Photoinduced transparency of effective three-photon absorption coefficient for femtosecond laser pulses in $Ge_{16}As_{29}Se_{55}$ thin films

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We report a dramatic change in effective three-photon absorption coefficient of amorphous $Ge_{16}As_{29}Se_{55}$ thin films, when its optical band gap decreases by 10 meV with 532 nm light illumination. This large change provides valuable information on the higher excited states, which are otherwise inaccessible via normal optical absorption. The results also indicate that photodarkening in chalcogenide glasses can serve as an effective tool to tune the multiphoton absorption in a rather simple way. © *2011 American Institute of Physics*. [doi:10.1063/1.3591978]

In recent years chalcogenide glasses (ChGs) have attracted much attention as promising candidates for ultrafast photonics and optoelectronics, owing to their unique properties of high Kerr nonlinearities at femtosecond time scales, third order optical nonlinearities two to three orders of magnitude higher than silica, good transparency in the infrared region, large Raman and Brillouin gain, easy synthesis methods, etc.[1–4] Needless to say, enhanced nonlinearity in ChGs has led to a number of potential applications in optoelectronics like ultrahigh speed demultiplexing, wavelength conversion, amplification, lasing, pulse compression, and optical limiting.[5–7] However, ChGs are also highly photosensitive and exhibit various light-induced effects.[8] Among the numerous light-induced effects shown by ChG, photodarkening (PD) is of crucial importance since it can severely affect the performance of nonlinear optical devices.[9,10]

Over the last few years, many researchers have shown that an intense ultrafast laser light can create PD in ChGs.[10–12] In all these experiments, cumulative effect of PD was studied when the sample was subjected to large number of intense short pulses. Though PD can be induced by femtosecond and cw laser, the mechanism of PD occurs for both the cases can be rather different. Zhang *et al.*[4] have shown that PD by femtosecond pulses increases the refractive index in As_2S_3, however cw illumination decreases it considerably. It was assumed that femtosecond laser irradiation induces charged defect pairs and self trapped excitons, which increase the polarizability of the medium. On the other hand, cw laser illumination results in the removal of homopolar bonds and the creation of more energetically favorable heteropolar bonds, which decrease the polarizability. As a result, the sign of change in nonlinear refractive index become opposite for cw and femtosecond laser irradiations. In all these studies, information on the nonlinear absorption of the photodarkened film to an intense ultrashort pulse is not reported. Moreover, the change in multiphoton absorption coefficient can provide valuable information on the higher excited states that are otherwise inaccessible to normal optical absorption measurements. In this letter, we have compared the nonlinear

absorption of ultrashort laser pulses (100 fs) on as-prepared and photodarkened films of $Ge_{16}As_{29}Se_{55}$ thin films deposited on a glass substrate. Our experimental results indicate a dramatic influence of PD on the effective three-photon absorption of chalcogenide glassy films to ultrashort laser pulses, which decreases with PD by an order of magnitude (from 6.8×10^{-27} to 9.2×10^{-28} m^3/W^2). These results also point out that multiphoton absorption can be effectively tuned by light induced methods.

Amorphous thin films of $Ge_{16}As_{29}Se_{55}$ of $\sim$1.0 μm thickness are deposited on a microscope glass substrate by conventional thermal evaporation. Figure 1 shows the optical absorption spectrum of the as-prepared sample. Data analysis using Tauc equation yields its band gap as 1.73 eV. When illuminated with a 532 nm diode pumped solid state laser of intensity of 1 W/cm^2, the film exhibits PD. During illumination, the optical absorption spectrum is recorded at 1 min interval and continued until it shows no further change. The change in absorption appears instantaneously, grows gradually, and saturates nearly after 40 min. At that point the band gap is shifted to 1.72 eV.
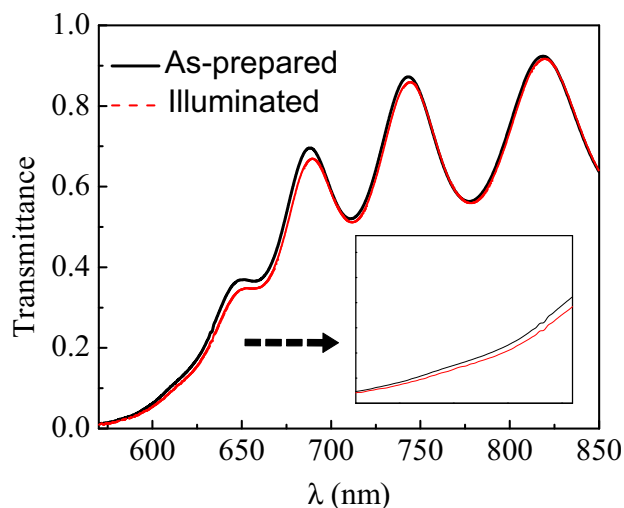

