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OPTICAL LIMITING BEHAVIOR OF INFRARED CHALCOGENIDE GLASSES

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Optical limiting properties of several chalcogenide glasses have been studied at 1.064 µm with a picoseconde pulsed Nd:YAG laser. These infrared glasses have been chosen in the ternary Ge-As-Se vitreous system, in which the glassy matrices present high third order non linear optical properties i.e. high non linear refractive indices (n_2) and high non linear absorption coefficients (β). When following the transmitted intensity versus the incident intensity these glasses show a real optical limiters behavior. Indeed, for example, for an incident intensity of 4 GW/cm^2 through a sample of $GeAs_2Se_2$ which presents a non linear absorption coefficient of 5.9 cm/GW, the transmitted intensity is only 0.62 GW/cm^2 for a sample thickness of 1.24 mm.

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1. Introduction

Using high power laser is very current in many applications and powerful laser beam can destroy optical sensors. So it is important to study materials with an optical limiting behavior to protect those detectors. More particularly, infrared materials showing such an optical limiting behavior can be of great interest for military applications. For example, an optical limiter could be added in the optical device of an infrared camera to protect the detectors against high power laser pulses. Optical limiters must also present different properties like a high linear transmission throughout the detector bandwidth, a good resistance to laser-induced damage and stability in time. Different non-linear optical phenomena such as non linear refraction, non linear absorption and non linear scattering can be used to obtain optical limiting properties which can be observed in different materials [1, 2]. Fullerene, fullerene derivative [3], or organometallic compounds [4] for example, exhibit reverse saturable absorption properties and an optical limiting behavior. Another non linear absorption, the multi-photon-absorption, leads to optical limitation in semiconductors or in several organic molecules offering donor-acceptor sites [5]. Other media like carbon nanotube suspensions [6, 7] or metal suspensions [8, 9] present also optical limiting properties.

In the case of chalcogenide glasses the transmittance range contains the two atmospheric windows 3-5 µm and 8-12 µm and these materials could be used for the realization of thermal camera for example. Furthermore, recent works have shown high third order non-linear optical properties for these materials. More precisely, high non linear refractive indices (n_2) combined with high two photon absorption (2PA) coefficients, have been measured using the Z-scan technique or Mach-Zehnder interferometry [10, 11, 12, 13]. The non-linear refractive index of chalcogenide glasses can be 400 to 800 times ($\approx 10^{-17}$ m^2/W) as high as the non-linearity of silica glass and the two photon absorption coefficient can reach 6 cm/GW [12]. The origin of those high third order non-linear optical properties is attributed to the highly polarizable electronic lone pair richness of chalcogenide glasses. Indeed, sulfur and selenium present two lone pairs and arsenic one lone pair highly polarizable. Then, it is of great interest to characterize the eventual optical limiting properties of these glasses.

2. Experimental

2.1. Glasses synthesis

Glasses used in optical devices need meticulous synthesis. The chalcogenide glasses are prepared in a silica tube under vacuum (10^{-5} mbar). High purity elements (Ge, As, Se) are used for the glass preparation (99.999 % purity). Arsenic and selenium present surface oxidation and need to be purified by a thermal treatment before the synthesis, arsenic oxide and selenium oxide being more volatile than As and Se respectively. After the purification, the elements are placed in a silica reaction tube. Then the tube is sealed and heated to 700-800 °C (depending on the composition) in a rocking furnace. The ampoule is maintained 12 hours at this temperature to reach a good reaction between the different elements and a good homogenization of the melt. The glass is obtained by quenching the melt and annealing it near its glass transition temperature (T_g) to reduce the mechanical stress produced by the cooling. The glass is cut in small disks (≈1mm thickness) which are polished with two plan and parallel sides. The Ge-As-Se glass forming region is given in the Fig. 1, on which are plotted the different glasses studied here for their optical limiting behavior.

