Raman gain measurements and photo-induced transmission effects of germanium- and arsenic-based chalcogenide glasses

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Abstract: The Raman gain spectra of millimeter thick As$_{2}$S$_{3}$ and As$_{24}$S$_{38}$Se$_{38}$ glasses and Ge$_{(23-x)}$Ga$_{x}$Sb$_{7}$S$_{(70-y)}$Se$_{y}$ with x = 0 and 5 and y = 0, 2, 5 have been measured using a direct nonlinear optics technique. The pump light originated from a picosecond Nd:YAG laser operating at 1064 nm and a tunable optical parametric generator and amplifier (OPG/OPA) was used as a source for the probe light. A peak material Raman gain coefficient of $(155 \pm 11) \times 10^{-13}$ m/W has been measured for the As$_{24}$S$_{38}$Se$_{38}$ glass. A reversible photodarkening effect which responds to picosecond pulses is also reported. Finally, surface optical damage threshold measurements were found to be less than 9 GW/cm$^2$ for the reported samples, values which are comparable to some TeO$_2$-based glasses with lower nonlinearities.

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References and links

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1. Introduction

Chalcogenide glasses have received increased interest due to their high linear and nonlinear indices of refraction and good transmittance into the infrared region. These materials are seen as potential candidates for infrared optics, photonic devices, reversible optical recording media, all-optical switching, and inorganic photoresists [1]. Asobe et al demonstrated the use of chalcogenide fiber to perform all-optical switching [2]. Waveguides have been fabricated out of chalcogenide glass and have shown to successfully perform all-optical regeneration of picosecond pulses [3]. Ge-Sb-S-based chalcogenide glasses have also been successfully poled and exhibit $\chi^{(2)} = 8.0 \pm 0.5$ pm/V [4]. A nearly stoichiometric As$_2$Se$_3$ fiber has been shown to have a nonlinear index of refraction of $n_2 \sim 930$ times higher than fused silica at 1550 nm and a peak material Raman gain coefficient $g_{\text{RG}} \sim 780$ times higher than the peak of fused silica [5]. A nearly identical composition was also used to demonstrate the first single-frequency Brillouin lasing using single-mode As$_2$Se$_3$ chalcogenide fiber,” Opt. Express 14, 4037 (2006).

Although traditional Raman scattering measurements can be made to study the vibrational modes – and hence the structure – of a material, these measurements are usually made with visible lasers close to the electronic band edge of the material under investigation. This can result in resonantly enhanced Raman gain spectra as reported by Rivero et al in heavy glasses such as tellurite glasses [7]. Since chalcogenide glasses have lower energy electronic band gaps than most tellurite glasses (defined to be TeO$_2$-based glasses), measuring the Raman gain spectrum from scattering measurements using visible lasers would provide unreliable data when projected to the communications wavelengths near 1550 nm. Unfortunately, resonantly enhanced Raman spectra can also affect the Raman spectral shape away from electronic resonances in the material under investigation, resulting in inaccurate projections of the Raman gain spectrum away from visible wavelengths [7].

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The values of $n_2$ in glasses of the Ge-Ga-Sb-S-Se system has recently been reported with a picosecond 1064 nm laser based on a nonlinear imaging technique developed to characterize optical nonlinearities by using a phase object [8]. It has been found that the values of $n_2$ of these chalcogenide glasses fall in the range 60 – 150 times higher than that of fused silica at 1064 nm [8]. The use of a picosecond source implies these values of $n_2$ include the nuclear contributions. These results raise the question of how the absolute value of the material Raman gain spectrum changes when the compositions are varied. For this reason, millimeter thick bulk samples in Ge-Ga-Sb-S-Se and As-S-Se systems were tested for their Raman gain spectra using a picosecond 1064 nm Nd:YAG pump beam and a tunable OPG/OPA as a probe beam using a direct nonlinear optics measurement technique [9]. A comparison between the Raman gain coefficients and values for $n_2$ measured at the same wavelength (1064 nm) – when scaled to fused silica – is also reported here. Surface optical damage threshold measurements at 1064 nm using 25 ps pulse lengths are reported, along with the reporting of a reversible photodarkening effect.

