Properties of Ge\(_x\)As\(_y\)Se\(_{1-x-y}\) glasses for all-optical signal processing

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Abstract: We present a systematic study of Ge\(_x\)As\(_y\)Se\(_{1-x-y}\) bulk chalcogenide glasses to determine the best composition for fabricating all-optical devices. The dependence of physical parameters such as the band-gap, glass transition temperature and third order optical nonlinearity (\(n^2\)) on composition has been studied and a relation between the bond-structure and elevated linear loss levels in high Germanium glasses has been identified. It is found that glasses with 11<x<13 % are most suitable for all-optical devices.

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References and links

compositions such as As-S and As-Se have been well characterised to between 8 and 16 microns in the infrared. Whilst the optical properties of some binary glasses with much higher nonlinearity are of interest for all-optical integrated photonic circuits.

Chalcogenide glasses, containing the chalcogen elements S, Se and Te covalently bonded with glass forming materials such as Ge, As, P, Sb or Si, are high nonlinearity materials with potential for integrated all-optical devices. They provide high linear refractive indices, low optical loss in the telecommunication bands (1310 nm and 1550 nm) and transmission out to between 8 and 16 microns in the infrared. Whilst the optical properties of some binary compositions such as As-S and As-Se have been well characterised and improved.
processing methods have been applied to As$_2$S$_3$ films to produce waveguide devices with high performance [10, 11]. As$_2$S$_3$ has a lower glass transition temperature ($T_g = 214^\circ$C) and lower optical nonlinearity (100 × silica) than desirable.

It is well accepted that substituting Se for S moves the band-gap from the visible to IR allowing the nonlinearity to be resonantly enhanced in the 1550nm telecommunications band. Furthermore, the addition of Ge with 4-fold bond coordination compared with As (3-fold) and S, Se (2-fold) produces a more 3-D glass network that increases $T_g$ [12]. Some properties of Ge-As-Se glasses which illustrate these trends have been reported in [3,4] with a glass containing 35% Ge stated to have nonlinearity 900× silica and a glass transition temperature of 380°C. These reports provide evidence that the nonlinear optical properties can be tuned by varying the Ge concentration. However, there is no systematic study of composition-dependence of the optical properties that includes linear optical losses as well as nonlinearity in Ge-As-Se system, or the relationship between the optical properties and bond structure. Optical losses are particularly important since all-optical devices must satisfy several figures of merit which take into account both linear and nonlinear absorption of light as well as factors related to thermal loading of devices due to optical absorption which becomes important at very high data rates [13].

In this work, we synthesized Ge$_x$As$_y$Se$_{100-x-y}$ bulk glasses with a wide composition range of 0<x<40 and 12<y<40 extending over the entire glass-forming region for these glasses [14, 15]. We report their linear and nonlinear optical properties, Raman spectra, Tauc gap and glass transition temperatures and relate them to requirements for all-optical switching.

2. Experiments

Chalcogenide glasses were typically prepared from 60-gram batches of high purity (5N) Germanium, Arsenic and Selenium metals. The raw materials were weighed inside a dry nitrogen glovebox and loaded into a pre-cleaned quartz ampoule. The loaded ampoule was dried under vacuum ($10^{-6}$ Torr) at 110°C for 4 hours to ensure removal of surface moisture from the raw materials. The ampoule was then sealed under vacuum using an oxygen-hydrogen torch and introduced into a rocking furnace used to melt the ampoule contents at 900°C. The melt was homogenised for a period of not less than 30 hours. Then the ampoule was removed from the rocking furnace at a predetermined temperature and air quenched. The resulting glass boule was subsequently annealed at a temperature 30°C below the estimated $T_g$ and then slowly cooled to room temperature. The properties of a sample of Ge$_{33}$As$_{12}$Se$_{55}$ made using this method was compared with commercial AMTIR-1 glass (Amorphous Materials Inc, Garland Tx), with no discernable differences found.

