OPTICAL PROPERTIES OF CHALCOGENIDE GLASSES

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1. INTRODUCTION

For the understanding of the nature of electronic processes in non-crystalline semiconductors it is necessary first of all to investigate their energy spectrum, the phenomena of charge carrier transfer, and the process of radiation interaction with such materials. The energy spectrum of electron states in the range $h\nu>E_g$ can be studied from the reflectivity spectrum of light in the fundamental absorption band where $h\nu$ is the energy of quantum and $E_g$ is the optical gap. Of special interest is the study of the optical features of non-crystalline semiconductors near the absorption edge. It is known that the absorption edge of non-crystalline materials is sensitive to the composition and to the material structure as well as to external factors such as electric and magnetic fields, optical, heat, electronic and other radiations. Under the influence of the mentioned factors optical parameters of non-crystalline semiconductors suffer reversible and irreversible changes. The study of such phenomena allows not only clarifying the mechanisms of light absorption in the matter at significant disorder of its structure, but also suggesting all possible practical applications, which are not always peculiar to crystalline semiconductors. However, to understand all these phenomena it is necessary to know the position of electron states, the position and the nature of the absorption edge, near which the majority of photo-stimulated phenomena in non-crystalline vitreous semiconductors take place. The study of optical properties of chalcogenide crystals and glasses is very important from the theoretical point of view because it allows to determine the energetic appropriateness of the interaction of the optical radiation with ordered and disordered solid state systems and to clarify how much the disorder influences the peculiarities of energy spectrum and optical phenomena in the mentioned above group of materials [1-7]. Short information concerning optical phenomena in the above mentioned group of materials will be given in this chapter. The peculiarities of energetic spectrum will be discussed too.

2. THE REFLECTIVITY SPECTRA OF CHALCOGENIDE CRYSTALS AND GLASSES. ELECTRON STATES.

The general method for the investigation of the energy spectrum of electron states in the range $h\nu\gg E_g$ is the study of the reflectivity spectrum of light in the absorption band, of photoemission and energetic losses of the electrons reflected by solids [1-7]. The reflectivity spectra of these materials were studied in the large energetic range (1.5-12.5 eV) that allowed investigating their electronic structure. Reflectivity measurements were performed at room temperature using the cleavage surface of As$_2$S$_3$ natural and artificially obtained single crystals as well as the surface of glasses (Fig.1). The obtained reflectivity spectra have the following peculiarities: The reflectivity spectrum of As$_2$S$_3$ crystals contains a few maxima. The main of them is placed at 4.0 eV and others appear in the range of 5-12.5 eV having a doublet form (Table 1). The reflectivity spectra of As$_2$Se$_3$ single crystal contains some reflectivity maxima, whose position are given in Table 1. The reflectivity spectra of As$_2$Te$_3$ crystals contain peaks at 3.0; 6.5 and 8.7 eV. Upon the crystal-glass transition only the broadest maxima remain at 3.0 and 8.8-10.0 eV [8-10]. The peaks in the reflectivity spectra of
glasses are very broad, but in main points repeat the peculiarities of reflectivity spectra of single crystals, especially it is true for the range of high energies. So, for the 10 eV ranges the peaks of reflectivity are situated at the same energies. In the range of energies $5.5 < \hbar \nu < 8$ eV the reflectivity peaks of glasses are shifted to the longer wavelengths in comparison with reflectivity peaks of crystals, but they have the same shape. The above mentioned peculiarities were confirmed by many authors. The magnitudes of energy for the peculiarities of optical transitions are given in Table 1 [8, 11-19] and they differ only a little although they were obtained by different authors who used, of course, different samples.

Fig. 1. The reflectivity spectra for crystalline (1,3) and vitreous (2,4) As$_2$S$_3$ (a) and As$_2$Se$_3$ (b), respectively.

**Table 1**

The energy positions of maxima of reflectivity and photoconductivity of As$_2$S$_3$ and As$_2$Se$_3$ compounds at 293K measured by reflectivity and photoconductivity methods (in eV).

<table>
<thead>
<tr>
<th>Composition</th>
<th>Structure</th>
<th>Light polarization</th>
<th>E</th>
<th>E1</th>
<th>E2</th>
<th>E3</th>
<th>E4</th>
<th>E5</th>
<th>E6</th>
<th>E7</th>
<th>E8</th>
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</thead>
<tbody>
<tr>
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<td>Non polarized</td>
<td>2.5</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>4</td>
<td>4.7</td>
<td>5.9</td>
<td>7.0</td>
<td>9.1</td>
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<td>2.61</td>
<td>2.83</td>
<td>3.03</td>
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<td>2.43</td>
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<td>6.3</td>
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<td>-</td>
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<td>4.43</td>
<td>6.3</td>
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<td>9.85</td>
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<td>~</td>
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<td>EIIc</td>
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<td>-</td>
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<tr>
<td>~</td>
<td>glass</td>
<td>Non polarized</td>
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<td>3.5</td>
<td>-</td>
<td>4.8</td>
<td>5.4</td>
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<td>1.77</td>
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<td>5.8</td>
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<td>9.3</td>
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<tr>
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<td>crystal</td>
<td>Non polarized</td>
<td>1.82</td>
<td>2.2</td>
<td>2.38</td>
<td>2.85</td>
<td>3.9</td>
<td>4.7</td>
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<td>~</td>
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<tr>
<td>As$_2$Se$_3$</td>
<td>glass</td>
<td>Non polarized</td>
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<td>3.2</td>
<td>3.6</td>
<td>5.3</td>
<td>5.3</td>
<td>9.3</td>
<td></td>
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</tbody>
</table>
It is worthy to note that the complexity of chalcogenide glasses band structure in the field of high energies (E >> Eg) was confirmed also by authors [20] who studied the cathodoluminescence spectra of As$_2$S$_3$ films under action of electron beam. Accordingly to these authors the cathodoluminescence spectra of As$_2$S$_3$ films contained maxima at 3.81; 4.06; 4.28; 4.32; 4.56; 4.81; 5.32 and 5.56 eV. From the comparison of these data with the data indicated in Table 1 one can see a very good coincidence. This confirms that not only reflectivity spectra but also cathodoluminescence spectra obtained in the conditions of electron beam action can be used for study of band structure of crystalline and vitreous semiconductors. As it was shown by authors [9] from the photoemission spectra $N_v(E)$ of these crystals have doublet bands in the range of 0-6 and 7-16 eV and are caused by two groups of occupied states. As far as As$_2$Te$_3$ crystals concern no doublet is observed in the spectral range 7-16 eV. It is surprising that in the case of As$_2$Te$_3$ compound the crystal-glass transition has no significant effect on the character of photoemission spectra [20] As it was indicated in [10] the changes in the short- range order of As$_2$Te$_3$ do not manifest themselves in the optical absorption and photoemission spectra. The reflectivity spectra obtained by Zallen and co-authors [18,21] were used by them for the calculation of $\varepsilon_2$ constant in the whole studied spectral range using Kramers-Kronig relations. Having compared the reflectivity spectra with the respective $\varepsilon_2$ spectra the authors observed that the peculiarities of both spectra were approximately at the same energies.

Energy interval for determination of $\varepsilon_2$ in the case of As$_2$S$_3$ was enlarged by Perrin and co-authors [22] by measuring the energetic losses of energy of electrons, which have a high maximum at 19.8÷20 eV for all crystallographic directions and a maximum at 19.2 eV for As$_2$Se$_3$ glasses. These maxima are due to oscillation of free electron plasma. Less pronounced maximum of electron energy losses is observed at 7-8 eV. In the range 3÷12 eV the spectrum $\varepsilon_2$ calculated from these data follows the spectral dependence obtained from the reflectivity spectra. At higher energies up to 35 eV the decreasing of $\varepsilon_2$ is observed for crystalline as well as for vitreous As$_2$S$_3$. The reflectivity spectrum of amorphous As$_2$S$_3$ films has been also investigated at room temperature in the vacuum ultra-violet light in the region between 35 and 55 eV. As it was shown by the authors a peak of reflectance was observed in the energy region around 44 eV. This peak in opinion of authors [23] corresponds to the 3d core levels of an As atom. As it follows from the theory [1] in crystals the positions of maxima of reflectivity and maxima of $\varepsilon_2$ at energies $E>E_g$ determine the value of the energies of direct band-band transitions in special points of Brillouin zone.

The theoretical analysis of the energy spectrum of the As$_2$S$_3$ crystal was made by authors [24] using the method of pseudopotential. The analysis was made along the symmetry axis 2, $\Lambda$ and along two directions perpendicular to each other in the plane perpendicular to axis $\Lambda$. If one considers the extrema which are nearest to the forbidden gap then one can observe that the maximum of the valence band in the point (0,0,0,2), which is placed in the symmetry plane, and minimum corresponds almost to the same energy. The difference between the minimum direct transitions and the minimum indirect transitions is less than 0.1 eV. This explains the small difference between the minimum direct and indirect transitions. One can also observe that accordingly with energy model calculated for As$_2$Se$_3$ the energy positions of reflectivity maxima can find correspondence with the values of electron energetic transitions.

Following from the band model calculated for As$_2$Se$_3$ by Gubanov and Dunaevschi [24] the energy distances at point $\Gamma$, between 2 valence bands and 3 conductivity bands permit
electron optical transitions at 3.25; 3.96; 4.98; 5.68; 6.96 and 8.68 eV. These data correspond in many cases with energy positions of the reflectivity maxima in the framework of fundamental band absorption of As$_2$Se$_3$ (see Table 1). This proves the concordance of experimental data with the theoretical model.

While reflectivity and $\varepsilon_2$ spectra of As$_2$S$_3$ and As$_2$Se$_3$ are compared it is necessary to take into account that the structure of these crystals has the same structure characterized by term isomorphism. This can be seen in Fig.2 [11] which represents the dependence of energy positions of the reflectivity maxima of crystals As$_2$S$_3$ versus the energy positions of the same values in the crystals As$_2$Se$_3$. The experimental data show the straight line with steepness equal to unity. So, in order to obtain the parameters of As$_2$S$_3$ energetic band-model it is enough to increase the corresponding parameters of As$_2$Se$_3$ band-model by the magnitude 0.7 eV.

The optical transitions of electron in crystals occur under the conditions when the rule of quasi-pulse conservation acts. At the same time Tauc and co-authors [5] suggested that at the large energetic distances from the margin bands the density of states $g_c(E_n)$ and $g_v(E_p)$ of crystals and of amorphous semiconductors of the same composition do not differ. Therefore $\varepsilon_2$ can be determined from formula

$$\varepsilon_2 \approx \frac{1}{\omega} \int P(E_n, E_p) g_c(E_n) g_v(E_p) dE_p$$

where $E_n = h\nu - E_g - E_p$ is a factor of weight, which depends on $E_n$ and $E_p$ and it is not constant when energy is changed in the wide interval. If the optical properties of crystals are determined by the reduced function of state density in the case of amorphous semiconductor these properties depend on combination of state density of both bonds, taken separately. The integration of expression (1) leads to erasing of fine structure, which is contained in $g_c(E_n)$ or in $g_v(E_p)$. This is why the details of the $\varepsilon_2$ spectra of amorphous semiconductors should be erased. This condition permits to determine the type of optical transitions, the energy distances between free and occupied states in different points of $K$ space as well as other peculiarities of the band structure of crystal.

In amorphous semiconductors the processes of optical absorption are possible without taking into account the law of quasi-pulse conservation which does not take place in such materials. The energetically bands in amorphous semiconductors can be discussed only from the point of view of density of states and not from the point of view of energy of electrons in $K$ space. Therefore one can not expect that the reflectivity spectra of amorphous semiconductors could be characterized by the same energy structures in $K$ space with Van Hove singularities.

