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Near-IR absorption of Ga:La:S and Ga:La:S:O glasses by free-electron laser-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 1.2×10^{-2} and $2.3 \times 10^{-2} \text{ cm}^{-1}$ was measured at $1.55 \mu\text{m}$ 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. Although not conclusive, our measurements suggest that the absorption is due to impurities and to the weak absorption tail.

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1. Introduction

Glasses based on gallium and lanthanum sulfides (GLS) have potential for photonic applications [1–3]. Their region of low attenuation ($\approx 0.7\text{--}5 \mu\text{m}$) 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 non-linearity [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 realization of practical devices is however a challenging task. While fiberizability of GLS glasses was demonstrated [2], attenuation is still of the order of dB per meter even in unstructured fibers [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 sulfide glass systems the weak absorption tail (WAT) of the electronic absorption

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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 μm 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 μm) [8]; however, when tuned in its third harmonic, it can deliver average output powers in excess of 100 W from 1 to 2.1 μm , making it ideal for near-IR absorption calorimetry.

2. Experimental

Two glass compositions were considered in this study; Ga:La:S, with nominal composition $65\text{Ga}_2\text{S}_3:35\text{La}_2\text{S}_3:5\text{La}_2\text{O}_3$ and Ga:La:S:O, with nominal composition $78\text{Ga}_2\text{S}_3:22\text{La}_2\text{O}_3$. Gallium and lanthanum sulfides 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 $^\circ\text{C}$; melts were quenched to room temperature and subsequently annealed at 20 $^\circ\text{C}$ 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 8.5 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 analyzing 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 minimize thermal disturbances.

The samples were clamped on an aluminum ring holder. Eight resistive temperature detectors (Pt thin film RTD) were attached to the holder. In our design the aluminum 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 non-linear 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 power density at the sample surface was about 0.2 kW/cm².

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

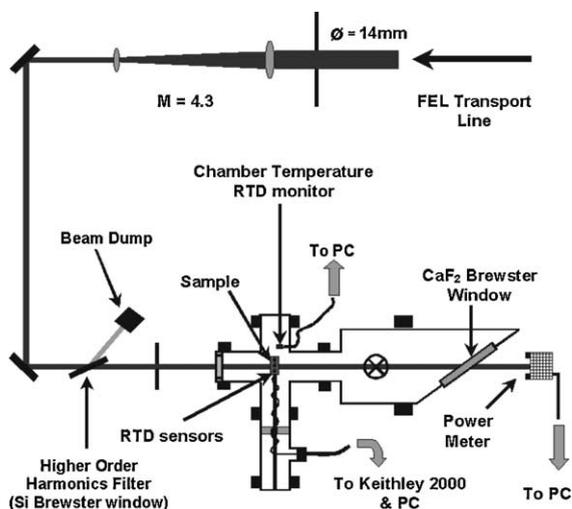


Fig. 1. Experimental set-up: laser beam path and calorimeter.

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 from interfaces. The total attenuation can be determined by differential transmission of samples with different thickness. We used ≈ 2 and ≈ 8 mm thick samples to measure the total attenuation of Ga:La:S and Ga:La:S:O (Fig. 4). Transmission of these samples was consistent within 0.05% T in a 10 mm diameter central area. Measurements were repeated after calorimetry in order to ensure that no modifications had occurred in the samples.

Fig. 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 min long, included recording the background, heating the sample for about 300 s and then monitoring the cooling. Three samples

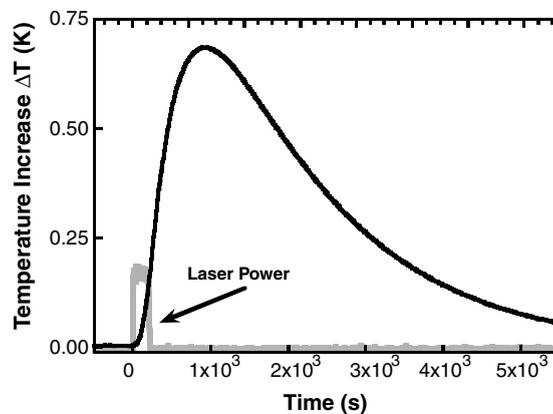


Fig. 2. Typical heating curve. Average power on the sample: 12 ± 1 W. Heating time: 210 s. Sample: Ga:La:S; thickness 7.62 ± 0.02 mm.

