Revista Mexicana de Física **43**, *No. 6 (1997) 960–965*

Nonresonant third-order optical nonlinearity of amorphous selenium with picosecond pulses

R. Rangel Rojo
Departamento de Óptica
Centro de Investigación Científica y Estudios Superiores de Ensenada
Apartado postal 2732, 22860 Ensenada, Baja California, Mexico

E. Haro Poniatowski and A. Muñoz Flores
Departamento de Física
Universidad Autonoma Metropolitana, Unidad Iztapalapa
Apartado postal 55-534, 09340 México D.F., Mexico

Recibido el 3 de noviembre de 1996; aceptado el 10 de enero de 1997

Abstract. We report the study of the third-order optical nonlinearities of amorphous selenium, using picosecond pulses at 1.064 μm, from a mode-locked Nd:YAG laser. The Z-scan technique was used to resolve the absorptive and refractive contributions to the nonlinear response of the material, including their sign. The chosen wavelength lies to the lower photon energy side from the absorption edge for the material studied, the interaction is therefore nonresonant and electronic in origin. We measured an $n_2 = -0.06$ cm^{2}GW^{-1}, with negligible two-photon absorption.We discuss the influence of two photon absorption on the nonlinearity observed.

Resumen. En este trabajo reportamos el estudio de las propiedades opticas nolineales de tercer orden del selenio amorfo, usando para ello pulsos a 1.064 μm, producidos por un laser de Nd:YAG de modos amarrados. Se uso la técnica de *barrido en z* para resolver las contribuciones absortiva y refractiva de la respuesta nolineal del material. La longitud de onda escogida, corresponde a energías del foton menores a la brecha de energía del material estudiado, por tanto, la interacción es no-resonante y de origen electrónico. Encontramos el valor $n_2 = -0.06$ cm^{2}GW^{-1}, con una absorción de dos fotones despreciable. Discutimos la influencia de la absorción de dos fotones en el proceso nolineal observado.

PACS: 42.65.-k; 42.65.An; 78.66.Qn

1. Introduction

There has been considerable interest in the study of the nonlinear interaction of on-resonance continuous wave light with amorphous chalcogenide glasses [1–3]. This interest stems, on one hand, from the possibility of using this interaction as a probe for the study of the photo-induced structural changes observed in this class of materials [4]. On the other hand, these photostructural changes give chalcogenide glasses a potential for optical data storage applications. More recently, the study of off-resonance interactions, involving the third-order nonlinear susceptibility $\chi^{(3)}(-\omega;\omega,-\omega,\omega)$, have attracted some

interest too [5–7] due to the ultrafast response times observed and the potential for all-optical switching applications. The chalcogenide glasses that have been studied in more detail are As_2S_3, $GeSe_2$, and non-stoichiometric related compounds. While the photoconducting properties of amorphous selenium have been studied in the past [8], little work has been done on its nonlinear optical properties. On-resonance degenerate four-wave mixing (DFWM) studies in amorphous selenium films showed a larger diffraction efficiency than that found in $Ge_{10}Se_{90}$ or Te_7Se_{93} [9] under the same conditions. This implied a larger on-resonance $\chi^{(3)}$ value for selenium than for the other compounds. Due to their potential use in ultrafast optical switching devices, it is interesting to investigate whether the non-resonant nonlinearity of selenium shows a similar enhancement over other chalcogenides as well.

The present work uses the beam distortion technique known as Z-scan [10], with picosecond pulses at 1.064 μm in order to study the off-resonance nonlinear response of an amorphous selenium thin film sample. By using such short pulses we minimized the possible presence of a thermal contribution in the nonlinearity observed. The Z-scan technique was chosen because it combines relative simplicity and high sensitivity and because, unlike other techniques like degenerate four-wave mixing, it yields direct information about $\mathrm{Re}\,\chi^{(3)}$ and $\mathrm{Im}\,\chi^{(3)}$, including their signs. Being able to resolve the real and imaginary parts of the nonlinearity is important because most all-optical switching applications are based on effects arising from $\mathrm{Re}\,\chi^{(3)}$, namely the nonlinear refractive index n_2. A knowledge of $\mathrm{Im}\,\chi^{(3)}$ is also important because nonlinear absorption processes usually represent limited performance conditions for such applications.

