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Self refractive non-linearities in chalcogenide based glasses

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Abstract

We report third order non-linear absorption and refraction measurements at 1.20 and 1.52 μm on selected gallium–Lanthanum sulfide-based glasses (Ga:La:S) showing negligible non-linear absorption and a refractive non-linearity close to one hundred times that of SiO_2 . Their potential use in telecommunication as base materials for all-optical switching practical devices is evaluated resulting in large figures of merit. The addition of a glass modifier to the Ga:La:S matrix has improved thermal and optical properties, resulting in ease of fibre drawing. The non-linear optical response of this new variant of the Ga:La:S family is studied.

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1. Introduction

Third order non-linear optical properties are of major interest in the development of optical devices. Although many materials have been explored as candidates for all-optical switching devices, third order non-linear measurements have been mainly performed at visible wavelengths. There are but few examples of third order non-linear measurements at wavelengths of interest in optical communications.

Any non-linear material suitable for an all-optical switching process should show a large third order optical non-linearity, fast response time, and minimal linear and non-linear absorption in the wavelengths of interest. Otherwise, a large absorbed power in a small volume would result in slow thermal drift in the refractive index. Furthermore, two-photon absorption (TPA) limits the optical power that can be transmitted and hence the attainable non-linear phase shift in the guiding structure. Assuming negligible linear absorption, it is customary to define the following figure of merit (FOM), $\text{FOM} = n_2 / (2\beta\lambda)$, where λ is the wavelength, n_2 is the real part of the non-linear refractive index and β the TPA coefficient [1]. For practical devices, this FOM should be much larger than 1 to avoid large TPA-induced attenuation.

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The family of chalcogenide glasses shows a large intensity dependent index of refraction without appreciable linear absorption at wavelengths for optical communications. Some chalcogenide glasses have already been demonstrated as effective all-optical switching devices [2]. Chalcogenides based on gallium–lanthanum sulphides (Ga:La:S) are of great interest particularly due to their low toxicity, high transition temperature ($T_g \sim 560$ °C) and excellent rare-earth solubility [3]. Improving the inherent properties of a glass is possible through the addition of glass modifiers. Wang et al. investigated the addition of CsCl to the Ga:La:S glass matrix with resulting improvements in optical properties and ease of fiber drawing of this modified glass [4].

We report non-linear absorption and non-linear refractive index measurements for selected variants of the Ga:La:S glass system. The measurements were at wavelengths of interest for optical communications. The selection of different glass compositions studied has been based on their viability to be drawn into fiber.

2. Experimental procedure

2.1. Glass fabrication

Most glasses based on the Ga:La:S system are fabricated in similar fashion. GLS glass (with molar composition $65\text{Ga}_2\text{S}_3:32\text{La}_2\text{S}_3:3\text{La}_2\text{O}_3$) is fabricated by melting a mixture of gallium sulphide, lanthanum sulphide and lanthanum oxide powders. Batches of powders are placed in a vitreous carbon crucible and melted in a tube furnace at 1150 °C for up to 24 h. The tube furnace has an argon-purged atmosphere, facilitating the removal of volatile impurities, particularly OH^- . The melt is quenched and the glass is annealed. Annealing is routinely done at 530 °C (below glass transition temperature) for about 24 h. The process of annealing removes residual stresses and thermal shock in the glass, which is introduced during the quench, making the glass suitable to be cut and polished.

The substitution of up to 30 mol% of La_2S_3 by La_2O_3 , (with resulting molar composition

$70\text{Ga}_2\text{S}_3:30\text{La}_2\text{O}_3$) results in a variant of GLS termed oxide–GLS (GLSO). GLSO glass has improved thermal stability during fiber drawing as compared to GLS; however, the higher oxide content in GLSO glass lowers the refractive index and deteriorates its spectroscopic properties [5]. The addition of a modifier such as a lanthanum halide to the Ga:La:S glass matrix has been successfully demonstrated and provides several important properties over GLS and GLSO glasses. Halide doped Ga:La:S glass (GLSOF) (molar composition $70\text{Ga}_2\text{S}_3:x\text{LaF}_3:(30-x)\text{La}_2\text{O}_3$) contains significantly less lanthanum oxide as compared to GLSO. This reduction in oxide content results in lower loss fiber due to reduction of hydroxyl impurities, while still maintaining thermal stability for fiber drawing [4,6].

