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REVIEW

# Research progress of third-order optical nonlinearity of chalcogenide glasses*

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Chalcogenide glasses (ChGs) are a promising candidate for applications in nonlinear photonic devices. In this paper, we review the research progress of the third-order optical nonlinearity (TONL) of ChGs from the following three aspects: chemical composition, excitation condition, and post processing. The deficiencies in previous studies and further research of the TONL property of ChGs are also discussed.

**Keywords:** chalcogenide glasses, nonlinear optics, optical property

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## 1. Introduction

As a macroscopic centrosymmetric material, chalcogenide glasses (ChGs), i.e., amorphous semiconductors constructed by chalcogen elements (S, Se, and Te),[1,2] and other elements such as Ge, As, Sb, etc., have attracted considerable attention due to their broad infrared transmittance region and large third-order optical nonlinearity (TONL, $\chi^{(3)}$)[3] with ultrafast response time ($<$ 100 fs). These unique properties, coupled with the flexible size and modifiable composition, make ChG an ideal material for infrared optics and nonlinear photonic devices.[4,5] Therefore, great efforts[2,6–9] have been made to design ChGs that match the specifications of each particular TONL-based optical device. To evaluate the performances of ChGs for nonlinear photonic applications such as all-optical switching, wavelength conversion for an optical communication system, a key prerequisite is to design bulk glass composition regarding the figure of merit (FOM)[6,10] that considers the trade-off among nonlinear refractive, nonlinear absorption, and incident wavelength. Therefore, understanding the dependence of the TONL property of ChGs on various factors will facilitate the development of chalcogenide materials that are designed and tailored for specific photonic devices. However, the latest review paper[11] on the TONL property of ChGs was published 15 years ago, which may limit the research in the field of chalcogenide photonics.

The aim of this paper is to highlight the recent studies on the TONL property of ChGs, review the research progress from three main aspects, i.e., chemical compositions, excitation condition, post processing, and discuss the further research of the TONL property of ChGs.

## 2. Mechanism

Maxwell equations describe the electromagnetic wave in which the magnitude of the polarization $\boldsymbol{P}$ is only related to the primary term of the electric field intensity $\boldsymbol{E}$. However, since the discovery of the first ruby lasers in the 1960 s and the subsequent discovery of various nonlinear effects, traditional concepts have been broken. When the medium is irradiated by an intense laser, the electronic cloud of the dielectric surface can produce distortion, so that the dielectric manifests a nonlinear response to the light. In theory, the nonlinear response originates from the harmonic motion of the bound electrons being exposed to an applied field. Accordingly, the total polarization $\boldsymbol{P}$ in electric field $\boldsymbol{E}$ satisfies the more general equation[12]

$$\boldsymbol{P} = \varepsilon_0 \left( \chi^{(1)} \cdot \boldsymbol{E} + \chi^{(2)} : \boldsymbol{EE} + \chi^{(3)} : \boldsymbol{EEE} + \cdots \right). \quad (1)$$

Here, $\varepsilon_0$ is the vacuum permittivity and $\chi^{(i)}$ is the $i$-th order susceptibility. $\chi^{(1)}$ is the linear susceptibility that represents the main contribution to $\boldsymbol{P}$ and affects the linear refractive index $n_0$ and the linear absorption coefficient $\alpha$. $\chi^{(2)}$ is the second-order susceptibility, in general, $\chi^{(2)} = 0$ for the medium having an inversion symmetry configuration in the molecular scale. However, from a macro perspective, glass is

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isotropic with an inversion symmetry center, the second-order contribution is ruled out. Also, $\chi^{(3)}$ is the third-order susceptibility, responsible for nonlinear phenomena such as nonlinear refraction, four-wave mixing (FWM), and third-harmonic generation (THG). In general, $\chi^{(3)}$ can be given by the following formula;

$$\chi^{(3)} = \mathrm{Re}(\chi^{(3)}) + \mathrm{iIm}(\chi^{(3)}), \tag{2}$$

where $\mathrm{Re}(\chi^{(3)})$ is the real part of $\chi^{(3)}$ contributed from nonlinear refractive index ($n_2$), and $\mathrm{Im}(\chi^{(3)})$ is the imaginary part contributed from the nonlinear absorption ($\beta$).[10] Therefore, the refractive index $n$ can be simply expressed as the addition of a linear and a nonlinear component, and their linear absorption coefficient $\alpha$ values are exactly the same. Moreover, most of the nonlinear effects in ChGs are contributed from the nonlinear refraction which manifests as the laser intensity-dependent refractive behavior. The intensity-dependent refractive index $n(I)$ and absorption coefficient $a(I)$ can be characterized by the coefficient $\beta$, defined through the following equations[13]

$$n(I) = n_0 + n_2 I, \tag{3}$$

$$\alpha(I) = \alpha_0 + \beta I, \tag{4}$$

where $\boldsymbol{I}$ is the intensity of the electromagnetic field propagating through the ChG, $n_0$ is the linear portion of refractive index, and $n_2$ is the nonlinear part. For an isotropic medium, $n_2$ relating to third-order susceptibility $\chi^{(3)}$ can be expressed as follows:[10]

$$n_2 = \frac{12\chi^{(3)}}{n_0}. \tag{5}$$

The commonly used methods for measuring the TONL property of ChGs are the Z-scan technique,[14] third-harmonic generation (THG),[15,16] optical Kerr shutter (OKS),[17–19] Mach–Zehnder technique (MZT),[20,21] spectrally resolved two-beam coupling (SRTBC), and so on. More or less, these testing methods have some limitations. For example, the THG method can only measure $\chi^{(3)}$ of optical material; the DFWM and OKS methods can measure $\chi^{(3)}$ and the nonlinear response time ($\tau$); the MZT, Z-scan, and SRTBC techniques can measure both the real and image parts of $\chi^{(3)}$, thus the characterization of the overall TONL for ChGs needs the combination of several testing methods.

