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Pulse duration dependent optical nonlinearities of Bi₂Se₃ thin films

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Abstract: Topological insulators, such as the Bi₂Se₃ material, exhibit significant optical nonlinearities. This work investigates the impact of the pulse duration on the nonlinear optical responses of Bi₂Se₃ layers. Scanning electron microscopy studies have been performed to reveal the crystalline structure of the samples. The nonlinear optical performance has been investigated for a wide range of pulse durations, from 400 fs to 10 ps, using 1030 nm laser excitation. The nonlinear absorption coefficients recorded in this study range from -1.45×10^{-7} m/W to -4.86×10^{-7} m/W. The influence of two different mechanisms on optical nonlinearities was observed and discussed. Identical experimental conditions have been employed throughout the studies allowing a direct comparison of the results.

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1. Introduction

2D chalcogenide thin films have gathered enormous attention due to their importance for optical applications such as optical data storage, mode locking, and super-resolution [1–3]. The giant optical nonlinearity associated with these complex materials makes them appealing for optical applications [4–6]. One of the widely studied materials of the chalcogenide family is the Bismuth Selenide (Bi₂Se₃). The Bi₂Se₃ belongs to the category of topological insulators [7,8], defined by the presence of an insulating bandgap in the bulk and conducting states on the surface [9]. The band gap of this material is known to be 0.2 to 0.3 eV [10–12]. The higher light transmission when compared to other topological insulators, the Dirac-like narrow band gap and the broadband optical response, allow Bi₂Se₃ to be a promising candidate for several photonic applications [8,13,14]. The complexity associated with the topological insulators calls for the precise optimization of their nonlinear optical (NLO) responses with respect to the material characteristics as well as the excitation conditions for optimal performances [4,5,8,15].

The optical nonlinearities of the Bi₂Se₃ material have already been studied using various techniques [8,16–18]. Such investigations have confirmed that the material holds record values of third-order nonlinear susceptibility [6,8,17,18]. The properties of Bi₂Se₃ and similar materials, such as the crystalline state and thickness, etc., can influence the topological properties and, consequently, the nonlinear optical properties [4,18,19]. Apart from the material itself, the laser excitation parameters can also alter the optical nonlinearities. For example, the laser excitation wavelength [8,17,18] and the pulse duration can dramatically modify the NLO response [15,20,21].

Our group very recently published on the thickness dependent third order optical nonlinearities of Bi₂Se₃ layers at visible and NIR excitation wavelength [18]. The published study confirms the above mentioned impact of material and excitation characteristics on NLO responses. The current work targets to shed light on the impact of the laser pulse duration on the NLO properties, which is expected to be incredibly beneficial for scientists working with saturable absorbers,

especially for those in the field of mode-locking. More specifically, pulse duration-dependent saturable absorption studies are carried out from the femtosecond up to the picosecond regime.

2. Experimental techniques

2.1. Material preparation and characterization

For the fabrication of thin films, Bi_2Se_3 pellets have been used to deposit the 40 nm thick Bi_2Se_3 thin layers using e-beam deposition (Bühler/Leybold Optics SYRUSpro 710), as described by our group elsewhere [4,18,22]. The thin films were deposited on B270 glass substrates. The thickness of the layers, as well as the deposition rate were monitored by using an in situ quartz microbalance that delivers a precision of ± 0.2 nm. The layers were deposited at a constant rate of 0.5 nm/sec in a vacuum chamber of pressure less than 10^{-6} mbar. An additional capping layer of SiO_2 (2 nm) was deposited on top of the Bi_2Se_3 layer to prevent post-deposition oxidation. The Bi_2Se_3 layers were then annealed in an oven at 190°C for 1 hour to achieve a good crystalline structure [18].

