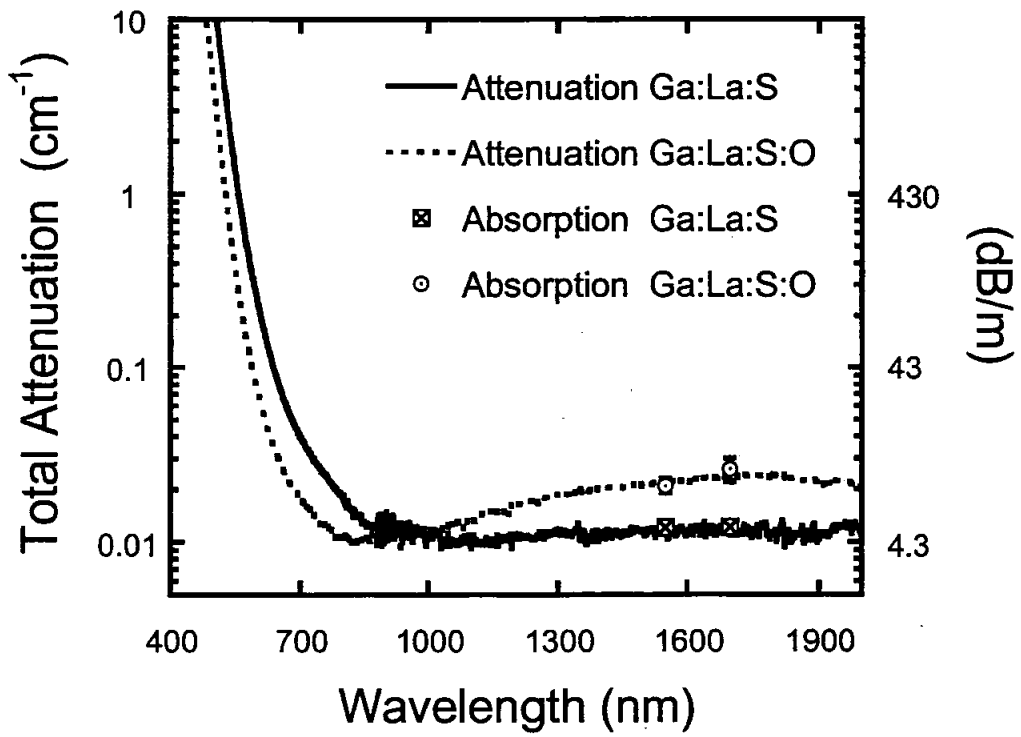


FIGURE 4