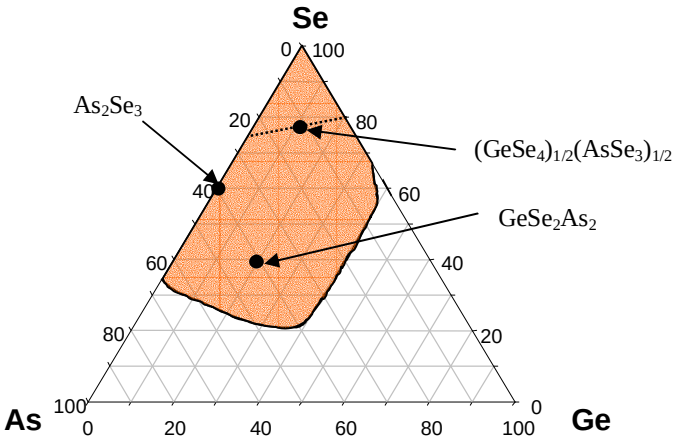

Fig. 1. Ge-As-Se glass forming region [14].

2.2. Optical limiting measurements set-up

The setup used for the optical limiting measurements is presented in Fig. 2. Excitation is provided by a Nd:YAG laser delivering 30 ps single pulses at 1064 nm. The input intensity is modulated by the mean of a half-wave plate and a Glan prism (not shown), in order to keep a linear polarized light for the probe, the reference and the pump beams. We use a control beam produced at the input of the set-up from the first reflection on the beam splitter (BS) in order to calculate the incident intensity onto the sample. This method is well adapted to our laser, which exhibits a good stability in the spatial intensity distribution but relatively large energy fluctuations from one laser shot to the other. The second reflection on the beam-splitter (BS) is used as a probe beam. Finally the transmitted (high intensity) pump beam is focused on the non-linear sample by the mean of the lens L (15 cm focal length). An image of this pump beam is formed on the CCD using lens L_2. The pump and probe pulses are spatially combined onto the sample at a sufficiently small angle (typically 4°). By mean of the prism P mounted on a translation stage we have the ability to perform temporal pump - probe experiments. Here the prism P is adjusted to produce perfect temporal overlap of the pulses (time-point zero between the pump and the probe). At the entrance of the cell and in the center of the pump beam, the pump peak-intensity I(0,0) lies within the $0–10^{16}$ W/m^2 range. The image of the non linear material (NL) input plane is formed on the CCD camera using lens L_2 (20 cm focal

length). The geometrical configuration of the set-up and the used focal lengths (for L_1 and L_2) allow us to acquire both images (due to the pump and the probe) with the same magnification (G = 2).

