Highly Nonlinear Ge–As–Se and Ge–As–S–Se Glasses for All-Optical Switching

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***Abstract*—We have synthesized Ge–As–Se and Ge–As–S–Se chalcogenide glasses designed to have large optical nonlinearities. Measurements reveal that these glasses offer optical Kerr nonlinearities greater than 500 times that of fused silica and figures of merit for all-optical switching >5 at 1.25 and 1.55 μm.**

***Index Terms*—Amorphous semiconductors, nonlinear media, nonlinear optics, optical communication, optical materials.**

ULTRAFAST all-optical switches (AOS) will be necessary in high bit rate communication systems. One route to ultrafast AOS 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 [$\mathrm{FOM} = n_2/(\beta\lambda)$ 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, $\mathrm{FOM} > 5$ is necessary [1]. As the nonlinear switching medium, glasses have advantages over other materials including ultrafast response time, compatibility with existing fiber technology, and substantially larger FOM because of their low optical losses.

Glasses containing 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 [2]. One motivation for examining glasses in the Ge–As–Se (selenide) and Ge–As–S–Se (sulfoselenide) systems is to extend our knowledge of chalcogenide nonlinear optical properties from the sulfide glasses studied previously [3]. Selenium, being heavier than sulfur, is known to raise the linear index and is expected to enhance the nonlinearity [1], [4]–[6].

In this letter, we report measurements of the nonlinear optical properties of Ge–As selenide and sulfoselenide glasses at the telecommunications wavelengths of 1.25 and 1.55 μm. We identify suitable glasses for AOS which combine Kerr nonlinearities greater than 500 times that of fused silica with small losses to offer FOM >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 nonlinear materials since it enables the design of an efficient switch with a two-photon resonantly enhanced nonlinearity.

TABLE I
SAMPLES FROM THE Ge–As SULFOSELENIDE AND SELENIDE GLASS SYSTEMS

name	λ_{gap} (μm)	composition
AZA	0.49	$Ge_{15.38}As_{30.77}S_{53.85}$
BGY	0.51	$Ge_{15.38}As_{30.77}S_{48.47}Se_{5.39}$
BGZ	0.54	$Ge_{15.38}As_{30.77}S_{43.08}Se_{10.77}$
BHA	0.56	$Ge_{15.38}As_{30.77}S_{32.31}Se_{21.54}$
BHB	0.58	$Ge_{15.38}As_{30.77}S_{26.92}Se_{26.92}$
BHC	0.59	$Ge_{15.38}As_{30.77}S_{21.54}Se_{32.31}$
BHD	0.61	$Ge_{15.38}As_{30.77}S_{10.77}Se_{43.08}$
BGV	0.64	$Ge_{15.38}As_{30.77}Se_{53.85}$
BIF	0.70	$Ge_{22.22}As_{44.44}Se_{33.33}$
BIG	0.68	$Ge_{20}As_{40}Se_{40}$
BIH	0.65	$Ge_{18.18}As_{36.36}Se_{45.45}$
BGX	0.64	$Ge_{16.67}As_{33.33}Se_{50}$
BGW	0.64	$Ge_{16}As_{32}Se_{52}$
BGV	0.64	$Ge_{15.38}As_{30.77}Se_{53.85}$
BGT	0.64	$Ge_{14.29}As_{28.57}S_{57.14}$
BGS	0.64	$Ge_{13.79}As_{27.59}Se_{58.62}$
BII	0.63	$Ge_{12.5}As_{25}Se_{62.5}$
BIJ	0.63	$Ge_{11.11}As_{22.22}Se_{66.67}$
BIK	0.64	$Ge_{10}As_{20}Se_{70}$

The major contributions to the third-order susceptibility in an isotropic medium come from one- and two-photon resonant processes [7]. 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 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 [8]. In this case, the FOM decreases monotonically with increasing normalized photon energy, $h\nu/E_{\mathrm{gap}}$. However, amorphous materials exhibit an exponential (Urbach) tail in their absorption edge, which leads to TPA below the half gap. In that case, n_2 may increase faster than TPA, and so the FOM would exhibit a peak just below the half gap. Three-photon absorption (3PA) may also be important when operating at high peak intensities and in this instance, optimum operating regions exist just below each multiphoton absorption edge [9].

