Highly nonlinear As–S–Se glasses for all-optical switching

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We have synthesized a series of chalcogenide glasses from the As–S–Se system that is designed to have strong nonlinearities. Measurements reveal that many of these glasses offer optical Kerr nonlinearities greater than 400 times that of fused silica at 1.25 and 1.55 μm and figures of merit for all-optical switching greater than 5 at 1.55 μm. © 2002 Optical Society of America

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Ultrafast all-optical switches (AOSs) will be necessary in high-bit-rate communication systems. One route to achieving ultrafast AOSs utilizes the intensity-dependent phase shift generated by the optical Kerr effect. The design of an efficient switch requires that the nonlinearity per unit nonlinear absorption, as embodied in the figure of merit {FOM [$=n_2/(\beta\lambda)$, with $n(I) = n_0 + n_2 I$ and $\alpha(I) = \alpha_0 + \beta I$]}, be large.[1] Specifically, for a Mach–Zehnder-based AOS, a FOM of >5 is necessary.[1] As nonlinear switching media, glasses have such advantages over other materials as ultrafast response time, compatibility with existing fiber technology, and substantially larger FOMs because of their low optical losses. Another intriguing proposed application of highly nonlinear glasses uses microresonators to generate solitons.[2]

Glasses that contain chalcogens (S, Se, Te) are among the most nonlinear glasses, and much effort has been devoted to their study. The optical properties of As_2S_3 glass have been characterized in both bulk and fiber forms, and an AOS has been fabricated from chalcogenide fiber.[3] It has been shown that the nonlinear index of refraction, n_2, increases when selenium is substituted for sulfur,[4,5] and recently, selenium-based chalcogenide glasses have been investigated as ultrafast AOS candidates.[1]

In this Letter we report measurements of the nonlinear optical properties of glasses in an As–S–Se system at the telecommunication wavelengths of 1.25 and 1.55 μm. We identify glasses that combine Kerr nonlinearities greater than 400 times that of fused silica with small losses to offer FOMs of >5. We also observe a peak in the FOM just below the half-gap ($h\nu/E_{\mathrm{gap}} = 0.5$). A maximum in the FOM near the half-gap is desirable for AOS materials because it permits the design of an efficient switch with a large nonlinearity.

The major contributions to the third-order susceptibility in an isotropic medium come from one- and two-photon resonant processes.[6] As the frequency of the incident field approaches one-half the frequency of a material resonance, the magnitude of the nonlinear index of refraction (n_2) is two-photon resonantly enhanced and is accompanied by two-photon absorption (TPA). As a first approximation, the dispersion of the nonlinearity in glasses is based on a model for crystalline semiconductors, assuming an infinitely sharp absorption edge.[7] In this case the FOM decreases monotonically with increasing normalized photon energy, $h\nu/E_{\mathrm{gap}}$. However, an amorphous material exhibits an exponential (Urbach) tail in its absorption edge, which leads to TPA below the half-gap. In that case, n_2 may increase faster than TPA, so the FOM will exhibit a peak just below the half-gap.

Our sample set consists primarily of glasses in the As–S–Se system and extends from selenium-deficient $As_{40}S_{60}$ to selenium-rich $As_{40}Se_{60}$. We also considered samples from As–S–Te and As–Se–Cu systems. The glasses were prepared from high-purity chemicals that were further purified in house by sublimation and distillation. The chemicals were placed in cleaned quartz ampoules, evacuated to $\sim 10^{-5}$ Torr, and sealed with an oxygen methane torch. The ampoules were heated at ~800 °C for 24 h, followed by quenching to ~200 °C for annealing and then slowly cooled to room temperature. We prepared bulk samples and measured linear absorption spectra to estimate the energy gap, where $\alpha(E_{\mathrm{gap}}) = 1000\ \mathrm{cm}^{-1}$ (see Table 1).

The nonlinear coefficients (n_2 and β) of these glasses were measured by use of spectrally resolved two-beam coupling (SRTBC).[8] SRTBC uses a standard pump–probe setup with the addition of a monochromator to measure the pump-induced shift of the probe spectrum. The sample is kept at the focus of the beams, and the energy transmitted through the monochromator at a fixed detuning from the center of the spectrum is monitored. SRTBC provides the sign and magnitude of the real and imaginary parts of the third-order susceptibility along with their dynamics and has demonstrated sensitivity to nonlinear phase shifts as small as 10^{-6} rad.[8,9] As shown in Fig. 1, the SRTBC signal is derivativelike when nonlinear refraction dominates. Nonlinear absorption appears as a downward unipolar contribution centered at zero delay, so a SRTBC signal with peaks and valleys of equal magnitude implies small nonlinear loss. Nonlinear absorption is also measured independently in a spectrally integrated scan. Two femtosecond

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Table 1. Linear and Nonlinear Optical Properties of the Measured Glasses

