CHARACTERIZATION OF HIGH REFRACTIVE AMORPHOUS $(As_4S_3Se_3)_{1-x}:Sn_x$ CHALCOGENIDE GLASSES

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Abstract. *The transmission spectra of bulk and thin films of $(As_4S_3Se_3)_{1-x}:Sn_x$ in the visible and infrared (IR) regions were investigated. Doping of $As_4S_3Se_3$ chalcogenide glass with Sn impurities essentially reduce the absorption bands of S-H (Se-H) and H_2O located at $v=5190$ cm^{-1} and $v=3617$ cm^{-1}, respectively. The amorphous $(As_4S_3Se_3)_{1-x}:Sn_x$ thin films exhibit photoinduced effects under the light irradiation with photon energy above the optical band gap $(hv{\geq}Eg)$, that make its perspective materials for registration of optical and holographic information. The modification of optical parameters (optical band gap E_g, absorption coefficient α, refractive index n) under light irradiation and heat treatment of the amorphous thin films with different amount of Sn was studied.*

Keywords: *Chalcogenide glasses, amorphous films, transmission spectra, refractive index.*

I.   Introduction

Chalcogenide glasses of As-S-Se system exhibit photostructural transformations, and are perspective materials for registration media, for fabrication of diffractive elements, and other optoelectronic applications [1]. It is well known that the optical properties (absorption coefficient a, refractive index *n*, optical band gap E_g) depend on the glass composition. In the last years, a special attention has been devoted to the metal impurity influence on the photostructural transformation in amorphous thin films doped with [2]. It was shown that the Sn impurity introduced in the As_2Se_3 glass network reduced the photodarkening effect. According to Mössbauer spectroscopy of [119]Sn in the $As_2Se_3:Sn$ glass system, new tetrahedral $Sn(Se_{1/2})_4$ and quasi-octahedral SnSe structural units can be formed, and which influence the photostructural transformations. In the present paper we report the optical transmission spectra and the modification of optical parameters (optical band gap E_g, absorption coefficient α, refractive index *n*) of the amorphous $(As_4S_3Se_3)_{1-x}:Sn_x$ thin films with different amount of Sn under light irradiation and heat treatment.

II. Experimental

The bulk chalcogenide glasses $(As_4S_3Se_3)_{1-x}:Sn_x$ $(0{\leq}x{\leq}0.1$ at.%) were prepared from the elements of *6N* (As, S, Se, Sn) purity by conventional melt quenching method. The thin film samples with thicknesses $d=0.5{\div}3.0$ μm were prepared by flash thermal evaporation of the synthesized initial glasses in vacuum onto glass substrates held at $T_{subs}=100$ °C. For optical transmission spectra measurements the double-beam spectrophotometer Specord M40 $(n=(19{\div}11)x10^3 cm^{-1})$, and the Spectrum 100 FTIR Spectrometer (PerkinElmer) $(n=400{\div}4000$ $cm^{-1})$ were applied. For calculation of the optical constants from the transmission spectra, the method proposed by Swanepoel and Tauc [3], and the computer program PARAV-V1.0 were used [4].

III. Results and discussion

The mid-IR transmission spectra of As_2S_3 and some $(As_4S_3Se_3)_{1-x}:Sn_x$ bulk glasses are shown in fig.1. Vitreous As_2S_3 doped with metals [5] are characterized by several well resolved absorption bands. For vitreous As_2S_3 these bands are located at the frequencies n=5190 cm^{-1} (S-H), n=3617-3522 cm^{-1} (H_2O), n=2482 cm^{-1} (S-H), n=1857 cm^{-1} (As-H), n=1597 cm^{-1} (H_2O), and n=1003 cm^{-1} (As_2O_3), and are summarized in table 1.

The characteristic absorption bands for pure As_2S_3 at ν=5190, 3617, 3522, 1857, 1597cm^{-1} are significantly reduced upon doping with Sn. At the same time for the $(As_4S_3Se_3)_{0.98}:Sn_{0.02}$ glass additional absorption bands located at n=5190, 3194, 2026, 1493 and 1500 cm^{-1} appear. The observed changes upon doping in the mid infrared region are most likely related to interactions of a portion of the introduced metal ion impurities with the inherent impurities of the host glass, such as hydrogen and oxygen atoms. Such interactions lead to the reduction of the relative intensity of bands associated with O-H, S-H, As-O and As-H bonds in the host glass. For the $(As_4S_3Se_3)_{1-x}:Sn_x$ bulk glasses with the composition x=0; 0.3; 0.4 no any absorption bands were observed.

