

## Third order nonlinearities in Ge-As-Se-based glasses for telecommunications applications

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We have studied the third order optical nonlinearities of Ge-As-Se-based glasses. The glasses have high melting and glass transition temperatures that offer the potential for integration with traditional compound oxide glasses into highly nonlinear, high-index-contrast fibers. We used *z*-scan and femtosecond pump-probe techniques to measure the nonlinear refractive index and two-photon absorption coefficient of the glasses at telecommunication wavelengths. Nonlinearities as high as  $\sim 900\times$  that of silica were measured at 1540 nm in  $\text{Ge}_{35}\text{As}_{15}\text{Se}_{50}$  with a glass transition temperature of 380 °C. © 2004 American Institute of Physics. [DOI: 10.1063/1.1805182]

High capacity optical systems require devices such as cross connects, add-drop filters, repeaters, and wavelength converters. While some of these functions are currently being performed electronically, it is expected that they may eventually be replaced with optical devices in which nonlinear materials will play an important role. A key property of such materials is the optical Kerr effect that produces a change in the index of refraction proportional to the optical intensity *I* and the nonlinear index coefficient  $n_2$ ,  $\Delta n = n_2 I$ . The Kerr effect has an ultrafast time response and could be the basis for ultrafast optical switches with low switching energy. Two-photon absorption also occurs when the photon energy is above half-gap in the material and limits the maximum phase shift achievable. A figure of merit  $n_2/\beta\lambda$ ,<sup>1</sup> where  $n_2$  is the nonlinear refractive index and  $\beta$  the two-photon absorption coefficient, can be defined to assess the material properties relevant for efficient optical switching. To achieve a nonlinear optical phase shift of  $\pi$ , necessary for a Mach-Zender optical switch, with a nonlinear transmission loss of 20%, a figure of merit of  $\sim 2$  is required.<sup>2</sup>

Chalcogenide glasses have large values of nonlinearity at 1.55  $\mu\text{m}$ , several orders of magnitude larger than the value for conventional silica glass.<sup>2</sup> Many such glasses have been previously studied.<sup>3–5</sup> Among these, the Ge-As-Se system is of interest due to high nonlinearity, high refractive index (2.4–2.65), suitable optical transmission at 1.55  $\mu\text{m}$  and a relatively broad glass formation region. In this paper, we focus on glasses with particular promise for fabrication into high-index-contrast highly nonlinear fiber for 1.55  $\mu\text{m}$  applications. Glasses from Ge-As-Se family have glass transition temperatures in the range of 150–390 °C making them suitable for integration with low refractive index compound-oxide glasses into high-index-contrast solid-core fiber. Highly nonlinear fiber can be used for applications including supercontinuum generation,<sup>6</sup> frequency metrology,<sup>7</sup> and wavelength conversion.<sup>8</sup> While nonlinear low-index-contrast fibers have been fabricated from chalcogenide material,<sup>9,10</sup>

high-index-contrast fibers offer the advantages of smaller modal volume, higher nonlinearity, and greater range of achievable dispersion. Such solid-core high-index-contrast fibers could be an alternative to structures in which air is used as the low-index-contrast material (e.g., chalcogenide fibers with air holes) and high-index-contrast chalcogenide-based photonic bandgap fibers.<sup>11</sup> However, the chalcogenide glasses used in the fiber core must have a glass transition and softening temperature compatible with that of lower index glasses used for the cladding. We have investigated several chalcogenide glasses with glass transition temperatures from 292 to 380 °C:  $\text{Ge}_{33}\text{As}_{12}\text{Se}_{55}$  (commercially available as AMTIR-1, from Amorphous Materials),  $\text{Ge}_{35}\text{As}_{15}\text{Se}_{50}$ ,  $\text{Ge}_{25}\text{As}_{10}\text{Se}_{65}$ , and  $\text{Ge}_{22}\text{As}_{20}\text{Se}_{58}$  (commercially available as GASIR1, from Umicore). The glasses are found to have nonlinearities between  $200\times$ – $900\times$  that of silica, and figures of merit  $n_2/\beta\lambda$  as high as 3.2.