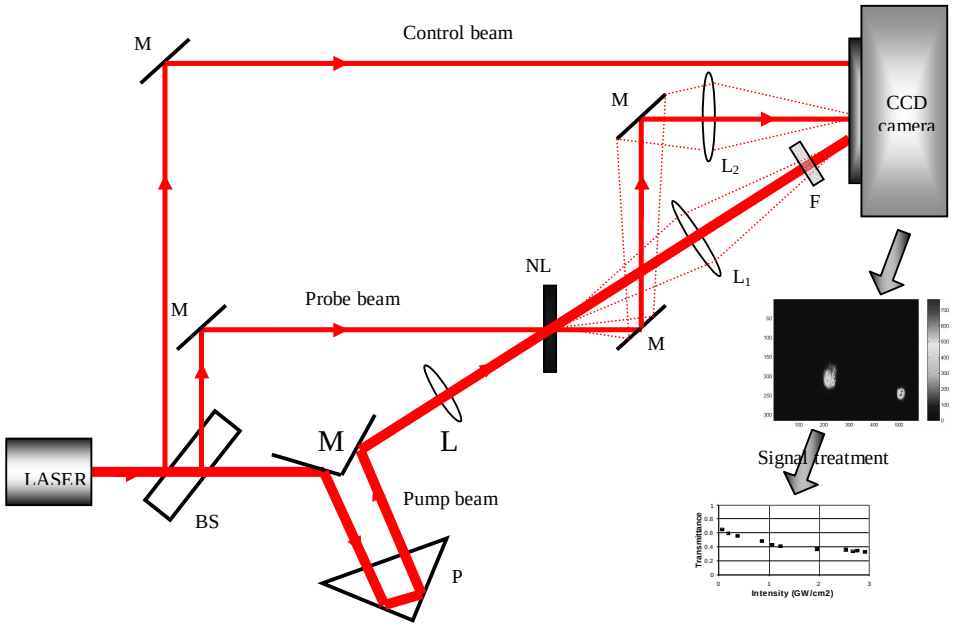

Fig. 2. Experimental set-up for the measurement of the optical limiting behavior of infrared chalcogenide glasses, NL: non linear sample, L: lens, M: mirrors, BS: beam splitters, F: Neutral filter, P: Prism.

The image receiver is a 1000 × 1018 pixels cooled CCD camera Hamamatsu C4880 used with a fixed gain. Camera pixels present 4095 gray levels. Neutral calibrated filters are necessary to use the camera within its linear range. The pixel is a 12µm × 12µm square. It must be noted that, in what follows, the intensity I(x,y) is measured considering an elementary area in the NL plane equal to $\Delta s = 6 \times 6\ \mu m^2$. One can note that the image produced by the probe beam is used to control optical damage that may occur after high intensity laser shot in the tested material.

3. Results

Physical and optical properties like the glass transition temperature, the linear absorption coefficient and the band-gap wavelength of several chalcogenide glasses are given in table 1. The glass transition temperature is varying between 117 ° C and 300 °C depending on the composition. The band-gap are at the end of the visible window, between 580 and 830 nm (the band-gap wavelength is given when the linear absorption coefficient reaches 10 cm^{-1}). The linear absorption coefficient at 1064 nm (Nd:YAG laser wavelength) is varying between 0.30 cm^{-1} and 0.61 cm^{-1}.

Table 1. Physical and optical properties of several chalcogenide glasses.

Composition	T_g (°C)	λ_{gap} (nm)	α_{1064} (cm^{-1})
As_2S_3 ($As_{40}S_{60}$)	195	584	0.30
$GeSe_4$ ($Ge_{20}Se_{80}$)	160	737	0.34
$GeSe_6$ ($Ge_{14}Se_{86}$)	117	746	0.41
$(GeSe_4)_{1/2}(AsSe_3)_{1/2}$ ($Ge_{11}Se_{11}Se_{78}$)	133	750	0.30
As_2Se_3 ($As_{40}Se_{60}$)	185	809	0.61
$GeAs_2Se_2$ ($Ge_{20}As_{40}Se_{40}$)	330	829	0.50

T_g, glass transition temperature; λ_{gap}, band-gap wavelength; α_{1064}, linear absorption coefficient at 1064 nm.

As an example, the Fig. 3 shows the transmittance spectrum for arsenic-selenium glass (As_2Se_3), obtained from a Varian spectrophotometer (Cary 5) between 0.5 µm and 2 µm and from a Bomem spectrophotometer (Michelson 100) between 2 µm and 20 µm. The high linear refractive index of chalcogenide glasses (between 2.4 –2.7) is responsible for high Fresnel reflections and leads to a maximum linear transmission of 66 % for As_2Se_3.

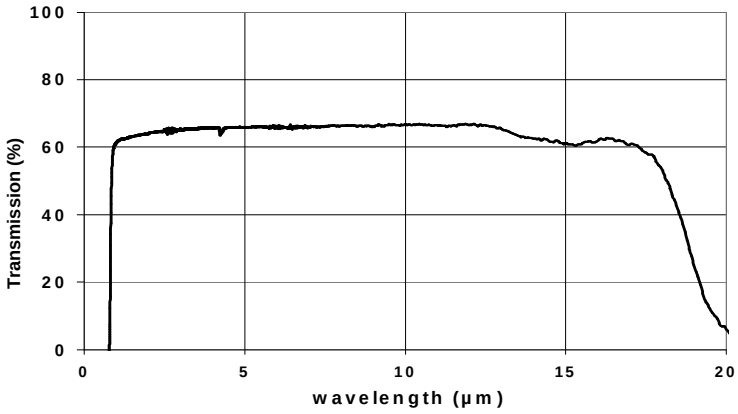

Fig. 3. As_2Se_3 infrared transmission window (1.44 mm thickness).