In addition, in order to rapidly assess the TONL performance of ChGs, some empirical or semi-empirical formulas based on the measurements are adopted, such as Boling, Glass, and Owyoung (BGO),[22,23] and Miller's rule;[10,24,25] the latter is expressed as follows:

$$\chi^{(3)} = [\chi^{(1)}]^4 \times 10^{-10}\,(\mathrm{esu}), \tag{6}$$

$$\chi^{(1)} = \frac{n_0 - 1}{4\pi}. \tag{7}$$

It can be deduced that $\chi^{(3)}$ increases with increasing $\chi^{(1)}$, i.e., a high TONL property is expected for ChGs with a high linear refractive index. Accordingly, the incorporation of heavy-metal elements into ChGs, thereby increasing linear refractive index ($n_0$) has already been confirmed to be an effective approach to enhancing TONL of ChGs. However, considering the flexible glass network of ChGs and dispersion in TONL, $\chi^{(3)}$ is not only determined by a linear refractive index, but also effected by the laser parameters, such as wavelength, intensity, etc., [25] thus different $\chi^{(3)}$ values could be obtained in ChGs with the same $n_0$ value, which will be demonstrated in detail in the following sections.

## 3. Chemical composition

The modifiable chemical compositions of glass material according to desirable properties make it possible to design specific nonlinear optical devices based on ChGs. As a category of amorphous semiconductor material, ChGs have very similar band-gap characteristics to those of crystalline semiconductor materials. However, compared with the crystalline semiconductor, ChG (amorphous semiconductors) contain quite a lot of defect units (wrong bonds, homopolar bonds, dangling bonds, and so on) and localized states in the band gap of ChGs, as a result of the flexible structure and intensive electron–lattice interaction in the ChG network.[26,27] Both indirect and direct electronic transitions exist simultaneously between the energy states, intensities of which depend on the chemical composition of ChG. Therefore, the relationship between TONL mechanisms of ChG and the chemical composition are more complicated than that of a crystalline semiconductor as well as the traditional oxide glass. Previous studies of the TONL properties of ChGs have indicated that the key factor to improve the TONL performance may be related to the number of lone-pair electrons and heavy-metal doping species,[21,28] such as in the cases of doping Bi, Pb, or Sb, etc. due to their large polarizability. Accordingly, a number of ChGs compositions within binary and ternary systems, have been developed and studied in order to optimize optical properties for various photonic applications. Therefore, the aim of this part is to summarize the compositional dependence of the TONL property of ChGs, and the correlation with the network structure of the ChGs is introduced as well.

In 1989, Nasu *et al.*[29] first gave the precise $\chi^{(3)}$ value of $As_2S_3$ glass by using the third-harmonic generation (THG) method. At the infrared wavelength of 1.9 μm, the $\chi^{(3)}$ value of $As_2S_3$ glass reached $2.2 \times 10^{-12}$ esu, which is 100 times higher than that of fused silica and in a similar magnitude to that of monomer-doped polymer known as high $\chi^{(3)}$ organic

material. Then, they investigated the TONL property of Ge–As–S–Se glass by the same method,[15] larger optical nonlinearity was obtained by substituting S atoms with Se atoms, and the maximum $\chi^{(3)}$ value reached $1.4.\times10^{-11}$ esu in the case of As–S–Se ChG at 1.9 μm, demonstrating that incorporation of Se is one of the effective keys to yielding a larger TONL in sulfide ChGs. More importantly, they discovered an ultrafast response time less than subpicosecond for the ChGs, which means that ChGs are suitable for optical switching devices requiring a high-speed response time of optical materials.

In 1990, the development of the Z-scan technique provided a simple and precise method of measuring both nonlinear refractive and nonlinear absorption behavior of optical materials. Marchese *et al.*[13] applied the Z-scan measurements to a new $GeS_2$-based (Ge–Ga–S) ChGs, and found a large variety of nonlinear refractive indices ($n_2$) in a range from $1.65.\times10^{-18}$ $m^2/W$ to $7.5.\times10^{-18}$ $m^2/W$ depending on the glass composition, and the enhancement of both nonlinear refractive and nonlinear absorption behaviors by doping halide (CsI) and heavy metal (Ag) were observed. Meanwhile, Zhou *et al.*[30,31] investigated the TONL of ChGs within the Ga–La–S system also by the Z-scan and THG method. At a visible wavelength of 532 nm, a large $n_2$ value of Ga–La–S glass (on the order of $10^{-17}$ $m^2/W$, one order higher than that of Ge–Ga–S ChG), as well as the large two-photon absorption coefficient ($\beta$, $\sim$ 40 cm/GW) are observed. By introducing $Na_2S$, PbS, and $Ag_2S$ into the Ga–La–S ChGs, the $\chi^{(3)}$ increases monotonically with reducing optical band gap ($E_g$) and increasing linear refractive index ($n_0$) as shown in Fig. 1, which proves the feasibility for modifying the TONL property of ChGs by the chemical composition, while similar experimental results were obtained in Ge–S binary glasses.[32]