$T_g$ was measured using a differential scanning calorimeter (DSC, Shimadzu DSC-50) with a scanning rate of 10K/min. The position of the dip in the DSC scans is defined as the $T_g$ [10] and it is within 0.5K. No devitrification or crystallisation was observed for the samples in this study. Following the annealing process, the glass boules were sectioned to form discs of 25 mm diameter and 1-2 mm thickness. The discs had opposite surfaces ground plane parallel and then polished to optical quality. Polished samples were inspected for internal defects and striae. Only samples relatively free from defects and striae were used in the measurements. We synthesized eight samples and added two commercially available Ge-As-Se glasses (AMTIR-1 – Amorphous Materials Inc; and GASIR – Umicore Optics) for our studies. Table 1 shows the compositions and respective mean co-ordination numbers (MCN) along with the corresponding sample names that will be used throughout this paper. The MCN is defined as the sum of the respective elemental concentrations times their covalent coordination number [16]. It has been established that many physical properties of glasses correlate with the MCN [17, 18] and in the case of the Ge-As-Se system an increase in the Ge concentration generally leads to an increasing MCN. These values can be used as a guide to the structure of these glasses. MCN < 2.4 represents a ‘floppy’ and weakly-bonded network while MCN > 2.67...
represents a ‘stressed-rigid’ region. The region of $2.4 \leq \text{MCN} \leq 2.67$ is termed as the ‘intermediate phase’ [15].

In order to accurately ascertain the position of the band edge of the bulk glass materials, very thin samples were required. Due to the physical characteristics of these chalcogenide glasses, it proved impossible to mechanically polish the bulk glass down to micron thicknesses, so a pressing technique was adopted. Small quantities of the bulk glass (milligram samples) were heated to a temperature 50 - 100 degrees above their glass transition temperature to soften the glass. The glass was then pressed onto a polished sapphire window substrate with a polished vitreous carbon plate using free weights. Uniform samples, few tens of microns thick, could be obtained and the sample was then cooled slowly to room temperature to avoid cracking. The pressing procedure was performed in an inert nitrogen atmosphere to prevent degradation of the bulk glass. Band gap measurements were performed on the bulk glass / sapphire substrate composite samples. The bandgap, $E_g$ was extracted from Tauc plots using the absorption spectra of these 10-30 µm thick glass samples.

The particular concentrations of the constituent elements were chosen to span the known glass forming region for this glass system [14,15]. Starting from As$_2$Se$_3$ glass, the addition of a small amount of Ge requires adjustment of the As and Se concentrations to avoid the known region of phase separation existing for Ge$\leq 15\%$. Ideally, for photonics applications, single-phase glasses with low linear absorption loss are desired as phase-separation is known to be detrimental [11]. Thus the compositions chosen with Ge$\leq 15\%$ lay close to but below the known lower boundary for phase separation. For moderate Ge concentrations (15-27%) a broad single-phase region exists which includes a commercial glass GASIR. At high Ge concentrations (Ge$\geq 27\%$) two factors determine the choice of As and Se content: firstly a second region of phase separation is avoided which occurs for As concentrations below about 15%; secondly the glass becomes increasingly under-stoichiometric in Se as Ge is added leading to an undesirable increase in the number of homopolar and defect bonds which are responsible for absorption by states in the band gap. Hence glass compositions were chosen that lay outside the region for phase separation with as high Se content as possible. However, commercial AMTIR-1 was included, although it is phase separated, for comparison with a single phase glass of the same Ge content, Ge33.

The linear refractive indices at 1550 nm were measured using a Metricon Prism Coupler. Raman spectral measurements were carried out using a micro-Raman system using a $\approx 5\text{mW}$, 808nm laser with backscattered spectra recorded using an Ocean Optics QE65000 spectrometer that provides a spectral resolution of about 4 cm$^{-1}$.

