

INFLUENCE OF RARE-EARTH ATOM (Sm) IMPURITY ON OPTICAL PROPERTIES OF CHALCOGENIDE GLASS-LIKE SEMICONDUCTORS OF Se-As SYSTEM

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The optical properties of $\text{Se}_{95}\text{As}_5$ composition CGS with different content of Sm impurity were investigated. The refractive index and extinction coefficient were determined. It is shown that dependence of these values on Sm atom concentration has a non-monotonous behaviour: Small concentration (up to 0.05 at %) increases their values and large concentration of impurity decreases the values of these parameters. Taking into consideration the structure of $\text{Se}_{95}\text{As}_5$ system, i.e. the presence of ordered microregions with high coordination number, separated one from another by regions with low atomic density it is concluded that optical properties can be explained within the Penn model.

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1. Introduction

Chalcogenide glass-like semiconductors (CGS) are perspective materials for use in IR technique, various switching, memory and also acousto-optical devices [1-3]. The applications are connected with the unique properties of the above mentioned materials as e.g. the change of the structure and electron properties induced by light, in particular occurrence of unpaired spins registered by electron spin resonance and photoluminescence with Stokes shift, etc. Knowledge of the mentioned parameters is also important for checking perspective material for optoelectronic aims. The choice of the composition depends mostly on the stability of structural and electronic properties [4].

2. Experimental method and samples

This paper deals with the investigation of $\text{Se}_{95}\text{As}_5$ system containing Sm impurity, especially determination of such fundamental parameters as optical width of the band gap, refractive index, also extinction coefficient which are closely related with atomic and electron structure of the material and energy spectrum of electron states.

The synthesis of $\text{Se}_{95}\text{As}_5$ composition CGS with Sm impurity has been carried out by melting appropriate amounts of chemical elements of special purity in vacuum quartz ampoules at above 900°C in rotary furnace with subsequent cooling in OFF regime. Impurity is introduced in the synthesis process. The impurity concentration is situated in the range 0.01÷1 at%.

The optical transmission spectrum has been studied by the method of two-beam spectroscopy in the energy interval 1÷2.8 eV. All the experiments have been carried out at room temperature.

3. Results and their discussion.

In Fig.1 there have been given optical transmission spectra of $\text{Se}_{95}\text{As}_5$ composition with various content of Sm impurity.

As it is seen from Figure 1 starting with the value of incident light wavelength 550 nm in spectra there have been observed interference maxima and minima that allow to calculate the optical coefficients (refractive index and extinction coefficient) as suggested in paper [11]. According to [11] the refractive index got from the region of the spectrum corresponding to photon energy where the light is poorly absorbed, is expressed by the formula:

$$n = \left[N + (N^2 - S^2)^{1/2} \right]^{1/2} \quad (1)$$

where,

$$N = 2S(T_M - T_m)/(T_M T_m) + (S^2 + 1)/2 \quad (2)$$

The T_M and T_m values of the transmission coefficient correspond to the maxima and minima in the transmission spectrum.

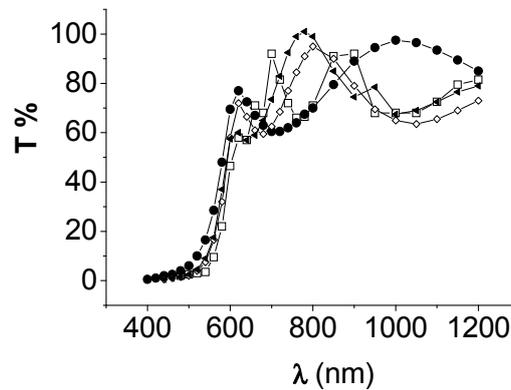


Fig.1. Optical transmission of $\text{Se}_{95}\text{As}_5$ CGS with various content of Sm impurity —□— $\text{Se}_{95}\text{As}_5$,
—●— $\text{Se}_{95}\text{As}_5\text{Sm}_{0.005}$, —◇— $\text{Se}_{95}\text{As}_5\text{Sm}_{0.05}$,
—▲— $\text{Se}_{95}\text{As}_5\text{Sm}_{0.6}$.