From the mentioned above it is quite clear why the reflectivity spectra of non-crystalline As$_2$S$_3$ and As$_2$Se$_3$ do not contain fine structure. At the same time in the region of high energies $7\div10$ eV reflectivity spectra of corresponding crystals and glasses are very alike. This can be understood if one takes into account that in the region of $7\div8$ eV $\varepsilon_2$ increases due to the beginning of a new absorption band. The latter is determined by electron transitions from the valence band, which is placed deeper. The lack of order does not influence very much the structure of this band.
Watanabe et al. [25] have pointed out the important role of intermolecular interaction in chalcogenide glasses, for which very strong dependence of the optical gap on the external pressure was discovered. The inclusion of the intermolecular interaction leads to marked change in the density-of-states spectra of the valence bands, giving smoothing and broadening of the structure. Such kind of alterations has been observed in the reflectivity spectra at addition of metal impurity to As$_2$S$_3$ (Fig.3) [26].

Introducing of rare earth Sm and Dy ions enlarges the main reflection peak, especially around its high-energy maximum at 3.5 eV. On the contrary, the transient metal Mn being added to the glass decreases the reflectivity in that band. It is seen from Fig.3 that the degree of the influence is increased with the impurity content growing from 0.1 to 0.5 at. % in both cases of Sm and Mn. The observed changes in the shape of the reflectivity spectrum look like the shift of the main peak to lower or to higher energy when the impurity atom of more (Mn) or less (Sm, Dy) electronegativity is introduced into the host glass. In the high-energy range (from 5 to 6 eV) the presence of impurity provides decreasing of reflectivity in the high-energy shoulder of the main peak (5.4…5.6 eV) and ~ 6 eV). The fall of reflectivity in this energy range may be associated with the effect of impurity on the degree of intermolecular interaction, as the latter significantly influences the density of states in the given energy interval. The changes in the intermolecular interaction have been revealed as increasing (in case of Mn) or decreasing (in case of Sm and Dy) of the interlayer distance, from X-ray diffraction examination.

On the basis of systematizing of the theoretical and experimental data of the investigation of optical properties of chalcogenide crystals and glasses some peculiarities of electron states in these materials were determined. The comparison of the reflectivity spectra of crystals and glasses of the same composition allows to clarify to what extent the optical properties are changed. It is shown that in the region near to optical gap single crystalline As$_2$S$_3$ and As$_2$Se$_3$ can not contain fine structure. At the same time in the region of high energies (7÷10 eV) reflectivity spectra of crystals and glasses are very alike because electron transitions occur with the participating of deeper valence bands which are less influenced by the lack of order.
3. THE ABSORPTION EDGE IN AMORPHOUS CHALCOGENIDES

3.1. THE MAIN FEATURES OF THE ABSORPTION EDGE

To elucidate the features of the absorption spectra caused by the losses of the far order, it is suitable to use such typical for non-crystalline semiconductors materials as arsenic sulfide and arsenic selenide. These materials possess such important advantages as the fact that they can exist in both amorphous and crystalline state. They are very convenient for optical investigation because their absorption edge is in the visible region of the spectrum. Besides that the vitreous materials can be obtained as bulk and thin film samples as well as in the form of fibres. Moreover the vitreous state of these materials is preserved at considerable deviation from the stoichiometry as well as at variation of the composition by introducing impurities and additions of other elements and alloys. At last, we shall point out that the structures of the bulk and thin-layer specimens do not differ significantly and consequently in the wide range of thickness the optical features of specimens slightly depend on thickness. This circumstance is very important for the investigation of the absorption coefficient in a wide spectral range. Many investigators paid attention to the mentioned advantages and devoted many of their works to the study of the absorption edge of vitreous arsenic sulfide and arsenic selenide. The results of the studied absorption edge of vitreous sulfide and arsenic selenide are shown in Fig.4a [7,27-29].

It is seen, that the results obtained by various authors are in a good agreement. There is some discrepancy only in the region of slight absorption (less than 1 cm\(^{-1}\)). The analysis of the experimental results shows that the absorption curves of amorphous sulfide and arsenic selenide as well as of other amorphous materials can be presented by three portions at high, medium and low absorption coefficient values. As it appears from Fig.4b the absorption edge of the amorphous arsenic sulphide in the region of high values of the absorption coefficient ($\alpha>10^4$ cm\(^{-1}\)) can be described by the square dependence of the type:

$$\alpha = A(T) / (\hbar \nu - E_g(T))^2$$

(2)

Coefficient $A(T)$ does not depend on the photon energy and slightly depends on temperature. $E_g$ is the energy value which according to [5] can be taken as the optical width of the forbidden gap. The determined from the graph dependence $(\alpha \cdot \hbar \nu)^{1/2}$ vs. $E_g$ value for

![Fig.3. Reflectance spectra of bulk glasses; As$_2$S$_3$ (1), As$_2$S$_3$+0.1 at.%Dy (2), As$_2$S$_3$+0.1 at.%Sm (3), As$_2$S$_3$+0.5 at.%Sm (4), As$_2$S$_3$+0.1 at.%Mn (5) and As$_2$S$_3$+0.5 at.%Mn (6).](image-url)
amorphous \( \text{As}_2\text{S}_3 \) appeared to be 2.35-2.38 eV. In the range of values 1÷310\(^3\) cm\(^{-1}\) the absorption coefficient depends on the exponential energy and can be described by the following ration:

\[
\alpha_0 \sim \alpha \exp \left\{ -\frac{E_o (T) - \hbar \nu}{\Delta} \right\} \text{ for } \hbar \nu < E_o
\]

(3)

where \( E_o \) approximately coincides with \( E_g \) value, but \( \Delta \) is equal \( \sim 0.05 \text{ eV} \). When the temperature decreases no structure appears, but the absorption edge first moves parallel to itself with the temperature coefficient \( 1.3 \times 10^{-3} \text{ eV} \) and then its position remains unchanged [30]. In the region of weak absorption (\( \alpha < 1 \text{cm}^{-1} \)) the absorption coefficient value strongly depends on the synthesis regime. At annealing of vitreous ingots the absorption edge moves to the area of large energies. However the exponential dependence of the type \( \alpha \sim \exp \hbar \nu / \Delta \), is

![Graph](image1.png)

**Fig.4a.** The absorption edge of vitreous \( \text{As}_2\text{S}_3 \) (1) and \( \text{As}_2\text{Se}_3 \) (2).

- Our data; ○ — [27]; △ — [29]; ▼ — [28].

also characteristic of this absorption edge section where \( \Delta \), is \( \sim 0.3 \text{ eV} \) [31].

Analogous results have been obtained when studying the absorption edge of the vitreous arsenic selenide and this is indicative of the fact that the features of the absorption edge of vitreous arsenic sulfide and arsenic selenide are common. However, this is not surprising, as these materials are analogous, they have the same structure both in the crystalline and in the vitreous state.

As it turned out, the absorption edge of other amorphous materials has the same shape as in the case of the sulfide and arsenic selenide, but the steepness of the exponential section edge and its position, as a rule, slightly differs [32]. Probably, the slope of the edge is influenced by the impurity as well as by the technology of amorphous alloys.
3.2. THE INFLUENCE OF DOPING ON THE ABSORPTION EDGE AND STRUCTURE OF AS2CH3 GLASSES.

Let us consider the influence of doping with different elements of the periodic table on the absorption edge of vitreous As$_2$S$_3$, A$_2$Se$_3$, typical representatives of vitreous semiconductors. From the elements of the first group silver has been chosen. With the increase of the concentration of silver impurities the absorption edge of the arsenic selenide shifts to the long-wave region and decreases its steepness [33]. According to these authors, the insertion of silver into the arsenic selenide with concentration from $8 \times 10^{19}$ to $5 \times 10^{21}$ cm$^{-3}$ results in the charged centres randomly distributed in the space and to the decreasing of the absorption edge steepness from 16.6 to 10.7 eV. The magnitude of energy, which characterises the enlarging of the absorption edge, is approximately equal to the change of the forbidden gap. This can be explained by enlarging of band edges caused by fluctuation of internal potential which appears due to chaotic distribution in space of the charge of doping atoms. The introduction of other elements may lead to the decreasing of the gap. For the example the introduction of the second group elements and particularly copper into arsenic sulfide shifts the absorption edge to the side of smaller energies to 0.4 eV [34].

The introduction of copper leads at the same time to the decreasing of the photo-darkening process [35]. The authors of paper [36] consider that in As$_2$S$_3$ and As$_2$Se$_3$ compounds copper does not generate deep defects, which could be detected by photoluminescence and EPR measurements. As it was established in the case of introduction of copper no structure modification occurs because the insertion of copper into the glass brings to the satisfaction of all chemical links. That means that Cu atoms become integral part of the amorphous lattice structure, but they do not have a significant effect on the tunnelling systems or the dichroism. This is because the tunnelling levels and the dichroism involve only local configurations. In the model proposed in [36] it was shown that introduction of copper determines the transition of chalcogen atoms from two fold to four fold coordination. This leads to the appearance near the top of valence bands of the electron metal-chalcogen states, which result in the decreasing of optical gap. It is understandable that this leads to the shift of absorption edge to the smaller values and to the disappearance of the photo-darkening effect.

The introduction of the elements of group three on the absorption edge of chalcogenide glasses can be demonstrated on the example of thallium. On the contrary, the case of silver and copper, which can be inserted into chalcogenide glasses only up to a few percents, thallium can be inserted, for example, in As$_2$Se$_3$ glasses in big quantities, because thallium creates with selenium weak bonds. In the systems As-Ch-Te, As-Ch-Ch-Tl (where Ch-Ch is S-Se or Se-Tl) the vitreous state is formed even in the case of large concentrations of thallium. The physical properties of such materials were widely studied in papers [37,38]. When inserting thallium into the arsenic selenide up to 0.1 am% the position of the absorption edge is unaffected however the Fermi level shifts to the conduction band because the concentration of negative defects D* is increased [39]. At the introduction of thallium in large concentrations the composition of the vitreous material changes giving rise to the shift of the absorption edge to smaller energies. In this case a definite amount of atoms plays the role of impurities manifested in the concentration increase of charged defects and the energy of activation conductivity.

Lanthanides belong to the third group of periodic table as well. These elements play nowadays very important role as luminescent additives in chalcogenide glasses for optoelectronic applications. The optical absorption of chalcogenide glasses is sensitive in the
case of their modification with heavy rare-earth metals. The authors [26] have shown that the addition of small amounts of dysprosium and samarium (0.1-0.5 at.%) leads to the shift of the absorption edge to longer wavelength and to an increase of the absorption above the edge (Fig.6) due to defects generated in the process of modification of the glass composition.

a)

![Absorption spectra of thin films](image)

**Fig. 6a.** Absorption spectra of thin films; As$_2$S$_3$ (1), As$_2$S$_3$+0.1 at.% Dy (2), As$_2$S$_3$+0.1 at.% Sm (3), As$_2$S$_3$+0.5 at.% Sm (4), As$_2$S$_3$+0.1 at.% Mn (5) and As$_2$S$_3$+0.5 at.% Mn (6).

b)

![Absorption spectra of bulk glasses](image)

**Fig. 6b.** The absorption spectra of bulk glasses; As$_2$S$_3$ (1), As$_2$S$_3$+0.1 at.%Sm (2), As$_2$S$_3$+0.5 at.%Sm (3), As$_2$S$_3$+0.1 at.%Dy (4), As$_2$S$_3$+0.1 at.%Mn (5) and As$_2$S$_3$+0.5 at.%Mn (6).

The influence of the elements of group four on the absorption edge can be demonstrated on the example of tin and germanium. Even the first investigation of the tin influence on electrical and photoelectrical properties of As$_2$S$_3$ glasses has shown that elements of the forth group having been introduced into glasses play a role of active impurity.

