Linear and non-linear optical properties of GeS₂ 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 GeS₂ 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 \( E_{\text{opt}} \) were calculated from the transmittance and reflectance spectra. The results showed that the doping of GeS₂ with Tl or Bi leads to increase in the refractive index by about 0.2–0.3. The non-linear refractive index, \( \gamma \), and the two-photon absorption coefficient, \( \beta \), 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

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 GeₙS(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 GeS₂ 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 GeS₂ changes the material type conductivity from p– to n–type. Small quantities of Bi or Tl cause some transformations in the glassy network of GeS₂ 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 GeS₂ 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 GeₓS₁₀₀₋ₓ and (GeS₂)₁₀₀₋ₓMeₓ 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 were deposited by conventional thermal evaporation from previously prepared bulk glasses.

<table>
<thead>
<tr>
<th>Composition</th>
<th>d [nm]</th>
<th>n (λ = 1550 nm)</th>
<th>A(_1) [nm]</th>
<th>A(_2) [nm]</th>
<th>E(_{g}^{\text{opt}}) [eV]</th>
<th>B [cm(^{-1/2})eV(^{-1/2})]</th>
</tr>
</thead>
<tbody>
<tr>
<td>GeS(_2)</td>
<td>987</td>
<td>2.11</td>
<td>3.395</td>
<td>231.48</td>
<td>2.56</td>
<td>593</td>
</tr>
<tr>
<td>Ge(<em>{20})S(</em>{80})</td>
<td>744</td>
<td>2.04</td>
<td>3.086</td>
<td>230.13</td>
<td>2.77</td>
<td>706</td>
</tr>
<tr>
<td>Ge(<em>{40})S(</em>{60})</td>
<td>1137</td>
<td>2.55</td>
<td>5.376</td>
<td>257.77</td>
<td>1.85</td>
<td>645</td>
</tr>
<tr>
<td>Ge(<em>{15})S(</em>{75})Ga(_{15})</td>
<td>1078</td>
<td>2.13</td>
<td>3.435</td>
<td>249.74</td>
<td>2.35</td>
<td>529</td>
</tr>
<tr>
<td>Ge(<em>{44.5})S(</em>{55.2})In(_{2})</td>
<td>766</td>
<td>2.12</td>
<td>3.407</td>
<td>245.81</td>
<td>2.34</td>
<td>530</td>
</tr>
<tr>
<td>As(<em>5)Ge(</em>{35})S(_{60})</td>
<td>878</td>
<td>2.43</td>
<td>4.736</td>
<td>267.55</td>
<td>2.07</td>
<td>588</td>
</tr>
<tr>
<td>Ge(<em>{32})S(</em>{68})Bi(_{4})</td>
<td>1122</td>
<td>2.06</td>
<td>3.181</td>
<td>240.98</td>
<td>2.47</td>
<td>576</td>
</tr>
<tr>
<td>Ge(<em>{31})S(</em>{69})Bi(_6)</td>
<td>764</td>
<td>2.41</td>
<td>4.706</td>
<td>252.28</td>
<td>1.89</td>
<td>459</td>
</tr>
<tr>
<td>Ge(<em>{32})S(</em>{68})Tl(_{4})</td>
<td>990</td>
<td>2.22</td>
<td>3.822</td>
<td>236.75</td>
<td>2.39</td>
<td>576</td>
</tr>
<tr>
<td>Ge(<em>{31})S(</em>{69})Tl(_{6})</td>
<td>1263</td>
<td>2.26</td>
<td>3.955</td>
<td>238.136</td>
<td>2.26</td>
<td>535</td>
</tr>
</tbody>
</table>

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:

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

where \(A_1\) and \(A_2\) are Sellmeier’s coefficients. The Sellmeier’s coefficients obtained for (1) with \(\lambda\) written in nm are presented in Table 1. At high values of the linear absorption coefficient \(\alpha\), where the condition \(\alpha d \geq 1\) is fulfilled, \(\alpha\) can be calculated from the equation:

\[
T = (1 - R)^2 \exp(-\alpha d)
\]

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

\[
(\alpha h\nu) = B(h\nu - E_g^{\text{opt}})^2
\]