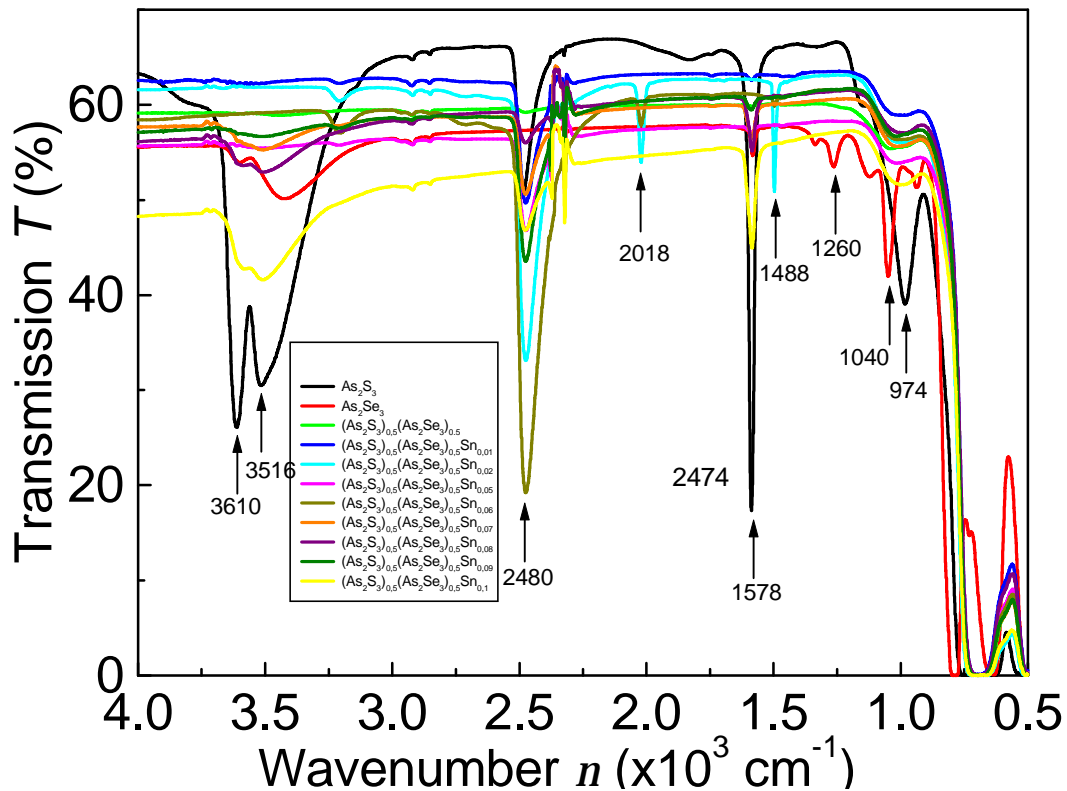Fig.2 shows the typical transmission spectra of some composition of amorphous glasses $(As_4S_3Se_3)_{1-x}:Sn_x$ thin films.

Fig.1. The transmission spectra of bulk samples of $(As_4S_3Se_3)_{1-x}:Sn_x$ glasses.

Table 1. Assignments of characteristic vibration bands for vitreous $(As_4S_3Se_3)_{1-x}:Sn_x$ bulk glasses.

Bond	Position (cm-1)	As_2S_3	As_2Se_3	x= 0	x= 0.01	x= 0.02	x= 0.05	x= 0.06	x= 0.07	x= 0.08	x= 0.09	x= 0.10
S-H (Se-H)	4878	4420	–	–	–	–	–	–	–	–	–	–
H2O	3584	3610	3607	–	–	–	–	–	–	–	–	3590
H2O	3496	3516	3427	–	–	–	–	–	3510	3506	–	3516
-S-H-	3215	–	2925	–	–	3213	–	3213	0	–	–	–
-S-H- (Se-H-)	2493	2480	–	–	2475	2480	2379	2475	2475 2372	2480 2372	2471 2380	2480 2380
CO2	2320	–	2317	–	2316	2320	2320 2372	2324	2320	2324	2316	2324
-C-O-S-	2020	–	–	–	–	2019	–	2019	–	–	–	–
-As-H-	1992	–	–	–	–	–	–	–	–	–	–	–
H_2O	1584	1578	1578	–	1590	–	1586	–	1582	1582	1590	1578
CS2	1497	–	1342	–	–	1495	–	1498	–	–	–	–
AsO (As_2O_3)	1052	974	937 1048 1130	1040	1015	1011	1030	1015	1022	1011	1022	1000
Phonon energy, cm^{-1}		804	832	768	762	775	767	767	767	764	767	771