In correspondence with the Mössbauer spectra tin is four-valence (Sn$^{4+}$) in the arsenic sulfide and arsenic selenide alloys and in the formation of the lattice all four valence electrons participate [40]. However, in the process of crystallization of glasses in the Mössbauer spectrum the lines appear which correspond to bivalent tin. In the As$_2$Sn$_x$ glasses tin atoms are inserted in the atomic network of glass, having the maximum valence 4$^+$. They do not form the energy levels in the forbidden band of the vitreous semiconductor. Under the influence of light illumination the appearance of two-valence tin, which is considered to be the recharge of tin centres, was observed.

The spectra of edge optical absorption (Fig.7a) of the AsSe films with various content of tin impurity are characteristic of amorphous semiconductors. The variation of the $E_{g opt}$ determined from Tauc plot for various tin content is shown in Fig.7b. It is seen that tin impurity lowers the optical gap, first (to 1 at.%) steeper, and then nearly proportional to the tin concentration. This fact probably indicates that at sufficiently high tin content there are formed new structural units with lower optical threshold energy, the presence of which lowers the mean value of the gap, as in alloys. This type of explanation for the variation of the optical gap upon tin content was suggested in [40] using the following structural units AsSe$_{1.5}$, As$_2$Se$_2$, As$_2$ and SnSe as possible constituents of the ternary chalcogenide glass. A similar consideration in the frame of “alloy” approximation based on structural units like Se, AsSe, AsSe$_{1.5}$ and SnSe$_2$ has been advanced in [41].
At intermediate values of the absorption coefficient in the range $h\nu < E_g$ the absorption edge behaves exponentially $\alpha h\nu \sim \exp \left(\frac{(h\nu - E_{go})}{E_{oo}}\right)$ (Fig.7). The Urbach edge arises from superposition of electron transitions from the valence band tail to extended states of the conduction band (and vice versa). As a rule the broader valence band tail is dominant, that is, the width $E_{oo}$ is characteristic of it. Between the apparent gap $E_g$ and the tail width $E_{oo}$ a simple correlation exists: $E_g = E_{go} - cE_{oo}$, where $E_{go}$ is the limiting value of the gap for a vanishing small tail width and $c$ is constant ($c = 5$ to $10$ for a-Si:H) [42]. If the tail width varies with the impurity content (or temperature), the extrapolations of the Urbach edges to higher energies for various impurity concentrations have to cross at a focus, the position of which corresponds to $E_{go}$. It is seen from Fig.7 that the slope of the exponential portions decreases with the increase of the tin content, and the largest slope corresponds to undoped AsSe. The above correlation fits to all alloys with the values $E_{go} = 2.15$ eV and $c = 5.2$, and the absorption at the end of the exponential tail is more than 100 times increased. The above described behaviour of the spectral dependence of the absorption in the exponential absorption region indicates that tin impurity induces broadening of the band tail states from 0.06 eV for undoped AsSe to 0.15 eV for AsSe:10%Sn. This broadening may be caused by formation of new Sn-based structural units as well, which add a compositional disorder to the existing structural one.

The observed behaviour of the Urbach edge is usually ascribed to the variation of the degree of structural disorder, in fact the medium range ordering, which includes both the thermal and frozen-in disorder. Hosokawa et al. [43] observed a fan-like decreasing of the Urbach slope of As$_2$S$_3$ and As$_2$Se$_3$ in a wide-range temperature interval 25 to 900 °C. Tichá et al. [44] obtained similar behaviour of spectra of glassy As$_2$Se$_3$ samples under thermal treatment with various quenching rates. The reasons for this behaviour and the role of disorder in formation of the Urbach edge, first stressed by Olley [45], are still under discussion. Here we wish to notice that the behaviour of this type is for the first time observed for the case of chalcogenide glass with varying impurity concentration.

As in the case of copper, metal impurities of III and IV group elements effectively reduce the photodarkening and its relaxation under light exposure in amorphous films of
As$_2$Se$_3$:0.5 at.% Me (Me=Sn, Mn, Sm and Dy) and of AsSe:Sn$_x$ (x=1 to 10 at.%) [46]. The degree of reduction becomes stronger as the impurity concentration is increased. Thermal treatment of the films at 100 °C in vacuum reduces the photodarkening, especially in undoped AsSe films, where there are numerous homopolar bonds. Doping of AsSe films by tin reduces the photodarkening for $x \leq 2$ at. % Sn. Changes in the optical transmission of AsSe:Sn and As$_2$Se$_3$:Me films under illumination may be described by a stretched exponential with the dispersive parameter $0.4 \leq \alpha \leq 1.0$. This fact indicates the presence of strong dispersion in the photo-darkening process. In the context of the "slip-motion" model [47], this dispersion may be naturally attributed to the multiple trapping of photo-induced holes. The strong effect of metal additives on the photo-darkening kinetics, especially on its response to thermal treatment, is in agreement with the model as well. In particular, with its tetrahedral type of coordination, tin should reduce the flexibility of the layer network, hence retarding the photo-darkening phenomenon. Doping of amorphous chalcogenide films by metals assists in stabilising the glassy matrix with respect to light exposure and thermal treatment (For details see p.6.4).

The influence of the elements of group five will be considered on the example of antimony. The structural pyramidal units As$_3S_3$ and Sb$_3S_2$ are preserved, but length of As-S bands increases. The latter leads to the shift of the absorption edge to smaller energies and to corresponding change of the optical band from 2.4 eV (for As$_2S_3$) to 2.1 eV (for As$_2$S$_3$Sb$_2$S$_3$). As a result of the introduction in the composition of the As$_{2-x}$Sb$_x$S$_3$ glasses of small quantities of antimony ($0 \leq x \leq 0.1$) the modification of refraction index occurs in the range 1.2 to 2 µm (C5). The same modification takes place in the case of introduction of antimony in As$_{2-x}$Sb$_x$Se$_3$ the values of antimony concentration ($0 \leq x \leq 0.3$) [48]. The modification of refractive index follows the relations:

$$n_1 = n_1(0) + (0,08 \pm 0,01) \cdot x \text{ for As}_{2-x}Sb_xS_3 \text{ system}$$

$$n_2 = n_2(0) + (0,22 \pm 0,01) \cdot x \text{ for As}_{2-x}Sb_xSe_3 \text{ system}$$

where $n_1(0)$ and $n_2(0)$ are refractive indexes respectively for As$_2S_3$ and As$_2$Se$_3$ glasses.

According to the authors [48-49] in the system As$_2S_3$-Sb$_2$S$_3$ the substitution of arsenic for antimony does not lead to considerable changes in the glass structure. The lack of the noticeable change of boring order upon arsenic substitution for antimony is the result of the fact that Sb$_2$S$_3$ structure consists of a trigonal pyramid which is similar to As$_2$S$_3$ structure. At the same time the arsenic atoms substitution for antimony influences the average order giving rise to gradual transition from layer As$_2S_3$ structure to continuous net structure which according to Chervinka [50] influences very much absorption in the infrared range.

The influence of the element of group six can be followed on the example of sulfur for selenium and sulfur for tellurium substitution in the As$_2S_3$ alloys. The optical features As$_2S_3$ and As$_2$Se$_3$ are very similar which follow from their structure. As many authors have shown upon sulphur substitution for selenium the absorption edge shifts to the region of smaller energies. Upon the substitution of sulfur for tellurium the absorption edge also shifts to the side of smaller energies [51-52], however the value of the steepness of the absorption edge increases. The authors of [53] consider, that upon the introduction of tellurium in small quantities the tellurium atoms substitute sulphur without changing the glass structure, while in large quantities the glass structure is deformed. The strong influence of tellurium on the absorption edge of the system As$_2$Se$_3$-As$_2$Te$_3$ was observed. Adding the tellurium to the alloys As$_2$Se$_3$-As$_2$Te$_3$ leads to the shift of the absorption edge to longer wavelength. If As$_2$Se$_3$ alloys have the maximum transparency at 0.8 µm then in the case of As$_2$Se$_3$-4As$_2$Te$_3$ the maximum transparency is in the region more than 1.4 µm. The optical gap determined from conductivity
and photoconductivity data is changed too while selenium is substituted by tellurium in the system \( \text{As}_2\text{Se}_3-\text{As}_2\text{Te}_3 \) from 1.5 eV (for \( \text{As}_2\text{Se}_3 \)) till 0.9 eV (for \( \text{As}_2\text{Se}_3-4\text{As}_2\text{Te}_3 \)).

The effect of doping on optical properties of chalcogenide glasses is very intensive in the case of addition of Mn, the transient metal (Fig. 6). The samples with 0.5 at.% Mn are practically opaque in the whole investigated spectral range (0.5 to 25 \( \mu \text{m} \)). The latter effect suggests the alteration of the macrostructure of the glass material at high Mn content. This suggestion was confirmed by mentioned authors by x-ray diffraction procedure [26]. These results indicate a significant modification of the mean distance between the disordered layers, induced by metals.

4. ABSORPTION EDGE IN THE MULTICOMPONENT ALLOYS

As it was established from investigation of optical properties of multi-component chalcogenide glasses the composition of glasses has a slight influence on the general aspects of the absorption edges. In both cases of binary stoichiometric glasses \( \text{As}_2\text{S}_3 \) and \( \text{As}_2\text{Se}_3 \) and non-stoichiometric glasses \( \text{As-S, As-Se, As-S-Se, As-Se-Te, As-S-Ge, As-Se-Ge, Ge-Bi-S, Ge-Sb-Bi-Se} \) and other the absorption edge is described quite well using only two exponential functions (in the regions of weak absorption and Urbach tail) and by quadratic function (in the range of high absorption). By changing the composition of glasses the position of absorption edge is changed too due to the change of optical gap. In the range of weak absorption the steepness of the absorption edge depends not only on the composition of glasses, but also on the technology of preparation, of additional components, on the history of samples. In the higher region of the absorption edge (1÷10^4 cm\(^{-1}\)) the steepness of the absorption edge can manifest a strong alteration, but it happens only in the cases when the changes of the composition of glasses is accompanied by the changing of the glass structure.

Really the glass structure change is directly connected with the absorption edge steepness. For example, upon changing the composition in the \( \text{As}_2\text{S}_3-\text{As}_2\text{Se}_3 \), \( \text{As}_2\text{Se}_3-\text{Sb}_2\text{S}_3 \) systems which are considered by many authors to be ideal solid solutions, the steepness of the absorption edge suffers slight changes influencing only its position, i.e. the optical gap. By changing the composition in the system \( \text{As}_2\text{Se}_3-\text{As}_2\text{Tl}_3 \), the width of the optical gap changes linearly with the composition as follows from relationship suggested by K. Shimakawa in [54], the use of which for various glasses was analysed in [55-56]:

\[
E_{g_{AB}} = Y E_{gA} + (1 - Y) E_{gB},
\]

(6)

where \( E_{gA} \) and \( E_{gB} \) are the optical gap components \( A \) and \( B \), \( Y \) is the share of element \( A \) volume.