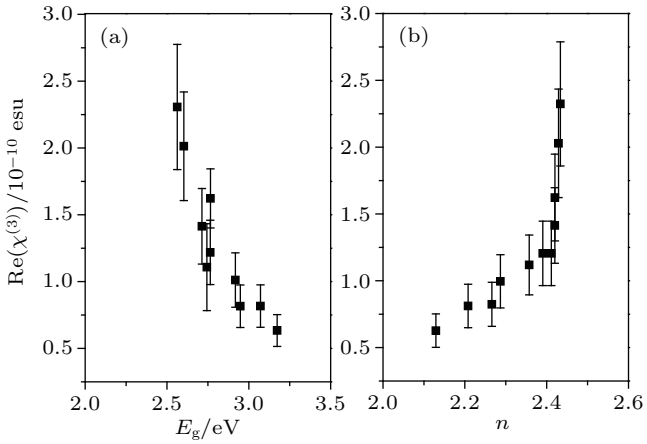



**Fig. 1.** Plots of the real part of $\chi^{(3)}$ of the binary $La_2S_3$–$Ga_2S_3$ glasses against (a) optical band gap ($E_g$), and (b) linear refractive index ($n_0$) (Zhou Z H *et al.* 1998).[30]

On the other hand, Cardinal *et al.*[33] first studied the correlation between glass structure and the TONL property of ChG by the Z-scan technique at the near infrared wavelength of 1.6 μm. In the As–Se–S ternary system, the maximum $n_2$ was obtained from ChG with a minimum As/(S + Se) molar ratio, and the $n_2$ value reached $8.9.\times10^{-18}$ $m^2/W$, exceeding 400 times that of fused silica. The large $n_2$ has been verified to be as a result of the formation of Se–Se homopolar bonds in the ChG network. Lenz *et al.*[34] reported that the TONL property of pure selenide (Se-based) ChGs, enhancement of $n_2$ had been observed in Ge–Se binary ChGs by heavy metal (Te or Sb) doping, but the maximum $n_2$ of $\sim$ 500 times that of silica was obtained from an $As_2Se_3$ glass. Troles *et al.*[21] added heavy metal Pb and Bi into As–Sb–S ChGs and obtained a large TONL as well, the maximum $n_2$ is $1.6.\times10^{-17}$ $m^2/W$, corresponding to 600 times that of silica glass.

In 2004, Cherukulappurath *et al.*[35] investigated the TONL property of telluride (Te-based) ChGs at 1.064 μm by the Z-scan method. In the Ga–As–Se–Te quaternary, the maximum $n_2$ reached $2.0.\times10^{-17}$ $m^2/W$, but the experimental results showed that the further addition of tellurium would exalt nonlinear absorption instead of enhancing the nonlinear refraction as a result of the shift of band gap energy towards the incident photon energy of 1.17 eV (at 1.064 μm). Meanwhile, Gopinath *et al.*[36] investigated the TONL property of Ge–As–Se ChGs with high Ge content for fabricating the high index-contrast and nonlinear fibers. They demonstrated that the Ge content has a great influence on the TONL properties of the Ge–As–Se ChGs, and the highest $n_2$ value of $2.4.\times10^{-17}$ $m^2/W$ was obtained from the ChG sample containing the highest Ge content: $Ge_{35}As_{15}Se_{50}$ (in unit mol%).

Since then, studies on the TONL property of ChGs focused on visible–transparent and environment-friendly (As-free) Ge–S–*X* (*X* is the third component) ternary systems. The researchers from Wuhan University of Technology gave a series of studies on the correlation between structure and TONL properties of Ge–Ga–S ChGs doped with transitional metal and halides. They demonstrated that the Ge–Ga–S ChGs possess an ultrafast nonlinear response time ($<$ 200 fs), which was kept unchanged with modification of the glass composition. The nonlinear refractive index $n_2$ (on the order of $\sim$ $10^{-18}$ $m^2/W$) of Ge–Ga–S ChGs is slightly smaller than those of As–Se based ChGs, and it can be modified by the introduction of various metals or halide compounds. For example, the introduction of light metal compounds with small polarization, such as $In_2S_3$,[37] CdS,[17] $CdI_2$,[18] etc, resulted in a reduction of the $n_2$ value, while the introduction of heavy metal halides with high polarization, such as $PbI_2$,[38] AgCl,[19] etc., increased the $n_2$ value. The researchers in Clemson University focused on the Ge–Sb–S/Se system, and they were particularly concerned with the dependence of the TONL property on bandgap energy ($E_g$) and the number of electronic lone pairs (ELPs) of the ChGs.[39] They indicated that $n_2$ of the Ge–Sb–S/Se ChGs could be promoted by the increase of Sb (one ELP per Sb ion) and Se/S(two ELPs per Se/S ions) con-

tent. Besides, they demonstrated that the red-shifting of the absorption band gap (decrease of $E_g$) with the addition of Sb content could also enhance the TONL property of the Ge–Sb–S/Se ChGs,[40] which is consistent with the experimental results from previous studies. The maximum value of $n_2$ as high as $1.05 \times 10^{-17}$ m$^2$/W was obtained in the ChGs containing the highest Sb content, reaching up to 500 times that for fused silica.

