

## OPTICAL PROPERTIES OF $\text{As}_2\text{S}_3\text{:Pr}$ AND $\text{As}_2\text{Se}_3\text{:Dy}$ AMORPHOUS COMPOSITES

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New composite materials consisting from arsenic sulphide ( $\text{As}_2\text{S}_3$ ) and arsenic selenide ( $\text{As}_2\text{Se}_3$ ) doped with rare-earth ions ( $\text{Pr}^{3+}$  and  $\text{Dy}^{3+}$ ) and polymers (polyvinyl alcohol (PVA) or polyvinylpyrrolidone (PVP)) were prepared and investigated. The optical absorption spectra of thermally evaporated amorphous  $\text{As}_2\text{S}_3$  and  $\text{As}_2\text{Se}_3$  thin films correlate with the transmission spectra of thick films prepared by chemical methods. For the samples  $\text{As}_2\text{S}_3\text{:Pr}^{3+}/\text{PVA}$  and  $\text{As}_2\text{Se}_3\text{:Dy}^{3+}/\text{PVP}$  an increasing of transparency in the visible region with respect to pure  $\text{As}_2\text{S}_3$  and  $\text{As}_2\text{Se}_3$  was observed. The investigated new composites are perspective for different photonic devices and sensors for different applications.

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### 1. Introduction

The development of new polymers and composite materials is very attractive for future implementation of new photonic and optoelectronic devices. Some general principles of nanotechnology and nanostructured materials, its properties and possible applications are presented by M. Muhammed & T. Tsakalakos in the review article [1]. Actually the definition of nanocomposite materials has broadened significantly and includes a large variety of systems and structures such as one-dimensional, two-dimensional (metal oxides, metal phosphates, chalcogenides), three-dimensional and amorphous materials. Now the main efforts are focused on the ability to obtain control of the nanoscale structures with the requested physical and optical characteristics through innovational synthesizing approaches. It was shown that the properties of nanocomposite materials depend not only of the properties of their individual host components but also on their morphology and interface characteristics.

The chalcogenide glasses ( $\text{As}_2\text{S}_3$ ,  $\text{As}_2\text{Se}_3$ ) exhibit a strong photoinduced effect under light irradiation with bandgap and UV light, and which have a wide applications as inorganic photoresists with high resolution, for preparing different diffractive elements for integrated optics and telecommunication systems. Because the chalcogenide glasses have a good solubility in different organic solutions, they present interest for fabrication of new composite materials involving polymers.

Low dimensional inorganic/polymeric nanocomposites represent an important and growing class of hybrid materials with promising physical and optical characteristics. Recently, a series of sulfides  $\text{Li}_x\text{TaS}_2$  nanocomposites prepared by the encapsulative precipitation method were obtained [2].  $\text{Me}_x\text{SnSe}_4$  mesostructured semiconducting porous structures with the bandgap between 1.4 and 2.5 eV also were fabricated [3]. Such semiconducting porous networks could be used for optoelectronics, photosynthetic and photocatalytic applications. At the same time it was shown that the photoinduced changes in chalcogenide glasses and polymers may be due by the atom displacements in these materials [4,5]. Because the organic polymers exhibit high photoinduced changes and low stability and on the contrast, the chalcogenide glasses – low photoinduced effects and good stability, the combination of these properties by creation of new composites based on chalcogenide glasses and

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polymers can allow to obtain new materials with new multifunctional properties. As an example, in [6,7] was shown, that doping of chalcogenide glasses with tin and rare-earth ions increase the stability of amorphous  $\text{As}_2\text{S}_3$  thin films against light irradiation and heat treatment.

The chalcogenide glasses (ChG)  $\text{As}_2\text{S}_3$  and  $\text{As}_2\text{Se}_3$  doped with rare earth ions are perspective materials for fiber optics amplifiers, recording media for high-resolution diffraction gratings, planar-integrated optical elements, all-optical switches, etc. A variety of nanocomposite materials based on  $\text{As}_2\text{S}_3$  and  $\text{GeSe}_3$  chalcogenide glasses was formatted under specific UV irradiation conditions [8]. It was established that applying lasers as a tool for photo-thermal synthesis it is possible to create a variety of multicomponent composites with new functional characteristics. Moreover, using the chalcogenide glass  $\text{As}_2\text{S}_3$  and commercial polymers, different integrated waveguides with low-loss ( $\sim 0.2$  dB/cm) were realized [9]. The ability of dissolution of amorphous  $\text{As}_2\text{S}_3$  in different organic solution (amines and nitriles, butylamine) by creating of large molecular fragments into the solution was shown in [10].

