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Linear and non-linear optical properties of GeS_2 doped with the elements from III and V group of the periodic table

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The present paper summarizes the results from a study on the linear and nonlinear optical properties of GeS_2 when adding elements from III and V group of the periodic table (Ga, In, Tl, As and Bi). The refractive index *n* and the optical band gap E_g^{opt} were calculated from the transmittance and reflectance spectra. The results showed that the doping of GeS_2 with Tl or Bi leads to increase in the refractive index by about 0.2–0.3. The non-linear refractive index, γ, and the two-photon absorption coefficient, β, were evaluated by applying a formula developed by Sheik-Bahae. Each of the films studied exhibits a high non-linear refractive index at the telecommunication wavelength, 40–250 times higher than that measured for fused silica.

Keywords: chalcogenide glasses, non-linear refractive index, Sheik-Bahae formula

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INTRODUCTION

The physical properties of chalcogenide glasses and their changes under exposure to light depend considerably on the composition and the conditions of deposition and illumination of the layers [1]. This is the reason for the intensive studies of the influence of the above parameters on the optical properties of thin films from the systems $Ge_xS(Se)_{1-x}$ [2, 3]. It is shown that the effect of photo-bleaching in thin Ge–S films is due to transformation of the homeopolar bonds in heteropolar ones and to a process of irreversible photo-oxidation [4, 5].

When a third element is incorporated in GeS_2 it leads to considerable changes in its structure and properties. The addition of gallium and indium in the chalcogenide glasses is intensively investigated since the both elements makes the glassy network an appropriate host for rare-earth elements [6]. The glasses from Ge - S(Se) - In systems are attractive as materials for ultra-fast all optical switching, fiber amplifiers and glass ceramics [6].Ternary Ge-S-Bi glasses were studied during the last decade because the addition of 6–8 at.% of Bi to GeS_2 changes the material type conductivity from p– to n–type. Small quantities of Bi or Tl cause some transformations in the glassy network of GeS_2 forming different structural units which leads to changes in the band gap as well as in the electrical [7] and optical [8-10] properties. However, the glasses from the Ge-S-Tl systems were not investigated systematically. Data for the structure and optical properties of Ge - S- Tl glasses and thin films can be found in [9, 10].

The aim of the present paper is to summarize the results of a study on the linear and nonlinear optical properties of GeS_2 when adding elements of group III and V of the periodic table (Ga, In, Tl, As and Bi).

EXPERIMENTAL DETAILS

The synthesis of glasses from Ge_xS_{100-x} and $(GeS_2)_{100-x}Me_x$ systems, where Me = Ga, In, Tl, As, Bi or Tl (for x = 4, 6 and 10 at.%) was accomplished in a silica ampoule at 970 °C for 14 h [10]. Cooling was carried out in ice water. Thin films were deposited on graphite and optical glass substrates BK-7, with a rate of evaporation of about 0.5 nm/s in high vacuum better than 10^{-3} Pa by thermal evaporation and stopping the process when the necessary film thickness was achieved. The composition of the thin films obtained was determined in a scanning electron microscope with an X-ray microanalyser Joel Superprobe 733 (Japan). The experiments were performed at an electron accelerating voltage of 25 kV and current of 1.4 nA and a scanning time of 200 s for each spectrum. Exposure was made by a halogen lamp

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(20 $mWcm^{-2}$) in air. The transmittance (T) and reflectance (R) were measured by a Cary 5E spectrophotometer (USA) in the range 350–2000 nm to an accuracy of ΔT =±0,1% and ΔR = ±0,5%.

RESULTS AND DISCUSSION

The thin films from $(GeS_2)_{100-x}Me_x$ systems where deposited by conventional thermal evaporation from previously prepared bulk glasses.

Table 1. Optical parameters (thickness, d, refractive index, *n*, Sellmeier coefficients A_1 and A_2, optical band gap, E_g^{opt} and slope parameter, B) of untreated thin GeS_2 - Me films.