FIG. 1. (Color online) The PD of $Ge_{16}As_{29}Se_{55}$ when irradiated with a 532 nm laser with an intensity of 1 W/cm^2. Inset shows expanded band gap region. The band gap of the as prepared and photodarkened film is 1.73 eV and 1.72 eV, respectively.

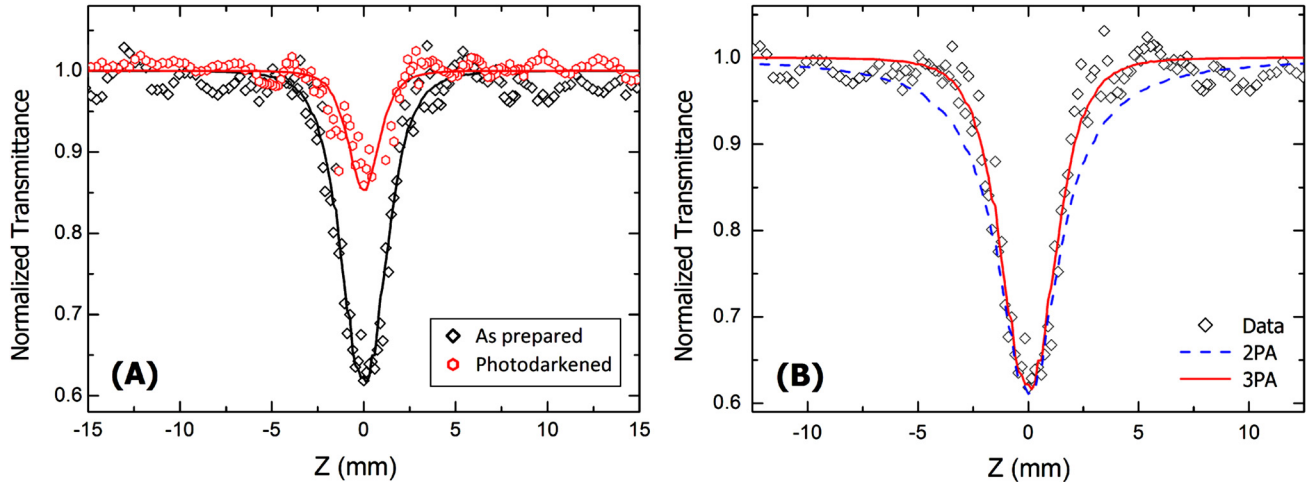a)Author to whom correspondence should be addressed. Electronic mail: adarsh@iiserbhopal.ac.in.

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FIG. 2. (Color online) (a) Normalized transmittance as a function of position in open aperture Z-scan using 800 nm 100 fs pulses. Symbolss represent data for the as-prepared and photodarkened $Ge_{16}As_{29}Se_{55}$ film; solid lines are respective theoretical fit. The effective three-photon absorption coefficient of the as prepared and photodarkened film is 6.8×10^{-27} m^3/W^2 and 9.2×10^{-28} m^3/W^2, respectively. The experimental results clearly indicate the photoinduced transparency in three-photon absorption coefficient by an order of magnitude. (b) Describing the numerical fit of the experimental data for two-photon and effective three-photon absorption processes. From the figure it is clear that an effective three-photon absorption process gives the best fit to the experimental data.