Ge–As selenide and sulfoselenide glasses (Table I) were synthesized from 40-g mixtures of elemental Ge, As, Se, and S with greater than 99.9995% purity (metals basis) that were loaded into 10-mm internal diameter fused silica ampoules under dry N_2. Prior to batching, the ampoules were etched

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in 5% HF : 5% HNO_3, rinsed in deionized water, and then dried at 1000 °C. The filled ampoules were evacuated to 10^{-6} torr, flame sealed, and then heated to 875 °C for at least 24 h in a rocking furnace. Cylindrical glass rods were formed by quenching the hot ampoules in water and subsequently annealed for about 1 h near the glass transition temperature. Bulk samples were prepared and linear transmission spectra were measured, from which the energy gap was estimated, where $\alpha(E_{\text{gap}}) = 1000\ \text{cm}^{-1}$ (Table I).

The nonlinear coefficients (n_2 and β) of these glasses were measured using spectrally resolved two-beam coupling (SRTBC) [10]. SRTBC uses a standard pump-probe setup with the addition of a monochromator to measure the dynamic 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 frequency 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} radians [10], [11]. Nonlinear absorption is also measured independently in a spectrally integrated scan. Two femtosecond laser sources were used in these measurements: a Cr : forsterite laser [12] at 1.25 μm and an Er-doped fiber laser [13] 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. An La–Ga–S glass of known nonlinearity was used as a reference sample [3].

Previous work has identified photostructural changes induced by the nonlinear excitation of chalcogenide glasses [14]. We observed a visible blurring of the transmitted laser beam profile, increased scattering, and SRTBC traces that became increasingly distorted with exposure time for the samples with the largest normalized photon energies (the selenides 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 before the onset of damage.

We observe a monotonic increase in n_2 with the progressive replacement of S by Se in the sulfoselenide glasses, and the gradual removal of Se at fixed Ge : As ratio from the selenide glasses (Tables II and III). As shown in Fig. 1, n_2 increases faster than β just below the half gap, consistent with our supposition about TPA. The FOM (Fig. 2) depends on the proximity of the frequency of the light to the two-photon absorption edge and the peak at $h\nu/E_{\text{gap}} \sim 0.45$ occurs when nonlinear refraction increases more rapidly than TPA with normalized photon energy. Additional experimental evidence of a peak in the FOM near $h\nu/E_{\text{gap}} \sim 0.45$ is found in As–S–Se glasses [13].

TABLE II
NONLINEAR OPTICAL PROPERTIES OF THE GLASSES MEASURED AT 1.25 μm

glass	$n_2/n_{2,\text{ fused silica}}$ ± 15 %	β (cm/GW) ± 15 %	FOM ± 20 %
AZA	190	0.040	9.5
BGY	210	0.15	2.8
BGZ	290	0.15	3.9
BHA	290	0.090	6.4
BHB	460	0.17	5.4
BHC	560	0.17	6.6
BHD	610	0.24	5.1
BGV	640	0.52	2.5
BIF	1200	7.4	0.32
BIG	880	2.8	0.63
BIH	720	1.0	1.4
BGX	870	0.26	6.7
BGW	800	0.36	4.4
BGV	640	0.52	2.5
BGT	530	0.26	4.1
BGS	640	0.28	4.6
BII	640	0.14	9.1
BIJ	550	0.45	2.4
BIK	660	0.42	3.1

TABLE III
NONLINEAR OPTICAL PROPERTIES OF SELECT GLASSES MEASURED AT 1.55 μm

glass	$n_2/n_{2,\text{ fused silica}}$ ± 15 %	β (cm/GW) ± 15 %	FOM ± 20 %
AZA	130	< 0.010	> 21
BHA	250	< 0.050	> 8.1
BHD	390	0.060	11
BIG	620	0.24	4.2
BII	450	0.040	18
BIJ	530	0.030	28

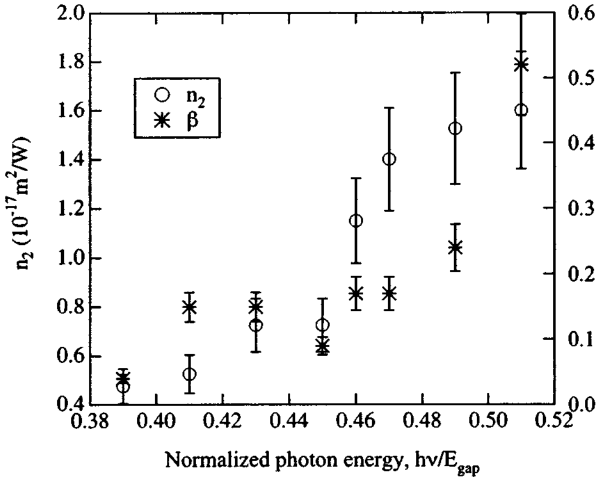

Fig. 1. Variation of n_2 and β with normalized photon energy in the Ge–As–S–Se system.