The samples of  $\text{Ge}_{33}\text{As}_{12}\text{Se}_{55}$ ,  $\text{Ge}_{35}\text{As}_{15}\text{Se}_{50}$ , and  $\text{Ge}_{25}\text{As}_{10}\text{Se}_{65}$  were prepared as follows. For each glass composition, 5N (99.999%) purity amorphous selenium shot, 7.5N (99.99995%) purity crystalline lump arsenic, and 6N (99.9999%) purity single crystal germanium were batched into a fused quartz looped tube along with a magnesium metal strip (4N purity). The tube was placed into a two-level furnace, with the looped portion of the tube, in the hotter furnace zone. Over  $\sim 12$  h, the As and Se components melted and were distilled from the loop into the lower part of the tube containing the Ge. After distillation, the lower portion of the tube was sealed, creating the melt vessel, and the loop containing impurities was discarded.<sup>12</sup> The melt vessel was placed into a rocking furnace at 900 °C for 12 h, homogenizing the glass melt. The melt was then placed into a second furnace at the expected glass transition temperature. This furnace was switched off, allowing the glass to cool slowly to room temperature. The glass boules were cut into flat disks of about 3 mm thickness and the facets were ground parallel and polished to optical quality. Samples of  $\text{Ge}_{33}\text{As}_{12}\text{Se}_{55}$  prepared in this manner were found to have similar  $n_2$ ,  $\beta$ , and bandgap energy to commercial samples

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purchased from Amorphous Materials. The sample of  $\text{Ge}_{22}\text{As}_{20}\text{Se}_{58}$ , a 3 mm thick sample with polished parallel faces, was purchased from Umicore.

To characterize the optical bandgap of the samples, linear transmission measurements were performed. Since glasses are amorphous, they lack a sharp absorption edge, and the optical bandgap is taken to be the point at which the absorption changes from a quadratic dependence on energy to an exponential dependence on energy (Urbach tail region<sup>13</sup>). A typical value of the absorption coefficient at this point is  $1000\text{ cm}^{-1}$  (Ref. 2) and is used here for the definition of the optical bandgap. Fits of the data to an exponential in the Urbach tail region yield the bandgap. To characterize the nonlinear refractive index  $n_2$  and two-photon absorption  $\beta$  coefficients of these glasses, a  $z$ -scan<sup>14</sup> setup was used. In the  $z$ -scan technique, a collimated Gaussian beam is focused onto a sample. The sample is translated through the beam focus and the transmission through an aperture behind the sample is measured. Simply removing the aperture allows the two-photon absorption to be measured. The data was fitted using the simplified expressions for open and closed aperture scans below,<sup>14,15</sup>

$$T_{op}(z) = 1 - \frac{\beta I_0 L}{2\sqrt{2}(1+x^2)}, \quad (1)$$

$$T_{cl}(z) \cong 1 + \frac{4x(\Delta\phi_0)(1-S)^{0.25}}{(1+x^2)(9+x^2)}, \quad (2)$$

where  $\beta$  is the two-photon absorption coefficient;  $I_0$ , the peak on-axis intensity;  $L$ , the sample length;  $x = z/z_0$ , where  $z$  is distance and  $z_0$ , the confocal parameter defined as  $z_0 = \pi w_0^2/\lambda$  with  $w_0$  defined as the beam waist;  $S$ , the aperture transmission; and  $\Delta\phi_0$ , the time-averaged peak-on-axis phase change defined as  $\Delta\phi_0 = 2\pi L n_2 I_0 / (\lambda\sqrt{2})$ . The expression for the open aperture scan assumes a Gaussian pulse shape. These expressions are valid for small phase shifts ( $|\Delta\phi_0| \ll 1$ ). Otherwise, one must use the exact formulas in Ref.15.

The experimental setup is as follows. An optical parametric oscillator (OPO), producing 150 fs pulses at a repetition rate of 82 MHz, was used as the laser source. The OPO output beam is coupled through 3 cm of standard single mode silica fiber (SMF) for spatial filtering. It is then recollimated and focused onto the sample. To measure  $n_2$ , an aperture is placed after the sample (closed aperture scan), and a lens images the apertured spot onto a large area Ge photodiode, connected to a lock-in amplifier. To measure the two-photon absorption coefficient, the aperture is removed (open aperture scan). To account for inhomogeneities in the samples, traces at attenuated intensities were also taken and subtracted from the high intensity scans. To separate the thermal lensing effects from those of the nonlinear index of refraction, the 3 cm of SMF was replaced with 50 cm of dispersion compensating fiber, which broadened the pulses to 1.5 ps. The  $z$ -scan setup was calibrated with samples of Si, GaAs, and  $\text{As}_2\text{Se}_3$ , whose  $n_2$  and  $\beta$  are known from the literature.