2. Glass elaboration

Effort have been made to develop glasses in the Ge–Sb–S system with a low Sb concentration and with an excess of S to present good physical stability and high nonlinear index suitable for use in novel optical applications. In order to increase the nonlinear refractive index, S has been replaced progressively by Se. It has been found that unlike Ge–Sb–S glasses, Ge–Ga–S are good host materials for incorporation of rare-earth because they have been shown to be capable of dissolving relatively larger amounts of rare-earth elements [10]. In these glasses, Ga$_2$S$_3$ acts as a co-former and introduces some modifications in the structural arrangement of the GeS$_2$ network, thus accommodating higher mol fractions of rare-earth. The glasses reported here do not contain any rare-earth ions.

Glasses in the system Ge$_{23-x}$Ga$_x$Sb$_7$S$_{70-y}$Se$_y$ with $x = 0$ and 5 and $y = 0, 2$ and 5 have been prepared is a 6 g batch from high purity elements (Ge Aldrich 99.999%, Ga$_2$S$_3$ Aldrich 99.99%, Sb Alpha 99.9%, As, S and Se Cerac 99.999%) [11]. Starting materials were weighed and batched inside a nitrogen-purged glove box and sealed using an oxygen gas torch under vacuum at a pressure of $10^{-4}$ Torr. Prior to sealing and melting, the ampoule and batch were pre-heated at 100°C for 4 h to remove surface moisture from the quartz ampoule and the batch raw materials. The ampoule was then sealed and heated for 24 hours at between 900 and 975°C, depending on the glass composition. Once homogenized, the melt-containing ampoule was air–quenched to room temperature from the furnace temperature between 900 to 975°C. After air-quenching, the ampoules were subsequently returned to the furnace for annealing for 15 hours at 40°C below the glass transition temperature, $T_g$. The same procedure was used for the arsenic-based compositions. The glass samples were then cut, optically polished and visually inspected.

3. Experimental procedure

Two different Raman experiments were performed on these samples. Primarily, the 1064 nm emission line from a high power pulsed picosecond Nd:YAG laser was used as the pump beam, and an OPG/OPA was used as a tunable probe. The data provided by this experiment provided the non-resonant, absolute magnitude of the Raman gain coefficient at discrete points in the Raman spectrum. The procedure to test for Raman gain in bulk glass samples using a 1064 nm pump wavelength has been previously reported in detail [9]. Additionally, traditional Raman scattering measurements were conducted using a backscattering geometry as described in Ref [7]. In the Raman scattering experiments, the germanium-based chalcogenide glasses were measured with a 1064 nm pump wavelength, and the arsenic-based materials were measured with an 840 nm pump wavelength. The data from the Raman scattering experiments is then scaled to the peak of the Raman gain spectrum obtained from the direct nonlinear optics measurements after correction for the Bose-Einstein
thermal population factor. The goal of overlaying the Raman scattering data over the direct Raman gain data is to provide greater detail as to the nature of the Raman spectrum.

4. Raman gain and damage threshold results and interpretations

Figure 1(a) is the Raman gain spectrum of Ge_{18}Ga_{5}Sb_{7}S_{70} with the Raman gain spectrum of 50TeO_{2} – 50Tl_{2}O – obtained from scattering measurements with a 1064 nm excitation wavelength and the peak of the Raman gain spectrum scaled to the value obtained with the direct nonlinear optics technique – overlaid for comparison since 50TeO_{2} – 50Tl_{2}O has the highest reported non-resonantly enhanced peak Raman gain coefficient in any tellurite glass to date [12]. Figure 1(b) is the Raman gain spectrum of As_{24}S_{38}Se_{38} with the Raman gain spectrum of fused silica overlaid and the amplitude multiplied by a factor of 100 for comparison. Each chalcogenide glass composition has a deep red color as its absorption tail trails deep into the visible wavelengths [11,13]. All of the reported samples are less than 2 mm thick.

Petit et al reported a two photon absorption (TPA) coefficient of $\beta < 0.1$ cm/GW for Ge_{18}Ga_{5}Sb_{7}S_{70}, so although TPA may have been occurring, it was seen as negligible for the Raman gain measurements in this glass composition [8]. The value of $n_{2}$ for Ge_{18}Ga_{5}Sb_{7}S_{70} was 65 times higher ($\pm$15% measurement accuracy) at 1064 nm pumping than fused silica [8]. This value is quite close in magnitude to the enhancement over fused silica of the peak in the Raman gain spectrum that occurs near $\Delta \nu \sim 10$ THz in these glasses. The excellent homogeneity and good surface smoothness enabled data with low error bars to be obtained on this sample. The main resonance near $\Delta \nu \sim 10$ THz is attributed to a vibrational mode of the GeS_{4} units. The resonance near $\Delta \nu \sim 14$ THz is due to S-S homopolar bonds in rings and chains. This resonance is typically much weaker than the GeS_{4} resonance near $\Delta \nu \sim 10$ THz.