The nonlinearity of a material may be changed through the modification of either its resonant or off-resonant parts. Quémard *et al.* [5] suggest that the concentration of lone electron pairs is the dominant factor in achieving large nonlinearities, and we have recently confirmed that n_2 increases with the most polarizable constituent (selenium) in As–S–Se glasses [13]. Typically, a change in the lone electron pair concentration modifies the energy gap so it is impossible to determine whether a corresponding change in the nonlinearity is due to lone-pairs or resonant enhancement. The selenide glasses studied here allow us to directly determine the impact of lone-pair concentration on the nonlinearity, since the energy gap remains constant with added selenium (Table II, samples BGX-BIK). In the absence of bandgap modification, we find no systematic increase of n_2 with rising Se content, and hence, lone pair concentration. In addition, lone electron pairs cannot account for the increase in

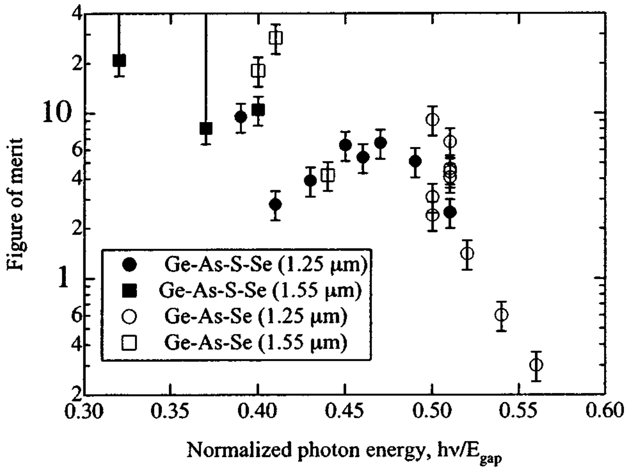

Fig. 2. Variation in the FOM with normalized photon energy in the Ge–As–Se and Ge–As–S–Se systems.

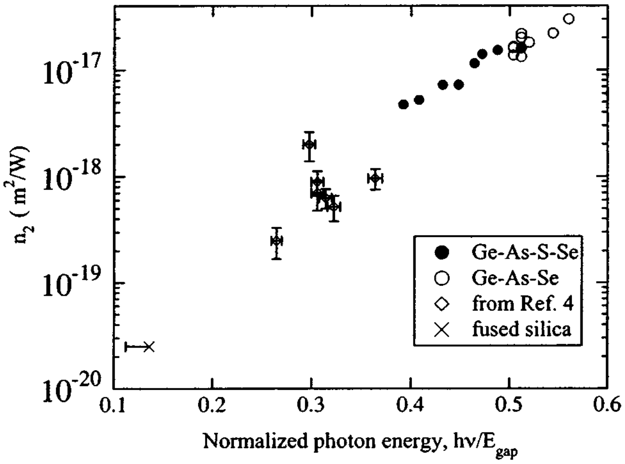

Fig. 3. Variation of n_2 with normalized photon energy in the selenide, sulfoselenide, sulfide, and heavy-metal-doped oxide systems, all at 1.25 μm. Fused silica is also shown for comparison. The horizontal error bars account for absorption edge conventions different from that used in this letter.

n_2 that we observe in samples BGX-BIF since the removal of Se reduces the pair concentration. Overall, we find that n_2 increases as the bandgap narrows in the selenide and sulfoselenide glass systems. When these results are combined with previous measurements of sulfide and heavy-metal-doped oxide glasses [3], we see that the general trend in the nonlinearity is accounted for by the normalized photon energy (Fig. 3). Therefore, when designing an AOS at a given wavelength, one would choose a glass with $h\nu/E_{\text{gap}} \sim 0.45$ to achieve both large n_2 and large FOM.

In conclusion, we find that chalcogenide glasses in the Ge–As–S–Se and Ge–As–Se systems simultaneously provide a large nonlinear index of refraction and a FOM that satisfies a standard criterion for AOS [1]. We find that the magnitude of the nonlinearity generally increases with normalized photon energy. We also observe that the FOM increases near $h\nu/E_{\text{gap}} \sim 0.45$, as qualitatively expected when the absorption edge is not infinitely sharp. Several of the glasses studied here have $n_2 > 800$ times that of fused silica and others have FOM >20. In particular, the sample BIJ achieves high values of n_2 and FOM (1.3×10^{-17} m^2/W and 28, respectively), and is, thus, quite promising for all-optical switching at 1.55 μm.

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