In 2008, Prasad *et al.*[41] studied the TONL property of Ge–As–Se ChGs at telecommunication wavelength (1550 nm) and first described the compositional dependence of $n_2$ in view of the topology of the glass network, which would put forward some guiding insights into future research in this field. The topological information for each Ge–As–Se ChG was quantified by a fundamental metric called mean co-ordination numbers (MCN), and the best TONL performance of the Ge–As–Se ChGs was obtained from glass samples with Ge content between 11 mol% and 13 mol% corresponding to the MCN value close to 2.5. More recently, Barney *et al.*[42] investigated the TONL properties of a group of stoichiometric $As_2S_3$–$As_2Se_3$ ChGs, and highlighted the dependence of $n_2$ on the arrangement of chalcogen atoms in the glass network by using neutron and x-ray total scattering technique, which gives a new option for the analysis of the compositional dependent TONL property of ChGs.

## 4. Dependence on wavelength

Like the linear optical properties, the nonlinear optical properties of optical materials also exhibit dispersions, namely wavelength dependence. For ChGs with high linear and nonlinear refractive index, the dispersion is significantly stronger than those of other glass systems, such as oxide glasses and fluoride glasses. Dispersion of the TONL property for optical materials is complicated, and it can be affected by various effects,[43] such as multi-photon absorption (MPA), Stark effect, Raman effect, etc. Besides, the electronic band structure of amorphous materials cannot be well concluded by these established theories suitable for crystal materials that have regular atomic arrangement, thus the TONL dispersion for ChGs has still not been well described. In this section, the published papers on dispersion for the TONL property of ChGs during the last couple of decades will be introduced.

Hall *et al.*[44] first found that the TONL susceptibility ($\chi^{(3)}$) of $As_2S_3$ glass at 1.06 μm was contributed from a resonant component, namely the imaginary part of $\chi^{(3)}$, which made it difficult to determine the $\chi^{(3)}$ value at the wavelength. Kobayashi *et al.*[16] measured the dispersion of TONL susceptibility ($\chi^{(3)}$) for $As_2S_3$ glass at longer wavelengths (from 1.55 μm to 2.2 μm) by using the difference frequency generation technique. The dispersion curve of $\chi^{(3)}$ is shown in Fig. 2, where it can be seen that the $\chi^{(3)}$ increases sharply before 1.75 μm toward a shorter wavelength due to the enhancement effect from the resonant effect from three-photon behavior, and the $\chi^{(3)}$ becomes almost constant at the wavelengths longer than 1.75 μm where the three-photon resonance is absent. In 2001, Quémard *et al.*[45] investigated both nonlinear refraction ($n_2$) and nonlinear absorption ($\beta$) of ChGs within a Ge–As–Se system by the Z-scan technique at wavelengths of 1.064 μm and 1.43 μm, and evaluated the TONL performance by FOM (defined as $\mathrm{FOM} = 2\beta\lambda/n_2$, where $\lambda$ is wavelength). They discovered that both $n_2$ and $\beta$ decreases with the increase of wavelength, but the decline rate of $n_2$ is much slower than that of $\beta$, resulting in improved TONL performance (smaller FOM) at longer wavelength. Later, Harbold *et al.*[46] investigated the TONL property of ChGs within a ternary As–S–Se system at two wavelengths of 1.25 μm and 1.55 μm for optical communication. They also observed the decrease of both $\beta$ and $n_2$ towards a longer wavelength, and explained such a variation trend by a two-photon resonant process. Accordingly, considering the Urbach tail for ChGs below the absorption edge (not infinitely sharp), the best TONL performance (maximum $\mathrm{FOM} = n_2/\beta\lambda$ defined in this work) was obtained from As–S–Se ChGs with bandgap energy ($E_g$) nearly twice that of the incident photon energy ($h\nu$), namely normalized photon energy ($h\nu/E_g$) at $\sim 0.45$.

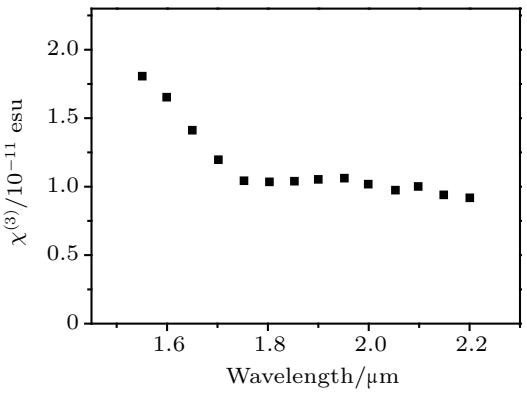



**Fig. 2.** Spectrum of $\chi^{(3)}$ for $As_2S_3$ glass (Kobayashi H *et al.* 1993).[16]

Wang *et al.*[47] recently gave the first attempt to model the TONL dispersion distribution of ChGs. They systematically measured both $n_2$ and $\beta$ of 51 ChG samples within five chalcogenide systems at near-infrared wavelengths from 1150 nm to 1686 nm by using the Z-scan method. Compared with these theoretical models for crystalline semiconductors established by Sheik–Bahae[48] and Dinu,[49] the TONL dispersion of ChGs (amorphous semiconductors) is in good consistence with that from Dinu's model (using $n_2E_g^4n_0^2$ and $\beta E_g^3 n_0^2$ cluster as a function of $h\nu/E_g$, within standard deviation below 12% as indicated in Fig. 3) for crystalline semiconductors with indirect transitions in the bandgap. However, the tail states originating from disorder and defects in the ChGs network were not

considered in Dinu's model, which might lead to considerable error in the estimation of both $n_2$ and $\beta$ for ChGs. In addition, multiple photon absorption (above two-photon absorption)[50] at a longer wavelength was also not considered in these published models, which would be a problem for estimation of TONL parameters of ChGs in longer wavelength regions, i.e., mid-infrared and far-infrared regions.