We have studied the optical limiting behavior of three chalcogenide glasses, $(GeSe_4)_{1/2}(AsSe_3)_{1/2}$, As_2Se_3 and $GeAs_2Se_2$. For the three glasses, we have measured the transmitted intensity when the incident intensity increases from 0.1 GW/cm^2 up to 4 GW/cm^2. The three different curves are shown on the Fig. 4. The straight line corresponds to the linear transmission for a material without non-linear effect.

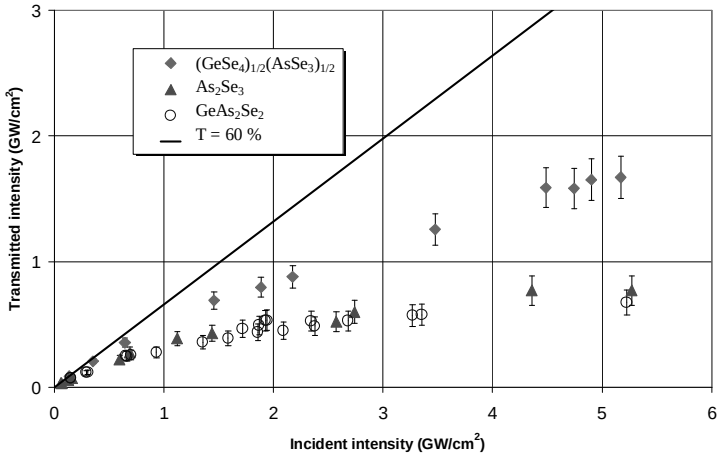

Fig. 4. Optical limiting behavior of $(GeSe_4)_{1/2}(AsSe_3)_{1/2}$(◆), As_2Se_3(▲) and $GeAs_2Se_2$(●). The sample thicknesses are respectively 1.18 mm, 1.44 mm and 1.26mm.

4. Discussion

We show in Fig. 5, how we can use the non-linear refraction (n_2) and the two photon absorption in optical limiting devices. In each case the transmission of the non-linear material decreases when the laser intensity increases. In our example we take a positive non-linear refractive index, which is the case for chalcogenide glasses. The two photon absorption can be observed only when the laser wavelength is between λ_{gap} and 2 λ_{gap}.