Petit et al have also shown that the nonlinear index increases very slightly with the replacement of Ge by Ga or S by Se in small quantities [8]. Because of their similar composition, the other glasses investigated in the Ge_{18}Ga_{5}Sb_{7}(70-y)Se_{y} system exhibit nearly the same Raman spectra as shown in Fig. 1(a), so only the magnitude of the peak is being reported for the resonance near $\Delta \nu \sim 10$ THz. As seen in Table 1, there is no measurable effect outside of the error bars on the peak of the Raman gain coefficient when Ga is introduced in the germanate glass network. A similar statement may be made by the small
replacement of S by Se in the peak Raman gain coefficient, although the value of the nonlinear refractive index has shown to increase upon this minor substitution [14].

Table 1. Peak Raman gain coefficients of the measured germanium and arsenic based chalcogenide glasses, ratio of \(n_2/n_{2,\text{silica}}\), and the surface optical damage threshold at 1064 nm using 25 ps pulse durations.

| Glass Composition | \(g_{\text{Raman}}\times 10^{13}\) (m/W) \(\Delta \nu\) (THz) | \(n_2/n_{2,\text{silica}}\) [Ref] | 1064 nm surface optical damage threshold (GW/cm²) |
|-------------------|-------------------|-----------------|----------------------------------|
| Ge\(_{23}\)Sb\(_7\)S\(_{70}\) | 71 ± 7 @ 10* | 55 [8] | 7.2 |
| Ge\(_{18}\)Ga\(_5\)Sb\(_7\)S\(_{70}\) | 65 ± 4 @ 10* | 65 [8] | 6.3 |
| Ge\(_{18}\)Ga\(_5\)Sb\(_7\)S\(_{68}\)Se\(_2\) | 68 ± 7 @ 10* | 53 [11] | 6.0 |
| Ge\(_{18}\)Ga\(_5\)Sb\(_7\)S\(_{65}\)Se\(_5\) | 72 ± 10 @ 10* | 63 [11] | 5.4 |
| As\(_2\)S\(_4\) | 74 ± 15 @ 10* | 73** [13] | 8.4 |
| As\(_2\)S\(_3\)Se\(_3\) | 155 ± 11 @ 7.8* | 406** [13] | 3.5 |
| 50TeO\(_2\)–50Tl\(_2\)O | 52 ± 3 @ 21.3 [12] | 33 [15] | 5.1 |
| SiO\(_2\) | 0.9 ± 0.2 @ 13.2 [9] | 1 | <100 |

* this work ** measured at 1.6 μm [13]

For comparison purposes, Table 1 also lists the same data for two oxide glasses – namely 50TeO\(_2\)–50Tl\(_2\)O and fused silica. The higher peak Raman gain coefficients than values for \(n_2\) (when ratioed to that of fused silica) in the Ge\(_{23} - x\)Ga\(_x\)Sb\(_7\)S\(_{70} - y\)Se\(_y\) system can be understood since the Raman spectrum is narrower and therefore must have higher peaks in order to satisfy the nonlinear Kramers-Kronig argument put forth by Hellwarth et al [16]. The peak Raman gain coefficients for Ge\(_{23} - x\)Ga\(_x\)Sb\(_7\)S\(_{70} - y\)Se\(_y\) with \(x = 0\) and \(y = 0, 2\) and 5 are roughly 50% larger that of the 50TeO\(_2\) – 50Tl\(_2\)O glass, but the bandwidth of the Raman shift is less than that seen in those glasses [12]. Hence, these chalcogenide glasses may prove to be more attractive as a high peak Raman gain material, but may not be considered for broadband Raman amplification when compared to tellurite glasses [12].

The surface optical damage threshold of these glasses falls in the same range as those of previously reported tellurite glasses [12]. The addition of Ga for Ge and Se for S lowers the surface optical damage threshold. Further studies on the surface optical damage thresholds as compositions are varied are necessary in order to provide conclusive systematic trends.