The thin films were subjected to spectrophotometric studies before and after annealing (Figure 1), using a Perkin Elmer lambda 1050 spectrophotometer. The as-deposited (i.e., the non-annealed layer) and annealed thin films were studied using the scanning electron microscopy (SEM) technique employing a Field Emission ZEISS Gemini 500 electron microscope with a four-quadrant backscattered electron (BSE) detector to reveal their nanoplate-type structures (see results and discussion). A detailed X-ray diffraction analysis of the Bi_2Se_3 layers has been previously published by our group [18]. A rhombohedral crystalline structure of the layers has been reported therein.

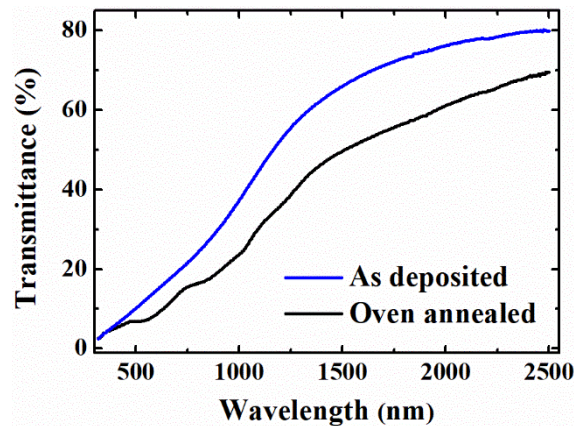


Fig. 1. Transmission spectra of the Bi_2Se_3 thin films

2.2. Nonlinear optical investigation

A traditional Z-Scan system has been employed to study the optical nonlinearity of the material as a function of the pulse duration, as mentioned elsewhere [4,18,23]. A hybrid (crystal/fiber), passively mode-locked laser delivering 400 fs duration pulses at 1030 nm has been employed. The oscillator provides pulses at a 40 MHz repetition rate. By means of a pulse picker and an acousto-optic modulator, both integrated in the laser system, the repetition rate can be adjusted. A repetition rate of 100 Hz has been fixed for the entire investigation to avoid the optical nonlinearities arising from laser-induced thermal effects. The pulse duration can be adjusted by

the laser itself within the range of 400 fs to 10 ps and all this available range has been employed for this work.

The laser pulses of a chosen duration have been directed and focused on the sample with a convex lens that provides a 40 μm focal spot diameter. The sample has been translated along the Z-axis (propagation axis of the beam) in order to be exposed to an intensity gradient. The laser beam transmitted through the sample carries information related to the optical nonlinearities of the sample and is divided into two parts with a beam splitter. One part was entirely collected by a photodetector using a focusing lens, also known as the “Open-aperture” Z-Scan, which allows the study of the nonlinear absorption characteristics of the material. The rest of the split beam has been collected into a far-field photodetector through a small aperture allowing only the central portion of the beam to enter the photodetector (“Closed-aperture” Z-Scan). The “Closed-aperture” arm has been used to study the nonlinear refraction behavior, which has been found to be negligible during this work. The laser intensities/ fluences have been at all cases carefully adjusted to avoid laser-induced damage of the Bi_2Se_3 samples while at the same time keeping high nonlinear optical signals.

3. Results and discussion

The transmittance spectra of the thin film before (as-deposited) and after annealing were recorded from 320 nm to 2500 nm. Figure 1 shows the results of the 40 nm thick Bi_2Se_3 film. The linear transmittance at 1030 nm was about 40% for the as-deposited film, which decreased to about 25% for the annealed sample.

Figure 2 shows representative SEM images of the as-deposited (Figure 2(a)) and annealed (Figures 2(b-d)) thin films. All the images have been recorded by applying the same acceleration voltage (10 kV). The image shown in Figure 2(a) has been obtained using a 40 kX magnification, while the three figures shown in Fig. 2(b-d) have been obtained with increasing magnifications, 2kX, 40kX and 100kX, respectively. The comparison clearly shows the appearance of nanosheet-like crystals which is in accordance with previous observations on this material [7,18,24,25].