The extinction coefficient k has been calculated by the formula.

$$k = \frac{\alpha\lambda}{4\pi} \quad (3)$$

The spectral dependences of refractive index (n) and extinction coefficient (k) for $\text{Se}_{95}\text{As}_5$ composition with various content of Sm impurity are illustrated in Fig. 2. As it is seen from this figure the values of n and k coefficient up to the value of incident light wavelength $\lambda=650$ nm

decrease monotonously with increasing λ , but its further increase does not influence these values.

In Fig.3 there have been presented the dependences of the refractive index (a) and extinction coefficient (b) of $\text{Se}_{95}\text{As}_5$ composition on Sm atom concentration. The Sm impurity influences the values n and k . Firstly a nonmonotonous behaviour; up to the value of concentration 0.005 at% (n increases, k decreases), then the fall of the first one and growth of the second one have been observed.

To explain the obtained results it is necessary to pay attention to structural peculiarities of the atomic arrangement and energy spectrum of electron states in $\text{Se}_{95}\text{As}_5$ system and changes taking place by the introduction of rare-earth element impurity. According to [12] for instance, arsenic selenide-typed CGS materials to which $\text{Se}_{95}\text{As}_5$ system is referred exhibit less labile and more rigid structure, As a consequence one forms ordered microregions with high coordination number separated one from another by regions with low atomic density.

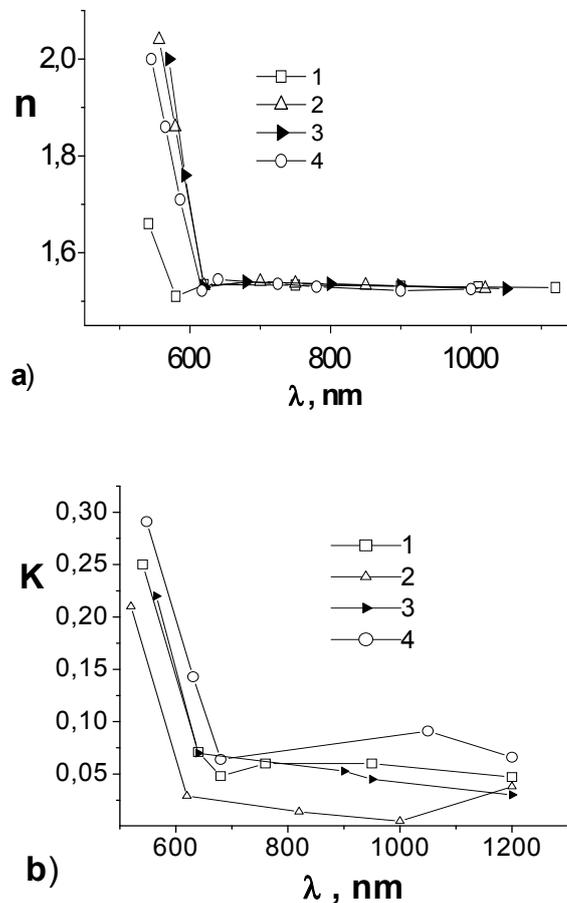


Fig.2 Spectral dependences of refractive index (a), extinction coefficient (b) of $\text{Se}_{95}\text{As}_5$ composition with various content of Sm impurity. 1- $\text{Se}_{95}\text{As}_5$, 2- $\text{Se}_{95}\text{AsSm}_{0.005}$ 3 - $\text{Se}_{95}\text{AsSm}_{0.05}$, 4- $\text{Se}_{95}\text{AsSm}_{0.6}$.

Such differences in the atomic arrangement brings about the fact that microscopic density ρ at the micro-region boundary with high coordination number becomes less than within the region that enables interpretation of obtained results with Penn model developed for materials

containing pores of small sizes to be carried out [13]. According to [13] the statistic refractive index n_0 is connected with plasma frequency ω_p and Penn energy band $\hbar\omega_g$:

$$n_0 = 1 + 2/3(\omega_p/\omega_g) \quad (4)$$

within Penn model $\hbar\omega_g$ must be decreased as square of average coordination number C , plasma energy being $\hbar\omega_p$, corresponding to excitation of electron localized mainly in dense regions of random net with high coordination number as square root from macroscopic atomic gas density (4). When magnitude $\hbar\omega_g$ is in agreement with spectrum maximum $k(\omega)$, ω_p is expressed by the formula:

$$\omega^2 = (4\pi \cdot e^2/m) \cdot (\rho N_A/A) \cdot n_v \quad (5)$$

where e and m are charge and mass of the electron; ρ is material density; A is molecular mass; N_A is Avogadro number; n_v is the number of valence electrons per atom.