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, \(h\nu\) is the photon energy and \(E_g^{\text{opt}}\) 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 Ge\(_2\) 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 \(h\nu < E_g^{\text{opt}}\). 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, \(n_2 [\text{esu}]\) or \(\gamma [\text{m}^2/\text{W}]\). It is known [15] that the intensity-dependent refractive index \(n'\) can be expressed as:

\[
n' = n + \gamma \quad I = n + \frac{n_2}{2} |E|^2
\]

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 \(\gamma\) can be expressed as:
\[ n_2[\text{esu}] = \frac{cn}{40\pi} \gamma[S^2] \] and

\[ \gamma = K \frac{h c \sqrt{E_p}}{2n^2 E_g^{\text{opt}}} G_2 \left( \frac{h \omega}{E_g^{\text{opt}}} \right) \] (5)

where \( E_p = 21 \text{ eV} \), \( K \) is found to be \( 3.1 \times 10^{-8} \) in units such that \( E_p \) and \( E_g^{\text{opt}} \) are measured in eV, and

\[ G_2(x) = \frac{-2 + 6x - 3x^2 - x^3 - \frac{3}{4} x^4 - \frac{3}{4} x^5 + 2(1 - 2x)^2}{64x^6} \] (6)

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

\[ \beta_{NL} = K \frac{\sqrt{E_p}}{n^2 E_g^{\text{opt}}} F_2 \left( \frac{2h \omega}{E_g^{\text{opt}}} \right) \] (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, \( \gamma \), 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 \( \gamma \) and \( \beta \) 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 \( \gamma \) from \( 1.33 \times 10^{-18} \text{m}^2/\text{W} \) for the thin Ge\(_{20}\)S\(_{80}\) film to \( 6.63 \times 10^{-18} \text{m}^2/\text{W} \) for thin layer with composition Ge\(_{40}\)S\(_{60}\) at wavelength \( \lambda = 1550 \text{ nm} \). The non-linear refractive index, \( \gamma \) of the glasses from Ge-S system depending on the germanium content is from \( \sim 4.8 \) to \( 250 \) times higher than that of fused SiO\(_2\). The influence of inclusions of 1-2 at \% of gallium and indium in thin Ge\(_2\) 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, \( \gamma \) (a) and non-linear absorption coefficient,\( \beta \) (b) for thin chalcogenide layers from the binary Ge\(_x\)S\(_{100-x}\) (for \( x = 28, 33 \) and 40) system.
Further increase of Ga or In content in the films to ~6 at% leads to increasing of the values of $\gamma$ to $\sim2.7 \times 10^{-18} \text{m}^2/\text{W}$. For comparison, $\gamma$ for GeS$_2$ is $\sim1.6 \times 10^{-18} \text{m}^2/\text{W}$.

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$_2$)$_{100-x}$Tlx films increase the non-linear refractive index, $\gamma$ from $2.33 \times 10^{-18} \text{m}^2/\text{W}$ to $3.71 \times 10^{-18} \text{m}^2/\text{W}$ at $\lambda = 1550 \text{ nm}$.

The highest value for the non-linear refractive index, $\gamma = 6.38 \times 10^{-18} \text{m}^2/\text{W}$ 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, $\chi^{(3)}$:

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

$$\chi^{(3)} = A \left[ \frac{E_0E_d}{4\pi(E_o^2 - h^2\omega^2)} \right]^4$$

where $A = 1.7 \times 10^{-10}$ (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 $h\omega$ 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 $\beta$ is a two-valued constant with either an ionic or covalent value ($\beta = 0.26 \pm 0.03 \text{ eV}$ and $\beta = 0.37 \pm 0.04 \text{ eV}$, respectively). According to [6] the
gallium and indium are four-fold coordinated in the glasses from Ge-S-Ga (In) systems forming tetrahedral units (GaS₄, InS₄) while the thallium atoms are univalent forming bonds with non-bridging sulfur in terminal bonds Ge⁻S⁻ from the type GeSₓTl [13]. The atoms of As and Bi are three-fold coordinated in the glasses from Ge-S-As(Bi) systems creating pyramidal structural units (AsS₃, BiS₃) [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 GeS₂ 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 SiO₂.

REFERENCES


ЛИНЕЙНИ И НЕЛИНЕЙНИ ОПТИЧНИ СВОЙСТВА НА ГЭС, 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 GeS₂ 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.