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 non-linear 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 non-linear component contributing to the total absorption, this should have caused a noticeable effect. As this was not the case in Ga:La:S and Ga:La:S:O samples, we concluded that non-linear 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]

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

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

As absorption can also occur at the sample interfaces due to defects and contamination, the total absorptivity is given in general by the sum of a bulk and a surface term. In the limit of low absorption and for a sample of thickness L : $\alpha \approx \beta L + 2\sigma$, where β is the absorption coefficient (Lambert–Beer law) and σ is the surface absorptivity, assumed to be equal for the two faces of the sample. By measuring samples with different thickness β and σ can be determined. Fig. 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 $(1.2 \pm 0.1) \times 10^{-2} \text{ cm}^{-1}$ for Ga:La:S and $(2.3 \pm 0.2) \times 10^{-2} \text{ cm}^{-1}$ for Ga:La:S:O.

Comparing these values with those shown in Fig. 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 region. Additional calorimetry measurements at 1.7 μm (also in Fig. 4) confirm this and the flat wavelength dependence of the loss, which is also seen in the transmission measurements. Absorption in this wavelength region is most likely caused by the WAT and by impurity absorption. Differ-

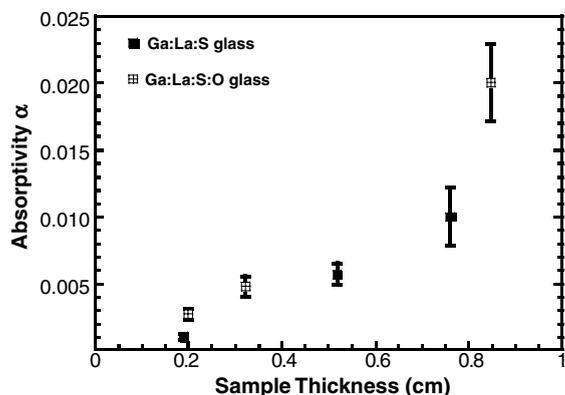


Fig. 3. Plot of the absorptivity as a function of the sample thickness for Ga:La:S and Ga:La:S:O samples.

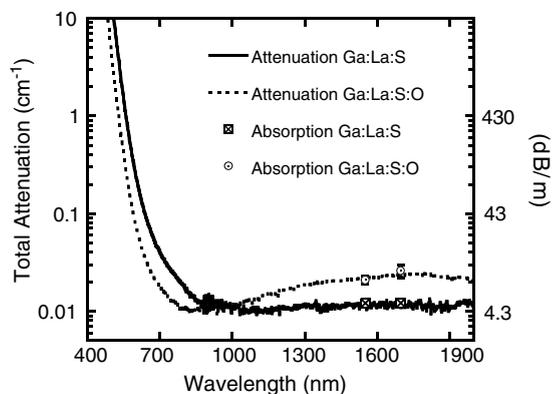


Fig. 4. Total attenuation of Ga:La:S samples (thickness: 1.96 and 7.62 (± 0.02) mm) and Ga:La:S:O (thickness: 2.00 and 8.48 (± 0.02) mm), measured by differential transmission spectroscopy. The data points at 1.55 and 1.7 μm show the absorption, as measured by calorimetry.

ences in the oxidation states of transition metal impurities could explain the difference in the absorption spectra of Ga:La:S and Ga:La:S:O. On the other hand, according to Ref. [5], the specific absorption coefficient of Fe in GLS is $0.6 \times 10^{-2} \text{ cm}^{-1} \text{ ppm}^{-1}$, hence impurity absorption cannot entirely account for the measured values.

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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