At the same time in the systems as \( \text{Ge}_{1-x}\text{S}_x \) in which the change of the composition leads to the change of the ratio of structural units \( \text{Ge-S, Ge-Ge, S-S} \) the deviation of the exponential values of the optical gap calculated according to formula (6) is observed. In the systems where there is a change of the composition and at the same time the ratio of the structural units changes as it was mentioned above the change of the steepness of the absorption edge occurs. This can be seen from the data of [57-59], where the optical features of the systems \( \text{As}_2\text{S}_3-\text{Ge} \) were investigated. With the enrichment of arsenic sulphide vitreous alloys by germanium the absorption edge shifts to longer wavelengths but the steepness of the edge increases rather sharply (to the germanium concentrations 7 at.%), and then changes more smoothly along the curve with the maximum corresponding to the composition given by formula \( \text{AsS}_{1.5}\text{Ge}_{0.73} \). The authors of [57-58] studied thin films of such compositions of \( \text{As}_2\text{S}_3-\text{Ge} \), which can be obtained in amorphous state only in the form of thin films, bulk
samples having polycrystalline structure. The experimental results of the absorption edge of
the materials As$_2$S$_3$-Ge are presented in Fig.8a. As it can be seen the increasing of germanium
in the glass leads to the shift of absorption edge to longer wavelengths. In the range of big
absorption coefficients the absorption edge can be described by formula:

$$\alpha \cdot h\nu \sim (h\nu-E_g)^{-2}$$

(7)

This relation was used for the determination of optical gap ($E_g$). Obtained values are
given in Fig.8b. One can observe that $E_g$ is changed almost proportionally when germanium is
introduced into the glass. For all studied compositions As$_2$S$_3$-Ge the exponential dependence
of absorption versus energy of photons is observed for all energies below $E_g$ (see Fig.8a).

![Fig.8a](image1.png) ![Fig.8b](image2.png)

**Fig.8a.** The dependence of absorption coefficient on photon energy $\alpha$ vs. $h\nu$ for amorphous As$_{1.5-x}$Ge$_x$ thin films. x: 1-0, 2-0.1, 3-0.19, 4-0.5, 5-0.73, 6-1.7, 7-2.0.

**Fig.8b.** The composition dependence of the band gap $E_g$ (1) and of the parameter of the Urbach edge $\Delta$ for the amorphous As$_{1.5-x}$Ge$_x$ thin films.

The steepness of the absorption edge is changed when composition of glass is
changed. When the concentration of germanium in the As$_2$S$_3$ glass is not too high (0÷7 at.%), $\Delta$ is changed drastically, but at higher values of concentration the parameter $\Delta$ suffers a small change and $\Delta$ follows a curve with maximum, corresponds to the composition As$_{1.5}$Ge$_{0.73}$ (Fig.8b). As one can note the absorption edge of As$_2$S$_3$-Ge glasses has the same shape as in
the case of As$_2$Ch$_3$ glasses having quadratic and exponential dependence versus energy of
photons (see Fig.7 and Fig.8).

With the temperature increase the optical gap decreases with the temperature
coefficient ($4÷8$) $10^{-4}$eV/° which is typical for vitreous semiconductors [60-61]. As the
authors of [62] who carried out complex investigations of the mentioned materials in the form
of heterostructures p-Si-As$_2$S$_3$-Ge$_x$ have shown the diminution of the forbidden gap width
with the addition of germanium to As$_2$S$_3$ is due to the fact that in the process of chalcogene
and arsenic substitution by germanium atoms the reorganization of the valence band structure
occurs when the edge of valence band moves up (Fig.9).

The influence of the glass structure on the position and steepness of the absorption
edge was pointed out by the authors in [63], who investigated the absorption edge in the
systems Te$_x$As$_{2-x}$S$_{3-x}$, where 0<x<1 and in the system As$_2$S$_{3-x}$Te$_x$, were 0≤x≤0.015.

As it was observed the increasing of the contents of tellurium shifted the absorption
edge to lower values. At the same time the steepness of the absorption edge ($\Delta$) is increased
while tellurium is added. It is considered that adding of a small quantity of tellurium into
As$_2$S$_{3-x}$Te$_x$ glass leads to the substitutions of sulphur atoms by tellurium atoms not changing
the structure of the glass. However, at a higher concentration of tellurium the structure of the
glass is deformed and the composition of the glass can be regarded as solution of As$_2$S$_3$ and As$_2$Te$_3$.

![Graph](image1.png)

Fig.9. The modification of the valence band edges (a), of the Fermi level (b), and the difference $E_{g2}$-$E_0$ on doping of As$_2$S$_3$ with Ge.

As far as the system As-S-Ge is concerned the results obtained in paper [64] were confirmed by measuring of the optical spectra of glasses As$_2$S$_3$-GeS$_2$ [62]. According to these data the glass alloy consists of structural units As$_{3/2}$S$_2$ and GeS$_{4/2}$. Increasing of GeS$_2$ concentration leads to increase of the level of ionicity due to the transition from trigonal structural units to tetrahedron ones. It is accompanied by shifting of the absorption edge to lower values although the shape of the absorption curve remains the same as in the case of other glasses.

The typical for chalcogenide glasses absorption edge with quadratic and exponential dependence of the absorption coefficient versus the energy of quanta is also observed in the system Ge-Bi-S [64]. The optical gap is decreased approximately linearly when the temperature is increased having the temperature coefficient $(4.6-4.9) 10^{-4}$ eV/K. These data correspond to data obtained in the other chalcogenide glasses.

Earlier it was shown that there is a clear dependence between $T_g$ and $E_g$ [65-66]. On the basis of the investigation of thin films of As$_2$S$_8$, As$_2$S$_3$, As$_2$S$_{1.5}$ S$_{1.5}$, As$_2$Se$_{1.5}$Te$_{1.5}$ it was found that for the atomization heat the following relation exists:

$$H_s(A-B) = \frac{1}{2}(H_s^A + H_s^B),$$  \hbox{(8)}

where $H_s^A$ and $H_s^B$ are atomization heat of elements $A$ and $B$.

In the binary alloys the relation gives the average number of coordination:

$$n = xN_A + (1-x)N_B = \frac{1}{2}(H_s^A + H_s^B),$$ \hbox{(9)}

where $N_A$ and $N_B$ are coordinator numbers of elements $A$ and $B$.

In the case of chalcogenide glasses having the same number of coordination the value of $E_g$ increases too. The correlation between the optical gap and the chemical composition of chalcogenide glasses proceeds from the analysis of the average atomization heat and the average coordinating number. It was found that when the atomization heat increased the width of the optical gap is increased for those vitreous materials which had the same value of the average co-ordination number.

A good correlation has been found between the width of the forbidden gap of the glasses and the bond length for the characteristic of which the sum of covalent radii in alloys with the coordinating number $n=2.4$ was used. For such alloys the plot of the dependence of $E_g$ on the reverse length of the inter-atomic bonds can be approximated by straight-line. In
such a way the atomization heat, the coordinating number, the length of the chemical bond are the parameters which coordinate well with the value of the optical forbidden gap of vitreous materials. In this case it is important to compare the mentioned parameters for the glass characteristics of one and the same coordinating number.

The most pervasive impurity in chalcogenide glasses is oxygen. The authors of [67] established that for oxygen concentration below \(10^{19}\) cm\(^{-3}\), the conductivity is independent of oxygen, but at concentrations exceeding the \(10^{19}\) cm\(^{-3}\) oxygen promotes doping by increasing the densities of dangling bond defects at 3-fold-coordinated chalcogens. For determining of this fact the compositions \(\text{Cu}_6\text{As}_4\text{S}_9\) and \(\text{Cu}_6\text{As}_4\text{Se}_9\) were studied because at these compositions the S (or Se) and Cu atoms were all tetrahedral coordinated and there exist only Cu-S and As-S (or CuSe and As-Se) bonds. Addition of oxygen to these glasses increased the conductivities by more than three orders of magnitude [68]. For oxygen concentrations higher than \(3\cdot10^{19}\) cm\(^{-3}\) the absorption was increased drastically. By comparison of last data with the data of conductivity one can conclude that in this case energy levels responsible for the impurity absorption could be associated with acceptor levels.

In conclusion we note that presented data are of great interest for discussing of the absorption edge nature in non-crystalline (amorphous) semiconductors that will be given in the next paragraph.

5. THE NATURE OF THE ABSORPTION EDGE IN NON-CRYSTALLINE (AMORPHOUS) SEMICONDUCTORS

The nature of the absorption edge in non-crystalline (amorphous) semiconductors has been discussed in literature for many years already. This is caused by the complexity of obtaining the optical characteristics of the amorphous semiconductors taking into consideration the first principles because of the complexity of their structure. It should be noted that due to this reason the nature of the absorption edge even in \(\text{As}_2\text{S}_3\) and \(\text{As}_2\text{Se}_3\) crystals is not completely understood. Moreover there is no unambiguous explanation of the exponential dependence, which is subordinated to the so-called Urbach rule.

In conformity with Urbach rule the steepness of the absorption edge depends on temperature as \(1/T\). It is supposed, that in crystals Urbach edge may occur as a result of different reasons, e.g., the interaction of coupled excitons with the lattice fluctuations [69], the widening of the absorption edge by the electric field [70]. To understand the physical mechanism of the formation of the exponential edge in semiconductors some theories have been worked out taking into account the defects [70-71]. Dexter [72] investigated the influence of the lattice deformation arising due to its oscillations on the width of the forbidden gap and the spectrum of the inter-band absorption. The absorption coefficient \(\alpha\), calculated by Dexter, corresponds Urbach rule, but only in a narrow range of temperatures and \(\alpha\) values. The exponential dependence of the absorption edge of crystals by Redfield’s [71] opinion is connected with the presence of internal electric field caused by the lattice defects. To calculate the absorption coefficient Redfield used Frantz-Keldish effect caused by the effect of the internal electric fields.

The explanation of the absorption edge in amorphous semiconductors creates more difficulties. For correct interpretation of the nature of the absorption edge of vitreous semiconductors it is necessary to take into account that in these materials the law of quasimomentum preservation is not realized, or is realized in the small regions[3,5]. According to the theoretical notions in the forbidden gap of amorphous semiconductors there
spread so-called tails of the state density, the form of which can be described by Gaussian or exponential function. Therefore in the first works on the absorption edge of the amorphous semiconductors the exponential section of the edge was considered as the result of optical transition between non-localized and localized states. However such an explanation is not enough motivated. Following Davis and Mott [73] the main objection against this explanation is the identical steepness of the absorption edge of the great majority of various materials. The authors are inclined to explain the exponential absorption edge in amorphous semiconductors by broadening of exciton line by the internal electric fields which suggests the presence of excitons and internal electric fields in amorphous semiconductors. There is no doubt about the presence of strong and internal electric micro-fields in them, yet the presence of excitons is problematic. As Bonch-Bruevich and Iskra showed [74] there exists a rather appreciable possibility of exciton disintegration in an internal field.

The suggestion that exponential absorption edge of Urbah type can arise from the effect of disorder upon exciton absorption was experimentally also shown by Olley [45]. For the evidence of this suggestion the author studied the changes of optical absorption of both crystalline and amorphous semiconductors during the introduction of disorder by heavy ion bombardment of crystals PbI2 by helium ions. The author has shown that such process leads to the quench of the exciton effects and to the appearance of experimental edge which broadens with increasing dose. Similar broadening Olley observed after bombardment of thin films of amorphous As2Se3 and amorphous Se at 25°K.

It is very important to note that the bombardment induced changes in absorption edge of mentioned materials can be annealed out merely by warming the films to room temperature, and they can then be rebombarded [45]. Lanthanides belong to the third group of periodic table as well. These elements play nowadays very important role as luminescent additives in chalcogenide glasses for optoelectronic applications. The optical absorption of chalcogenide glasses is sensitive in the case of their modification with heavy rare-earth metals. The authors of [26] have shown that the addition of small amounts of dysprosium and samarium (0.1-0.5 at.%) leads to the shift of the absorption edge to longer wavelength and to an increase of the absorption above the edge (Fig.6) due to defects generated in the process of modification of the glass composition.

These results can be regarded as convincing evidence that the Urbach edge observed in amorphous semiconductors arises from inherent structural defects, which are manifested by both broken and strained bonds.