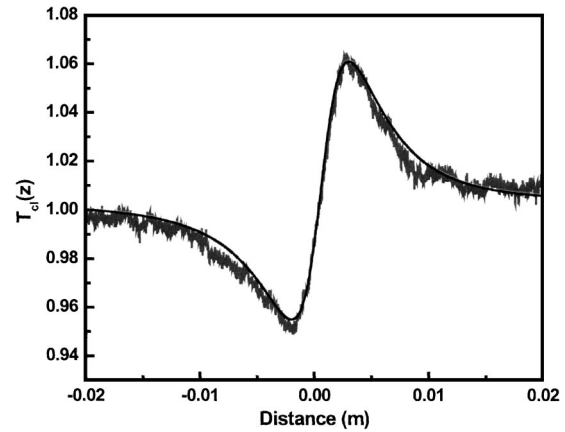


FIG. 1. Transmission vs position for closed aperture scan of  $\text{Ge}_{33}\text{As}_{12}\text{Se}_{55}$  at an intensity of  $0.16\text{ GW/cm}^2$ .

Additionally, a pump-probe technique was used to verify some of the values obtained for two-photon absorption coefficients, as the sensitivity is higher than that of the  $z$ -scan. In the pump-probe, a high intensity pump beam and a low intensity probe beam are focused collinearly through the sample. After the sample, a polarizer rejects the pump and allows detection of only the probe. Since the wavelength of the laser, 1540 nm, corresponds to an energy that is well below the bandgap of the sample, induced changes in absorption are dominated by two-photon absorption. The two-photon absorption coefficient can be determined from the data with the knowledge of the incident intensity. A combination of pump-probe and  $z$ -scan measurements allowed determination of the two-photon absorption coefficients of the chalcogenide glasses studied.

Figs. 1 and 2 show typical  $z$ -scan open- and closed-aperture traces. At 1540 nm, the nonlinear refractive index  $n_2$  of  $\text{Ge}_{33}\text{As}_{12}\text{Se}_{55}$  was measured to be  $15 \times 10^{-18}\text{ m}^2/\text{W} \pm 25\%$  and the two-photon absorption coefficient  $\beta$ ,  $0.4\text{ cm/GW} \pm 25\%$ . Values of  $n_2$  in the other materials investigated ranged from  $6.0\text{--}24 \times 10^{-18}\text{ m}^2/\text{W}$ , and that of  $\beta$ , from  $0.4\text{--}0.5\text{ cm/GW}$ . When determining the intensity incident on the sample, Fresnel losses on the front sample surface were included. No evidence of thermal effects for any of the glasses can be seen in the data. Data was taken with intensities as high as  $170\text{ MW/cm}^2$  and no damage to the samples was observed.

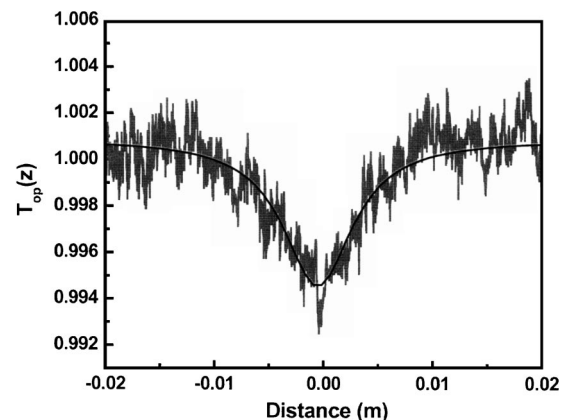


FIG. 2. Transmission vs position for open aperture scan of  $\text{Ge}_{33}\text{As}_{12}\text{Se}_{55}$  at an intensity of  $0.16\text{ GW/cm}^2$ .

TABLE I. Properties of Ge-As-Se glasses. The measurements of  $n_2$  and  $\beta$  assume a 19% Fresnel reflection from the glasses. The bandedge is defined where the absorption coefficient is equal to  $1000\text{ cm}^{-1}$ .