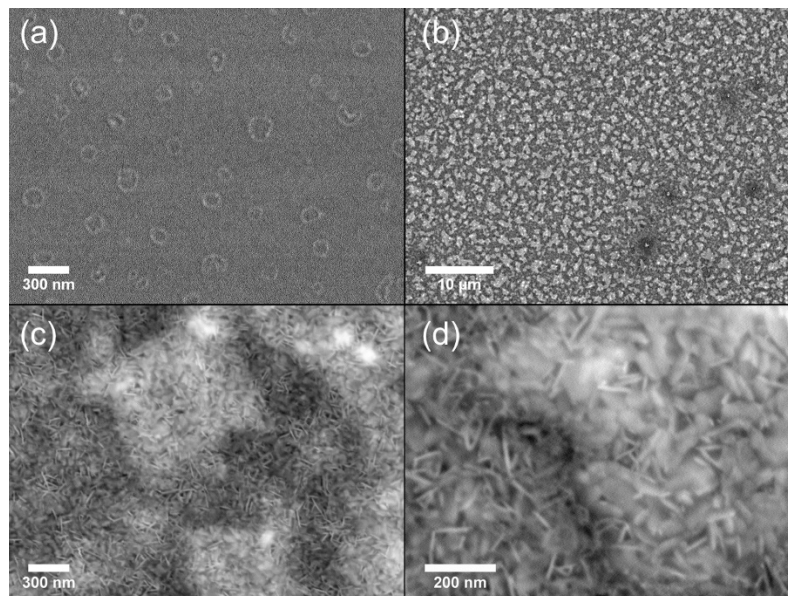


Fig. 2. Scanning Electron Microscopy images of the (a) as-deposited layer and (b-d) annealed layers. The (b-d) images correspond to different magnifications.

The well-known Z-scan technique [23,26] has been employed for investigating the impact of the pulse duration on the optical nonlinearities using pulse durations from 400 fs to 10 ps. The selected pulse duration range is of significant importance as the carrier dynamics/fast relaxation of the 2D topological insulators take place at the femtosecond-picosecond regimes [9,27]. Consequently, studies carried out at these time scales can offer precious information concerning the NLO dynamics of the layers.

The first approach has been to perform NLO studies while keeping a constant incident laser intensity on the sample. The significance of this approach is that the nonlinear absorption coefficient of several 2D materials is usually intensity dependent [28]. This fact, combined with the pulse duration dependent character of the layers, renders the problem highly complex. Indeed, modifying the pulse duration and intensity at the same time can induce effects from both pulse duration and intensity simultaneously. Consequently, the interpretation of the results is complicated. One needs to keep a constant intensity to see only the pulse duration dependent effect on the nonlinearities. However, keeping the intensity constant is challenging. Two factors contributing to the complexity need to be discussed, as explained next.

First, the NLO responses of Bi_2Se_3 can be investigated within a specific range of peak intensity. This range of intensity lies between the threshold intensity for NLO procedures to appear and the material's laser-induced modification threshold. It is good to note that, for proper NLO detection and analysis, a significant signal-to-noise ratio is required, but without surpassing the modification threshold of the layers. Exceeding the modification threshold would result in an alteration of the crystalline structure of the layers or even an ablation of the surface. Secondly, the laser damage threshold of several materials is known to decrease with increasing the pulse duration [29,30]. Such a phenomenon has also been observed in this work, as it has been found out that the modification threshold has been decreased by an order of magnitude while changing the pulse duration from the femtosecond to the picosecond regime. This abrupt decrease of the modification threshold is the second factor that contributes to the challenging nature of this study. This complexity makes the NLO investigations almost impossible for a long range of pulse durations by keeping a constant intensity.

Consequently, our first target has been to find an intensity that can guarantee a high signal-to-noise ratio in a maximum pulse duration range without damaging the investigated layers. It has been found out that an intensity of 4 GW/cm^2 can allow high-quality measurements for pulse durations ranging from 400 fs to 1.6 ps. A further increase of the pulse duration was impossible as the layer was modified at this specific intensity, as the laser-induced modification threshold decreased abruptly, as discussed before. Longer pulse durations have been studied using a second approach, which will be discussed in the following paragraphs.