2.2. Optical measurements

The transmittances of the materials were measured in order to determine the optical absorption edge (or optical gap), ϵ_g as well as the linear refractive indices at 1.20 and 1.52 μm . Chalcogenide glasses, like almost all amorphous materials, exhibit an optical absorption edge which is not sharp, but obeys an exponential dependence on photon energy. Beyond the optical gap, the absorption, α , changes its behavior and becomes $\alpha(\omega) \propto (\hbar\omega - \epsilon_g)^2/\omega$ [7]. Thus, the value of the absorption edge at room temperature (shown in Table 1) was obtained by linearly extrapolating $(\omega\alpha(\omega))^{1/2}$ versus $\hbar\omega$. The linear refraction indices were computed with data from the transmittance spectra. A standard SF59 glass sample was used for calibration of all optical experiments.

Non-linear measurements were carried out using the Z-scan technique [8]. In this experiment, a focused Gaussian laser beam induces a self-focusing effect on a sample that is moved along the propagation path of the beam. The transmittance of the material as a function of its distance to the focusing plane of the beam is recorded in the far field through a small aperture. The transformation of phase distortion into amplitude distortion during beam propagation allows measurement of the change of the refractive index, Δn . If this variation is related to a third order non-linear optical pro-

Table 1
Composition and linear optical properties of studied Ga:La:S based glasses

	Molar composition (mol%)					Refractive index ^a		Absorption edge ^a (nm)
	Ga ₂ S ₃	Na ₂ S	La ₂ S ₃	La ₂ O ₃	LaF ₃	1.20 μm	1.52 μm	
GLS	65	–	32	3	–	2.42	2.41	545
GLSO	70	–	–	30	–	2.25	2.25	500
GLSOF	70	–	–	15	15	2.28	2.26	497
GNS	68	32	–	–	–	2.16	2.14	473

^a Experimental uncertainty: $|\delta n_{\max}| < 1.6\%$, $|\delta \epsilon_{g \max}| < 1.7\%$.

cess, then $\Delta n = n_2 I$, where n_2 is the non-linear refractive index, $I = (n_0 c / 8\pi) |E(\omega)|^2$ the time-averaged intensity of the optical field $E(\omega)$, n_0 the linear refractive index and c the speed of light [9]. The determination of the non-linear absorption coefficient was carried out through the so called open aperture (or near field) configuration for Z-scan as described in Ref. [10].

By fitting the Z-scan data with a thin lens model [11] (provided that the thin lens condition is met, i.e. the thickness of the sample is much smaller than the Rayleigh range of the beam, z_0) it is possible to extract values for the non-linear refractive index, n_2 , the thermo-optic coefficient, and the TPA coefficient, β . Pure electronic effects and thermo-optic effects can be differentiated because of the distinctive z -dependence of the normalized power transmitted by the sample.

The laser source used in the Z-scan experiment was an optical parametric amplifier pumped by a regeneratively amplified femtosecond Ti:sapphire laser. The output of the system was a linearly polarized pulsed beam with a repetition rate of 230 kHz. At the working wavelengths (1.20 and 1.52 μm), the pulse duration was typically 130 fs and the power incident on the sample ~ 200 kW.

Uncertainties in the experimental data arise when determining the intensity at the sample. To reduce them, a standard SF59 sample was used as a reference, with a published value of $n_2 = 3.20 \times 10^{-15} \text{ cm}^2/\text{W}$ at $\lambda = 1.06 \text{ μm}$ [12]. Since this (and the wavelengths we worked at) are far beyond the energy gap of SF59 (Fig. 1) it can be assumed that the non-linear dispersion in the range of wavelengths of interest is negligible. Hence, we considered that the value of the non-linear refractive index for SF59 at 1.06 μm holds for 1.20 and 1.52 μm and used it as reference. This as-