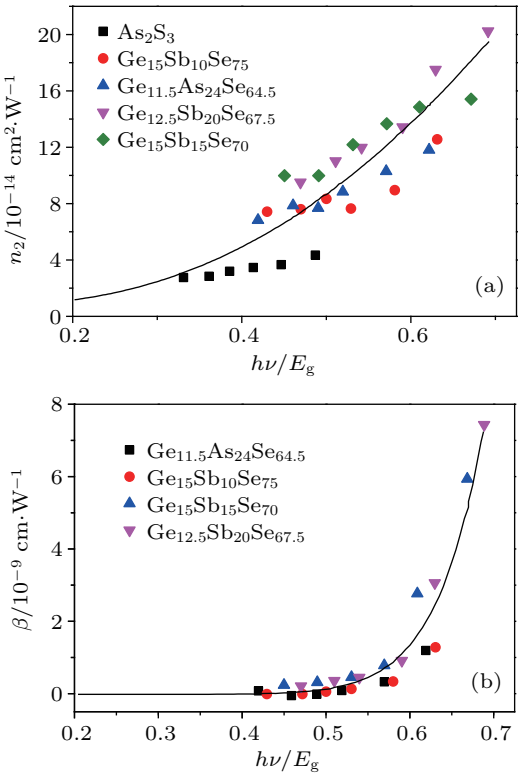



**Fig. 3.** (color online) Plots of (a) nonlinear refractive index ($n_2$) and (b) nonlinear absorption coefficient ($\beta$) versus normalized photon energy ($h\nu/E_g$) for the ChGs, respectively (Wang T *et al.* 2014).[47]

The development of chalcogenide mid-infrared (MIR) photonic devices, especially supercontinuum generation and Raman gain laser have promoted the study of TONL dispersion ChGs at MIR wavelengths. By employing the MIR femtosecond laser from an optical parametric amplification (OPA) system, the TONL dispersion of ChGs at the MIR wavelength can be investigated, but the relevant work is still limited. Our group have recently studied the TONL property of Ge–Sb–Se ChGs at wavelengths beyond 2 μm[51] by the Z-scan method using femtosecond laser pulses generated from the OPA system, and studied the MIR dispersion for the TONL property of the ChGs. As the value of $n_2$ varies with wavelength as shown in Fig. 4, the $n_2$ value of the Ge–Sb–Se ChGs at the MIR wavelength of 2 μm is significantly larger than those at both 1.55 μm and 2.5 μm. Since $1/3E_g$ of the ChGs ($E_g$ at $\sim$ 1.8 eV) matches the incident photon energy of 2 μm ($h\nu = 0.62$ eV), the relatively large $n_2$ at 2 μm can be attributed to the resonance effect originating from the strong three-photon absorption (3 PA). Accordingly, multiple ($> 2$) photon absorption occurs at a longer wavelength, which leads to anomalous dispersion behavior that needs to be considered in a study of the TONL property of ChGs in this wavelength region.

Our very recent study[52] showed that the impurity absorption of ChGs, appearing at the MIR wavelength, could also influence the TONL property of ChGs. By utilizing the Z-scan method assisted with the MIR OPA system, the negative influence of impurity (–OH group at $\sim$ 3 μm) on the nonlinear refraction behavior of ChGs in the Ge–Sn–Se ternary system was found. The $n_2$ of the Ge–Sn–Se ChGs at 3 μm attenuated significantly (with an average decrease rate of 66%) as compared with that at 3.5 μm, which indicated that the optical absorption from vibration of impurity units at the MIR wavelength needs serious consideration in the study of the MIR TONL dispersion of ChGs.

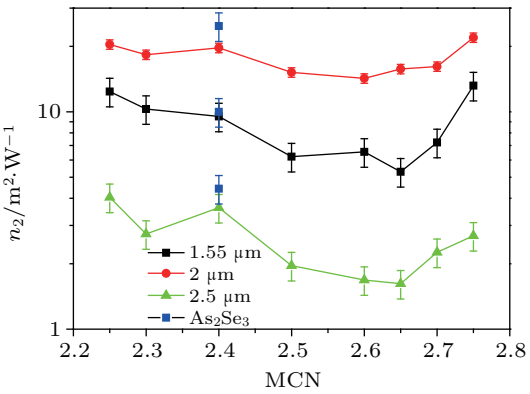



**Fig. 4.** (color online) Plots of nonlinear refractive index ($n_2$) versus mean co-ordination numbers (MCN) of the Ge–Sb–Se and $As_2Se_3$ ChGs ( Dai S *et al.* 2015).[51]

## 5. Laser intensity

It is believed that a large number of lone-pair electrons and defects existing in the ChGs matrix result in a 'soft' feature of the glass network, which can be easily distorted in external excitation, such as light irradiation and heat radiation, leading to the formation of new network structures. Therefore, the properties of ChGs show photosensitive behaviors, and so do the TONL properties which will be discussed in the following section.