According to [14] band gap within Penn model $\hbar\omega_g$ has to decrease as the square of average coordination number C but plasma energy $\hbar\omega_p$ corresponding to collective excitation of spectral gas localized mainly in dense regions of random net with high coordination number as the square root from macroscopic atomic density.

In this case for instance equation 4 for a-Si has a form [15]:

$$n^2 = 1 + 2/3(\omega/\omega_g) \cdot (\rho/\rho^0)^{1-4f} \quad (6)$$

where, $f = d \ln C / d \ln \rho$; C is the average coordination number. Index “zero” stands for the parameter of completely coordinated substance.

If we assume that Sm atoms are introduced as Sm^{3+} ions and small quantities mainly fill existing vacancies they cause elimination of heterogeneities related with density shortage in mentioned regions and simultaneous growth of heterogeneity degree in the distribution of charged centres, thus encouraging electrostatic potential fluctuations. As a result is produced the increase of refractive index and extinction coefficient (Fig.3). In Fig.4 there is presented the dependences of Penn band width of $\text{Se}_{95}\text{As}_5$ system CGS including Sm impurity defined from Fig.2.b. It is seen that impurity influence on value of Penn band width has a complex behaviour. Low concentration (up to 0.05 at%) decrease and high ones increase gradually the coefficients, indicating the complex influence of Sm impurity atom on the concentrations of localized states in mobility gap.

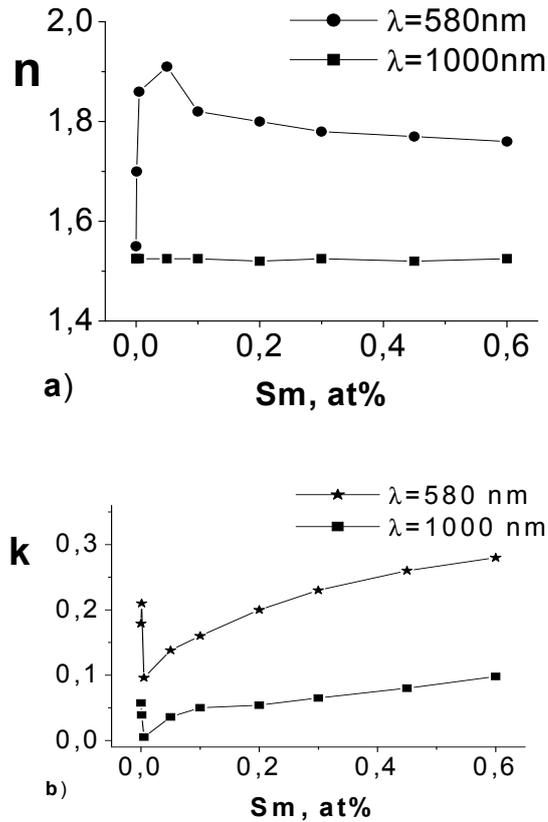


Fig.3. Spectral dependences of refractive index (a) and extinction coefficient (b) of $Se_{95}As_5$ composition on Sm atom concentration.

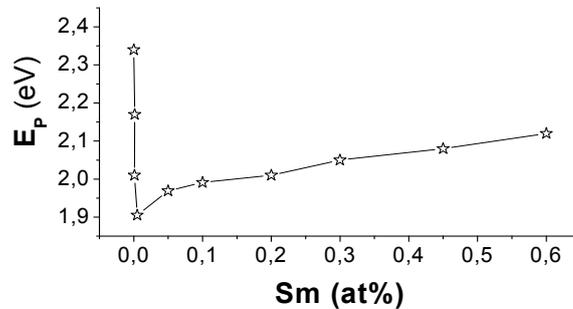


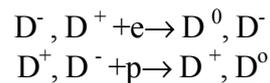
Fig.4 Dependence of Penn band gap of $Se_{95}As_5$ system CGS on Sm atom concentration.