2. EXPERIMENTAL SET-UP

The Z-scan technique is based on the observation of the change in the far-field pattern of a focused Gaussian beam, due to distortion when the sample is scanned through the focal plane, along the optical axis. This distortion is caused by the nonlinear response of the sample. When nonlinear absorption is present, transmission changes however can be due to both refractive and absorptive nonlinear processes. A detector gathering all the transmitted light will detect changes due to the change in the nonlinear absorption with position, whereas an apertured detector will detect changes due to the effect of both nonlinear absorption and refraction in the sample.

The sample studied was an 0.8 μm thick selenium film, grown by evaporation onto a Corning 7059 glass substrate. The absorption spectrum of the sample is shown in Fig. 1. From this spectrum, it is evident that linear absorption at the laser wavelength is very low. The optical bandgap (E_g) of selenium is 2.1 eV, and the photon energy ($\hbar\omega$) of the light employed was 1.165 eV. Operation was therefore close to a two-photon absorption resonance, $\hbar\omega/E_g = 0.55$.

The laser employed was a Nd:YAG laser, with active-passive mode-locking, producing 20 ps (FWHM) pulses with a 1.064 μm wavelength and a 10 Hz repetition rate, according to the laser manufacturer specifications. The pulses are Gaussian in shape, and are focused down to a spot size (HW1/eM in irradiance) r_0 of 21 μm, resulting in a beam with a diffraction length (Rayleigh range) $z_0 = 2.5$ mm. The beam waist was measured

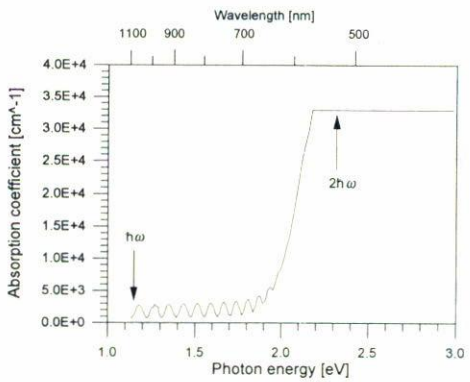

FIGURE 1. Amorphous selenium thin film absorption spectrum. The oscillations observed for low photon energies (long wavelengths) are due to Fabry-Perot effects in the film. The flat line for photon energies > 2.2 eV is due to detection limitations in the spectrometer used. Also shown are the photon energy of the Nd:YAG laser and the corresponding two-photon energy.

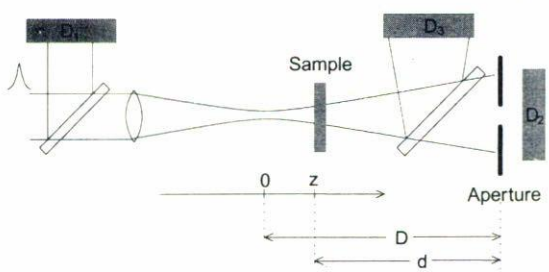

FIGURE 2. Schematics of the experimental set-up for the Z-scan technique, see text for details.

by imaging the focal plane into a CCD camera and measuring the gaussian profile of the beam. From this, it is easily seen that the sample thickness L fulfills $L \ll z_0$, a condition needed in the analysis of the Z-scan results. Figure 2 shows schematically the set-up used to perform the experiments. The signal of a detector D_2 placed behind a finite aperture in the far field is recorded while the sample position z along the optical axis is scanned through the focal plane. The used of a beam splitter in the far field, makes it possible to detect the apertured detector and a non-apertured detector D_3, sensitive to absorption changes only, simultaneously. Large area silicon photodiodes are used to detect the signals. The detected signals are processed in a box-car integrator, and they are calibrated against a calibrated pyroelectric energy meter.

3. RESULTS AND DISCUSSION

Figure 3 shows the experimental results for the transmittance through the closed-aperture detector for a pulse energy of 8.3 μJ, corresponding to an on-focus peak irradiance, inside the sample, of 23 GW/cm^2. The transmittance is normalized to the linear transmittance value, measured when the sample is away from the focal plane of the beam.