From the transmission spectra *T=f(l)*, using the expressions $a = \frac{1}{d}\ln\frac{(1-R)^2}{T}$, $n = \left[M + (M^2 - n_s^2)^{1/2}\right]^{1/2}$, $M = \frac{2n_s}{T_m} - \frac{n_s^2 + 1}{2}$, where and the dependence $(ahn)^{1/2} = A(hn-E_g)$, the absorption coefficient - *a*, the refractive index of our materials - *n*, n_s - refractive index of glass substrate (n_s=1.51±0.01) , and the value of the optical band gap E_g were determined, respectively. Here *d* – is the thickness of the sample (cm), *R* – the reflection coefficient, *A* - is a constant. In chalcogenide glasses the absorption edge is broader than in crystalline analogues and this is caused by a broad energy distribution of electronic states in the band gap due to disorder and defects. The absorption edge in the high absorption region (a>10^4 cm^{-1}) is described by a quadratic function $a \propto \frac{1}{hn}(hn - E_g)^2$. Dependence in the Tauc coordinates $(ahn)^{1/2}$ *vs.* *(hn)* gives the value of the optical band gap energy, E_g, and determined as the energy difference between the onsets of exponential tails of the allowed conduction bands.
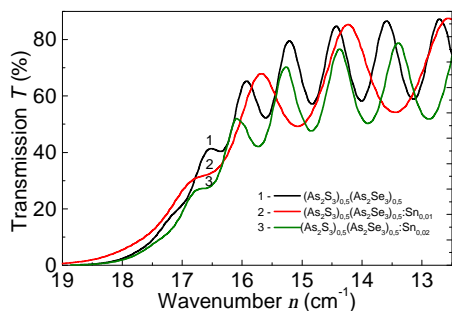

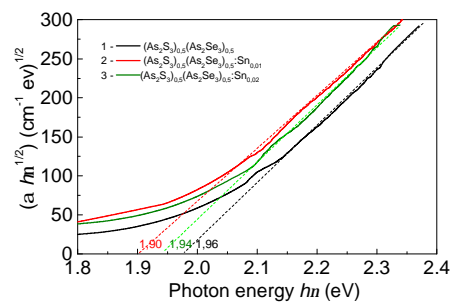Fig.2. The transmission spectra of some amorphous $(As_4S_3Se_3)_{1-x}:Sn_x$ thin films.

Fig.3. The absorption spectra in the Tauc coordinates $(a\,hn)^{1/2}$ *vs* *(hn)*.

Fig.3 represents the absorption spectra in the Tauc coordinates $(\alpha\, h\nu)^{1/2}$ vs $(h\nu)$. As one can see the Sn impurities in the $As_4S_3Se_3$ increase the absorption coefficient α and decrease the optical band gap energy Eg, as was observed in the case of the amorphous AsSe:Sn films [6]. These peculiarities indicate that the tin impurities in chalcogenide glasses induce a broadening of the electronic tail states in the conduction bands and shift the Urbach edge in the red region of the spectrum. This broadening of the electronic tail states can be attributed to the formation of new tetrahedral structural units containing Sn, and which leads to the additional structural disorder to that existing in the matrix of chalcogenide glass.

Fig.4 represents the dispersion curves of the refractive index $(n^2-1)^{-1}=f(hn)^2$. Increasing of the Sn content in amorphous $(As_4S_3Se_3)_{1-x}$:Sn_x thin films leads to increase the refractive index n. The values of the refractive index n at the wavelength l=633nm are n=2.52±0.02 for x=0, and n=2.74±0.02 for x=0.02, respectively.