Recently new nanocomposites based on semiconductors (PbS) and polymer, chalcogenide glasses ( $\text{As}_2\text{S}_3$ ) and polymer for electroluminescence and different diffractive elements were investigated [11,12]. High photoluminescence gain from  $\text{Nd}^{3+}$ -ion-implanted  $\text{As}_2\text{S}_3$  planar waveguide at 1090 nm was observed. By thermal evaporation and subsequent ion implantation were obtained thin films of  $\text{As}_2\text{S}_3$  and  $\text{As}_{24}\text{S}_{38}\text{Se}_{38}$  doped with  $\text{Er}^{3+}$ , which shows a luminescence peak situated at 1536 nm [13]. In such way, it was demonstrated that the combination of thermal evaporation and ion implantation is an efficient method for the fabrication of rare-earth-doped waveguides, avoiding any solubility limitation. At the same time the penetration depth for the implanted species is very small ( $\sim 42$  nm) for the  $1\div 2$   $\mu\text{m}$  film thickness. In order to increase the absorption length the method is apply to obtain multilayer structures. For this reason, investigation of new nanocomposites thin film structures based on doped with rare earth ions chalcogenide glasses and polymers are actually.

The aim of this paper is to demonstrate the possibilities of fabrication of new composite materials based on rare-earth doped chalcogenide glasses dispersed in polymeric matrix. A series of composites films of  $\text{As}_2\text{S}_3:\text{Pr}^{3+}$ /polymer and  $\text{As}_2\text{Se}_3$ /polymer were prepared by chemical methods. The new composite materials exhibit changes in optical properties under UV irradiation. These changes depend on the species and concentration of the rare-earth dopant.

## 2. Experimental

The composite films were obtained from the solution of rare earth doped chalcogenide glasses ( $\text{As}_2\text{S}_3$  and  $\text{As}_2\text{Se}_3:\text{Pr}$ , Pr concentration – 0.1 at.%, 0.5 at.% and 1.0 at.%) and polyvinyl alcohol (PVA)  $[-\text{CH}_2\text{CH}(\text{OH})-]_n$  in different proportions. Then the liquid solution was deposited uniformly on the glass substrate and thermally treated in order to obtain dry layers suitable for optical measurements. In the same manner were obtained composites containing  $\text{As}_2\text{Se}_3$  and  $\text{As}_2\text{Se}_3:\text{Dy}$  (Dy concentration – 0.1 at.%, 0.5 at.% and 1.0 at.%) and polyvinylpyrrolidone (PVP)  $[\text{C}_6\text{H}_9\text{NO}]_n$ , also in different proportions. The thickness of the films was  $3\div 50$   $\mu\text{m}$ , and the concentration of chalcogenide glass varied from 33 up to 100 mass % with respect to the mass of polymer. For optical transmission spectra measurements, an SPECORD UV/VIS (0.4-0.8  $\mu\text{m}$ ) and SPECORD 61 NIR (0.8-3.2  $\mu\text{m}$ ), CARL ZEISS JENA production were used.

It was established that the chemical composition of the composite materials under study corresponds to the initial components in the mixture, namely  $\text{As}_2\text{S}_3$ ,  $\text{As}_2\text{Se}_3$ ,  $\text{As}_2\text{S}_3:\text{Pr}$ ,  $\text{As}_2\text{Se}_3:\text{Dy}$ , PVP and PVA. The prepared composite films are homogeneous, yellow-colored (for composites containing  $\text{As}_2\text{S}_3$ ) and auburn-colored (for composites containing  $\text{As}_2\text{Se}_3$ ). Microscope investigations show that the composite films contain clustered spheroids of approximately equal sizes and which are homogeneously distributed in the polymer matrix. The sizes of the spheroids are in the range of 100 nm up to several micrometers, and increase with increasing of the chalcogenide glass concentration in the composites. The typical *SEM TESCAN* image with the distribution of nanoparticles and microscopic clusters of the polymer/inorganic nanocomposite PVA/ $\text{As}_2\text{S}_3$  and PVA/ $\text{As}_2\text{S}_3:\text{Pr}^{3+}$  (the ratio  $\text{As}_2\text{S}_3:\text{PVA} = 100:100$ ) is shown on Fig.1 and 2, respectively. In PVA/ $\text{As}_2\text{S}_3$  composites we can not observe some organization of the chalcogenide glass particles in the polymeric matrix. On the

other hand, in PVA/As<sub>2</sub>S<sub>3</sub>:Pr<sup>3+</sup> composites we can observe some clustering, due to the presence of the rare-earth doped glasses.

### 3. Results and discussion

Fig.3 shows the absorption spectra for As<sub>2</sub>S<sub>3</sub>:PVP nanocomposites before and after UV irradiation. The increasing of the concentration of chalcogenide glass in the polymer lead the shift of the absorption edge to lower energies and increasing of the slope of the absorption edge. This indicates to an increasing of the degree of ordering of the films. At the same time increasing of rare-earth ions concentration in chalcogenide glass decreases the level of absorption of the composite material (Fig.4).