Composition	d [nm]	*n* (λ = 1550 nm)	A_1	A_2 [nm]	E_g^{opt} [eV]	B [$cm^{-1/2}eV^{-1/2}$]
GeS_2	987	2.11	3.395	231.48	2.56	593
$Ge_{20}S_{80}$	744	2.04	3.086	230.13	2.77	706
$Ge_{40}S_{60}$	1137	2.55	5.376	257.77	1.85	645
$Ge_{31}S_{63}Ga_6$	1078	2.13	3.435	249.74	2.35	529
$Ge_{34.6}S_{63.2}In_{2.2}$	766	2.12	3.407	245.81	2.34	530
$As_5Ge_{35}S_{60}$	878	2.43	4.736	267.55	2.07	588
$Ge_{32}S_{63}Bi_4$	1122	2.06	3.181	240.98	2.47	576
$Ge_{31}S_{63}Bi_6$	764	2.41	4.706	252.28	1.89	459
$Ge_{32}S_{64}Tl_4$	990	2.22	3.822	236.75	2.39	576
$Ge_{31}S_{63}Tl_6$	1263	2.26	3.955	238.136	2.26	535

The results from X-ray microanalysis for their composition are given in Table 1. The refractive index, *n* and thickness, *d* of thin Ge - S - Me films were calculated from the interference extrema in the transmission spectra using Swanepoel's method [11, 12]. The program used to calculate *n* will determine it to an accuracy of ± 0.5 % for an error in the transmittance of ± 0.1 % [12]. The calculated values for *n* were extrapolated by Sellmeier's equation:

$$n^2(\lambda) = 1 + \frac{A_1\lambda^2}{\lambda^2 - A_2{}^2} \quad (1)$$

where A_1 and A_2 are Sellmeier's coefficients. The Sellmeier's coefficients obtained for (1) with λ written in nm are presented in Table 1. At high values of the linear absorption coefficient α, where the condition αd ≥ 1 is fulfilled, α can be calculated from the equation:

$$T = (1-R)^2 \exp(-\alpha d) \quad (2)$$

Analysis of the strong absorption region ($10^4 \le \alpha \le 10^5$) has been carried out using the following well-known quadratic equation, often referred to as Tauc's law [13]:

$$(\alpha h\nu) = B(h\nu - E_g{}^{opt})^2 \quad (3)$$

where B is a substance parameter, which is in an inverse proportion to the width of the localized states in the density of states diagram, hν is the photon energy and E_g^{opt} is the so called Tauc's gap. The results for the optical parameters of thin Ge-S-Me films are summarized in Table 1. It is seen that the inclusion of 2-6 at % of In, Tl, Bi, As in GeS_2 leads to increasing of the refractive index and to decreasing of the width of the optical band gap, respectively. The influence of the gallium is not too notable due to the similar polarizability of its atoms to those of germanium.

Further we will consider the non-linear response of the chalcogenide medium to intense light with photon energies $\hbar\omega < E_g^{opt}$. We know that two-photon absorption would be involved in the interband transitions in that case [14]. One of the associated effects is the inducing of non-linear refractive index, *n_2[esu]* or *γ [m^2/W]*. It is known [15] that the intensity-dependent refractive index *n'* can be expressed as:

$$n' = n + \gamma \qquad I = n + \frac{n_2}{2}|E|^2 \quad (4)$$

where n is the linear, weak-field refractive index, I denotes the intensity and E - the strength of the applied optical field, and n_2 gives the rate at which the refractive index increases with increasing the optical intensity. For prediction of the non-linear refractive index we have applied a formula, developed by Sheik-Bahae et al. [19] for crystalline semiconductors and successfully applied for the glasses and thin films from Ag-As-S-Se systems [16-17]. In the simple model n_2 and γ can be expressed as:

$$n_2[esu] = \frac{cn}{40\pi}\gamma[SI] \text{ and}$$

$$\gamma = K\frac{\hbar c\sqrt{E_p}}{2n^2 E_g^{opt4}} G_2\left(\frac{\hbar\omega}{E_g^{opt}}\right) \qquad (5)$$

where E_p = 21 eV, K is found to be 3.1 x 10^{-8} in units such that E_p and E_g^{opt} are measured in eV, and γ is measured in m^2/W, ħ is the reduced Plank's constant, c – the speed of light in vacuum and G_2 is a universal function:

$$G_2(x) = \frac{-2+6x-3x^2-x^3-\frac{3}{4}x^4-\frac{3}{4}x^5+2(1-2x)^{\frac{3}{2}}\Theta(1-2x)}{64x^6} \qquad (6)$$

where Θ is the Heaviside step function. In the same approximation, the two-photon absorption, β_{NL}, originally defined by $\alpha' = \alpha + I\beta_{NL}$ (α' being the intensity-dependant absorption coefficient), can be expressed:

$$\beta_{NL} = K\frac{\sqrt{E_p}}{n^2 E_g^{opt3}} F_2(2\hbar\omega / E_g^{opt}) \qquad (7)$$

where

$$F_2(2x) = \frac{(2x-1)^{3/2}}{2x^5}$$ for 2x > 1 and $F_2(2x) = 0$, otherwise. That means that two-photon absorption occurs only for photon energies higher than at least half of the optical band-gap. It is shown [18] that the two-photon absorption possibly accompanying the high non-linear refractive index, γ, could prevent the optical switching effect, thus seriously limiting the applicability of any high third order nonlinear material in all-optical switches. In Figs. 1-3 the dispersion of γ and β for chalcogenide layers from binary Ge-S and ternary Ge-S-Me systems are shown. For the films from binary Ge-S system it was obtained that the increase of Ge-content leads to approximately 5 times increased value of γ from $1.33\times10^{-18} m^2/W$ for the thin $Ge_{20}S_{80}$ film to 6.63 $\times10^{-18} m^2/W$ for thin layer with composition $Ge_{40}S_{60}$ at wavelength λ = 1550 nm. The non-linear refractive index, γ of the glasses from Ge-S system depending on the germanium content is from ~ 4.8 to 250 times higher than that of fused SiO_2. The influence of inclusions of 1-2 at % of gallium and indium in thin GeS_2 films can be seen in Fig. 2. Due to similar polarizability of the gallium and germanium atoms, the inclusion of 4 at % of gallium affects poorly the non-linear parameters.

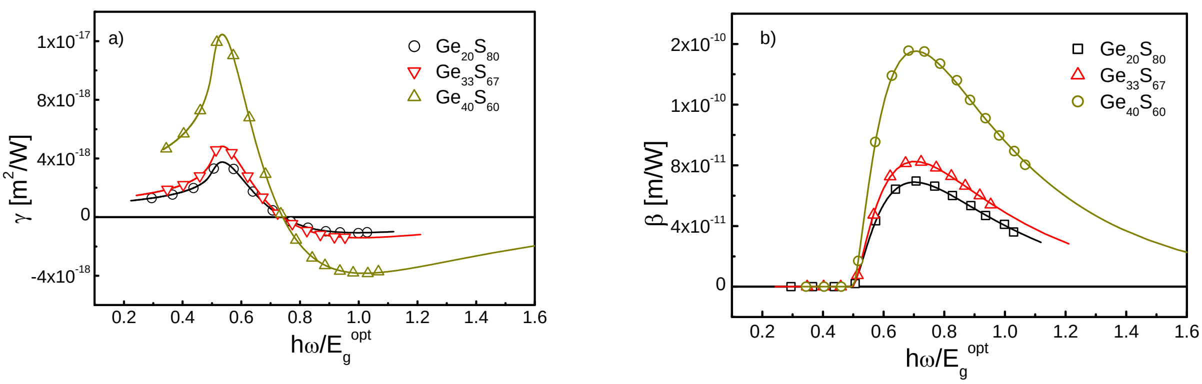

Fig. 1. Dispersion of the non-linear refractive index, γ (a) and non-linear absorption coefficient,β (b) for thin chalcogenide layers from the binary Ge_xS_{100-x} (for x= 28, 33 and 40) system.