From the above discussed results one can make another conclusion that the thermal treatment influences optical properties of amorphous materials. The evidence of this fact one can find for example in paper [75]. In the last paper [44] studying the temperature dependence of the Urbach edge of glassy As2S3 prepared by slow (∼10^{-3}Ksec^{-1}) cooling and rapid (into cold water) quenching from temperature 600°C the slope of Urbach edge decreases for low cooling rate. It was proved by X-ray diffraction, differential scanning calorimetry (DSC) measurements and density determination. It is worthy to note that under slow cooling the structure of glassy As2S3 is improved. In opinion of the authors the structure improvement (under very slow quenching rate) proceeds owing to the decrease of the wrong bonds density and simultaneous increase of the medium range order. As it was shown above, any mechanism of explaining the nature of the absorption edge of amorphous semiconductors should take into account the presence of incidental internal micro fields which in these materials can arise as a result of lattice distortion, the freezing of fluctuations in the inter-atom distance, introduced admixtures and others.
There is every reason to consider that the nature of the absorption edge in strongly
doped semiconductors and in the amorphous ones are alike. The presence of a great analogy
between the strongly-doped crystalline semiconductors with a clustered structure and
amorphous semiconductors has been referred to by Ryvkin and the collaborators in their works [76].

Redfield [77] associated the nature of the exponential “tail” absorption in strongly-
doped semiconductors with Frantz-Keldish effect on the internal electric fields created by the
ionized impurities. This idea was further developed by Shklovskii and Efros [78], who
proceeding from the theoretical consideration, obtained in the case of strongly-doped
semiconductors and exponential absorption edge.

Some time before the idea of large-scale fluctuations had been used by Fritzshe [79] for
analyzing the discrepancy of concentration values of local states near Fermi level determined
by optical and electrical methods. If it is taken into account that part of large-scale fluctuations
is caused by deviations in inter-atomic distances which can be considered as frozen phonons
of high concentration, then these phonons must not change with temperature (up to \( T_g \)) the
steepness of the absorption edge [60]. Bonch-Bruevich [80,81] proposed the theory of inter-band
optical transitions in disorder systems for two extreme cases, when the incidental internal field
immediately changes in space and when this condition is not deliberately fulfilled. Examining
the optical transitions between the states of the continuous spectrum of the nearly intrinsic
semiconductor at low temperatures for the case of slowly changing internal field the following
exponential dependence of the absorption coefficient on the quantum energy was also
obtained;

\[
\alpha \sim \exp\left(\frac{h\nu}{\omega}\right)
\]

(10)

\[
\omega = \left(\frac{\varphi_2}{g}\right)^{1/3}; \quad \varphi_2 = \frac{3h}{4mc^2} \langle (\Delta U) \rangle^2
\]

(11)

where \( U \) is potential energy of electrons in the internal field and \( t_1 = \langle U^2 \rangle \). So the steepness of
the absorption edge is determined by the average square fluctuation product of the potential
electron energy \( \langle (\Delta U)^2 \rangle \).

The theory of inter-band absorption being applied to the vitreous semiconductors in the
system As\(_2\)S\(_3\)-Ge allowed to obtain the values of \( \langle (\Delta U)^2 \rangle \). These data show the value of
square average fluctuation of potential energy derivate of electron when germanium is
introduced into As\(_2\)S\(_3\). From this point of view the most disordered alloy is As\(_{1.5}\)Ge\(_{0.73}\) or As\(_3\)S\(_6\)Ge\(_3\).

On the basis of analysis of the absorption threshold of amorphous semiconductors the
information concerning the distribution of the density of states in band tails was obtained. This was
obtained taking into account the following conditions: (a) the law of pulse conservation is not
fulfilled; (b) the function of matrix element \( M(\omega) \) does not depend on photon energy \( h\nu \). Then
the function \( \varepsilon_2(\omega) \) can be written in the following way:

\[
\varepsilon_2(\omega) = M(\omega)\rho_{\text{conv}}(\omega)
\]

(12)

where

\[
\rho_{\text{conv}}(\omega) = \int_{-\infty}^{v} \rho_\nu(\omega')\rho_\nu(\omega' + \omega)d\omega'
\]

(13)

Therefore for determining of the function \( M(\omega) \) it is necessary to use formula (12) and
(13). At the same time it is known that this mentioned above spectral function is difficult to
calculate from the first principles. Dersch, Overnot and Thomas [82] make use of the theory
developed by Miller and Thomas [83]. They have taken into consideration not only the static
disorder but the dynamical one too conditioned by the phonons. These authors have found that $M(\omega)$ has a weak maximum near $\omega=\varepsilon_2-\varepsilon_\nu$, which is in full agreement with the results of work [84]. In this case $M(\omega)$ is changed by approximately 2 times.

Bonch-Bruevich showed that in the case of long-wave fluctuations of the potential the matrix element strongly depends on the photons energy. The authors of [82] in collaboration with M.Grunvald calculated $M(\omega)$ on the basis of the accepted by them Hamilton model for a one-dimensional circuit. As a result of this they showed that for investigated case $M(\omega)$ was a dropping (lowering) function which completely determined the optical spectrum in the tail section. That was in full agreement with Bonch-Bruevich’s results.

On the basis of ideas developed by Mott, Davis and Sttreet [84,85], Kolobov and Konstantinov [86] showed in the case of unfigurational coordinate model of amorphous semiconductors Urbach law can be obtained only in the case when the maximum of conductivity band corresponds to the maximum of the valence band. As it was shown by many authors the exponential form of the absorption threshold in amorphous semiconductors is determined by the density of states in the band tails, the latter being connected with disorder induced by impurities. Some authors accepted that logarithm of state density (H1) $\ln g(E)$ is proportional to $F^\nu$, where for the three-dimensional case $\frac{1}{2} \leq n < 2$. Exponential index $n$ is a function of correlation length of disorder $L$ and of energy $E$.

If the correlation disorder length caused by the joint effect of the structural and oscillating distortion lies in the range of $L=(2-5)\AA$ but the potential fluctuation is proportional to $(\varepsilon\nu)^2$ then as authors [87,88] showed the determining function of the absorption edge is the state density. In such a way in this case Urbach tail of the absorption edge directly follows from the function form of the state density and the value $n(L,E=1)$. Yet, in these authors’ opinion, the above mentioned arguments may not take place in strongly doped semiconductors where the typical values $L$ are 25-50\AA and -the potential fluctuation is evaluated as 0.04 (eV)$^2$.

In Tauc’s opinion [87] two reasons for the formation of states in the band tail should be pointed out. The first of them is due to the disorder of the lattice structure of the glass as a result of angle fluctuations and band lengths. The states arising as a result of this can be called proper electron states of the band tails. Parallel with these states in the forbidden gap can arise due to the broken bonds and impurities. However it should be mentioned that the electron states could be caused by the fundamental characteristics of non-crystalline solid bodies that is by the structure disorder. Since the absorption edge of amorphous semiconductors is caused by the structure disorder there arises the question, whether it is possible to get some information about the glass structure investigating the form of the absorption edge. The answer to this question was got in work [88] in which the author analyzed the absorption edge of the vitreous As$_2$S$_3$ taking into consideration the thesis that two types of disorder are additively created in non-crystalline semiconductors. One of them has a thermal nature that is a pure form there exists in crystals and the other type is a structure disorder, which together with the thermal disorder is present in amorphous semiconductors. This thesis was used as the basis for interpreting the power index $\sigma$ in the expression for the absorption coefficient:

$$\alpha = \alpha_0 \exp \left[ \frac{(h\nu-E_0)}{\sigma} \right]$$  \hspace{1cm} (14)

where $\alpha_0$ and $E_0$ are the material constants, $\sigma$ is the reverse value of the absorption edge slope, which, in the author’s opinion, expresses the disorder degree.

In crystals:

$$\sigma = A k T^*$$  \hspace{1cm} (15)

where $A$ is the constant, $k$ is Boltzmann invariable, $T^*$ is the efficient temperature making a contribution to the fluctuating atom shift.
In non-crystalline materials:

$$\sigma = AkT^* + \theta_s$$

$$\alpha = AkT^*$$  \hspace{1cm} (16)

where $\theta_s$ is the contribution of the structural disorder. Interpreting analytical expression of parameters $T^*$ and $\theta_s$ and taking into account that the electron capture brings to additional disorder the authors obtained for $\sigma$ the following expression:

$$\sigma = Ak[(\theta_1/2)\coth(\theta_1/2T) - f(\theta_2/2)\tanh(\theta_2/2T)] + gT_f$$  \hspace{1cm} (17)

where $\theta_1 = 4\omega/k$, $\omega$ is the frequency of the fluctuating atom shift, $k\theta_2$ is the energy of the electron excitation, $\theta$ is the contribution of the structures disorder, which takes into account the glass prehistory:

$$\theta_1 = gT_f + h$$  \hspace{1cm} (18)

Experimentally measuring $d\varepsilon/dT$ in the region $T > T_g$ it is possible to evaluate $g\omega$ and by adjusting the expression for $\sigma(T)$ with the experiment $f$ and $\theta_2$ values are obtained. Using the above given procedure the author of [89] has found the value for $\sigma$ in the case of glass like AsSe$_2$ to be equal 56 meV at 77K while the experimental value constitutes 52 meV which shows a surprisingly good coincidence. From this analysis one more conclusion can be drawn: as in the expression for $\sigma$ the first term $AkT^*$ depends on temperature, then for $\sigma$ to be independent of temperature it is necessary the second term $\theta$ to be also dependent on temperature and in such a way to compensate the first term of $AkT^*$. This means that with the increase of temperature on the glass-like As$_2$Se$_3$ the structure must change.

In such a way, exponentially the absorption edge in amorphous or so-called Urbach rule in amorphous semiconductors was subjected to a thorough analysis by many investigations. At the same time it should be underlined: the last investigation connecting the nature of Urbach absorption edge in amorphous semiconductors with their structure for the first time allows not only to bring arguments for the explanation of the absorption edge form but also to use the experiments for investigating the absorption edge to get information about the structure of glass-like materials [89]. If Urbach absorption edge in amorphous semiconductors arouse a great discussion, in the area of weak absorption it has received a more unambiguous explanation.

The absorption edge of glass-like semiconductors in the area of weak absorption ($\alpha \leq 1$ cm$^{-1}$), as it was already shown, strongly depends on the synthesis regimes and can be described by the exponential function of the type described by formula (14). Taking into consideration the structural sensitivity of this section of the absorption edge it is possible to suppose that it is connected with the optical transitions with the participation of non-localized and localized states found deep in the forbidden gap. The authors of [31] consider, that the section of weak absorption is connected with the deep fluctuations potential, which can arise because of the loss of distant long-range order, defects or impurities. They counted the concentrations of local states making contribution to absorption. The value of the general concentration of local states obtained from this calculation turned out to be equal to $10^{16} - 10^{17}$ cm$^{-3}$. Such an order of concentrations of local states ($N$) in the forbidden gap of the glass-like arsenic sulfide was also found in other experiments. However the experiments on magnetic susceptibility give for $N$ greater values of the order $6 \cdot 10^{17}$ cm$^{-3}$.

The problem of the nature of the weak-absorption tail recently was studied using the constant-photocurrent method (CPM) [90]. As it was established the weak-absorption tail detected by CPM is substantially smaller than that evaluated from transmission measurements. At the same time the steepness of the weak-absorption tail in As$_2$S$_3$ determined from CPM measurements is equal to 80 meV instead of the value 300 meV, found
by utilization of optical method. Besides, at low temperatures Urbach tail detected by the CPM appears to be blue-shift. In $\text{As}_2\text{S}_3$ and GeSe at 10-150K and 150÷400K respectively spectral features are qualitatively similar to those in $\text{As}_2\text{S}_3$, i.e. the weak-absorption tail is substantially redressed and the non-photoconduction spectral gaps appear [90]. That means that thermal excitation of holes from the gap states is nearly impossible in the weak absorption region.