According to the plots presented in Fig.3 and Fig.4 we state that small concentrations of Sm impurity atoms increase, but high concentrations decrease density of localized states in mobility gap of the material under the investigation that must bring about the similar change of such parameters and charge centre concentrations and characteristic energy of Urbach absorption, and also values of optical absorption coefficient corresponding to the given region.

We have shown in [6] that Sm impurity in small concentration up to 0.005at% increases the mentioned parameters. High concentration of Sm^{3+} ion impurities distributing all over the matrix due to chemical activity have an attraction for the ends of negatively charged (C_1^-) Se chains and favours formation of structural elements of $SmSe_3$. As a result the concentration of the broken bonds is decreased and this decrease is accompanied by a decrease in localized state

densities in mobility gap connected with charged defects (U^- -centres) and weakening of electrostatic potential fluctuations. The last fact leads to the gradual decrease of refractive index and extinction coefficient (Fig.3) and also decrease of band gap in the Penn model. Simultaneous influence of above- mentioned facts brings about the decrease of characteristic energy of Urbach absorption and charged defect concentration that controls the Urbach absorption. As a result there is produced the “brightening” of the material that at large concentration of Sm impurity is observed .

To clarify the role of charged defects D^- and D^+ in optical properties of $Se_{95}As_5$ system CGS including Sm impurity we investigate spectral distribution of optical absorption coefficient by the presence of background intrinsic lighting. “Photobrightening” observation only in the region of weak tail absorption and also display of maximum depending on photoinduced change of optical absorption coefficient on the concentration of introduced Sm atoms at 0.005at% , i.e. at the concentration when optical absorption coefficient and charged defect concentration have a maximum value points to the fact again that light absorption in the given region of spectrum is caused by transitions between band and states D^- and D^+ which concentrations are decreased as compared with equilibrium state concentration by photoexcitation. It is expected that by photoexcitation there has been taken place capture of electrons and holes on paired defect according to reaction



as a result concentrations of D^+ , D^- centres in comparison with equilibrium D^0 state concentration have been decreased. Capture of non- equilibrium carriers on paired defects D^+ , D^- with negative effective correlation energy is accompanied by local reconstruction of the structure. Reverse behaviour of photoinduced changes of light optical absorption coefficient indicates that the reconstruction like this has an elastic character, i.e. disappears at the transition of centre from excited state D^0 , D^- or D^+ , D^0 , with trapped carrier into main one D^+ , D^- during the inter-centre recombination.

The behaviour of the CGS materials is due to the fact that their most local states are related to charged defects D^- and D^+ (U^- -centres with negative effective energy of electron correlation) whose concentration can be supervised by the introduction of impurity atoms shown as charged centres that allow the parameters of electric charge transfer and photosensitivity to be improved significantly [4-9].

Use of rare-earth elements [RE] as impurities due to charged centres influence the U^- centre concentrations and, therefore, the electron properties. Apart this the mentioned impurities form states in the gap attributed to 4f states of RE ions and, in this case, the optical width of CGS band gap overlaps in energy to the utmost possible number of transitions permitted by RE ions (Sm) that leads to significant change of optical, photoelectric and electrical properties [7-10]. The mechanism of electron processes responsible for above-mentioned peculiarities requires a more complex investigation of the structure and physical properties of these materials

4. Conclusions

Proceeding from the considerations developed in this paper one can treat that influence of Sm impurity on the optical properties of $\text{Se}_{95}\text{As}_5$ as related to changes, that occur in the atomic structure and energy spectrum of electron states in the frame of the Penn model.