<table>
<thead>
<tr>
<th>Name</th>
<th>Composition</th>
<th>Mean co-ordination number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ge5</td>
<td>Ge$<em>5$As$</em>{30}$Se$_{65}$</td>
<td>2.4</td>
</tr>
<tr>
<td>Ge11</td>
<td>Ge$_{11}$As$<em>2$Se$</em>{67}$</td>
<td>2.44</td>
</tr>
<tr>
<td>Ge12</td>
<td>Ge$<em>{12.5}$As$</em>{25}$Se$_{62.5}$</td>
<td>2.5</td>
</tr>
<tr>
<td>Ge15</td>
<td>Ge$<em>{15}$As$</em>{34}$Se$_{51}$</td>
<td>2.64</td>
</tr>
<tr>
<td>Ge18</td>
<td>Ge$<em>{18}$As$</em>{23}$Se$_{59}$</td>
<td>2.59</td>
</tr>
<tr>
<td>GASIR</td>
<td>Ge$<em>{22}$As$</em>{20}$Se$_{58}$</td>
<td>2.64</td>
</tr>
<tr>
<td>AMTIR-1</td>
<td>Ge$<em>{33}$As$</em>{20}$Se$_{55}$</td>
<td>2.78</td>
</tr>
<tr>
<td>Ge33</td>
<td>Ge$<em>{33}$As$</em>{20}$Se$_{7}$</td>
<td>2.86</td>
</tr>
<tr>
<td>Ge35</td>
<td>Ge$<em>{35}$As$</em>{15}$Se$_{50}$</td>
<td>2.85</td>
</tr>
<tr>
<td>Ge39</td>
<td>Ge$<em>{39}$As$</em>{16}$Se$_{45}$</td>
<td>2.94</td>
</tr>
</tbody>
</table>
Photo-thermal deflection spectroscopy (PDS) [19] was employed to measure the optical loss. In our system a 500W ORIEL Xenon Arc Lamp combined with a monochromator was used to create a pump source that could be focussed to form an illuminated stripe (≈ 12mm x 1mm) on the surface of a glass sample enclosed within a cell filled with tetrachloroethylene. The monochromator delivered light in a ≈ 5nm wide band, tuneable from 400-1700nm and a focussed He-Ne laser probed the temperature gradient created in the fluid just above the surface of the sample due to absorption of the pump by the glass. The refractive index gradient caused by the temperature gradient deflects the probe beam and this deflection was monitored using a position-sensing detector. The light from the arc lamp was chopped so that a lock-in amplifier could be used to discriminate against noise in the system. The noise floor typically corresponded to absorption of about 0.05 dB/cm at 1550nm. Calibration was performed by overlapping PDS data with that from a Cary 5000 spectrophotometer in regions of higher absorption.

The nonlinearity was measured using the Z-scan technique [20] modified by replacing the ‘open’ and ‘closed’ aperture channels with a single InGaAs camera (Sensors Unlimited SU320-1.7RT) and viewing the beam projected onto a screen. A ‘movie’ of the output beam pattern was recorded as a function of sample position and both the total transmitted power and that passing through a virtual aperture were calculated from the sequence of recorded images. An Optical Parametric Generator (Light Conversion TOPAZ) pumped by a Ti:sapphire laser (Clark MXR) producing ≈ 150 fs pulses at 1500 nm at a repetition rate of 250 Hz was used for the measurements. Calibration of the input power was made using a Thorlabs DET-410 photodiode. The camera output was digitised using an NI-PCI 1409 acquisition card and the image analysis performed in software using NI-LabVIEW. The programme averaged 200 frames per image to minimise noise. A virtual aperture was applied and the beam centre tracked throughout the scan. The closed-aperture profile was extracted using a pixel summation in the aperture region. Similarly, an open aperture scan was obtained by summing all pixels in the image after background correction. The camera was calibrated against incident power so as to ensure that any deviation from linearity in the camera response was tracked and corrected. This modified technique provides accuracy (± 10%) comparable to that of the conventional technique while eliminating errors in the Z-scan caused by any sample inhomogeneity or lack of parallelism of the polished samples.