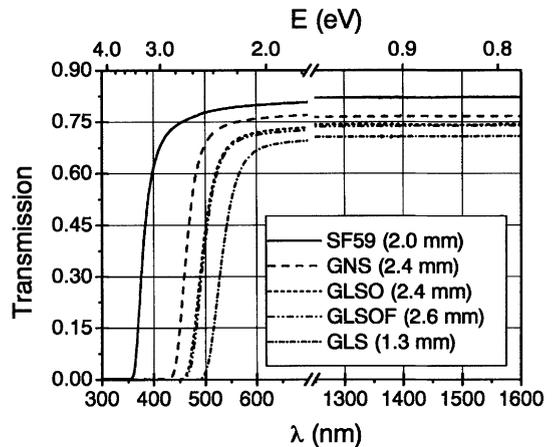


Fig. 1. Transmission spectra for samples under study together with SF59 for reference purposes. Transmission spectra for GLSO and GLSOF samples are too close to be clearly resolved in the figure.

sumption was proved correct after cross-checking our GLS non-linear measurements with those already published: comparison between measured and published data for GLS glass showed little variation [13,14]. Typical intensities inside the samples were around 2 GW/cm² and no optical damage was observed.

3. Results

Fig. 1 shows the experimental transmission spectra of the samples under study, together with SF59 for reference purposes. The spectra present an extended transparent region from the visible to the IR that shows no linear dispersion from 650 nm onwards. Linear refractive indices and optical absorption gaps computed from the spectra are

collected in Table 1. The measured values for GLS, GLSO and SF59 glasses were compared with those already published [15] (and Schott catalogue), showing a maximum deviation of $\pm 1.6\%$ in the linear refractive indices and $\pm 1.7\%$ in the values of the optical absorption edges. These data show that the absorption edges of all samples are beyond 2.28 eV (below 545 nm).

An experimental Z-scan trace and actual fit for GLSO glass at 1.52 μm is shown in Fig. 2. This Z-scan trace is representative for all the samples under study, and it is characteristic of a positive variation of the refractive index with increasing intensity and the absence of absorptive non-

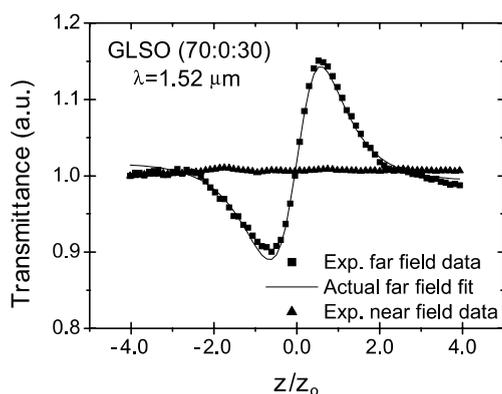


Fig. 2. Experimental near and far field Z-scan traces (open and closed aperture configuration, respectively) for GLSO and actual far field data fit.

linearities. Thermo-optic effects were not expected since samples are transparent at the wavelength used for the measurements and the repetition rate was low enough [16]. The absence of any thermo-optic effects was confirmed after fitting the data with the model described in [11].

Table 2 lists the non-linear optical refractive indices and absorption coefficients at 1.52 μm for the glasses studied in this work, along with other chalcogenide glasses for comparison. It can be seen that n_2 is higher than $10^{-14} \text{ cm}^2/\text{W}$ for all the Ga:La:S based glasses. Measurements at 1.20 and 1.52 μm yielded the same value within experimental resolution confirming the assumed flatness of the non-linear dispersion. Non-linear absorption (multiple photon absorption) measurements were carried out in search of both two and three photon effects; no TPA was expected as the optical absorption edges of all the samples are below 545 nm, which is less than half the shortest wavelength used in the measurements. However, three-photon absorption could become significant near $\epsilon_g/3$. No non-linear absorption, regardless of its origin, could be resolved in a 2% (maximum experimental resolution, Fig. 2) full scale open aperture Z-scan trace. We therefore estimate $\beta < |0.01| \text{ cm/GW}$ at both 1.20 and 1.52 μm for all the samples. After calibrating the experiment as described above the maximum experimental uncertainty is $\pm 17\%$, which is typical of Z-scan experiments.