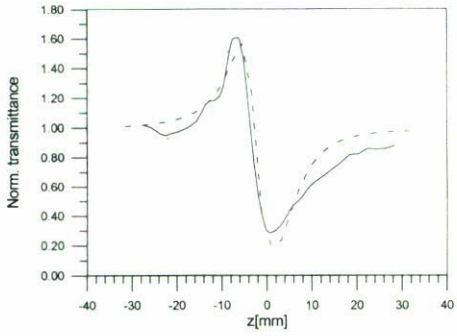

FIGURE 3. Closed-aperture Z-scan measurements in a 0.8 μm thick Se sample. The aperture transmittance was $S = 0.22$. The peak irradiance was 23 GWcm^{-2}. The solid line represents the experimental data, and thebe dotted line the fit made to the data.

The results show the signature of a negative n_2 for Se, a pre-focal transmittance maximum (peak) followed by a post-focal transmittance minimum (valley). The unapertured -"open" D_3 detector showed no discernible transmittance changes for the irradiance used, indicating a small value of the two photon absorption coefficient.

The experimental results can be modeled assuming that the nonlinear response of the sample consists of an absorption coefficient and a refractive index that are dependent on the light irradiance I in the following way:

$$\alpha(I) = \alpha_0 + \beta I, \tag{1}$$

$$n(I) = n_0 + n_2 I, \tag{2}$$

where n_2 is the nonlinear refractive index, directly proportional to $\mathrm{Re}\,\chi^{(3)}$ [$n_2 = \mathrm{Re}\,\chi^{(3)}/(n_0^2\,\varepsilon_0\,c)$], and β is the two photon absorption coefficient, $\beta = 4\pi \mathrm{Im}\,\chi^{(3)}/(\lambda n_0^2\,\varepsilon_0\,c)$, when SI units are used. In order to model the closed-aperture Z-scan results, a detailed calculation of the beam propagation through the sample, and through free space from the sample back-face to the plane of detection has to be made. The evolution of the beam inside the sample is calculated by solving the relevant wave equation for the electric field envelope $E(z, r, t)$, assuming the field is a gaussian function of the radial coordinate r, and z is the sample position relative to the focal plane. The fact that no transmittance changes through the "open aperture" detector are detected, gives an upper limit for the value of the β coefficient. Under these circumstances, since no transmittance changes were detected within a 1% (roughly the error on the experimental results), we can establish that $\beta < 5.6$ cm/GW [11].

Since the experimental results show the effect of nonlinear absorption to be negligible, the nonlinear propagation through the sample can be calculated considering linear absorption and the nonlinear phase change $\Delta\phi_{NL}(z'; z, r, t)$ as a function of z' position within the sample as [12]

$$\frac{d\Delta\phi_{NL}}{dz'} = \frac{2\pi}{\lambda} n_2 I. \tag{3}$$

The total nonlinear phase change $\Delta\phi_{NL}(L;z,r,t)$, with L the sample thickness, in the external self-focusing approximation, *i. e.* when the effect of induced phase changes on beam propagation inside the sample is negligible, will be obtained by integrating Eq. (3) over the sample thickness, with $I(z') = I_0 \exp(-\alpha_0 z')$. The electric field at the apertured detector plane, situated a distance D from the focal plane, $E_{\rm ap}(z+d,r,t)$ is calculated using the Huygens-Fresnel formalism [12]

$$E_{\rm ap}(z+d,r,t) = \frac{2\pi}{\lambda}\exp\left(\frac{i\pi r^2}{\lambda d}\right)\int_0^\infty r'dr' E_{\rm out}(z,r',t)\exp\left(-\frac{i\pi r'^2}{\lambda d}\right)J_0\left(\frac{2\pi r r'}{\lambda d}\right), \quad (4)$$

where $E_{\rm out}(z,r,t) \propto \sqrt{I(L,z,r,t)}\exp[i\Delta\phi_{NL}(L;z,r,t)]$ is the electric field at the sample exit face, and J_0 is the zeroth-order Bessel function. Finally, the apertured detector transmittance $T(z)$ is obtained by integrating $I_{\rm ap} \propto |E_{\rm ap}(z,r,t)|^2$ up to the aperture radius $r_{\rm ap}$ given through $S = 1 - \exp(-2r_{\rm ap}^2/\omega^2(D))$, where S is the linear aperture transmittance and $\omega(D)$ is the beam spot-size in the aperture plane in the absence of the sample.