The absolute value of \( n_2 \) can be obtained directly from a Z-scan trace for an ideal Gaussian beam if the pulse characteristics such as peak power, pulse duration (\( \tau_p \)) and pulse energy are known accurately. However the output beam from the TOPAZ parametric generator is only an approximation to a Gaussian. Therefore, we chose to make relative Z-scan measurements of the Ge-As-Se bulk glasses against known standards such as silica \( (n_2 = 2.5 \times 10^{-16} \text{ cm}^2/\text{W}) \) [21] and As\(_2\)S\(_3\) \( (n_2 = 3.0 \times 10^{-14} \text{ cm}^2/\text{W}) \) [22] to obtain absolute values for the nonlinear refractive indices.

3. Results and discussion

3.1 Optical loss measurements

In general the optical loss in bulk chalcogenide glasses includes intrinsic and extrinsic contributions. Intrinsic losses can be due to single or multi-photon excitations and Rayleigh scattering. Extrinsic mechanisms are those associated with the presence of impurities such as hydrogen or oxygen that result in deviations from stoichiometry. In addition, extrinsic loss an be due to structural imperfections and bond defects in the glass structure. PDS is a zero-background technique which is especially suitable for measuring weak absorption in the exponentially decaying absorption tail created by defects in the structure [19]. In contrast, it is difficult to measure small levels of absorption against the 100% background in a spectrophotometer because the absolute transmission is masked both by reflection losses and any sample inhomogeneities.
Figure 1 shows the dependence of the linear absorption loss at 1200 nm on the Ge concentration. Values at 1200 nm are quoted since in some samples the absorption at 1500 nm fell below the noise floor of the instrument. In general we found that absorption at 1500 nm was 2-3 times lower than that at 1200 nm. Losses range from as low as ~ 0.05 dB/cm for As$_2$Se$_3$ to several dB/cm for compositions with Ge $\geq$ 33%. Interestingly the AMTIR-1 sample (Ge$_{33}$As$_{12}$Se$_{55}$) had significantly lower losses than the Ge33 sample (which has the same Ge content). It should be noted in particular that there is an abrupt increase in loss for Ge $>$ 30%.

![Fig. 1. Linear absorption loss profile at 1200 nm, with varying Ge content, for bulk glasses](image)

In the context of all-optical processing the optical losses limit the effective length of the device and hence the total nonlinear phase change that can be obtained from the Kerr nonlinearity. In general there is a maximum ultra-fast index change ($\approx 10^{-5}$–$10^{-4}$) that can be achieved before higher order nonlinear effects appear. Furthermore in chalcogenide glasses it has been found that optical damage occurs at intensities of a few GW/cm$^2$ using ps duration pulses which again places an upper limit on the nonlinear index change [23]. Taking these factors into account implies that all-optical devices will need to have propagation lengths of at least few tens of cms and propagation losses must, therefore, be 0.2 dB/cm or lower at 1550 nm. Clearly the measurements presented in Fig. 1 suggest that only glasses with low Ge content satisfy this criterion.

3.2 Glass transition temperatures, optical gap and Raman spectra:

$E_g$ and $T_g$ are important parameters as they govern the optical properties as well as the thermal stability of Ge-As-Se glasses for all-optical devices. Figure 2 shows the dependence of these two physical parameters on the Ge content. In the low-germanium glasses, $E_g$ increases steadily with Ge content. $E_g$ is relatively constant in the region of 22% $\leq$ Ge $\leq$ 33% and then decreases for compositions with Ge $> 33\%$. As expected, $T_g$ increases monotonically with Ge content from 200 °C for Ge5 to 386 °C for Ge39.

The trend of $E_g$ and $T_g$ can be explained by studying changes in the fundamental glass structure depending on the concentration of the constituent elements. It is known that including heavier elements such as Ge can enhance the $T_g$ of chalcogenides by increasing the cross-linking of bonds within the network [24]. This increase in $T_g$ therefore correlates with a steadily increasing mean coordination number as the glasses move from the intermediate to the stressed-rigid phase.
Fig. 2. Variation of bandgap (E_g, open squares) and glass transition temperature (T_g, filled circles) with Ge content for Ge-As-Se bulk glasses