The plot $(n^2-1)^{-1}$ vs. $(hn)^2$ (Fig.4) allows to determine the oscillator parameters by fitting straight line through a set of experimental points. By extrapolating the fitting line towards $(hn)^2$=0, one can obtain the static refractive index $n(0)$, and the static dielectric constant $e(0)=n^2(0)$. The dispersion of the refractive index is related to the electronic absorption spectrum through the Wemple equation based on the single electronic oscillator model [7] $(n^2-1) = \dfrac{E_d E_0}{E_0} - (hn)^2$, where E_0 is the average electronic energy gap, and E_d is the dielectric oscillator strength.
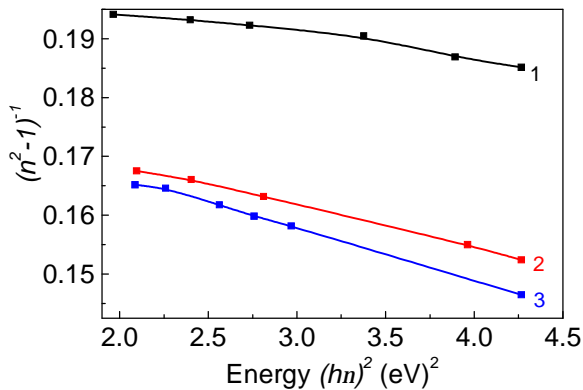

Fig.4. The dependence of the refractive index $(n^2-1)^{-1}$ vs. $(h\nu)^2$ for amorphous $(As_4S_3Se_3)_{1-x}$:Sn_x thin film. x: 1-0; 2-0.01; 3-0.02.
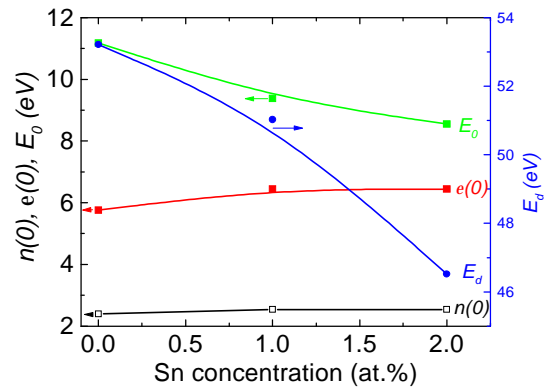
Fig.5. The calculated parameters n(0), ε(0), E_0 and E_d for as-deposited amorphous $(As_4S_3Se_3)_{1-x}$:Sn_x thin films.

Large values of the refractive index n, E_0 and large E_d lead to a large dispersion throughout the chalcogenide glass material. From equation (2) we obtain: $(n^2-1)^{-1} = \dfrac{E_0}{E_d} - (\dfrac{1}{E_0 E_d})(hn)^2$.

Using the plot from fig.4, the E_0 and E_d were calculated with the values E_0=0.93±0.03eV and E_d=7.44 ±0.03eV, respectively (Table 2). For $As_{12.6}Ge_{23.8}S_{63.6}$ was found that $E_0 \gg 2E_g$ [8]. In our case amorphous $(As_4S_3Se_3)_{1-x}$:Sn_x thin films $E_0 \approx (4\div6)E_g$.

IV. Summary

Doping of $As_4S_3Se_3$ chalcogenide glass with tin impurities essentially reduces the absorption bands intensity of S-H (Se-H) and H_2O located at $v = 5190$ cm^{-1} and $v = 3617$ cm^{-1}, respectively. From the transmission spectra the optical parameters (optical band gap E_g, absorption coefficient

α, refractive index n), the average electronic energy gap E_0, and the dielectric oscillator strength E_d for amorphous $(As_4S_3Se_3)_{1-x}:Sn_x$ thin films with different amount of Sn were calculated.

Table 2. The optical parameters of amorphous $(As_4S_3Se_3)_{1-x}:Sn_x$ thin films.

Nr.	Film composition	$a \cdot 10^4$, cm^{-1} ($h\nu$=2.3 eV)	$Eg \pm 0.03$, (eV)	$n \pm 0.02$ (l=633nm)	$n(0) \pm 0.02$	$e(0)$	$E_0 \pm 0.02$, (eV)	$E_d \pm 0.02$, (eV)
1.	$As_4S_3Se_3$	2.44	1.96	2.52	2.40	5.76	11.18	53.21
2.	$(As_4S_3Se_3)_{0.99}:Sn_{0.01}$	3.17	1.90	2.70	2.54	6.44	9.38	51.02
3.	$(As_4S_3Se_3)_{0.98}:Sn_{0.02}$	3.07	1.94	2.74	2.54	6.44	8.55	46.52

V. Acknowledgment

VI. References

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