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***Abstract*—This study investigates polarization-dependent photoinduced effects in As_2S_3 and As_2Se_3 thin films excited by fs-laser pulses operating in the telecommunications range. The findings demonstrated the localized formation of structural defects, including crystallization, and revealed anisotropy-induced birefringence that varied with laser parameters.**

Keywords—*Photoinduced effects, thin films, femtosecond laser, structural defects.*

I. Introduction

Chalcogenide glasses are amorphous materials composed of sulfur, selenium, or tellurium, combined with elements such as arsenic or germanium [1]. These materials exhibit extensive light-induced effects, including photocrystallization, photoamorphization, and polarization-dependent effects, which enable reversible or irreversible transformations [2], [3], [4]. The density and reversibility of these effects depend on various factors, including the energy of the excitation photon and phonon, as well as the type of excitation, whether it is sub-bandgap, above-bandgap, or super-bandgap [5]. This ability to tune these characteristics makes chalcogenide glasses highly valuable for integrated optics, photonic devices, and optical communications [4], [6].

Research over the past decades has extensively studied light-induced effects in chalcogenide glasses, including sub- and above-bandgap excitation [5]. Specifically, one of the most extensively studied photoinduced phenomena is photocrystallization, which has been found to be influenced by light polarization [4], [7].

Despite advances, limited research exists on the nonlinear optical behavior of chalcogenide glasses in the telecommunications range (sub-bandgap excitation). This knowledge gap extends to the nonlinear optical regime, where studies addressing the formation and effects of photoinduced structural defects are still scarce. Understanding how femtosecond laser-induced modifications influence both the linear and nonlinear optical properties is essential for the development of advanced photonic applications. Characterizing the nonlinear optical properties of thin films at the micro- or nanoscale presents additional challenges, as many of these properties strongly depend on film thickness. Moreover, exposure to high-intensity irradiation can potentially damage the material or induce irreversible structural transformations [8].

Among the available techniques for probing nonlinear optical responses, nonlinear elliptical rotation (NER) stands out as a highly sensitive and non-destructive method. This technique is particularly advantageous for thin films, as it enables the investigation of ultrafast and low-signal phenomena without requiring high input intensities that could damage the sample [9].

Here, structural nonlinear optical properties and defect evolution of arsenic sulfide (As_2S_3) and arsenic selenide (As_2Se_3) thin films under femtosecond laser irradiation in the telecommunications regime were studied. Nonlinear elliptical rotation was used to investigate the nonlinear refractive index and its relationship with the polarization-dependent effects of induced photoanisotropy and photocrystallization.

II. Methods

Chalcogenide solutions were prepared by dissolving arsenic trisulfide or arsenic selenide in propylamine (133 g/L) within a nitrogen glovebox. Thin films of As_2S_3 and As_2Se_3 were produced using spin-coating at 2000 rpm for 10–20 seconds on glass substrates. The films were vacuum baked at 60 °C for 1 hour and then at 110 °C for 7 hours, resulting in a thickness of 500 nm. Optical properties were analyzed using a Shimadzu UV-1800 spectrophotometer. The linear refractive index was determined by analyzing the absorption spectrum using the Pointwise Unconstrained Minimization Approach (PUMA), which is a mathematical algorithm based on a point-to-point error minimization problem.

NER measurement was performed using a femtosecond Ti:sapphire laser system (Dragon from K&M Labs), operating at 780 nm with a pulse duration of 40 fs and a repetition rate of 1 kHz, along with an optical parametric amplifier to achieve wavelengths in the telecommunications spectral range.

Figure 1 displays the single-beam NER setup. Polarization states were controlled using a quarter-wave plate and the laser beam was focused onto the sample with a 20x microscope objective. Hence the beam passes through a spinning analyzer before reaching a photodetector. Finally, the polarization rotation signal was monitored using a dual-phase lock-in amplifier to determine changes in polarization states.

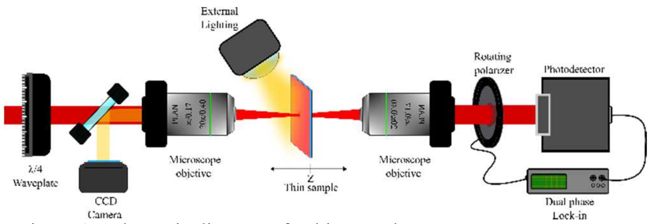

Figure 1. Schematic diagram of a thin sample NER

III. RESULTS AND DISCUSSION

A. Linear optical characterization

Figure 2 displays the optical absorption spectra for both samples. The Tauc plot (insets) was applied for the effective optical bandgap determination. The bandgap energy (E_g) values obtained were 2.15 eV for As_2S_3 and 1.07 eV for As_2Se_3, respectively.