Action of the UV irradiation, in dependence of the ChG concentration in PVA slightly influences the shape of the absorption edge [14]. Although at the initial time of UV irradiation some bleaching effect take place, further irradiation lead to the well known for amorphous semiconductors photodarkening effect [8]. The degree of photodarkening depends on the composition of the nanocomposites and is higher for As<sub>2</sub>S<sub>3</sub>:PVA (ratio 100:100), and As<sub>2</sub>S<sub>3</sub>+0.25 at.% Pr:PVA (ratio 37,5:62,5).

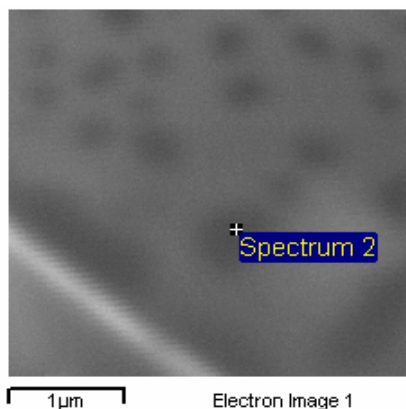


Fig.1. SEM image of the typical structure of the polymer/inorganic composite PVA/As<sub>2</sub>S<sub>3</sub>.

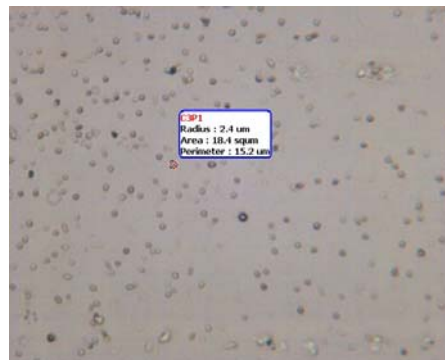


Fig.2. SEM image of the typical structure of the polymer/inorganic composite PVA/As<sub>2</sub>S<sub>3</sub>:Pr.

Some peculiarities in the absorption spectra of the investigated nanocomposites were observed. Fig.5 shows that in the absorption spectra an inflection point located at around  $h\nu=2.5\pm 2.9$  eV ( $\lambda=0.4\div 0.5$  μm) is observed. In the low energy region ( $h\nu < 2.5$  eV) the absorption of the As<sub>2</sub>S<sub>3</sub>+0.25 at.% Pr:PVA is higher than the similar undoped As<sub>2</sub>S<sub>3</sub>:PVA nanocomposites. In the same time in the high energy region ( $h\nu > 2.5$  eV) the absorption of the As<sub>2</sub>S<sub>3</sub>+0.25 at.% Pr:PVA is lower than the similar undoped As<sub>2</sub>S<sub>3</sub>:PVA nanocomposites.

This effect is in a good correlation with the photodarkening effect observed by us in different investigated amorphous chalcogenides [6,7]. The composites structures from rare earth doped chalcogenide glasses and polymers give a good opportunity for its applications as recording media for fabrication of different diffractive elements for optoelectronics [12].

Fig. 6 represents the spectral dependence of the absorption coefficient for the composite film structures As<sub>2</sub>Se<sub>3</sub>:PVP before and after UV irradiation. It was shown that increasing of the chalcogenide glass component in the in the composite material lead to the shift of the absorption edge to lower energies. At the same time, some increasing of the absorption coefficient and of the slope of the absorption edge was observed (Fig.7).

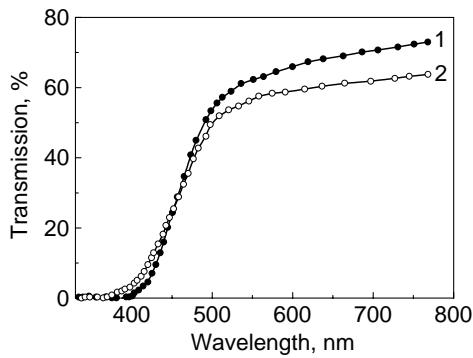


Fig.3. The transmission spectra of as-deposited composite structures  $As_2S_3:PVP$  (1), and irradiated with UV irradiation (2).

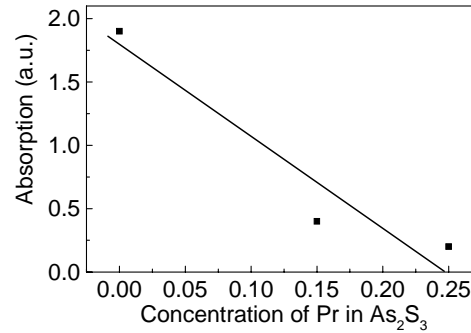


Fig.4. The absorption level of the composites  $As_2S_3:Pr:PVA$  vs. Pr concentration in  $As_2S_3$ .