Figure 3 represents the saturable absorption response of the Bi_2Se_3 layers at constant intensity for different pulse durations. More specifically, in Fig. 3(a) “Open-aperture” Z-Scans are shown for pulse durations ranging from 400 fs to 1.6 ps. Figure 3(b) shows the corresponding nonlinear absorption coefficient (β) values as a function of the pulse duration. The normalized transmittance shown in Fig. 3(a) is observed to be increasing when the thin film is at the focal plane of the lens. In other words, the transmittance through the sample increases when exposed to a relatively higher intensity, which indicates the saturable absorption behavior of the Bi_2Se_3 thin film. This behavior is related to the Pauli's blocking which is well known to result to saturable absorption attribute in the case of topological insulators [6,8,17]. The origin of the Pauli's blocking in the case of the Bi_2Se_3 material is of high complexity due to the multiple valence/ conduction bands as well as surface states [13,31]. The description of the transitions that may arise during the laser excitations employed in this work have been discussed previously so they will not be detailed here [32,33]. No nonlinear refraction behavior was observed under the current experimental conditions. The absence of nonlinear refraction can be attributed to the giant nonlinear absorption arising in the case of 2D materials, like the Bi_2Se_3 . This behavior has been previously demonstrated and

discussed by our group in the past in the case of the Sb_2Te_3 material [4]. This investigation shows that the nonlinear absorption coefficient has an obvious dependence on the laser pulse duration. The Z-Scan saturable absorption peak as well as the nonlinear absorption coefficient, are positively correlated with the pulse duration. A rather big influence of the pulse duration on the nonlinear absorption coefficient is seen at the first part of the curve, which corresponds to the femtosecond regime. In particular, an increase of about 40% is observed while increasing the pulse duration from 400 fs to 660 fs. For higher pulse durations, a less significant increase is occurring. The highest β values obtained by this approach have been $-2.42 \times 10^{-7} \text{ m/W}$ and correspond at 1.6 ps pulse duration, the longest pulse duration employed in this case.

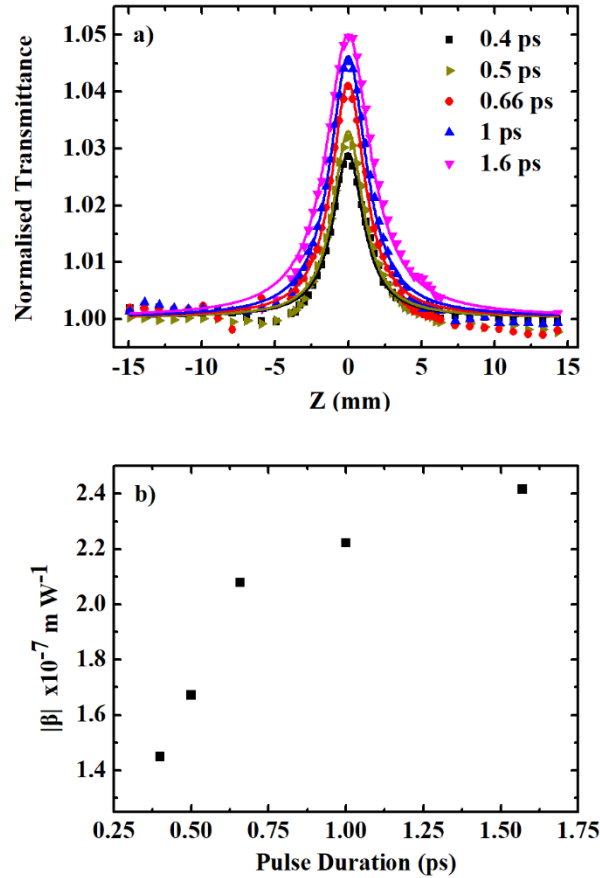


Fig. 3. (a) The “open-aperture” Z-Scan curves represent the normalized transmittance of 1030 nm laser pulses of 4 GW/cm^2 peak intensity for different pulse durations. (b) The corresponding nonlinear absorption coefficient (β).