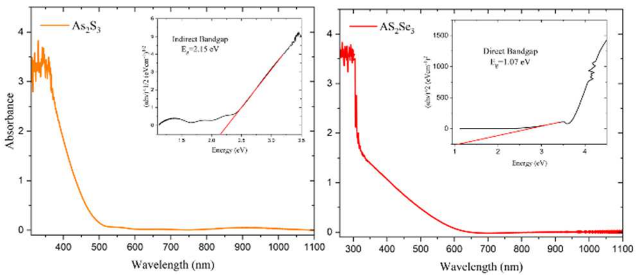

Figure 2. Absorption spectra of the As2S3 and As2Se3 thin films.

In Fig. 3, the transmittance spectra of the two samples are shown, where the oscillatory behavior is due to interference fringes resulting from the film thickness. The values of the linear refractive index calculated by the PUMA were 2.078 for As_2S_3 and 1.971 for As_2Se_3. However, the values for the refractive index found in the literature are 2.4 for the As_2S_3 and 2.7 for the As_2Se_3 [10]. This difference is mainly associated with the thin film thickness.

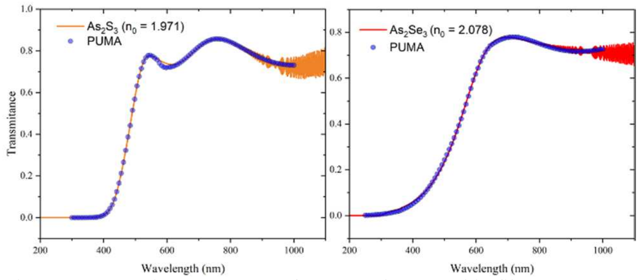

Figure 3. Transmittance spectra of As_2S_3 and As_2Se_3 thin films.

B. NERs measurement

The spectrum of the nonlinear refractive index (n_2) as a function of the wavelength for both samples is shown in Fig. 4. A high dispersion in the n_2 was observed. It is important to note that these materials are primarily recognized for exhibiting a wide range of photo-induced effects [4]. Among these effects, many depend on the polarization of the incident light [11]. As a result, the NER signal could be affected by these structural phenomena.

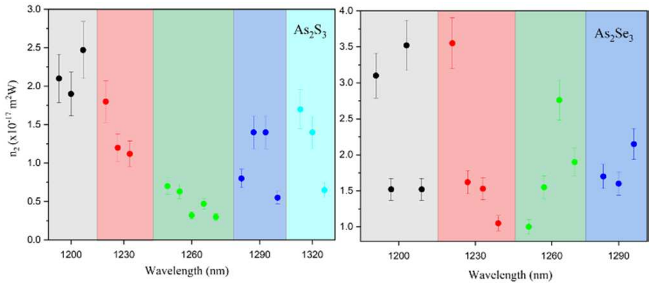

Figure 4. Spectra of the nonlinear refractive index of As_2S_3 and As_2Se_3 thin films obtained by NER technique.

Therefore, to determine the origin of the material's nonlinearity, an analysis of the amplitude behavior of the NER signal ($<\alpha>_{lock-in}$) as a function of the quarter-wave plate rotation degree (ϕ) was performed. Equation (1) describes the ellipse rotation signal as a function of the sample position.

$$<\alpha(z)>_{lock-in}=\frac{\omega\sin(2\phi)\,Bz_0I}{8c^2\epsilon_0 n_0\sqrt{2}}\left[arctan\left(\frac{z_B}{z_0}\right)-arctan\left(\frac{z_A}{z_0}\right)\right] \quad (1)$$

This expression relates the α(z) angle with the angular frequency (ω), the intensity of the laser beam (I), the speed of light (c), and the B coefficient, which is correlated with the nonlinear refractive index. The last term is known as the focalization regime and is associated with the sample thickness (L) and the Rayleigh length.

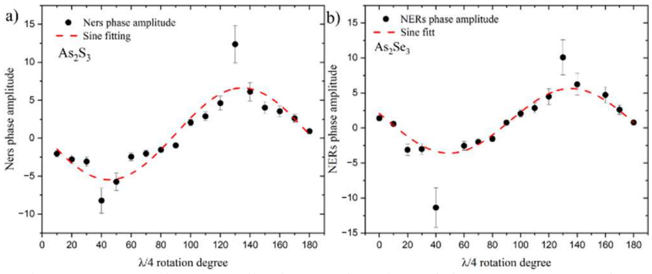

Figure 5. NER phase amplitude as a function of the quarter-wave plate rotation for both thin films.