Table 1 also presents the Raman gains of some As-based glasses. The highest peak Raman gain coefficient has been measured at \((155 \pm 11) \times 10^{13}\) m/W with the direct nonlinear optics approach using 1064 nm pumping in the As\(_2\)S\(_3\)Se\(_3\) glass. The two main Raman bands shown in Fig. 1(b) are attributed to an intermolecular mode resulting from the antisymmetric As-S-As stretching vibration located near \(\Delta \nu \sim 10\) THz and to mixed As\(_n\)S\(_n\)Se\(_{n-3}\) pyramids located near \(\Delta \nu \sim 7.8\) THz. The Raman gain spectrum of As\(_2\)S\(_4\) is nearly identical to Fig. 1(b) if the resonance near \(\Delta \nu \sim 7.8\) THz is completely removed. The peak Raman gain coefficient increases when S is systematically replaced by Se in the As-based glass matrix, in accordance with measured values of \(n_2\) in the same glasses [14]. As observed in the germanium based glasses, the replacement of S by Se in As-based glasses lowers the surface damage threshold as presented in Table 1.

5. Photodarkening results

Figures 2(a) – 2(c) display how the probe beam transmission through the As-based glasses is affected by the amount of pump light at the sample – negative values for the probe beam axes relate to the offset voltage at the boxcar data acquisition unit. The solid line represents the slope of the transmission curve of the probe beam when the photodarkening effect is not present [as in Fig. 2(a)] and the open circles represent the experimentally obtained data. It has been observed that as the amount of Se increases by replacing S, the extent of photodarkening at the probe wavelength, placed at the Raman gain peak in these experiments, increases as...
seen in Fig. 2(c) for the As$_2$Se$_3$ glass. In Figs. 2(a) – 2(c), the transmission of the probe beam is adversely affected by the amount of pump light at the sample with increased Se content. This directly affects the ability to measure Raman gain in the probe polarization parallel to the pump polarization in higher concentration Se samples. The photodarkening effect did not allow testing of the Raman gain spectrum of As$_2$Se$_3$. Conversely, the probe polarization that is orthogonal with respect to the pump polarization does not suffer from this effect. The reason for this has been attributed as coupling between optical phonons and the incoming electric field for sub-band gap irradiation [17]. These experiments differ from the work done in Ref. [17] as the probe beam was placed at the Raman gain peak to couple to the strongest optical phonons in the glass. In Fig. 2(b), the box around 0.4 GW/cm$^2$ indicates the linear regime in which the Raman gain of As$_{24}$S$_{38}$Se$_{38}$ was measured. It was found that the photodarkening effect is reversible between laser shots (10 Hz repetition rate, 25 ps pulse duration) and disappears if the pump beam is blocked from the sample and only the probe beam is transmitted through the sample. The photodarkening effect is consistent everywhere in the samples and shows no sign of “memory” after the strong pump beam is blocked. The probe beam transmission of the Ge-based glasses listed in Table 1 has also been measured and no photodarkening effect was observed. Due to the thin nature of the samples tested and the experimental restriction of measuring less than 10% Raman gain of the input probe beam, pump depletion is not considered to be an issue before the samples experience surface optical damage at higher pump powers where pump depletion may develop.

6. Conclusions

Several glasses in the As- and Ge-based chalcogenide families have been characterized for their Raman gain performance and surface optical damage threshold using picosecond 1064 nm irradiance...
nm pumping utilizing a direct nonlinear optics measurement technique. A peak material Raman gain coefficient of \((155 \pm 11) \times 10^{-13} \text{m/W}\) is reported for the \(\text{As}_{24}\text{S}_{38}\text{Se}_{38}\) glass, which is the highest value reported to date with this technique. In general, the Raman gain values agree well with values of \(n_2\) when compared to the values obtained for fused silica with 1064 nm pumping. Surface optical damage thresholds are less than 9 GW/cm² for all of the samples tested, which is in the same range as some tellurites which exhibit lower nonlinearities. A reversible photodarkening effect which responds to 25 ps pulse lengths has been reported. Linear and nonlinear (multi-photon) absorption measurements are ongoing for these glasses in order to verify how the figure of merit (gain vs. loss) compares to current technology.

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