A second approach has been employed to study the dependence of pulse durations longer than 1.6 ps. In this case, the NLO behavior has been studied at a constant peak laser fluence of 1.6 mJ/cm^2 . This fluence has been sufficient to study the 2D layers throughout almost the whole pulse duration range investigated during this work, except for pulse durations longer than 5 ps. Figure 4(a) presents the “Open-aperture” Z-Scan signals as a function of pulse duration at constant laser peak fluence, while Fig. 4(b) represents the evolution of the corresponding nonlinear absorption coefficient. From Fig. 4, one can note that the “Open-aperture” Z-Scan peaks are decreasing with increasing the pulse duration, while the nonlinear absorption coefficient

is increasing and then staying almost constant for pulse durations higher than a few picoseconds (about 3 ps). Two mechanisms may arise in this case and can explain this phenomenon.

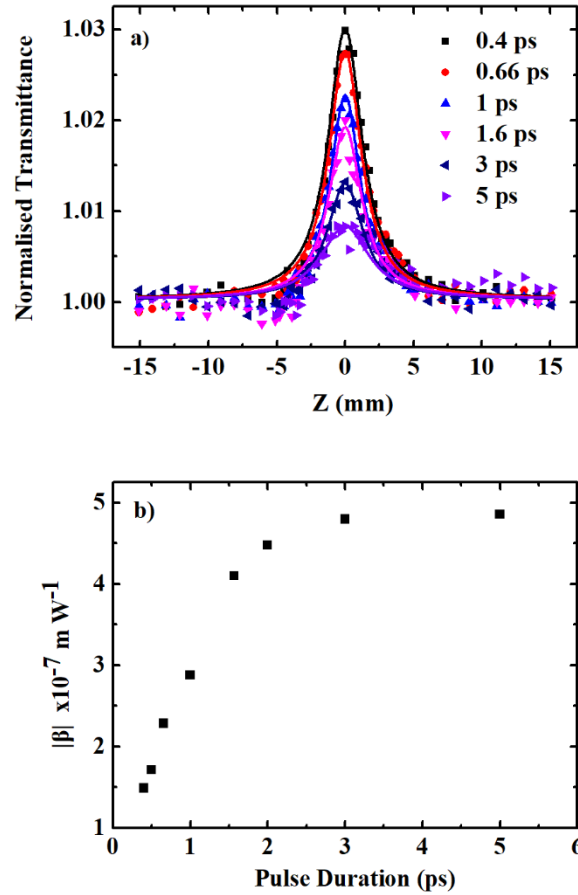


Fig. 4. (a) The “open-aperture” Z-Scan curves represent the normalized transmittance of 1030 nm laser pulses at 1.6 mJ/cm^2 peak fluence for different pulse durations. (b) The corresponding nonlinear absorption coefficient (β) as a function of the pulse duration.

Firstly, keeping the fluence constant results in a gradual decrease of the intensity as the pulse durations become longer. This gradual decrease of the intensity can result to a significant increase of the optical nonlinearities in the case of topological insulators. Indeed, a previous study on Bi_2Se_3 nanosheets [8] has demonstrated that increasing the excitation intensity from 7.3 GW/cm^2 to 43.6 GW/cm^2 can result to an increase of the absorption coefficient from $-2.1 \times 10^4 \text{ cm/GW}$ to $-0.34 \times 10^4 \text{ cm/GW}$ and consequently at a significant loss of the saturable absorption performance. This has been attributed to a simultaneous contribution of two mechanisms, firstly, a ground state bleaching which is due to the Pauli blocking along with a free carrier absorption which is enhanced while increasing the incident laser intensity. Similar attribute has been observed for other 2D materials such as Bi_2Te_3 , Bi_2TeSe_2 and $\text{Bi}_2\text{Te}_2\text{Se}$ [8]. Secondly, the modification of the pulse duration results to a change of the dynamics of the photo-excited carriers in the 2D layers, thus to a modification of the optical nonlinearities, as it has been clearly demonstrated during the first series of experiments of this work. One can conclude that both mechanisms play an important role on the findings shown in Fig. 4(b) and can explain the fact that the nonlinearity remains almost constant in the picosecond regime for longer pulses than 2 ps.