The structural peculiarities of $\text{Se}_{95}\text{As}_5$, i.e. the presence of ordered micro-regions with high coordination number separated one from another with low atomic density, cause the complex influence of the Sm impurity on the optical parameters (optical absorption coefficient, refractive index and extinction coefficient). We consider that Sm impurity appears in the form of Sm^{3+} ions and in low quantities, mainly by filling the existing vacancies. They eliminate the heterogeneities related to the density shortage in mentioned regions and leads simultaneously to the rise of heterogeneity degree in distribution of charged centres, thus encouraging the strengthening of the electrostatic potential fluctuations. High concentration of Sm ion impurity distributes all over the matrix due to its chemical activity. Sm has an attraction for the ends of negatively charged (C_1^-) Se chains and favour the formation of SmSe_3 structural elements. As a result, one forms a decreased concentration of broken bonds accompanied by a decrease of the localized state density in the mobility gap related to charged defects (U^- centres) and weakened electrostatic potential fluctuations. Such behaviour of the impurity atoms leads to nonmonotonous change of the optical absorption coefficient, refractive index and extinction coefficient, and also Penn band gap, depending on impurity concentration of rare-earth elements.

References

- [1]. Electron phenomena in chalcogenide glass- like semiconductors. Chief Editor K. D. Tsendin, Sankt Petersburg. pp.320, (1996).
- [2]. Tanaka Keiji. Nonlinier Optics in Glasses: How can we analyze? // Book of Abstracts 7th Int. Conf. On Solid State Chemistry. Czech Rep., Pardubice, p. 60, (2006).
- [3]. Zakery A., Elliott S, R. J. Non-Cryst. Sol., 330, 1,(2003).
- [4]. Isayev A.I., Kazakova L.P., Lebedev E.A., Mekhtiyeva S.I., Yatlinko I.I. "Method of Se-As-typed chalcogenide glass-like semiconductor production " A.S. №1512015., Moscow,1989.
- [5]. Kazakova L.P., Lebedev E.A., Isayev A.I., Mekhtiyeva S.I., Zakhrova N.B, Yatlinko I.I FTS., 27,959,1993.
- [6]. Kazakova L. P., Lebedev E. A., Zakharova N. B., Yatlinko I. I., Isayev A.I., M S. I., J. of Non – Cristalline solids **167**, 65, (1994).
- [7]. Isayev A. I., Mekhtiyeva S.I., Rzayev A. K. Turkish.J. of Phisics, **22**, 263, (1998).
- [8]. Mekhtiyeva S.I., Ibraqimov ,N.I, Isayev A. I., Zeynalov V. Z., Mamedov E. A, Turkish. J. of Phisics, **26**, 449,(2002).
- [9]. Isayev A.I., Kazakova L.P., Lebedev E.A., Mekhtiyeva S.I., Yatlinko I.I. "Local states controlling carrier transfer in glass-like semiconductors of Se-As system and influence of galogen impurities. "CV.: Defects in semiconductors st. Petersburg. pp. 61., (1992)
- [10]. Ya.Y.Klyava. FSS, 27, 1350 (1985)
- [11]. Swanpoel R. J. Phys.E. Sci Instrum,16, p. 1214, (1983).
- [12]. Popov A., I., In: Semiconductors and Semimetals (Amsterdam, Elsevier Inc.,2004) v.78 p. 51.
- [13]. Physics of Hydrogenated Amorphous Silicon. Ed.2: Electron and vibrational properties. Edited by Joanopoulos J. Jukovsky J. –M; Mir, 1998, pp. 447, [Translation from

English: The Physics of Hydrogenated Amorphous Silicon II. Electronic and vibrational properties, Edited by Joanopoulos J. D and Jukovsky G (Berlin – Hiedelberq-N.Y. Tokyo, Springer Verlag, 1984)]

[14]. Phillips J, C., Phys.Status. Solidi, b44, K1 (1971).1

[15]. Shevchik N. J., Paul W. “Voids in amorphous semiconductors” J. Non – Cryst. Solids **16**, 1, p 55-71. (1974).

[16].A.I.Isayev, S.I.Mekhtiyeva, N.Z.Jalilov, R.I. Alekperov, V .Z. Zeynalov, The optical absorption of $Se_{95}As_5$ system doped by atoms of samarium , Optoelectronics and Advanced Materials–Rapid Communic. Vol.1 Iss. 8, 368 -372 (2007).