Material	Bandgap (nm) $\pm$ 4%	$n_2 (\times 10^{-18}\text{ m}^2/\text{W})$ $\pm$ 25%	$\beta$ (cm/GW) $\pm$ 25%	Glass transition temp ( $^{\circ}\text{C}$ )	Softening temp ( $^{\circ}\text{C}$ )	Figure of merit $n_2/\beta\lambda$
Ge <sub>35</sub> As <sub>15</sub> Se <sub>50</sub>	639	24.6	0.5	380	474	3.2
Ge <sub>33</sub> As <sub>12</sub> Se <sub>55</sub>	600	15	0.4	362	476	2.4
Ge <sub>22</sub> As <sub>20</sub> Se <sub>58</sub>	614	9.2	0.4	292		1.5
Ge <sub>25</sub> As <sub>10</sub> Se <sub>65</sub>	585	6.0	0.4	305	436	1.0

Table I summarizes the results. The value of  $n_2$  measured at 1540 nm ranges from  $\sim 200\times$  to  $\sim 900\times$  the value of silica. One of the highest values reported for other chalcogenide glasses is  $900\times$  that of the value of silica, but the glass transition temperature is quite low (As<sub>2</sub>Se<sub>3</sub> 188  $^{\circ}\text{C}$ ).<sup>3</sup> As more germanium is added to the samples, the glass transition temperature increases as well as the nonlinear refractive index and the figure of merit, making the glass more favorable for fiber-based applications. The bandgap energy also decreases. However, high germanium content makes Ge-As-Se glasses more prone to crystallization.<sup>16</sup> The nonlinear figure of merit  $n_2/\beta\lambda$  is  $\approx 3.2$  for Ge<sub>35</sub>As<sub>15</sub>Se<sub>50</sub>, the highest value reported for glasses that can be codrawn into fiber with low-index glasses.

From the data in Table I, one can see that a small variation in composition can have a large effect on  $n_2$ . Just a few percent variation in composition causes the nonlinear refractive index of the samples to increase by a factor of 4 while the two-photon absorption coefficient increases more slowly. The value of nonlinearity increases as the wavelength of operation approaches the half-bandgap. As the wavelength of operation shifts closer to half the bandgap, both two-photon absorption and  $n_2$  increase due to resonant effects. Because the glasses exhibit an Urbach absorption tail below the bandgap,  $n_2$  increases faster than  $\beta$  below half gap, leading to a maximum in the figure of merit slightly below the half-bandgap.<sup>3</sup>

Correlations of the nonlinear properties with composition are relatively well understood for binary chalcogenide glasses such as Ge-Se.<sup>5,6</sup> These correlations are usually explained in the framework of the “lone electron pair approach.” According to this theory, the nonlinearity of the chalcogenide glasses increases with the concentration of the highly polarizable lone electron pairs.<sup>5,6</sup> However, variations of the nonlinear response we have observed cannot be satisfactorily explained in the framework of this model. For example, in this study, the highest value of  $n_2$  was observed for the glass containing the highest Ge content: Ge<sub>35</sub>As<sub>15</sub>Se<sub>50</sub> which has the lowest concentration of lone electron pairs among all compositions studied. We have also observed an unexpected rise of nonlinear refractive index for compositions in which part of selenium is substituted with arsenic: compositions Ge<sub>22</sub>As<sub>20</sub>Se<sub>58</sub> and Ge<sub>33</sub>As<sub>12</sub>Se<sub>55</sub> vs composition Ge<sub>25</sub>As<sub>10</sub>Se<sub>65</sub> (Table I). These observations are similar to that made by Quémard *et al.*<sup>4,5</sup> for the same family of chalcogenide glasses. Apparently, the contribution to polarizability from the lone electron pairs is not the predominant factor influencing the nonlinear properties of ternary Ge-As-Se

glasses. Additional factors, such as glass structure or density, the presence of unpaired electrons,<sup>16</sup> and the presence of defect states must be taken into account. While the structure of the amorphous chalcogenide glasses can be viewed as an assembly of different structural units, such as GeSe<sub>4</sub> and AsSe<sub>3</sub>, the situation is further complicated by the opportunity for both homopolar (e.g., Ge-Ge) and heteropolar bonds (e.g., Ge-Se). This leads to a variety of “defect” gap states, which can contribute to the nonlinearity. For the glasses reported herein, the smallest nonlinearity is seen for Ge<sub>25</sub>As<sub>10</sub>Se<sub>65</sub>, which is expected to be closest to the stoichiometric ideal, highlighting the importance of defect gap states.

In summary, we have investigated several Ge-As-Se chalcogenide glasses with high melting temperatures suitable for high-index-contrast, high nonlinearity fiber. Ge<sub>35</sub>As<sub>15</sub>Se<sub>50</sub> has a nonlinearity of  $24 \times 10^{-18}\text{ m}^2/\text{W}$ , and a figure of merit of 3.2. Such materials show great potential for telecom applications that might use highly nonlinear, high-index-contrast fiber.

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