Figure 5 represents the evolution of the imaginary part of the nonlinear susceptibility and the figure of merit, as a function of pulse duration at constant intensity (Fig. 5(a,b)) and at constant fluence (Fig. 5(c,d)). These results are also presented in Table 1. It has to be noted that in the case of 10 picoseconds pulse duration, the signal-to-noise ratio was low in the case of the 1.6 mJ/cm^2 constant fluence irradiation. For this reason, the fluence has been increased to be 3.2 mJ/cm^2 , as it is mentioned in Table 1. This fluence change can have an impact to the NLO response. For this reason the measurement has not been added to the aforementioned graphs. However, it is shown in Table 1 in order to allow the completeness of the experimental data for the largest range of pulse durations possible.

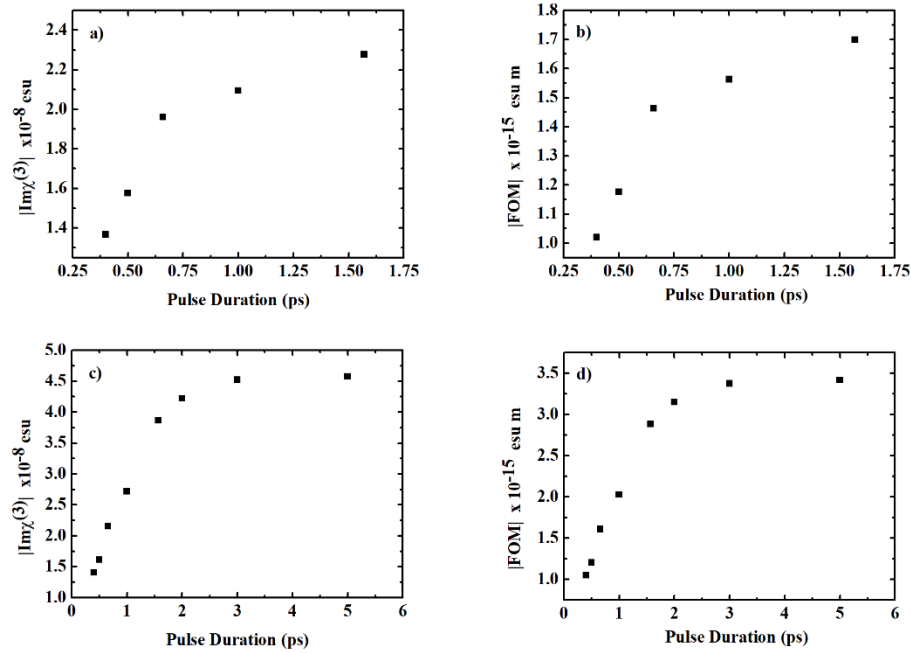


Fig. 5. The nonlinear parameters obtained at a constant intensity of 4 GW/cm^2 (a,b) and constant fluence of 1.6 mJ/cm^2 (c,d) are represented. The absolute value of imaginary part of third order nonlinear susceptibility ($\text{Im}\chi^{(3)}$) (a,c) and the Figure of merit (FOM) (b,d) as a function of pulse duration is represented.