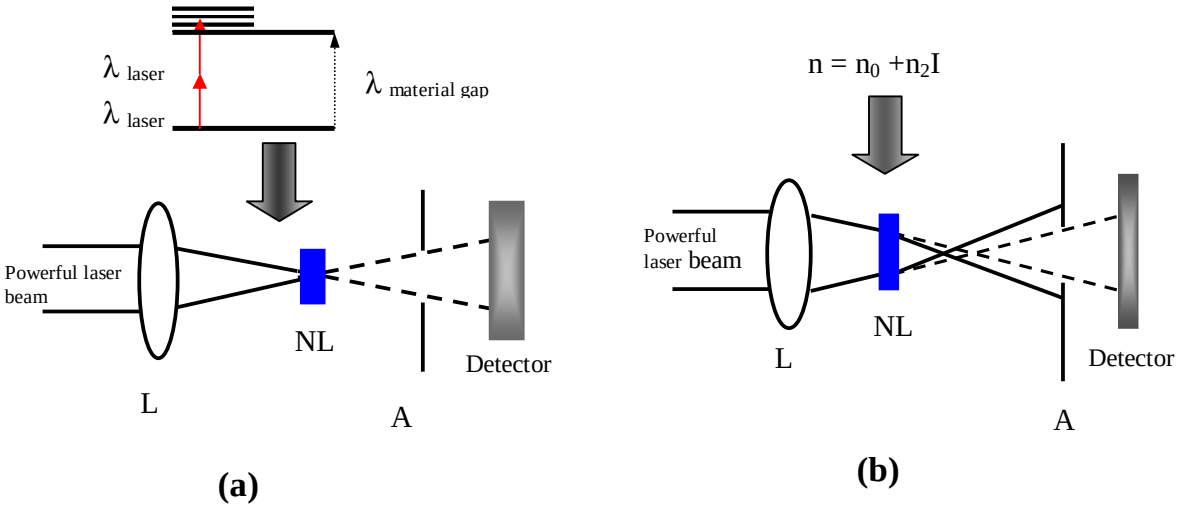

Fig. 5. Optical limiters based on third order non linear optical properties: (a) two photons absorption, (b) non linear refraction. L : lens, NL : non linear material, A : Aperture.

High non linear refractive indices (n_2) combined with high two photon absorption (2PA) coefficients, have been previously measured using the Z-scan technique and Mach-Zehnder interferometry [12, 13]. These results are presented in Table 2. Then we have studied the optical limiting behavior of three chalcogenide glasses, $(GeSe_4)_{1/2}(AsSe_3)_{1/2}$, As_2Se_3 and $GeAs_2Se_2$ chosen for their strong two photon absorption coefficients measured by Z-scan at 2.7, 4.5 and 5.9 cm/GW respectively (Table 2).

Table 2. Comparison of non linear refractive index and two photons absorption coefficient between a Mach - Zehnder interferometer method and a Z - scan method for several chalcogenide glasses and CS_2.

	Mach-Zehnder interferometer		Z-scan	
	β (cm/GW)	n_2 x 10^{-18} (m^2/W)	β (cm/GW)	$n_2 \times 10^{-18}$ (m^2/W)
CS_2	0.0	3.1	0.0	3
As_2S_3	0.08	5.0	0.1	4.5
$GeSe_4$	1.8	8.3	1.7	13
$GeSe_6$	1.7	11.5	1.5	17
$(GeSe_4)_{1/2}(AsSe_3)_{1/2}$	2.5	12	2.7	22
As_2Se_3	4.4	19	4.5	18
$GeAs_2Se_2$	5.4	10	5.9	18.5

β, two photon absorption coefficient; n_2, non linear refractive index.

We can see (Fig. 4) for the tested glasses that the transmitted intensity moves away from the reference line when the input intensity increases. This indicates for those three glasses a real behavior of optical limiters. Indeed for an incident intensity of 5 GW/cm^2 through the $GeAs_2Se_2$ glass, the transmitted intensity is only 0.67 GW/cm^2. If the glass sample had not presented optical limiter behavior the transmitted intensity would have been 3 GW/cm^2 (Table 3). The glass sample divides by four the transmitted intensity. However when the input intensity exceeds 5.5 GW/cm^2 all the glassy samples were locally damaged by the laser beam.

Table 3. Optical limiting efficiency of studied glasses.

I_{inc} (GW/cm^2)		1	2	3	4	5
	$I_{inc} \times T_{lin}$ (GW/cm^2)	0.6	1.2	1.8	2.4	3
$(GeSe_4)_{1/2}(AsSe_3)_{1/2}$	I_{trans} (GW/cm^2)	0.53	0.80	1.20	1.25	1.65
	ΔI (GW/cm^2)	0.06	0.4	0.6	1.16	1.35
	$I_{inc} \times T_{lin}$ (GW/cm^2)	0.66	1.32	1.98	2.64	3.3
As_2Se_3	I_{trans} (GW/cm^2)	0.38	0.50	0.65	0.73	0.8
	ΔI (GW/cm^2)	0.28	0.82	1.33	1.91	2.5
	$I_{inc} \times T_{lin}$ (GW/cm^2)	0.6	1.2	1.8	2.4	3
$GeSe_2As_2$	I_{trans} (GW/cm^2)	0.27	0.45	0.57	0.62	0.67
	ΔI (GW/cm^2)	0.33	0.75	1.23	1.78	2.33