To understand the bond structure of Ge_xAs_ySe_1-x-y glasses, we measured their Raman spectra which are shown in Fig. 3. We can classify the glasses into two distinct regimes based on the dominant peaks in the Raman spectra: 0% ≤ Ge ≤ 15% (low Ge, Fig. 3(a)) and 22% ≤ Ge ≤ 39% (high Ge, Fig. 3(b)). In the low Ge compositions the dominant peaks are As-Se (230 cm⁻¹) and Ge-Se (193 cm⁻¹) associated with [AsSe₃] pyramidal structures and [GeSe₄] tetrahedrons respectively [25]. With increasing Ge content, the As-Se peak reduces in intensity and shifts to higher wavenumbers. The dominant peak then becomes that associated with Ge-Se and this shifts to lower wavenumbers as the Ge content in the glass is increased. For high-Ge concentrations, broad shoulders appear both at low wavenumbers (170-180 cm⁻¹) and high wavenumbers (300 cm⁻¹). The strong shoulder at 170 - 180 cm⁻¹ increases in intensity rapidly as the Ge concentration rises. Previously, these bands have been attributed to defect bonds such as Ge-Ge, As-As or Se-Se [26].
Qualitatively these spectra suggest that the number of defect bonds increases rapidly at high Ge concentrations and this would be expected to cause an increase in the strength of the defect-induced absorption tail within the bandgap. It should be noted that the measured variation in the bandgap itself (Fig. 2) does not correlate with the changes in absorption (Fig. 1).

To quantify the numbers of defects bonds, the Raman spectra were decomposed into as many as seven Gaussian curves whose position and intensity were tracked to determine the relative bond concentrations and their vibrational frequencies. Figure 4 shows that the integrated area of Raman peak in the 170-180cm\(^{-1}\) region associated with defects closely reflects the optical loss trend shown in Fig. 1 for Ge > 22%. From this result we conclude that the observed rise in linear loss is associated with an increasing number of defect bonds in the high Ge glasses and hence only those glasses with low to moderate Ge concentrations are suitable for all-optical processing. Recall that Ge33 had a higher loss than AMTIR-1 although they have the same Ge content. The Raman spectrum for Ge33 (MCN = 2.86) showed significantly higher defect bond peaks compared with those for AMTIR-1 (MCN = 2.78) as seen in Fig. 4, resulting in the higher loss level.
3.3 Linear and nonlinear refractive indices

Values of the linear ($n_0$) and nonlinear ($n_2$) refractive index are shown in Fig. 5. The linear index is highest at either extremes of the composition range and dips for 22% < Ge < 33% to a value of ≈ 2.54 at 1550nm. According to the empirical Miller’s Rule, $n_2 \approx n_0^4 \times 10^{10}$ (esu) [27] hence the highest third order nonlinearities are expected for glasses near the extremes of the composition range. The measurements confirm this trend although only a small drop in nonlinearity occurs between As$_2$Se$_3$ and Ge12. In this range the nonlinearity is around 350x that of silica. No significant levels of two-photon absorption could be detected in these Ge-doped glasses from the open aperture z-scans indicating two-photon absorption coefficients < few $10^{-11}$ cmW$^{-1}$ (the limit due to fluctuations in the Z-scan signal). This suggests that all the glasses tested satisfied the nonlinear figure of merit introduced by Stegeman and Wright [13], namely $n_2 / \beta \lambda > 1$.

Our values for the $n_2$ of As$_2$Se$_3$ are in reasonable agreement with values reported in [1] at 1060 and 1043 nm measured using the Z-Scan technique. They are also in agreement with values determined from self-phase modulation in optical fibres and waveguides [28, 29]. However, the values quoted in [2] using the SRTBC technique are more than twice the values obtained by our own Z-Scan measurements and twice those reported in [28, 29]. Note that dispersion of the nonlinearity of As$_2$Se$_3$ indicates that the value is enhanced at 1430 nm relative to 1500 nm [29] but this can explain only a small part of this discrepancy.
For Ge between 18% and 33% both the linear and nonlinear refractive indices are reduced. Taken in conjunction with the loss data in Fig. 1 this reinforces the notion that glasses with low Ge concentration are favourable whilst the data on $T_g$ in Fig. 2 suggests that the Ge concentration should still be chosen to be as high as possible to increase the glass transition temperature. One can therefore conclude that Ge values 11-13% provides the best combination of optical and physical properties corresponding to a co-ordination number close to 2.5.