As represented in Figure 5, the nonlinear parameters have a clear, strong dependence on the pulse duration. This fact is mainly related to the relaxation processes of the 2D layers, which are of high complexity. As it has been previously mentioned, many different processes can arise depending on the structure of the layers and the laser excitation parameters, such as electron-electron thermalization and electron relaxation through the longitudinal optical phonon cascade emission [27]. The pulse duration dependence is an important aspect that has to be considered, especially while employing the Bi_2Se_3 material for applications, in particular mode-locking. More specifically, the efficiency of the employed layers/ crystals will strongly depend on the pulse duration of the laser pulses that are used for the mode-locking and has to be considered in order to avoid discrepancies during the design of the laser systems and their final performance.

From both experiments, it is obvious that the pulse duration has a significant impact on the NLO response. An increase in the nonlinear absorption coefficient (β) from $-1.45 \times 10^{-7} \text{ m/W}$ (400 fs) to $-2.42 \times 10^{-7} \text{ m/W}$ (1.6 ps), has been observed in the first study done by keeping the intensity constant. Similarly, from the studies carried out at constant fluence, the β values were

Table 1. Nonlinear Optical Parameters (1030 nm excitation wavelength)

Pulse Duration (ps)	Constant intensity studies (4 GW/cm ²)			Fluence constant studies (1.6 mJ/cm ²)		
	Beta x10 ⁻⁷ (m/W)	Im $\chi^{(3)}$ x10 ⁻⁸ (esu)	FOM x10 ⁻¹⁵ (m esu)	Beta x10 ⁻⁷ (m/W)	Im $\chi^{(3)}$ x10 ⁻⁸ (esu)	FOM x10 ⁻¹⁵ (m esu)
0.4	-1.45	-1.37	-1.02	-1.49	-1.40	-1.05
0.5	-1.67	-1.58	-1.18	-1.71	-1.61	-1.20
0.66	-2.08	-1.96	-1.46	-2.29	-2.15	-1.61
1	-2.22	-2.09	-1.56	-2.88	-2.72	-2.03
1.6	-2.42	-2.28	-1.70	-4.10	-3.86	-2.88
2	NA	NA	NA	-4.48	-4.22	-3.15
3	NA	NA	NA	-4.80	-4.52	-3.38
5	NA	NA	NA	-4.86	-4.58	-3.42
10	NA	NA	NA	-3.95 ^a	-3.73 ^a	-2.78 ^a

^aThe irradiation fluence was 3.2 mJ/cm² fluence for 10 ps pulse duration; NA-not available.

observed to be increasing from -1.49×10^{-7} m/W (400 fs) to -4.86×10^{-7} m/W (5 ps). The FOM are the values which are more convenient to compare with reported values as they account for the possible variations and contributions that can arise across different types of thin film depositions, thicknesses, and crystalline states. The FOM values observed in the current work range from -1.02×10^{-15} m esu (400 fs) to -3.42×10^{-15} m esu (5 ps). It has to be noted that while the samples are irradiated with picosecond pulses, the electrons have enough time to relax within the pulse [9,27]. The relaxation process is complex, as the electrons can be found in many different states, including metastable states [32,34–37]. This relaxation can explain the less significant increase of the optical nonlinearity while the pulse duration increases at the picosecond regime, compared to a similar increase of the pulse duration at the femtosecond regime. These facts are in very good accordance with those obtained by Park et al. [32], who obtained transient bleaching and ultrafast relaxation within similar timescales. Further intensity dependent studies, as well as pump-probe studies will be necessary in order to provide a better understanding on how the modification of the laser intensity, as well as the pulse duration can modify the nonlinear optical responses.

4. Conclusion

In conclusion, the optical nonlinearities of Bi₂Se₃ layers have been studied at the femtosecond and picosecond regimes. The studies have been performed by keeping a constant intensity or a constant fluence, as much as possible in order to allow a direct comparison between the results of the current work. A significant impact of the pulse duration on the nonlinear optical response has been observed. Consequently, considering the strong pulse duration-dependent character of the nonlinear optical response of the Bi₂Se₃ material is very important for photonic applications such as mode-locking, where 2D materials are nowadays frequently used.

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Data availability. Data underlying the results presented in this paper are not publicly available at this time but may be obtained from the authors upon reasonable request.

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