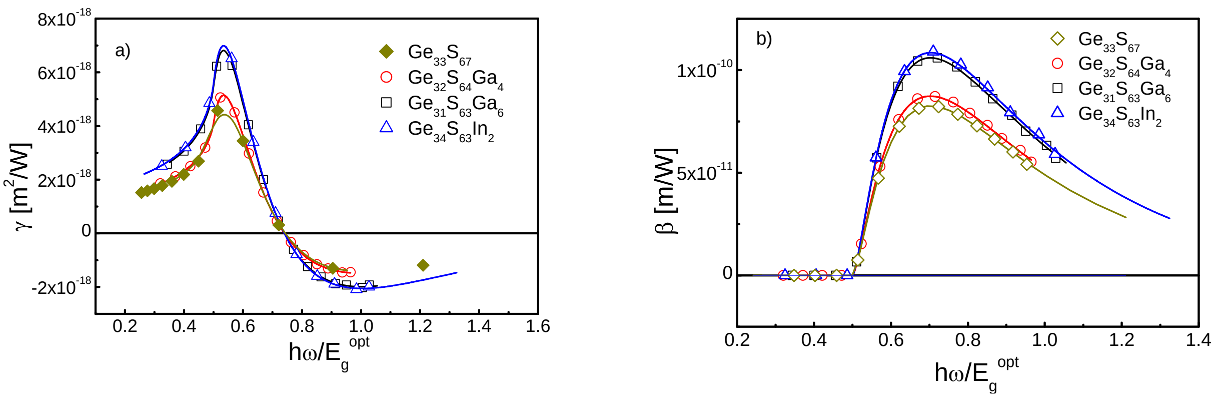

Fig. 2. Dispersion of the non-linear refractive index, γ (a) and non-linear absorption coefficient, β (b) for thin chalcogenide layers from the ternary Ge-S-Ga(In) systems.

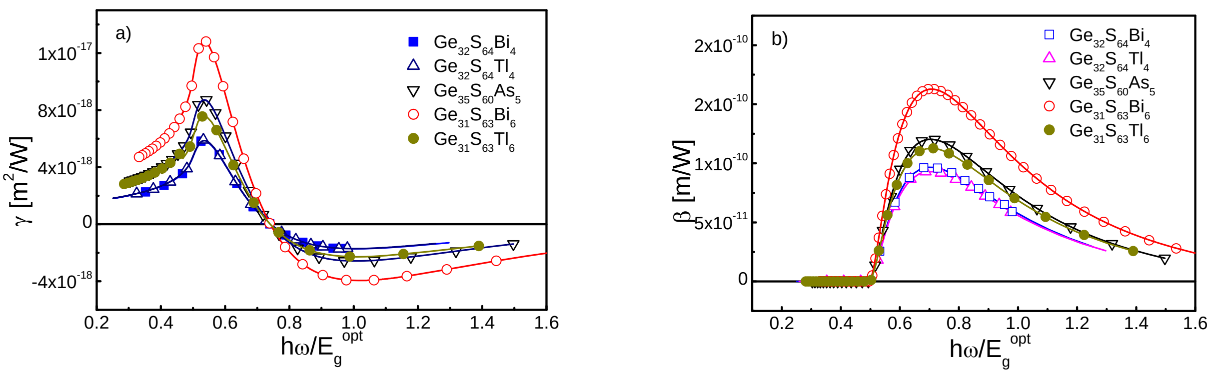

Fig. 3. Dispersion of the non-linear refractive index, γ (a) and non-linear absorption coefficient,β (b) for thin chalcogenide layers from the ternary Ge-S-As(Bi, Tl) systems.