PD in $Ge_{16}As_{29}Se_{55}$ thin films can be understood by considering the compositional heterogeneities created during thermal evaporation of the film on the glass substrate.[13] During deposition, various nonstochiometric atomic fragments of Ge–Se and As–Se are formed from the vapor phase. When such a film is illuminated with 532 nm cw light, a considerable fraction of metastable homopolar bonds present in the atomic fragments are broken and subsequently converted into energetically favored heteropolar bonds.[13] The reduction in As homopolar bonds results in PD but that of Ge atoms leads to photobleaching.[13] However, since the amount of Ge in the present composition is significantly lower than As, the net result is PD. At this point, it is reasonable to assume that PD in our sample is accompanied by a change also in the complex nonlinear optical susceptibility χ^n ($n > 1$, real part of χ gives nonlinear refraction and imaginary part refers to nonlinear absorption) of the medium. Effectively, multiphoton absorption also expected to change with PD since the nonlinear absorption coefficients are related to the nonlinear optical susceptibility. Wherrett has predicted that for a direct band gap crystalline semiconductor, N photon absorption coefficient strongly depends on the optical band gap and can be written as[14]

$$K_N \propto \left(\frac{e^2}{\hbar c}\right)\hbar^{N-1}\frac{P^{2N-3}}{n^N E_g^{4N-5}}F_N\left(\frac{N\hbar\omega}{E_g}\right), \qquad (1)$$

where K_N, e, $\hbar$, c, P, n, and E_g are the N photon absorption coefficient, electronic charge, (Plank's constant)/2π, velocity of light, momentum element, linear refractive index, and band gap, respectively. The function F_N in Eq. (1) takes the form

$$F_N\left(\frac{N\hbar\omega}{E_g}\right) = \frac{(N\hbar\omega/E_g - 1)^{1/2}}{(N\hbar\omega/E_g - 1)^{4N-3}}. \qquad (2)$$

Following Eqs. (1) and (2), the magnitude of multiphoton absorption at a particular wavelength strongly depends on the optical band gap of the material. Though the calculations are for direct band gap materials, such strong dependency of multiphoton absorption is also assumed for indirect band gap

materials like ChGs. We made such an assumption based on the previous results obtained for two-photon absorption measurements in chalcogenide as well as oxide glasses.[15,16] The nominal band gap of as-prepared $Ge_{16}As_{29}Se_{55}$ is 1.73 eV and after PD it has changed to 1.72 eV. Hence, we presume that the shift in the optical band gap ΔE_g of 10 meV will produce a substantial change in the multiphoton absorption coefficient.

A standard Z-scan setup was used for the determination of three-photon absorption in $Ge_{16}As_{29}Se_{55}$. The experimental setup was the same as described by Sheik-Bahae *et al.*[17] In our setup, a Ti:sapphire laser system (TSA-10 Spectra Physics) was used for excitation at 800 nm. The nominal input pulse width (full width at half maximum) of this chirped pulsed amplifier laser was 100 fs, as measured using autocorrelation traces obtained from second harmonic generation in a thin BBO crystal. The laser was run in the single-shot mode and the repetition rate was approximately 1 Hz. Precautions were taken to avoid the sample damage: by limiting the peak input energy to a few microjoules and making the repetition rate at 1 Hz such that any damage due to sample heating could be avoided. Two pyroelectric energy probes were used as detectors, of which one monitored the transmitted energy through the sample, while the other monitored input laser energy. The laser was focused using a plano-convex lens and samples were moved along the z-axis (along the propagation direction of the laser) by a micrometer stage having a resolution of 2.5 μm. The whole experiment was automated on a Linux based platform.

Figure 2 shows the open aperture Z-scans recorded at 800 nm for the as-prepared and photodarkened samples. It is seen that a three-photon absorption type process gives the best fit to the experimental data. However, the excitation wavelength region corresponding to a genuine three-photon absorption in our samples is below 1700 nm because the optical band gap is at 1.72 eV. Therefore, genuine three-photon absorption is not the cause for the observed three-photon type process. The possible alternative mechanism is that under intense excitation with femtosecond laser pulses at 800 nm, a strong two-photon absorption process takes place