Table 2

Non-linear optical properties and FOM of Ga:La:S based glasses along with the highest non-linear chalcogenide glasses to our best knowledge

	λ_{meas} (μm) ^a	n_0	n_2 ($10^{-14} \text{ cm}^2/\text{W}$) ^b	β (cm/GW)	FOM	Absorption edge (nm)	Author
GLS	1.52	2.41	2.16	<0.01	>7.1	545	This work
GLSO	1.52	2.25	1.77	<0.01	>5.8	500	This work
GLSOF	1.52	2.26	1.39	<0.01	>4.6	497	This work
GNS	1.52	2.14	1.01	<0.01	>3.3	473	This work
Ge _{0.28} Se _{0.60} Sb _{0.12}	1.5	2.6	9.4	0.2	1.6	690	[21]
As ₂ Se ₃	1.5	2.8	13.0	0.4	1.1	700	[21]
As ₂ S ₃	1.06	2.6	5.7	0.26	1.0	520	[22]
Ge ₃₀ Se ₇₀	1.06	–	21	1.1	0.9	705	[23]
Ge ₁₀ As ₁₀ Se ₈₀	1.06	–	22	2.7	0.39	760	[23]

^a Wavelength used for each measurement.

^b Experimental uncertainty for samples measured in this work: $|\delta n_{2\text{max}}| < 17\%$.

4. Discussion

The refractive non-linearity results for Ga:La:S based glasses show values close to a hundred times that of silica glass ($n_{2\text{SiO}_2} = 0.024 \times 10^{-14} \text{ cm}^2/\text{W}$ [17]). This demonstrates Ga:La:S based glasses have larger off-resonant non-linearities than oxide and heavy metal oxide glasses [13,18]. On the other hand, the small TPA of Ga:La:S based glasses is one of their most outstanding features. When considering practical all-optical switching devices, both the non-linear refractive index and the TPA coefficient must be taken into account.

The large off-resonance non-linear refractive index of Ga:La:S based glasses is attributed to the large hyperpolarizability of the sulfide anions and cations with filled outer d shells (Ga^{3+}) [19]. The non-linearity of the similar structure $70\text{Ga}_2\text{S}_3: x\text{La}_2\text{S}_3:y\text{La}_2\text{O}_3:(30-x-y)\text{LaF}_3$ glasses increases with increasing contents of sulfides as the sulfide anion hyperpolarizability is larger than that of the O^{2-} anion which in turn is larger than that of the fluorine anion. The fact that the positive non-linear refractive indices of the Ga:La:S glasses are predominantly due to bound electronic effects [13], and the small TPA showed by these glasses account for the absence of measurable non-linear dispersion at the working wavelengths, as the process responsible for TPA also gives a significant contribution to n_2 [20].

Table 2 presents the non-linear refractive indices of Ga:La:S based glasses compared to those of the, to our best knowledge, highest non-linear chalcogenide glasses (as reported in literature). Although n_2 values for Ga:La:S based glasses are 5–7 times smaller than those of other chalcogenide glasses, the non-linear absorption values for Ga:La:S glasses are much smaller. This leads to a FOM for Ga:La:S based glasses (defined as above) much larger than 1 and among the highest in the family of chalcogenide glasses (Table 2). The improved fiber drawing ability of GLSOF glasses should allow the realization of low loss single mode fiber and, although FOM for GLSOF glasses is slightly lower as compared with GLS, this is an acceptable tradeoff. Thus, GLSOF glass is a promising candidate for practical all-optical switching devices with fiber-based geometry.

5. Conclusion

In summary, the large non-linearity of Ga:La:S glasses with negligible non-linear absorption at the telecommunication wavelengths indicate great potential for all-optical switching devices. Furthermore, material optimization of Ga:La:S glass with the addition of a third component results in a trade-off between non-linear optical property versus glass workability. This shows that Ga:La:S based glasses are among the best candidates for practical photonic applications in the form of fibers.

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