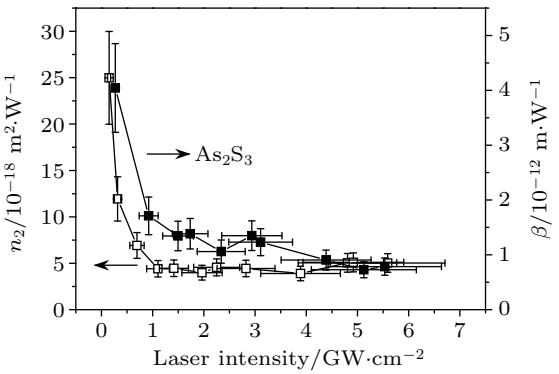



**Fig. 5.** Nonlinear refractive index ($n_2$) and nonlinear absorption coefficient ($\beta$) of $As_2S_3$ versus laser intensity at wavelength of 1.064 μm. Curves are for guiding the eye and correspond to simple interpolation between the experimental data (Smektala F *et al.* 2000).[53]

In 2000, Smektala *et al.*[53] first observed the changes of the TONL property of both $As_2S_3$ and $As_2Se_3$ ChGs at different laser intensities. Figure 5 gives the experimental results for $As_2S_3$ ChGs, from the figure it can be seen that both $n_2$ and $\beta$ (at 1.064 μm) of the glass decrease significantly with the increase of laser intensity ($I$) and nearly reach a saturated level at $I > 1$ GW/cm$^2$, and the value of $n_2$ drops from $25 \times 10^{-18}$ m$^2$/W to $5 \times 10^{-18}$ m$^2$/W. For the $As_2Se_3$ ChG, an even greater variation, from $160 \times 10^{-18}$ m$^2$/W to $18 \times 10^{-18}$ m$^2$/W was obtained. According to the theory for the free-carrier contributed TONL property of semi-conductors, the $I$-dependent nonlinear refractive index $n_2(I)$ can be expressed as the following formula:

$$n_2(I) = n_2 + \frac{n_{2S}}{1 + I/I_S}, \tag{8}$$

where $n_{2S} \gg n_2$, and $I_S$ is the saturation intensity on the order of MW/cm$^2$. They attributed the intensity dependence of $n_2$ to the saturable effect of the two-photon resonance in the band structure at a high $I$ level, but the detailed origin of such a phenomenon was not discussed.

Boudebs *et al.*[54] investigated experimentally and theoretically the intensity-dependent nonlinear refractive behavior of $As_2S_3$ and $As_2Se_3$ ChGs at 1.046 μm. They developed a novel model for the nonlinear optical property of ChGs by incorporating a fifth-order nonlinear index $n_4$ (the quintic nonlinear index), and proposed a simplified linear formula used for describing the optical nonlinearity of the ChGs as follows:

$$n_2^{\text{eff}} = n_2 + n_4 I, \tag{9}$$

where $n_2^{\text{eff}}$ is the effective nonlinear refractive index. By linearly fitting the experimental results given in Fig. 6, $n_2$ of $2.2 \times 10^{-17}$ m$^2$/W and $n_4$ of $-7.9 \times 10^{-31}$ m$^4$/W$^2$ are obtained for $As_2S_3$, and $n_2$ of $5.8 \times 10^{-18}$ m$^2$/W and $n_4$ of $-6.3 \times 10^{-32}$ m$^4$/W$^2$ are obtained for $As_2Se_3$. However, the model remains unable to explain the sharp decrease of $n_2^{\text{eff}}$ at low laser intensity (especially for $As_2Se_3$ ChG), and it only considered two-photon nonlinear absorption for simplicity at the near-infrared wavelength. For wavelengths in the longer (mid- and far-infrared) region in which multiple ($> 2$) photon absorption for ChGs occurs, a more precise model needs to be established.

Ogusu *et al.*[55] discovered the enhanced intensity-dependent behavior of nonlinear refraction for $As_2S_3$ ChG after silver-doping at a wavelength of 1.05 μm. They obtained a nonlinear refractive index ($n_2$) of Ag-doped (20 at.%) $As_2Se_3$, nearly 2–4 times that of the undoped, and ranges from $2 \times 10^3$ to $2.7 \times 10^4$ times that of fused silica, varying with the intensity changing of the incident laser, which cannot be interpreted by Boudebs's model (as indicated by the experimental curves shown in Fig. 7). Therefore, the detailed origin of this phenomenon remained unclear and was not discussed in their study. Moreover, the nonlinear absorption coefficient (TPA, $\beta$) became intensity-independent after silver doping, while $\beta$ of the undoped decreased with increasing input laser intensity, which led to the increase of the figure of merit (defined as FOM $= 2\beta\lambda/n_2$).

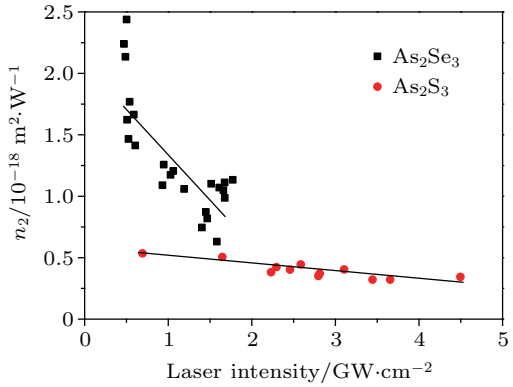



**Fig. 6.** (color online) Evolution of the measured effective nonlinear index coefficient as a function of laser intensity in $As_2S_3$ and $As_2Se_3$. The points represent the experimental data, and the solid lines refer to the linear regression fits using Eq. (9). Note the negative slopes for both materials (Boudebs G *et al.* 2003).[54]