			$\lambda = 1.25\ \mu$m			$\lambda = 1.55\ \mu$m		
Glass	n_0 at 1.55 μm	λ_{gap} (μm)	$n_2/n_{2,\text{fused silica}}$ ($\pm$15%)	β (cm/GW) ($\pm$15%)	FOM ($\pm$20%)	$n_2/n_{2,\text{fused silica}}$ ($\pm$15%)	β (cm/GW) ($\pm$15%)	FOM ($\pm$20%)
$As_{40}S_{60}$	2.45	0.52	260	0.16	3	220	<0.030	>12
$As_{40}S_{50}Se_{10}$	2.49	0.55	400	0.14	6	380	0.16	4
$As_{40}S_{40}Se_{20}$	2.55	0.59	360	0.22	3	300	0.060	8
$As_{40}S_{30}Se_{30}$	2.62	0.62	580	0.38	3	430	0.15	5
$As_{40}S_{20}Se_{40}$	2.70	0.64	920	1.04	2	460	0.25	3
$As_{40}S_{10}Se_{50}$	2.76	0.67	1000	1.4	2	560	0.14	7
$As_{40}Se_{60}$	2.81	0.70	1200	2.8	1	930	0.14	11
$As_{39}Se_{61}$	2.81	0.70	–	–	–	660	0.28	4
$As_{40}Se_{55}Cu_5$	2.93	0.79	–	–	–	850	0.29	5
$As_{25}S_{55}Te_{20}$	2.52	0.79	–	–	–	470	0.15	5

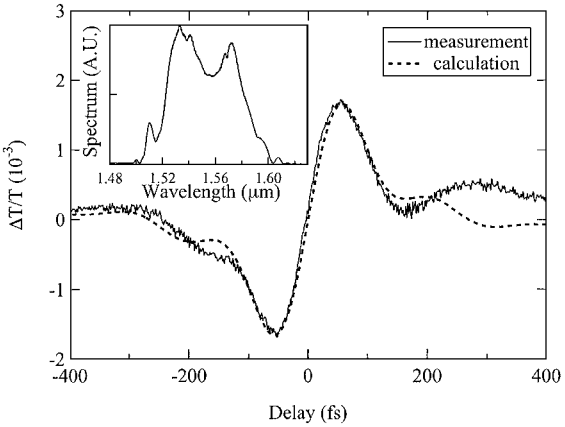

Fig. 1. Representative SRTBC signal obtained with the EDFL. The calculated signal is derived from a zero-phase Fourier transform of the laser spectrum (inset). The difference between measurement and calculation for positive delay is due to the nuclear contribution to the nonlinearity.[9]

laser sources were used in these measurements: a Cr:forsterite laser at 1.25 μm and an Er-doped fiber laser (EDFL) at 1.55 μm. By keeping the intensity at the sample below 200 MW/cm^2 and using femtosecond pulses, we ensured that the effects of higher-order nonlinearities were negligible. A La–Ga–S glass of known nonlinearity was used as a reference sample.[10]

SRTBC signals measured with the EDFL (Fig. 1) deviate from the analytic form presented in Ref. 8 because of the laser's structured spectrum (Fig. 1, inset). In the current work, the signals obtained with the EDFL were verified numerically by use of the electric field derived from a Fourier transform of the actual laser spectrum; the pulses were assumed to be chirp free. Experimentally, chirp is minimized with a silicon prism sequence and the time–bandwidth product is close to the transform limit. At 1.55 μm, the influence of TPA on the SRTBC signal was below the sensitivity of our measurements, so n_2 was determined by scaling from the reference sample.

Some selected glasses in the As–S–Se system were studied previously but not in a systematic manner, and the nonlinear parameters of these materials were published elsewhere.[1,3–5] The variation in these results is large; for example, the spread in n_2 for $As_{40}S_{60}$ is nearly a factor of 6. The size of this range may be attributed to variations in the glass's stoichiometry, quality, and melting conditions. We have duplicated the measurement of $As_{39}Se_{61}$ reported by Lenz *et al.*[1] to within 30% (the sample reported as $As_{40}Se_{60}$ in Ref. 1 is actually $As_{39}Se_{61}$).

Photostructural changes induced by the nonlinear excitation of chalcogenide glasses were identified previously.[11] We observed a blurring of the transmitted laser beam profile, increased scattering, and SRTBC traces that became increasingly asymmetric with lengthening exposure time for the samples with the largest normalized photon energies ($As_{40}Se_{60}$ and $As_{40}S_{10}Se_{50}$ at 1.25 μm). By attenuating the incident beam and monitoring the SRTBC traces for two to three times longer than the actual acquisition time, we ensured that the measurements were completed without damage to the samples.