I_{inc}, incident intensity; T_{lin}, linear transmittance; I_{trans}, Transmitted intensity; $\Delta I = (I_{inc} \times T_{lin}) - I_{trans}$

In order to identify the origin of the optical limiting behavior we have determined the different transmittances (total, linear and non linear). For that, we used three acquisitions on the CCD: a first acquisition without the sample to control the intensity, a second acquisition with the sample at high intensity for measuring the total transmission (T_{tot}), a last acquisition with the sample and with a weak intensity to control the linear transmitance (T_{lin}).

The non linear transmittance (T_{nl}) induced only by the non linear effects is :

$$T_{nl} = T_{tot} / T_{lin} \tag{1}$$

The theoretical expression of a non-linear transmittance ($T_{nl\text{-}theoretical}$) produced by two photon absorption is given by the equation (2) [15]:

$$T_{nl\text{-}theoretical} = \frac{1}{1+\beta I_0 L_{eff}} \tag{2}$$

$$L_{eff} = \frac{1-\exp(-\alpha L)}{\alpha} \tag{3}$$

With α is the linear absorption coefficient, β is the non-linear absorption coefficient and L the sample thickness.

We calculated the theoretical non linear transmission obtained by the equation (2) using the two photon absorption coefficients measured by Z-scan (Table 2). The comparison between the calculated non linear transmission and the experimental non linear transmission for the glass $(GeSe_4)_{1/2}(AsSe_3)_{1/2}$ is given in the Fig. 6. The theoretical curve (continuous line) is given by the equation (2) for a non linear absorption coefficient of 2.7 cm/GW and 1.18 mm sample thickness. The experimental non linear transmitance which represents only the non linear contributions is determinated from the equation (1). The experimental points are in good agreement with the theoretical curve. This indicates, as expected, that the optical limiting behavior is principally induced by the two photon absorption.

5. Conclusion

We have studied three glasses of the ternary Ge-As-Se system, which present high two photons absorption coefficients. Those three glasses exhibit an optical limiting behavior characterized with help of a Nd:YAG pulsed laser at 1.064 µm. For the $GeAs_2Se_2$ glass sample, the transmitted intensity is divided by four compared to the linear transmission for a 1.26 mm thickness sample. The comparison between the theoretical non linear transmission induced by a two photons absorption effect and the experimental non linear transmittance shows that the optical limiting properties are principally due to the non linear absorption. The optical limiter behavior of such infrared glasses is of interest for applications in the protection of infrared detectors.

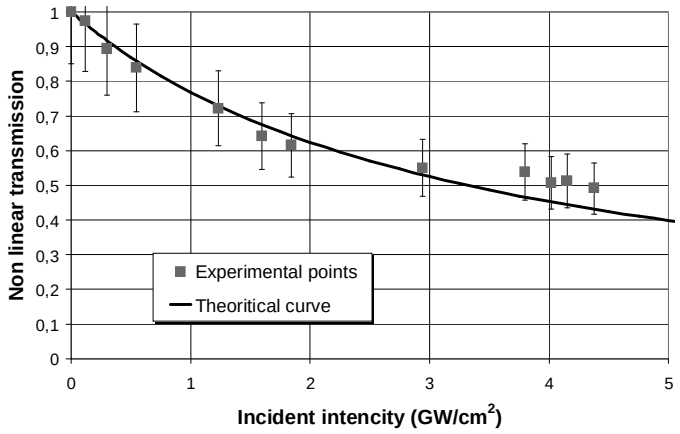

Fig. 6. Theoretical non linear transmittance and experimental points for $(GeSe_4)_{1/2}(AsSe_3)_{1/2}$ glass (1.18 mm sample thickness and β =2.7 cm/GW).

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