Figure 3 also shows the best fit to the experimental closed-aperture Z-scan data obtained using the beam propagation algorithm outlined here. An n_2 value of $-(0.06 \pm 0.02)$ cm^{2}GW^{-1} is extracted from the theoretical fit. The observed value for n_2 is three orders of magnitude larger than the ones observed for As_2S_3 and $Ge_{33}As_{12}Se_{55}$ at the same wavelength [5]. The upper limit for the two-photon absorption coefficient β that can be inferred from the present experiments, $\beta < 5.6$ cmGW^{-1}, is consistent with what has been measured for these other chalcogenides. The energy bandgap of amorphous Se is very similar to that of the chalcogenides studied in the cited work, and resonance conditions are therefore very similar. As in those studies, two-photon absorption is certainly present, and should enhance the nonlinearity. However, the nonlinear refractive index measured in this case is anomalously large for the existing resonance condition even taking into account the two-photon absorption enhancement. From this, we can conclude that some other effect or mechanism must be present to account for the measured n_2 value. Anomalously large n_2 values have been observed in metal-doped chalcogenides, for example [13]. One possible explanation for this behaviour in the case of Se, can be an structural one, the large refractive nonlinearity observed could originate in the fact that selenium tends to form chains and rings that are planar, whereas other chalcogenides like $GeSe_2$ tend to form tetrahedral structures. This could in principle produce a two-dimensional confinement of the electrons that could in turn enhance the nonlinearity. Other mechanisms that can be present are free-carrier absorption or exciton enhancement, both produced by two-photon transitions. In fact, the influence of the latter, has been observed in the on-resonance nonlinearity of amorphous Se clusters [14].

4. CONCLUSIONS

We have measured the nonresonant nonlinear refractive index for an amorphous selenium thin film. The large n_2 value found in the present studies would seem to be in line with the larger nonlinearity observed on- and near-resonance for selenium over other chalcogenide glasses. However the large discrepancy with results for other chalcogenides

in the present off-resonant condition would seem to indicate that processes other than two-photon absorption could be present. Further studies are needed to elucidate this point. In particular, time-resolved techniques such as DFWM could be used to find out whether there is a further enhancement by one of the other processes mentioned above. Such mechanisms would have a finite response time, given by the recombination time of the carriers, and could then be separated from two-photon absorption, that has an instantaneous response time. Recent results with an excite-probe technique with 100 fs long pulses at 850 nm [15], show an induced absorption effect that recovers within 50 ps, that can be attributed to free-carrier absorption, and would point in this direction, but further work will be needed to completely elucidate this point.

REFERENCES

1. J. Hajto and I. Janossy, *Phil. Mag. B* **47** (1983) 347.
2. L. Toth, J. Hajto, and G. Zentai, *Solid State Comm.* **23** (1977) 185. (1977) 185.
3. E. Haro-Poniatowski, M. Fernandez Guasti, E.R. Mendez, and M. Balkanski, *Opt. Commun.* **70** (1989) 70.
4. E. Haro *et al.*, *Phys. Rev. B* **32** (1985) 969.
5. R. Rangel-Rojo *et al.*, *Opt. Commun.* **109** (1994) 145.
6. V. Chumash *et al.*, *SPIE Proceedings*, **2287** (1994) 183.
7. M. Asobe, K. Suzuki, T. Kanamori, and K. Kubodera, *Appl. Phys. Lett.* **60** (1992) 1163.
8. P.H. Keck, *J. Opt. Soc. Am.* **41** (1951) 53.
9. E. Haro-Poniatowski, M. Fernandez Guasti, S. Camacho Lopez, and F. Ruiz, *Physica A* **207** (1994) 329.
10. M. Sheik-Bahae *et al.*, *IEEE J. Quantum Electron.* **26** (1990) 760.
11. See for example section 3.4.2 of R. Rangel Rojo, "Picosecond third-order nonlinearities in organic materials and chalcogenide glasses", Ph.D. Thesis, Heriot-Watt University, Edinburgh (1994).
12. E.W. Van Stryland *et al.*, *Opt. Engineering* **24** (1985) 613.
13. T.I. Kosa *et al.*, *J. Non-Cryst. Solids* **164-166** (1993) 1219.
14. V.P. Mikhailov, *1944 IEEE Nonlinear Optics: Materials, Fundamentals, and Applications*, (1995) 251.
15. R. Rangel Rojo and V. Garces Chavez, presented at XXXIX Congreso Nacional de Física, *Suplemento Bol. Soc. Mex. Fís.* **10** (1996) 110.