Further increase of Ga or In content in the films to~ 6 at % leads to increasing of the values of γ to ~2.7 $\times 10^{-18}$ m^2/W. For comparison, γ for GeS_2 is ~1.6 $\times 10^{-18}$ m^2/W.

The influence of inclusion from Tl and Bi on the non-linear optical properties of Ge-S-Me films is demonstrated in Fig.3. The increase of thallium content from 4 to 6 at % in thin $(GeS_2)_{100-x}Tl_x$ films increase the non-linear refractive index, γ from 2.33×10^{-18} m^2/W to 3.71×10^{-18} m^2/W at λ = 1550 nm.

The highest value for the non-linear refractive index, γ = 6.38×10^{-18} m^2/W we obtained for the thin film with composition $Ge_{31}S_{63}Bi_6$, which was approximately 4 times higher than those for the thin GeS_2 coating index of fused SiO_2. To understand the role of the different metals, which are subject of the investigation of the present work we used the proposed in [19] formula for the non-linear refractive index n_2 and non-linear optical susceptibility, $\chi^{(3)}$:

$$n_2 = \frac{12\pi\chi^{(3)}}{n_0}, \text{ where}$$

$$\chi^{(3)} = A\left[\frac{E_o E_d}{4\pi(E_o^{\,2} - \hbar^2\omega^2)}\right]^4 \qquad (10)$$

where A = 1.7.10^{-10} (for $\chi^{(3)}$ in esu). E_0 and E_d are dispersion parameters in the Wemple Di Domenico model [20]. n_0 being the limit of the refractive index dispersion as ħω approaches 0. It is seen from equations (10) that the non-linear refractive index is in direct proportion to the fourth power of the dispersion energy, E_d. According to [20] the dispersion energy, E_d is related with the coordination number, N_c of the cations by the following equation - $E_d = \beta N_c Z_a N_e$, where Z_a is the formal chemical valence of the anion, N_e is the effective number of valence electrons per anion, and β is a two-valued constant with either an ionic or covalent value (β = 0.26 ± 0.03 eV and β = 0.37 ± 0.04 eV, respectively). According to [6] the gallium and indium are four-fold coordinated in the glasses from Ge-S-Ga (In) systems forming tetrahedral units (GaS_4, InS_4) while the thallium atoms are univalent forming bonds with non-bridging sulfur in terminal bonds Ge^{+}-S^{-} from the type GeS_4Tl [13]. The atoms of As and Bi are three-fold coordinated in the glasses from Ge-S-As(Bi) systems creating pyramidal structural units (AsS_3, BiS_3) [5, 8].

CONCLUSION

In the present work it is demonstrated the influence of elements of III and V group of the periodic table (Ga, In, Tl, As and Bi) on the linear and non-linear optical properties of thin Ge-S-Me films. The results showed that the doping of GeS_2 with Tl or Bi leads to increase in the refractive index by about 0.2-0.3.Applying the formula proposed by Sheik-Bahae et al. [15], it was found that the non-linear refractive index can be in the range of 4-250 times higher than that of fused SiO_2. The increase in the linear and non-linear refractive indices was explained on the basis of the model, proposed by Wemple and DiDomenico [20].

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ЛИНЕЙНИ И НЕЛИНЕЙНИ ОПТИЧНИ СВОЙСТВА НА GES_2 ДОТИРАН С ЕЛЕМЕНТИ ОТ III И V ГРУПА НА ПЕРИОДИЧНАТА ТАБЛИЦА

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(Резюме)

Настоящото изследване е обобщение на резултатите от проучване на линейни и нелинейни оптични свойства на GeS_2 при добавяне на елементи от III и V група на периодичната таблица (Ga, In, Tl, и Bi). Резултатите показват, че внасянето на Tl или Bi води до увеличаване на линейния и нелинейния показатели на пречупване.