6. PHOTO-INDUCED ABSORPTION

The interaction of radiation with vitreous materials provokes irreversible and reversible changes of atomic and electronic structure. For example, under radiation influence the structure of vitreous materials changes, new defects appear, films crystallization or amorphization take place, phase transition or transition from one unstable state to another unstable state occurs [7]. All these phenomena and some others will be discussed in next chapter. In this chapter attention will be paid only to reversible phenomena due to interaction of light with non-equilibrium excited carriers and phonons. Different models of photo-induced absorption will be discussed: the model on the basis of interaction of light with multiple trapped carriers in localized states, the model of photo-induced non-linear absorption due to interaction of light with non-equilibrium localized phonons, the cooperation model on the basis of the coherent generation of the non-equilibrium phonons, the model of two-photon and two-step absorption.

6.1. PHOTO-INDUCED ABSORPTION ON THE BASIS OF MODEL WITH CARRIER MULTIPLE TRAPPING IN LOCALIZED STATES.

It was found by many authors that transport phenomena in noncrystalline semiconductors including chalcogenide glasses are conditioned by interaction of excited nonequilibrium carriers with traps distributed quasicontinuously in the forbidden gap [91-95]. However the excitation of non-equilibrium carriers in such systems also leads to many peculiarities of optical properties and mainly to photo-induced optical absorption. It is to note that in the specific conditions of experiment photo-induced changes in chalcogenide glasses are observed at very small levels of light excitation as high as $10^{-6}$-$10^{-2}$ W/cm² [96,97]. Such optical changes hardly may be explained by photo-structural transformations. They can be interpreted using electron transitions in the framework of electron and phonon systems of chalcogenide samples, taking into account the existence of high concentration of localized states distributed quasicontinuously in the forbidden gap of these materials. While chalcogenide glass samples are excited by the light with energy of $h\nu\geq E_g$ non-equilibrium carriers appear in free bands (Fig.10).

Very quickly they are captured by the tail states proportionally to their density, since the capture coefficient is supposed to be the same for different values of trap energy $E_o$. The probing light with energy $h\nu<E_g$ excites the trapped carriers in the band of localized states, that leads to an additional optical absorption in a wide range of energy that leads to photo-induced absorption due to pure electron processes (Fig.11). As it has been shown by the authors of [93,94,97,98], who had developed the model with carrier multiple trapping in localized states the distribution of carriers trapped on the localized states in the gap can be determined by several processes. These processes are the capture of charge carriers on the traps, their subsequent thermal activation and then their repeated trapping. In the case of continuous illumination the equations representing the generation of carriers, multiple
trapping of excess carriers on localized states and their thermal activation and recombination may be written as follows:

\[ \frac{dp(t)}{dt} = G - R_{pc(t)}p(t) \]  \hfill (18)

\[ \frac{dp(t,E)}{dt} = \frac{1}{\sigma_0 N_t} [g(E) - p(t,E)] p_c(t) - \nu_o \exp(-E/kT)p(t,E) \]  \hfill (19)

\[ \rho(t) = \rho_c(t) + \int_{0}^{\infty} dE \rho(t,E) \]  \hfill (20)

where \( p \) is the full density of excess holes, \( p_c \) is the density of mobile holes, \( E \) is the energy of a localized state, \( p(t,E)dE \) is the density of holes localized in the energy range from \( E \) to \( E + dE \), \( t \) is the time interval after switching on the illumination (\( t>0 \)), \( G \) is the generation rate of the carriers, \( \sigma_0 \) is the time of life of carriers between captures, \( g(E) \) is the energy distribution of localized states, \( \nu_o \) is the attempt-to-escape frequency, \( T \) is the temperature and \( k \) is the Boltzmann constant. Equations (18-20) are written for holes, but can easily be rewritten for electrons. Equation (18) represents the generation and recombination of excess carriers; equation (19) the kinetics of carrier trapping and their thermal activation, and finally equation (20) gives the ratio of mobile and trapped carrier numbers. Equations (18-20) take into account the recombination of delocalized holes with localized electrons and do not take into consideration the recombination of mobile electrons with trapped holes.

The photoinduced absorption coefficient \( \Delta \alpha \) for probing light frequency \( \omega \) is determined by the density of excess charge carriers localized in the energy range \( 0<E>h\omega \) [97]:

\[ \Delta \alpha(\sigma, t) = \sigma^{-1} C \int_{0}^{\ h\omega} dE \rho(t,E) \]  \hfill (21)

where \( C \) is a constant which is inversely proportional to the refractive index (for not too large a frequency range one can assume to be a constant).

In the case of exponential distribution of localized states, which is the most frequently used model for trap distribution in chalcogenide glasses, we can write:

\[ g(E) = (N_i/E_0) \exp(-E/E_0) \]  \hfill (22)

where \( N_i \) is the total density of traps and \( E_0 \) is the characteristic energy of distribution.

The photoinduced absorption stationary state coefficient \( \Delta \alpha \) for the case of sufficiently
long exposure time can be written as follows:

\[ \Delta \alpha_{st}(\omega) = \omega^{-1}CNt(kT/Eo)(G/RN^2\sigma_o\nu_o)^{1/(1+y)} x \exp[(\hbar \omega/kT) - (\hbar \omega/Eo)] \]  

(23)

and

\[ \Delta \alpha_{st}(\omega) = \omega^{-1}CNt(G/RN^2\sigma_o\nu_o)^{1/(1+y)} \exp(-\hbar \omega/Eo) \]  

for \( \hbar \omega > E \)  

(24)

where \( E \) is the energy of the quasi Fermi level determined as

\[ E = kT(1+y)^{-1} \ln (RN^2\sigma_o\nu_o/G) \]  

(25)

and \( y \) is the dispersion parameter, \( y = kT/Eo \).

The solutions for photo-induced absorption time dependences after switching of the exciting light were presented in [97].

![Graphs](image)

**Fig.11.** The spectral distribution of photoabsorption steady state coefficient \( \Delta \alpha \) in \( \text{As}_2\text{S}_3 \) (a) and \( \text{As}-\text{S-}\text{Se} \) (b) fiber at \( T=300 \text{ K} \) (1) and \( T=77 \text{ K} \) (2) for illumination with an Ar-laser at \( P=10^{-2} \text{ W/cm}^2 \).

The maximum on photo induced absorption kinetics curves observed for small photon energy can be explained as a result of excess carrier redistribution on shallow states. At the first moment after switching on the illumination the main part of the excess carriers is trapped in the shallow states at the bottom of the conduction band. However, as time goes on because of the thermal release of the carriers and their multiple trapping an increasing number of excess carriers are trapped on the deep states. The ratio of the number of excess carriers localized on shallow states to the number of excess carriers localized on deep states, changes with time. This process leads to the appearance of a maximum on the PA time dependence curve.

The intensity dependence on the photo-induced absorption coefficient, as follows from analytical solutions of (18-20), has a power-law character. The following causes the increasing of the photo-induced absorption coefficient with decreasing temperature. When the temperature decreases the probability of thermal activation of the trapped carriers decreases too, this fact leading to an increasing density of localized carriers and, respectively, to an increase in PA.

The proposed model is in a good correlation with experimental results [91-99] though
this component of photo-induced absorption is not to high because the concentration of
localized states quasicontinuously distributed in the forbidden gap with small exceptions is
less than $10^{18} \text{cm}^{-3}$. So the photo-induced absorption controlled by optical transitions from
localized states to free bands will be by $10^4$ times less than absorption due to the contribution
of optical transitions between free bands.

Usually the experiments for study of photo-induced absorption are undertaken on thin
films. That means that number of absorbed photons, which is proportional to the thickness of
sample, is very low, because the thickness of films is as a rule of order of 0.5-10 $\mu$m. The
measured optical signal of probe light can be increased if the thickness of the sample would
be increased. Especially good results give the experiments on fiber samples of chalcogenide
glassy semiconductors. Investigation of interaction of light radiation with fiber samples of
ChG led to possibility to study many peculiarities of photo-induced absorption in ChG.
Indeed the use of optical fibers rather than thin films or bulk samples enabled us to better
observe small changes in the optical absorption caused by lateral excitation by light from the
region $h\nu>E_g$ and even in the case of $h\nu<E_g$. This takes place due to the fact of longer
optical path in the fibers. Besides that, the using of fibers instead of bulk samples allows to
decrease the thresholds of power needed for developing of nonlinear optical processes [100].

As it was shown in our previous papers [96,97] while chalcogenide glass fibers are
excited by the light with the energy of $h\nu>E_g$ their optical losses are increased. The latter is
observed using the probing light with the energy $h\nu<E_g$. In this experiment the probing light
with a photon energy $h\nu<E_g$ was launched into the input face of the fiber. At the output of the
fiber the intensity of the probing light, transmitted through the fiber, was measured. When
illuminating the fiber lateral surface with a continuous band gap light the intensity of the
probing light at the output of the fiber decreased from its initial value (in the dark) because of
the manifestation of the photo-induced absorption. A rather low intensity of the exciting light
was employed in the experiments, therefore no structural photo-induced changes occurred.
The absence of the structural changes was confirmed by a complete restoration of the initial
optical transmittance of the fibers after the cessation of the exciting light. The restoration rate
depended on the illumination conditions and on the glass composition. The spectral
distribution of the photo-induced absorption coefficient measured in the energy range of the
probing light 0.6-1.6 eV is presented in Fig.11 for the As-S-Se fibres.
Similar dependences were observed for As-Ge-Se fibres. We note the exponential character of
the spectral dependence at $\alpha$ for a rather large energy range that is in a good agreement with
analytical solution of given above. The illumination of the fiber at a lower temperature (77K)
leads to a significant increase of photo-induced absorption with respect to the room
temperature illumination.

The intensity dependence of the photo-induced absorption coefficient exhibits a power
I-law behavior, $\Delta \alpha \sim P^n$, when the intensity of the exciting light $P$ is varied by about four
orders of the magnitude (Fig.12a). The value of $n$ changes in dependence of the probing light
photon energy in the range 0.3-0.5. The photo-induced absorption kinetics measurements were
carried out in a time interval of $10^{-2}$-$10^4$ s after switching on the exciting light for the As$_2$S$_3$,
As-S-Se and As-Ge-Se fibers. The typical curves for As-Ge-Se fibers are shown in Fig.13.

The character of the photo-induced absorption kinetics depends on the illumination
conditions, such as the temperature, the probing light photon energy and the power of the
exciting light. Experimental results confirm the model with carrier multiple trapping in
localized states, distributed continuously in the gap [101].
The dependence of $\Delta \alpha$ steady-state value upon light intensity for As$_2$S$_3$ (a) and As-Ge-Se (b) fibers at $T=300$ K. The photon energy of probing light, eV: 1-0.7, 2-0.8, 3-0.95, 4-0.98, 5-1.08, 6-1.2, 7-1.3.

The qualitative analysis of experimental results in terms of the multiple trapping enables us to evaluate some parameters of localized state distribution and carrier transport. For example, the temperature dependence of the photo-induced absorption coefficient can be used to determine the characteristic energy of localized state distribution $E_0$. Taking into account that in real conditions the dispersion parameter $\gamma < 1$, and the second term in the right side of (7) is less than the first one, we can approximate the temperature dependence of the PA coefficient as follows:

$$\ln(\Delta \alpha) = \ln C_1 - \left(\frac{kT}{E_0}\right) \ln A - S$$

(26)

where $C_1 = \omega t^2 / \kappa C N_1$, $A = R N_2 t_0 / (G t^2) > 1$ and $S$ is the additional negative term which depends weakly on temperature:

$$S = \exp\left(-\frac{h \omega}{E_0}\right) A^{t_0 E_0}$$

(27)

Figure 14 shows how the value of the $S$ term for different temperature can be determined from experimental curve $\Delta \alpha(T)$.