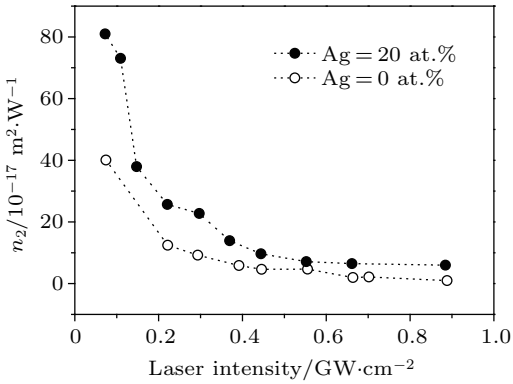



**Fig. 7.** Dependence of nonlinear refractive index ($n_2$) on laser intensity for Ag content $x = 0$ and $x = 20$ at.% (Ogusu K *et al.* 2004).[55]

To the best of our knowledge, the above three papers are the only work that reported the influence of laser intensity on the TONL property for ChGs, which means that such a behavior has not been considered seriously by the researchers in the circle of chalcogenide materials and devices. In fact, the variable $n_2$ with respect to laser intensity for ChGs (especially for $As_2S_3$ and $As_2Se_3$ ChGs) is important for the infrared photonic applications, such as Raman laser supercontinuum generation, which shows variable performances at different excitation intensities. The mechanism responsible for the intensity-dependent nonlinear property of ChGs is complicated, and it could relate to laser parameters, such as wavelength, laser pulse frequency, repetition rate, and chemical composition of ChGs. For implementing the chalcogenide photonic devices that need to be specifically designed and tailored, in-depth study of this phenomenon and establishing an appropriate theoretical model are necessary.

## 6. Post-processing

ChGs, similar to oxide glass systems, possess a metastable network structure, which have a tendency to relax when excited by external stimulation. The chalcogen atoms (S, Se, and Te) constitute a main network structure of ChG by connecting with other metal atoms As, Ge, Sb, etc., and the bond strength of the formed covalent bonds is weaker than those of oxide glass systems. Therefore, in a similar condition of external stimulation, the network structure of ChG is more likely to be changed, resulting in the modification of the corresponding properties. By post-processing ChGs, the TONL property can also be modified, and relevant studies mainly focused on laser irradiation and heat treatment, which will be reviewed in the following subsections.

### 6.1. Laser irradiation

Xiang *et al.* first reported the enhancement of the TONL property of ChGs by means of laser irradiation, which was observed from a Ge–Ga–Cd–S ChG by using the femtosecond optical Kerr shutter (OKS) technique at a wavelength of 830 nm.[56] They found that the OKS signals of the ChG increased continuously with the increase of irradiation (pump laser of the OKS) duration and were saturated at two different laser intensities (as shown in Fig. 8), while no changes in glass structure occurred. Therefore, the overall third-order susceptibility ($\chi^{(3)}$) of the ChGs can be rewritten as

$$\chi^{(3)}=\chi_0^{(3)}+\chi_{\text{extra}}^{(3)}, \tag{10}$$

where the initial value of $\chi_0^{(3)}$ and the photo-induced one $\chi_{\text{extra}}^{(3)}$ were calculated to be $4.0.\times10^{-13}$ esu and $5.0.\times10^{-13}$ esu respectively, constant at both irradiation intensities of 19 GW/cm$^2$ and 30 GW/cm$^2$ indicating the absence of intensity-dependent effects. Besides, the irradiation enhancement of $\chi^{(3)}$ is metastable, and it would be reduced by changing the polarization of the pump laser or keeping the sample in darkness. Accordingly, such a behavior can be attributed to photon-induced anisotropy, which can be described by the intimate valence alteration pair (IVAP) model. The three-hold coordinated sulphur or nonsulphur atoms with positive charges and the one-fold coordinated sulphur atoms were considered to be the IVAP, which shows that the dipole moments are dependent on the polarization status of the pump beam and contribute significantly to the TONL property of the ChG.

Zhang *et al.*[57] observed the changes of the photon-induced effects on the TONL property by irradiating an $As_2S_3$ glass with different laser sources. Switching between enhancement and attenuation of the TONL property of the $As_2S_3$ glass was observed, depending on the wavelength and repetition rate of the laser source: the $n_2$ value was enhanced by irradiating the femtosecond laser at 780 nm, while it was suppressed after irradiation by a continuous-wave (cw) laser at 579 nm. The opposite change in $n_2$ can be attributed to the presence of different photon-induced effects under different processing conditions, namely photodarkening at 780 nm and photoexpansion at 579 nm. Therefore, it is believed that the irradiation processing can be used to manipulate the TONL property of ChGs. However, these photon-induced effects are metastable, both photodarkening and photoexpansion will disappear through a self-annealing process, which means that the change of $n_2$ induced by lasers will recover after the irradiation has been removed.

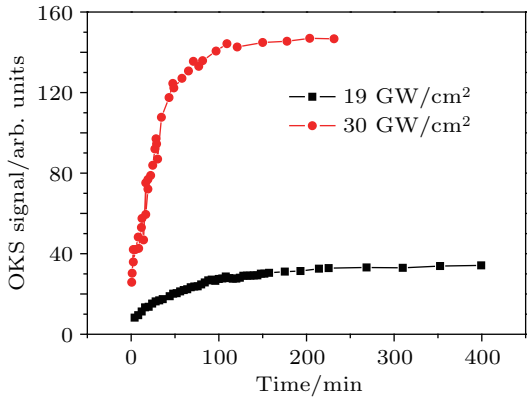



**Fig. 8.** (color online) Time-dependent OKE peak values for light intensity of 19 GW/cm$^2$ and 30 GW/cm$^2$. The solid curve is to guide the eye (Xiang H *et al.* 2006).[56]

### 6.2. Thermal treatment

Compared with those photon induced effects, the thermal treatment of ChGs that caused the structure to permanently change or crystallize in the glass network as proposed by Zhang *et al.*,[58] has been considered as a more effective and stable method to modify various properties of the optical materials. The ChGs with micro-crystal grains within the glass network, namely chalcogenide glass-ceramics (ChGCs) has been found to exhibit enhanced hardness, rare-earth luminous intensity, as well as nonlinear optical properties.