In the As–S–Se glass system the overall trend is an increase in n_2 with the addition of selenium (Table 1), in agreement with previous results.[4,5] $As_{40}Se_{60}$ has the largest value of n_2 of all the samples that we measured at 1.25 and 1.55 μm, i.e., 3.0×10^{-17} and 2.3×10^{-17} m^2/W, respectively. The rapid increase in n_2 (Fig. 2) at $h\nu/E_{gap} \sim 0.45$ is consistent with two-photon resonant enhancement. The FOM (Fig. 3)

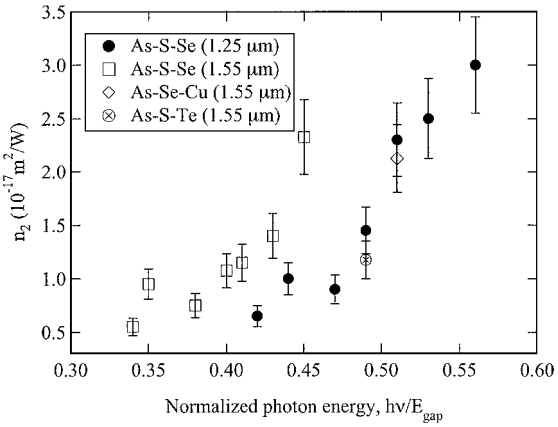

Fig. 2. Variation of n_2 with normalized photon energy. Results for $As_{40}Se_{55}Cu_5$ and $As_{25}S_{55}Te_{20}$ glasses are shown for comparison with $As_{40}Se_{60}$.

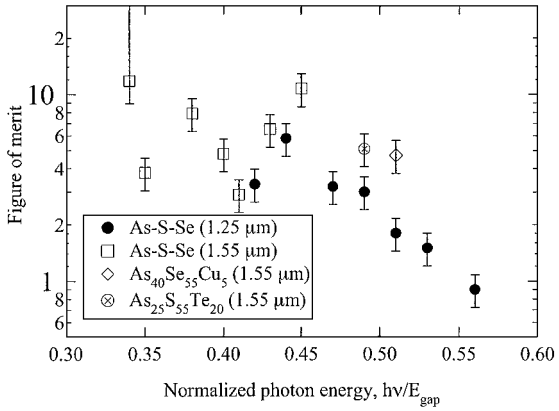

Fig. 3. Variation in the FOM with normalized photon energy. Results for $As_{40}Se_{55}Cu_5$ and $As_{25}S_{55}Te_{20}$ glasses are shown for comparison with $As_{40}Se_{60}$.

depends on the proximity of the wavelength to the TPA edge, and the peak in the FOM at $h\nu/E_{\mathrm{gap}} \sim 0.45$ is consistent with our supposition about TPA in glasses. Additional experimental evidence of a peak in the FOM near $h\nu/E_{\mathrm{gap}} \sim 0.45$ is found in Ge–As–S–Se glasses.[12] The unexpectedly large differences in n_2 and the FOM measured for $As_{39}Se_{61}$ and $As_{40}Se_{60}$ are reproducible. We are unable to explain the difference based on either sample purity or structure, and understanding this sharp variation will require further experiments.

Within the context of a model for the nonlinear index of refraction in glasses,[11] one obtains a large value of n_2 by maximizing the linear index of refraction, n_0, and minimizing E_{gap}, subject to the constraint that the TPA edge remains shorter than the wavelength of the light. We attempted to improve on the excellent nonlinear optical properties found in the As–S–Se system at 1.55 μm by modifying n_0 and E_{gap} relative to $As_{40}Se_{60}$. Copper incorporated into the glass $As_{40}Se_{55}Cu_5$ increased n_0 and decreased E_{gap}. Measurements revealed that n_2 is essentially unchanged and TPA increases, so the FOM decreases. $As_{25}S_{55}Te_{20}$ should have larger TPA because its E_{gap} is smaller than that of $As_{40}Se_{60}$. The measurements revealed that both n_2 and FOM are smaller in $As_{25}S_{55}Te_{20}$ than in $As_{40}Se_{60}$. These two examples show that the constraint on n_0 and E_{gap} that arises from the need to avoid TPA limits any further optimization of $As_{40}Se_{60}$ for operation at 1.55 μm.

In conclusion, we have found that chalcogenide glasses in the As–S–Se system simultaneously provide a large nonlinear index of refraction and a FOM that satisfies a standard criterion for AOSs.[1] In the samples with a FOM of >5, nonlinear phase shifts of π rad can be produced without damage for intensities of ≤ 200 MW/cm^2. We observed that the FOM increases substantially near $h\nu/E_{\mathrm{gap}} \sim 0.45$, as is qualitatively expected when the absorption edge is not infinitely sharp. These experiments confirm that the nonlinearities are determined largely by the abundance of the most-polarizable constituent, in this case selenium. In particular, $As_{40}Se_{60}$ achieves high values of n_2 and FOM (2.3×10^{-17} m^2/W and 11, respectively) and is thus quite promising for use in an AOS at 1.55 μm.

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