We have compared our data on optical nonlinearity with the model developed by Sheik-Bahae et. al. [30] for direct gap semiconductors which predicts that the third order nonlinearity is enhanced due to the proximity of a two photon transition across the band gap when the photon energy is $0.54\cdot E_g$. Figure 6 shows that the dispersion of the nonlinear refractive index for various compositions as a function of $E_g$ is in close agreement with the model in [30] (solid curve). At 1500 nm the value of the incident photon energy $hf = 0.83$ eV and, therefore, the highest nonlinearity can be expected in compositions with $E_g \approx 1.53$ eV. The data generally support this trend although some scatter is apparent most likely due to the limitations inherent in the parabolic band model when applied to glasses with substantial numbers of defect states. Interestingly, since $E_g$ reflects the average energy of the bonds in the glass, when the preferred bond structure can be predicted, it is possible to ‘tune’ the bandgap via composition in a predictable way to achieve higher non-linearity [12]. This result is in agreement with Tanaka’s findings [31] which show that the Sheik-Bahae model provides a good prediction of the dependence of nonlinearity with band-gap for chalcogenide amorphous semiconductors, at least near the two-photon absorption edge.
We also considered the results of Quemard et al [1] who reported a lone-pair electron model to explain the variation of \( n_2 \) with composition for binary Ge-Se systems. This model suggests that increasing the amount of Se increases the number of polarisable lone-pair electrons and enhances the third order nonlinearity. However, no such correlation was found between the Se content and the nonlinearity for the more complex \( \text{Ge}_x\text{As}_y\text{Se}_{100-x-y} \) bulk glasses with \( 0 < x < 40 \) and \( 12 < y < 40 \) and our result is in agreement with this.

4. Conclusion

Ge-As-Se bulk glasses with varying composition have been fabricated. Glass transition temperature and optical properties such as linear absorption loss, bandgap and nonlinear refractive index (\( n_2 \)) at 1500 nm have been characterised. We find that for \( \text{Ge}_x\text{As}_y\text{Se}_{100-x-y} \) bulk glasses with \( 0 < x < 40 \) and \( 12 < y < 40 \) the linear absorption loss increases with increase in Ge content with losses of \( \sim 0.05 \) dB/cm for low Ge glasses to \( > 1 \) dB/cm for Ge in excess of 33%. This increase correlates with increasing numbers of defect bonds in glasses that become over-stoichiometric in Ge as supported by our results from Raman spectroscopy. Whilst \( T_g \) is enhanced as more Ge is added into the glass matrix, the rise in absorption is a serious issue for all-optical devices ruling out glasses with the highest \( T_g \). The nonlinear refractive index (\( n_2 \)) of up to \( 9.0 \times 10^{-13} \) cm\(^2\)/W (350 x silica) at 1500 nm has been measured with low Ge content glasses Ge5 and Ge11. The dispersion of nonlinear refractive index with \( E_g \) for Ge-As-Se chalcogenide glasses follows a two-band model, and thus the highest nonlinearities are achieved if \( E_g \) is tuned into the range 1.56 – 1.70 eV.

The application of these glasses in all-optical devices requires the chosen composition to have low linear losses, high third order nonlinearity as well as the highest possible glass transition temperature. These criteria are best satisfied by \( \text{Ge}_x\text{As}_y\text{Se}_{100-x-y} \) bulk glasses with \( 11 < x < 13 \) (MCN \( \approx 2.4-2.5 \)) where the As:Se ratio can be chosen so as to avoid regions of phase separation. These glasses also lie close to the region where the network is stress-free but rigid [18]. Glasses in this region display reasonable absorption losses < 0.1 dB/cm at 1500 nm; nonlinearities about 350 x silica; negligible two-photon absorption and \( T_g \) around 250°C. Hence they appear to be the most suitable for fabrication of all-optical devices.
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