that considerably populates the excited states, followed by a one-photon absorption from the excited states.[18] This stepwise process will appear similar to a genuine three-photon absorption process if an intensity-dependent transmission measurement like the Z-scan is performed. Therefore such processes, which mimic genuine three-photon absorption, are called effective three-photon absorption in the Z-scan literature.[19] For an effective three-photon absorption process, the normalized transmittance through the sample can be written as[20]

$$T = [(1 - R)^2 \exp(-\alpha_o l)/p_o \sqrt{\pi}]$$
$$\times \int_{-\infty}^{+\infty} \ln[\sqrt{1 + p_o^2 \exp(-2t^2)} + p_o \exp(-t^2)]dt, \quad (3)$$

where T is the light transmission through the sample, R is the surface reflectivity, and α_o is the linear absorption coefficient. P_o is calculated as $[2\gamma(1-R)^2 I_0^2 L_{eff}]^{1/2}$, where γ is the effective three-photon absorption coefficient and I_o is the on-axis peak intensity. L_{eff}, the effective sample thickness is described by $[(1-\exp(-2\alpha_0 l)]/2\alpha_0$, where l is the sample thickness. The Z-scan curves were fitted by numerical integration of Eq. (3) and effective three-photon absorption coefficients were determined. Effective three-photon absorption coefficient of the as-prepared film is 6.8×10^{-27} m³/W² and the same for the photodarkened film is 9.2×10^{-28} m³/W². Evidently, the value of effective three-photon absorption coefficient decreases dramatically by about an order of magnitude, as a result of PD. Although the change in optical band gap by PD is very small ($\sim 0.5\%$), the change in effective three-photon absorption coefficient is dramatic and is nearly 87%. In this context, we propose that a small change in optical band gap can produce substantial change in multiphoton absorption in ChGs. Therefore, PD can be effectively used to manipulate the multiphoton absorption process in ChGs. Additionally such light induced methods are in a way much simpler than the known methods in thin films for tuning the multiphoton absorption process and may find potential applications in optoelectronics. At this stage it is worthwhile to qualitatively compare our observations with the method proposed by Garcia, where to use Franz–Keldysh effect (FKE) to tune the multiphoton absorption.[21] In FKE, the electric fields required are very large (on the order of a few kilovolts) to produce a substantial change in the multiphoton absorption,[22] however in our samples it can be done with a very low power laser correspond to the optical band gap of the material.

Having demonstrated the strong sensitivity of photoinduced transparency of effective three-photon absorption with PD, we attempt to explain the observed effects. There is little doubt that the huge change in effective three-absorption coefficient is due to other aspects of PD, we recognize that $Ge_{16}As_{29}Se_{55}$ thin film contains a large number of nonstochiometric atomic fragments of As_2Se_3 and $GeSe_2$. During PD, a considerable amount of such defects are annealed out using the lone pair π electrons of the chalcogen atom. At this point we conjecture that light induced structural rearrangements in $Ge_{16}As_{29}Se_{55}$ will produce changes in the energy levels at the higher excited states in addition to the changes near the optical band gap as well as a substantial reduction in hyperpolarizability of the ChG medium. As a result, effective three-photon absorption reduces considerably. Nonlinear refractive index measurement by Zhang *et al.*[4] in As_2S_3 have shown that the hyperpolarizability of the ChG medium decreases with PD. Nonlinear absorption measurements in oxide glasses also have shown that the two photon absorption coefficients changes with hyperpolarizability.[16] Photoinduced change in effective three-photon absorption thus provides valuable information about the changes occurring at the higher excited states, which was otherwise inaccessible to normal optical absorption measurements.

In conclusion, our experimental results show a strong influence of PD on the nonlinear interactions of $Ge_{16}As_{29}Se_{55}$ thin film to intense ultrashort femtosecond laser pulses. In this case, effective three-photon absorption coefficient changes dramatically, by an order of magnitude. Our experimental results also point out that multiphoton absorption can be effectively tuned by light induced methods, which may find potential applications in optoelectronics. Moreover, the change in effective three-photon absorption coefficient also provides valuable information on the hyperpolarizability of the glassy medium and photoinduced changes in higher excited states before and after PD, which are not readily accessible to normal optical absorption measurements.

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