Figure 5 illustrates that both films exhibit the expected sinusoidal behavior, where the phase amplitude is minimized for linear polarization (0° and 90°) and maximized for circular polarization (45° and 135°). Such sinusoidal behavior (red dotted lines) is normally associated with an electronic nonlinear phenomenon.

However, various authors report that chalcogenide glasses also exhibit induced birefringence and other effects such asphotoanisotropy and photoinduced dichroism when interacting with polarized light. Specifically, an optical anisotropy was observed in these materials for different polarization states (linear, circular, and elliptical polarizations) and irradiation times [11], [12]. Therefore, other orientational factors may also be present in the NER signal [8].

To explore this idea, NER measurements were conducted as a function of the excitation wavelength using various intensities. This approach is based on the observation that Eq. (1) shows a direct relationship between the rotation angle of the NER and the incident intensities. Figure 6 presents a comparison of the NER signatures obtained at 1230 nm and 1260 nm using different intensities. The absence of a systematic dependence on intensity in our measurements supports the hypothesis that structural or orientational effects contribute substantially to the NER signal, reducing confidence in a purely electronic interpretation.

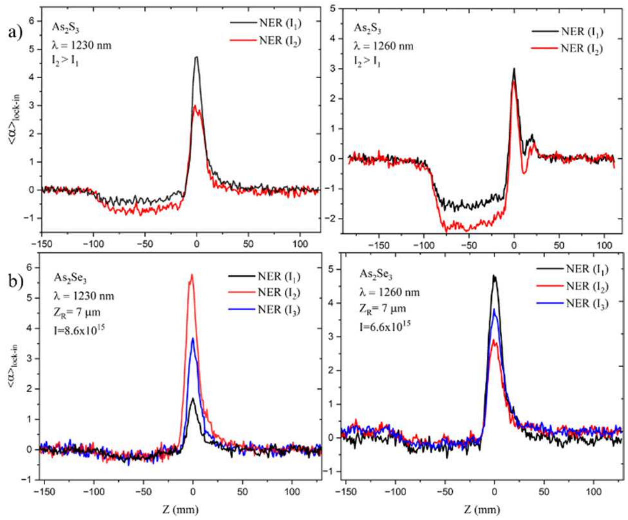

Figure 6. NER signatures comparison for different incident intensities for a) As_2S_3 and b) As_2Se_3 thin films.

Additionally, sample inspection indicate that the laser irradiation led to the formation of local structural defects. This altered surface exhibited NER signals even at relatively low intensity levels. This finding was further confirmed by conducting successive measurements. Figure 7 shows both situations. The first measure (NER_{Mea_1}) was taken at a low enough intensity that it did not modify the material's surface, while the second (NER_{Mea_2}) was taken with the same intensity but in a region that had already been modified.

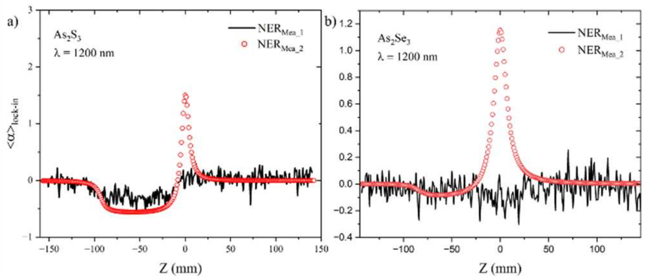

Figure 7. NER signature comparison for measures performed with a no ablation intensity inside (black line) and outside (red dots) of a modified zone.

It is possible to observe that this light-induced local defect is also producing a rotation of the incident light polarization. Therefore, the photoinduced structural change, along with the lack of relationship between the NER signal and the incident intensities, confirms the influence of the polarization-dependent linear effects, which overshadow the nonlinear effects, thereby disrupting the NER measurements.

IV. Conclusions

In this study, evidence of photoinduced effects was observed in As_2S_3 and As_2Se_3, including signals consistent with crystallization and polarization-dependent anisotropy, during femtosecond laser irradiation at telecommunications wavelengths. The NER detected signal variations that align with structural changes observed at the surface, which complicates distinguishing between electronic nonlinear responses and structure-dependent linear effects. This overlap between linear and nonlinear effects, particularly in polarization-dependent regimes, highlights the complexity of interpreting NER signals in chalcogenide materials. Consequently, the findings suggest that careful control of irradiation conditions and the use of complementary characterization techniques are essential for isolating the nonlinear responses in these systems. Overall, the work contributes to a deeper understanding of light–matter interactions in chalcogenide thin films and offers valuable insights for their application in future photonic devices.

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