The first study on the TONL property of ChGCs was reported by Lin *et al.*[59] They obtained $\beta$-$GeS_2$ nanocrystals ($\sim$ 100 nm in diameter) in Ge–Ga–S ChGs by thermal treatment, and observed the increase of both $n_2$ and $\beta$ values of the ChGCs due to the presence of the nanocrystals. More importantly, as shown in Fig. 9, the maximum figure of merit (FOM$=n_2/\beta\lambda$) was amplified from $<1$ to 11.64 at 850 nm as a result of the quantum size effect from the $\beta$-$GeS_2$ nanocrystals. Later, Shen *et al.*[60] introduced halide (CsCl) as a nucleating agent into the Ge–Ga–S ChGs in order to precipitate more uniform and smaller crystal particles by means of heat treatment. They obtained Ge–Ga–S–CsCl ChGCs containing both $Ga_2S_3$ and $GeS_2$ nanocrystals with particle sizes of 2 μm$\sim$ 5 μm and $\sim$ 80 nm respectively, and

the ChGCs possess a maximum TONL susceptibility $\chi^{(3)}$ of $4.34 \times 10^{-11}$ esu, which is nearly four times that of the as-quenched ChGs without thermal treatment, demonstrating that the quantum size effect could be promoted by crystals with smaller sizes.

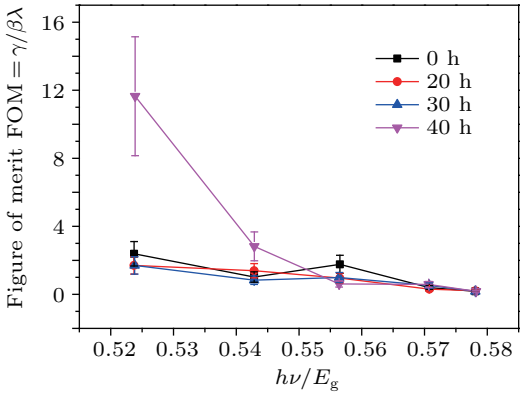



**Fig. 9.** (color online) Plots of figure of merit (FOM) versus normalized photon energy ($h\nu/E_g$) of the Ge–Ga–S ChGs after heat treatment at 466 °C for different times (Lin C *et al.* 2011).[59]

Our previous work[61] found that gold (Au) can be a suitable nucleating agent for the preparation of Ge–Ga–S ChGCs, and the Au-doped ChGCs after thermal treatment possess fine-distributed $\alpha$-$Ga_2S_3$ single-crystals with an average particle size of $\sim$ 40 nm independent of the duration of the treatment. Performance improvement of the TONL property for the Au-doped ChGCs was observed, and the maximum $n_2$ at a wavelength of 800 nm reached $2.4 \times 10^{-17}$ m$^2$/W, twice that of the as-quenched ChG due to the size effect from the quasi-quantum dots. Besides, it is of interest to find that a larger $n_2$ was obtained in the ChGC with a smaller number of the particles, indicating that the nano-crystals promoted TONL performance also exhibits quenching behavior.

Our recent study[62] presented the TONL property of selenide (Se-based) ChGCs within the Ge–Sn–Se ternary system. By introducing a small amount of Sn (5 mol%) as a nucleating agent into the Ge–Se binary system, $GeSe_2$ and $SnSe_2$ combined crystals with an average size of $\sim$ 100 nm could be observed after thermal treatment. Due to the local field effect from the Ge(Sn)$Se_2$ nanocrystals, the Ge–Sn–Se ChGCs exhibited a superior TONL property. The maximum $n_2$ that was obtained from the ChGC sample treated for 12 hours reached $5.3 \times 10^{-16}$ m$^2$/W, almost one order higher than that of the as-quenched Ge–Sn–Se ChG, and this $n_2$ value is also the largest found in the literature, to the best of our knowledge.

To date, the studies on the post-processing modified TONL property of ChGs have still been very limited, and there remain a number of scientific problems to be solved, such as the spectral modeling of the irradiation modified TONL as well as the detailed dependence on laser parameters, and the optimizing of the precipitation of crystalline for the TONL property of ChGs, including crystal type, size, shape, and so on. However, the experimental results obtained from the reported work made us believe that the modification of the TONL property of ChGs by post-processing will become one of the focusing topics in studying and developing new chalcogenide materials in the future.

## 7. Summary

Chalcogenide glasses (ChGs) are amorphous semiconductor materials, presenting infrared transparency and superior third-order nonlinear (TONL) property with a response time on the femtosecond scale, which make them a perfect candidate for infrared nonlinear optical devices. In this paper, the research progress of the TONL property of ChGs has been reviewed from three aspects, i.e., composition dependence, excitation condition, and post processing. It is clear that most of the reported studies focusing on the dependence of the TONL property on chemical composition were based on the fundamental theory of glass science, while theoretical research relating to the modification of the TONL property by taking advantage of the characteristics of ChGs, such as large dispersion, photon sensitivity, and crystallization behavior is still very limited, thus there remain a number of scientific problems to be solved. We believe that understanding the mechanisms behind the above problems will significantly promote the development of infrared technology based on chalcogenide photonics.

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