The linear approximation $\ln(\Delta \alpha)$ against $T$ must be a tangent to the experimental curve $\ln(\Delta \alpha)$ against $T$ at low temperatures, i.e. where the magnitude of term $S$ is negligible (see equation 27). The temperature dependence of the term $\ln(S)$ obtained from figure 14 must exhibit a linear behavior when it is represented as a function of $T$:

$$\ln S = -\frac{h \omega}{E_0} + \left(\frac{kT}{E_0}\right) \ln A$$

(28)
Therefore, by plotting the magnitude of term $\ln S$ against $T$ and extrapolating it to $T=0$ (Figure 14b) one can find the magnitude of the characteristic energy of the distribution of traps $E_0$.

![Fig.14a. The temperature dependence of the steady-state absorption coefficient in As$_2$S$_3$ fibers.](image)

Note that both linear functions in figure 0.14 must have the same slope, i.e. $(l/E_0)\ln\alpha$. In this way, the magnitude of $E_0$ obtained from the PA temperature dependence is about 0.26 eV, i.e. is in a good agreement with the value 0.3 eV, given in the literature for $E_0$ in the field of weak absorption (we remind that measurement were undertaken with the light $h\nu<E_g$ [89].

The fact that the dependence of photo-induced absorption has a power low character following the square-root function confirms that carriers excited in the process of photo absorption as well as carriers participating in photoconductivity recombine according to bimolecular mechanism [102]. This can be used for determining the magnitude of drift mobility. Orenstein and Kastner [103,104] have shown that photo-absorption and carrier mobility are governed by the same localized carriers. For low mobility semiconductors the diffusion limited recombination can be presented by Langevin equation:

$$b = (e/\varepsilon\varepsilon_0)(\mu_u + \mu_p)$$  \hspace{1cm} (29)

In the case $\mu_u << \mu_p$:

$$\theta_1 = 4\alpha/\varepsilon$$  \hspace{1cm} (30)

On the other hand $b$ can be determined from the fractional change in optical transmission through approximated formula [103,104].

$$b = 4\sigma^2 F\gamma(1-R)/\varepsilon^2$$  \hspace{1cm} (31)

where $\alpha$ is the absorption coefficient for excitation light, $F$ is incident photon flux, $\gamma$ is the quantum efficiency and $R$ is the reflectivity for excitation light. From the temperature dependence of steady-state photo-induced absorption measurements the authors of [105] found the temperature dependence of the bimolecular rate coefficient “$b$” in As$_2$S$_3$ glass which was used for determining of the temperature dependence of the time-averaged drift mobility in As$_2$S$_3$ glass (Fig.15).
The temperature hole drift mobility in As$_2$S$_3$ was found to be temperature activated at high temperatures, and almost temperature independent below approximately 130 K. The hole mobility at room temperature was found to be of the order of $10^{-10}$ cm$^2$/v.sec, which correlates with the results obtained from electrical measurements. The recombination radius $R_0$ was estimated to be about 20 Å, which is quite close to the value of the recombination radius, obtained for As$_2$S$_3$ by Orenstein and Kastner [104].

6.2. PHOTO-INDUCED NON-LINEAR ABSORPTION IN CHG WITH PARTICIPATING OF NON-EQUILIBRIUM LOCALIZED PHONONS.

The excitation of the non-equilibrium carriers with the energy $h\nu>E_g$ photons leads to the appearance of hot electrons and holes. Their thermalization in the non-crystalline systems is accompanied by the generation of the non-equilibrium localized phonons (fractons) [7, 106-107]. The phonons with the wave-length of the order of the magnitude modulation length of the random potential in the ChG drastically change the form of the potential, which modulates the bottom of the conduction band and the top of the valence band of the ChG. In such a way non-equilibrium localized phonons open a new channel of the interband light absorption. For this reason the absorption coefficient increases with the increasing of the light intensity and the phenomenon can be explained by means of photo-induced light absorption in ChG with the participation of the fractons [105-109]. In fact, the coefficient of the interband light absorption can be represented as a sum of two parts [109]:

$$\alpha = \alpha_0 + \beta_n n$$

(32)

where $\alpha_0$ is the part of the absorption coefficient, which does not depend on the temperature, $\beta_n$ is the part of the absorption coefficient, which depends on the mean number of the localized phonons $n$. Thus, in the process of the interband light absorption the transitions with the simultaneous participation of light quanta and localized phonons play an essential role. The second part of the absorption coefficient in eq. (32) essentially changes in the process of the relaxation of the excited electrons into the localized states in the optical gap of ChG. This relaxation is accompanied by the coherent generation of the non-equilibrium phonons $\Delta n = n - n_0$, where $n_0$ is the mean number of the equilibrium localized phonons [109].

The authors of [104,105,107-110] studied the non-linear absorption by laser pulses in thin film samples of chalcogenide glasses As-S, As-Se, Ge-Se, As-S-Ge and others (0.2-5.0 μm thickness). It was shown, that when the input light pulse (with $h\nu\geq E_g$) intensity was relatively low the transmission of thin ChG films did not manifest the non-linear effect.
However, an increasing of the incident light intensity over some threshold values \(I_0\) leads to a non-linear character of the light transmission by ChG films [7,105,104,107,108]. The characteristic value of the threshold light intensity depends on the ChG film composition, wavelength of excitation, temperature and the laser pulse duration (Fig.15).

As a result of the non-linear light absorption a change of time profile of the laser pulses is observed which leads to a hysteresis-like dependence of the output light intensity on the corresponding value of the input intensity (Fig.15). The authors of [109] have shown that a contribution to non-linear absorption in ChG can have cooperative phenomena in the process of the generation of coherent phonon pulses by hot electrons.

![Fig.15](image)

**Fig.15.** Intensity dependence of the light transmission of a-As\(_2\)S\(_3\).

Among randomly distributed quantum wells of quasielectrons one can always pick out the quasiequidistant subgroups of two-level states in such randomly distributed states. For example, if we consider a single localized electron with the transition energy \(h_{\omega\alpha} = E_{2\alpha} - E_{1\alpha}\) one can always find the large number of other localized electrons with the same transition energy between the ground and excited states. Therefore, let us introduce the subgroup distribution function \(p^{\alpha}\) of the electron states in the quantum wells with the same energy distance \(h_{\omega\alpha}\). Every subgroup \(\alpha\) of coupled electrons generates localized phonons with the proper frequency \(h_{\omega\alpha}\). The certain quasiequidistant subgroup can generate a coherent Dicke pulse of the non-equilibrium localized phonons. The localized phonons decay into the acoustic phonons. Anderson et al. [111] proposed the analogous two-level systems. Such two-level systems occur when the certain numbers of excited atoms (or group of atoms) have two equilibrium positions. The mechanism of the excitation of the localized kinetics is given in [109].

Solving these equations in the stationary conditions the authors obtained for the non-linear absorption coefficient \(\alpha (I_s) = dI_s (z)/I_s dz\) the following expression:

\[
\alpha = \alpha_0 + \beta n \\
n = n_0 + \Delta n
\]

(33)

(34)

where coefficients \(\beta\) and \(\alpha_0\) do not depend on light intensity.

It is clear that with the increasing of the light intensity the absorption coefficient increases. As it was mentioned above such increasing was experimentally observed.
When the time duration of the excitation pulse is shorter than the decay times of the localized electrons the authors of [109] obtained for the relaxation of the non-linear absorption coefficient after the passage of the short-pulse through the sample of ChG in the quasistationary case the following expression:

\[
\alpha(I) = \alpha_0 + \beta \sum \frac{d\alpha^2}{\tau\alpha} \text{sech}^2 \left( \frac{d\alpha}{\tau\alpha}(t-t_{0\alpha}) \right)
\]  

(35)

where \(t^\alpha\) is the delay time of the subgroup \(\alpha\). From this expression one can see that the relaxation depends on the cooperation law between the localized electrons. Every function sech\(^2\) in the last equation has the maximum, when \(t=t_{0\alpha}\). The sum on \(\alpha\) takes into account all subgroups of the equidistant two-level states, which have different delay times. In this case relaxation law of the absorption coefficient can be more broadened than that in the case of single group of the equidistant two-level states. The broadening depends on the explicit form of the subgroup distribution function \(p^\alpha\) [109]. As it has been established by the authors of [7,104,105,107,112] such delay of photo-induced absorption was observed experimentally.
6.3. PHOTO-INDUCED NON-LINEAR ABSORPTION DUE TO TWO-PHOTON AND TWO-STEP ABSORPTION

The first investigations of the non-linear absorption of nanosecond laser pulses with $h\nu < E_g$ in ChG were reported by Lisitsa, Fekeshgazi et al. [113,114]. The dynamics of such induced absorption with subpicosecond and picosecond time resolution have been investigated by Fork, Shank et al. [115] and by Ackley, Tauc et al [116]. These authors showed that as a result of ChG strong excitation with $h\nu < E_g$, an additional induced absorption appears, which exhibits maximum amplitude during the excitation pulse and relaxes with several time constants. This kind of photo-induced absorption (when $h\nu$ is far from the absorption edge $E_g$) appears only at strong laser excitation of ChG. The mechanisms of two-photon (or two-step) absorption and of the carrier localization and redistribution on states in the gap were proposed to explain the photo-induced absorption in ChG. For intraband excitation of As$_2$S$_3$ thin films ($E_g = 2.4$ eV) the authors of [113,114] utilized 100 Fs laser pulses (pumping at 2.0 eV, and probing at 2.14 and 1.4 eV). The dynamics of the induced absorption relaxation is shown in Fig. 17 [112] which is composed of two parts, a first one, coherent, shaping as the cross-correlation of the pump and probe pulses, followed by a second less intense and slower component.

From the slower component fitting parameters, using the model of a non-degenerate two-photon absorption process, followed by a direct absorption of the probe pulse by carriers in localized states (two-step absorption), the measured depletion time (from 54 Ps to 61 Ps) depends on the pumping rate (from 1.5 $\mu$J to 0.75 $\mu$J pumping, respectively) [112]. In such a way the authors of [112] observed a competition between two-photon and two-step absorption. It is for the reason that the pump pulse energy is lower than the gap. In this case the excitation can excite carriers into localized states in the gap by one photon processes or into delocalized states by two photon transition. A probe pulse can be absorbed by two photon transitions and by transition of carriers in localized states, which are directly pumped by one-photon processes. Beside that, there is a possibility of excitation of non-equilibrium states.

So the theoretical and experimental researches of the photo-induced absorption phenomena give the information concerning possible mechanisms of photo-induced absorption which include many models described above. The realization of one or another model depends on concrete experimental conditions: composition of glass, the wavelength and intensity of pump and probe light, temperature etc.

6.4. RELAXATION OF PHOTODARKENING

The variety of light-induced structural transformations in amorphous chalcogenide films is rather wide and attracts scientific as well as technical interest [117]. The arsenic chalcogenide films usually become darkened under light irradiation in the region of the fundamental absorption edge. As the composition of a glass determines both the structural units and the mean coordination number of the amorphous solid, the effect of the composition in glassy systems As-S(Se) on the degree of photostructural transformations has been studied in detail. Lesser attention has been devoted to the influence on photodarkening of foreign impurity atoms introduced in a glass. At present, due to the application of metal-doped chalcogenide glasses as optoelectronic materials this problem has attracted new interest.

In the present work we report the results of the study of photodarkening and its kinetics in amorphous a-As$_{40}$Se$_{60}$ films separately doped with 0.5 at.% of metals Sn, Mn and rare-earths Sm, Pr and Dy, and a-As$_{50}$Se$_{50}$ films doped with various amount of Sn (1 to 10 at.%).
The films of thickness 1-6 µm were prepared by flash thermal evaporation in vacuum of the synthesized material onto glass substrates held at 100 °C. A He-Ne laser (λ=0.63 µm) was used as a source of light exposure. Thermal effects were examined by annealing of a part of the films in vacuum at 100 °C for 30 min.

All As_{40}Se_{60}:Me and As_{50}Se_{50}:Sn films underwent typical photodarkening under illumination with a clear red shift of the absorption edge after exposition. The changes in the optical transmission \( T(t)/T(0) \) of the As_{40}Se_{60}:Me films as functions of the exposure time \( t \) are shown in Fig.18a for untreated and annealed films, respectively. At a constant light intensity the plots characterise the decay of the optical transmittance with the increase of the dose of absorbed photons. Note that 0.5 at.% of metal impurity significantly reduces the photodarkening effect, especially for Sn and Dy [118]. In annealed films the specific metal impurity reduces the photodarkening in the same manner as for untreated films, but this reduction is lowered to about 2/3. The addition of metals hinders the photodarkening, i.e. impurities play stabilising role in the glass structure with respect to light exposure. Increasing of the metal concentration also reduces the photodarkening (Fig.118b).

The reduction in transmission with exposure time in As_{50}Se_{50}:Sn_{x} films is shown in Fig.19a for untreated and annealed samples, respectively. The figure demonstrates the effect of impurity concentration and heat treatment on the photodarkening. The effect of annealing is different for the films with low or high tin concentration. In the former case annealing weakens the photodarkening, and in the latter case it is increased. Inversion occurs at about 2 at. % Sn in AsSe, when the effect of annealing is weak.

To obtain a unified basis for comparison of the transmission relaxation, \( T(t) \), we have used so called stretched exponential presentation for the relaxation curves:

\[
T(t)/T(0) = A_0 + A \exp\left[-(t-t_0)/\tau\right]^{1-\alpha} (36)
\]

Here \( t \) is the exposure time, \( \tau \) is the apparent time constant, \( A \) characterizes the exponent amplitude, \( t_0 \) and \( A_0 \) are the initial co-ordinates, and \( \alpha \) is the dispersion parameter (\( 0<\alpha<1 \)). Approximation of the decays with the aid of standard computer fitting is shown in
Figs. 18a and 18b by solid lines. The parameters of the stretched exponent $t_0$, $A_0$, $A$, $\tau$ and $\alpha$ have been determined for all compositions of the untreated and annealed films.

The parameter $A=1-A_0$ characterises the growth of optical losses on photodarkening. With the increase of tin content in $\text{As}_50\text{Se}_{50}$ films from $x=0$ to $x=10$, the $A$ parameter decreases by about eight times in the case of untreated films and approximately twice for the annealed films. The variation of the kinetic parameters $\alpha$ and $\tau$ of the stretched exponential is most interesting. The $\alpha$ parameter is found to be less than unity and to lie between 0.43 and 0.93 for all samples, slightly increasing after annealing, especially in $\text{As}_40\text{Se}_{60}$ and $\text{As}_40\text{Se}_{60}:\text{Sm}$ films. The time constant $\tau$ of the photodarkening process depends much stronger on the sort of impurity, increasing in the impurity series $\text{Sm-Mn-Sn-Dy}$, particularly after annealing. The behaviour of the parameters $\alpha$ and $\tau$ of the photodarkening process on the impurity concentration is shown in Fig. 19b for $\text{As}_50\text{Se}_{50}:\text{Sn}_x$ samples.

The dispersion parameter $\alpha$ is close to 0.5 for almost all $\text{As}_50\text{Se}_{50}:\text{Sn}$ films, with greater values for samples with the highest Sn content. In untreated films, the time constant $\tau$ decreases with increasing of $x$ (approximately by 300 s per 1 at.% Sn), while in annealed films it rapidly increases (at about 3000 s per 1 at.% Sn), with the exception of the richest composition $x=10$. This fact indicates that in films containing impurities the photodarkening process proceeds many times slower, especially in annealed films.

The red shift of the absorption edge on photodarkening indicates the narrowing of the optical gap of the film, and it is believed to be due to broadening of the valence band, the top of which is formed mainly by states of lone-pair electrons of the chalcogen atom. Recently, a novel model for photodarkening in $\alpha$-$\text{As}_2\text{Se(S)}_3$ has been proposed \cite{117,119}, in which photoexcited charge carriers in extended states are considered as responsible for photodarkening. Unlike the previous conceptions, the new model takes into account the layered cluster structure of chalcogenide glasses. During exposure the layer is negatively charged due to capture of photoexcited electrons, and repulsive forces are built between the layers. These forces cause enlargement of the interlayer distance (leading to photoexpansion) and slip motion along the layers. This latter process alters the interaction of lone-pair electrons between the layers leading to the photodarkening effect. The model \cite{117,119} offers a good basis for consideration of the effect on photodarkening of impurity atoms with coordination different from that of the host glass atoms, as in the case of metals under study. The foreign metal atoms provide bridging between the layers and hence reduce the slip motion, thus suppressing the photodarkening.

The metals Mn, Sm, Pr and Dy enter the host glass as 2+ or 3+ ions, and, due to charge and large ion dimensions, induce deformations in the host matrix. The Sn environment was found to be a tetrahedrally co-ordinated species. From the X-ray investigation of the first diffraction peak (FSDP) in $\text{As}_40\text{Se}_{60}$ glasses doped with 0.5 at.% of Sn, Mn, Sm, Pr and Dy it was concluded \cite{120} that disordered layers of the glass structure are locally distorted by insertion of the metal atoms that bond to selenium. A high covalence of the Me-Se bond gives rise to strong directional bonds and the layers become more rigid while high metal ionicity diminishes the stiffness of the layers. The Sm and Dy atoms with higher electronegativity produce a shift of the interlayer distance towards a lower value, i.e. rare-earth atoms play the role of network modifiers that smooth the disordered $\text{As}_40\text{Se}_{60}$ layers allowing for a better packing at a smaller thickness.

Mn and especially Sn exhibit lower electronegativity and induce a shift of the interlayer distance towards higher values. In $\text{As}_50\text{Se}_{50}+5$ at.% Sn the interlayer distance was found to be enlarged to 5.50 Å (comparable to 5.47 Å in undoped $\text{As}_50\text{Se}_{50}$ film). This effect
can be ascribed to the role of a network former played by the more covalent atoms. In this case the interlayer distance is increased due to the increase of the effective thickness of the layers. The impurity therefore strongly affects the network of the host glass in both the short-range and medium-range order, and we may expect a significant influence on the relative motion of the layers.

The results of the present work together with the slip-motion model [117,119] may be used to estimate the behaviour of metal impurities in the photodarkening process. The effect of impurities is manifested mainly through retardation of the photodarkening process due to their presence. The time constant of the process in undoped films is several times increased after doping, the strongest effect (24 times) is found for Dy impurity. The presence of metal impurities strongly enhances the annealing effect in comparison with the undoped film.

The difference in the photodarkening time constant for the untreated and annealed films grows with increasing impurity content. In the context of the model [117,119] this fact clearly indicates the strong retardation of the slip motion of the layers due to presence of the impurity. As the metals in the host glass tend to create directional bonds, some bridging links should appear between the layers, especially during the annealing process. The structure with metal impurities requires therefore some excess slip forces, i.e. leads to greater doses and time constants. Furthermore, creation of clusters, such as SnSe₂, may lower the density of the typical for As₅₀Se₅₀ lone-pair defects thus lowering the charge state of the layers and, finally, the photodarkening. This effect is particularly important at high dopant contents when the impurity approaches its dissolution limit and actually changes the number of structural units in the glass. In the untreated films the changes in the structure after introducing the impurity occur first of all in the layers, and the enlargement of the interlayer distance promotes the slip motion, thus yielding a slight decrease of the time constant of the process.

The fact that the photodarkening kinetics may be described by a stretched exponential is an indication of dispersion in the kinetic mechanism, i.e. the time dependence of the process rate. The photoinduced absorption is limited by a dispersive process with the exponent $\alpha \approx 0.5$. In our case it is the dispersive character of hole transport that may cause the dispersive character of the relaxation after photogeneration. Indeed, the transport of photoexcited holes is included in the model at the stage where the layer clusters are charged due to capture of charge carriers.

![Fig.19a](image1.png) Excess absorbance induced by light absorption during the exposition. Only the curves for the As₅₀Se₅₀ films without Sn and doped with 10 at.% Sn are shown, both for untreated (u) and annealed (a) samples. These curves bracket the whole range of excess absorbance.

![Fig.19b](image2.png) The dependence of the kinetic parameters $\tau$ and $\alpha$ on Sn content for untreated (untr) and annealed (ann) As₅₀Se₅₀ films. The dashed lines are drawn as guides for the eye.
Charge transport in chalcogenide glasses is known to be highly dispersive due to a wide distribution of capture times in the multiple-trapping process [121]. For glasses like a-As$_{40}$Se$_{60}$ the dispersive parameter $\alpha$ of hole transport is close to 0.5, in accordance with the value found from the stretched exponential presentation of photodarkening kinetics. The fact that $\alpha$ is increasing with the addition of metal impurities indicates that the dispersion of transport is decreased. This is in general accordance with both the stabilization of the structure and the expected alteration of the density of the defect centres. In particular, a specific path of impurity conduction has been detected for As$_{40}$Se$_{60}$ glasses doped with Mn and Dy [120].

7. CHALCOGENIDE GLASSES IN OPTOELECTRONICS

In the Center of Optoelectronics many devices were developed on the base of ChG, which can change their electrophysical and optical parameters under applying of electrical field, exposition by light electron beam, X-ray irradiation etc [122]. At the same time they manifest resistance to nuclear radiation. Besides that, ChG could be obtained using very simple technologies and in many cases (but not in all cases) they do not need very high purity. It allows producing industrially electrical switches, xerographic and thermoplastic media, photoresistant and holographic media, optical filters, optical sensors, thin films waveguides, nonlinear elements, etc. (Fig.20).

![Application of Chalcogenide Glasses in Optoelectronics](chart)

**Fig.20.** Fields of application of chalcogenide glassy semiconductors.

New materials, thin film structures and optic fibers based on chalcogenide vitreous semiconductors such as As$_2$S$_3$, As$_2$Se$_3$, AsSe, As-S-Sb, As-S-Ge doped with rare-earth ions (Dy, Sm, Nd, Ho, Pr, etc.) were developed. The rare-earth dopants are of profound importance in modern optoelectronic technology because of their excellent luminescent properties that have permitted fabricating optical amplifiers and lasers for optical fiber telecommunication.

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windows at 1.3 µm and 1.5 µm. On the base of thin film heterostructures ITO-Sb₂S₃/As₂S₃, SnO₂-As₂Se₃/TlSbSe₂-Al, Si-SiO₂/As₂Se₃-Al, SnO₂-As₂Se₃/Sb₂Se₃-Al a set of photosensitive elements was designed with controlled spectral sensitivity for application in xerography and photothermoplastics, as photo- and electron-resists, photoelectric sensors and transformers.

The main advantages of these elaborations lie in heightened sensitivity due to wide interval of spectral susceptibility associated with high optical resolution. A wide variety of light-induced and electron beam changes in ChG allows to fabricate on the basis of these effects planar and three-dimensional optical waveguides as well as gratings for integrated optics [123]. At the present new glasses and optical fibres doped with rare earth ions were prepared, which are perspective for different applications in telecommunication systems, as ultra-fast all optical switching, and for toxic chemical sensing.

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