The absorption coefficient and of the slope of the absorption edge of the investigated composite film structures are influenced by the Dy concentration in the chalcogenide glass (Fig.8). Increasing of the Dy content in the film structure composite drastically decrease the absorption in the spectral region of high energies ( $E > 2.5$  eV). In the region of low energies ( $E < 2$  eV) some increasing of the absorption coefficient take place for the composite  $PVP:As_2Se_3+1.0$  at.% Dy.

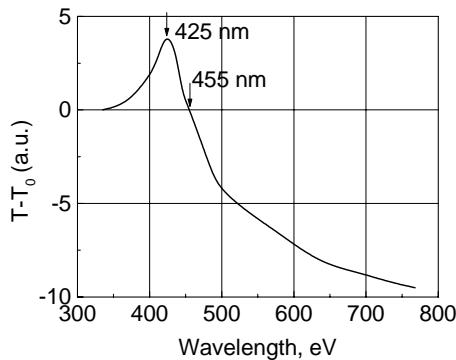


Fig. 5. The decrement of the transmission spectra  $T-T_0$  vs. wavelength  $\lambda$  under UV irradiation of the composite structures  $As_2S_3:PVP$ .

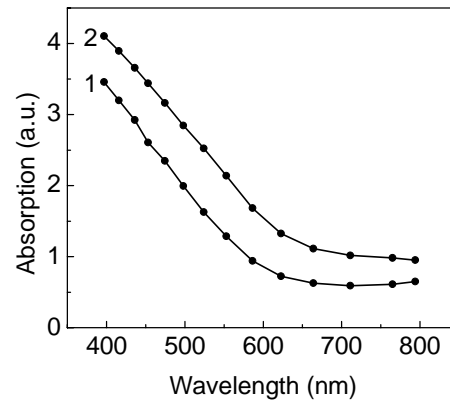


Fig. 6. The absorption spectra for the composite film structure  $As_2Se_3:PVP$ . 1 – for as-deposited; 2 – UV irradiated during 30 min. The ratio of chalcogenide glass/polymer components in mass % is 100:100.

UV irradiation of the composite thin film structures  $As_2Se_3+0.5$  at.% Dy:PVP during 30 min (Fig.7) shifts the absorption edge to lower energies ( $\Delta\lambda=135$  nm) and increase the absorption (photodarkening). For the composite film structure  $As_2S_3:PVP$  the shift of the absorption edge is smaller and consists  $\Delta\lambda=74$  nm. In fact the degree and behaviour of photodarkening effect in composite film structures  $As_2Se_3+Dy:PVP$  depend on the concentration of the Dy ions in the initial chalcogenide glass.

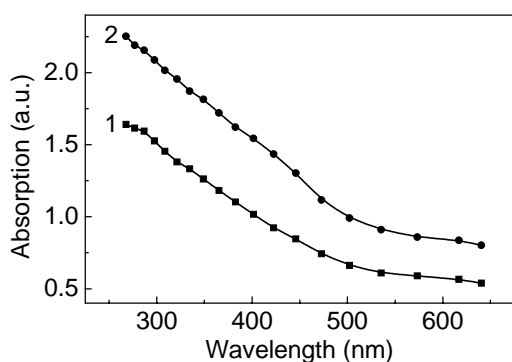


Fig. 7. The absorption spectra for the composite film structure  $As_{40}Se_{60}+0.5$  at.% Dy:PVP. 1 – for as-deposited; 2 – UV irradiated during 30 min. The ratio of chalcogenide glass/polymer components in mass % is 100:100.

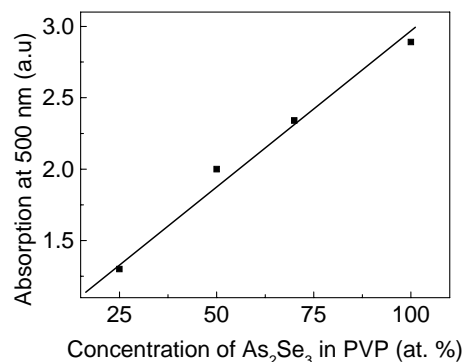


Fig. 8. The dependence of absorption of the composite films on the  $As_2Se_3$  concentration in PVP (at. %).

In our previous work [6] it was shown that, the impurities of Dy in amorphous  $As_2Se_3$  films reduce the photodarkening, and the relaxation process become slower. This effect was explained on the base of the “slip-motion” model, elaborated for photodarkening in amorphous  $As_2S_3$  and  $As_2Se_3$  films [6,7]. According to this model, during the exposure the layers are 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 offers a good basis for consideration of the effect on photodarkening of impurity atoms with co-ordination different from that of the host glass atoms, as in the case of rare earth ions under study. The foreign metal atoms provide bridging between the layers and hence reduce the slip motion, thus suppressing the photodarkening [6,7].

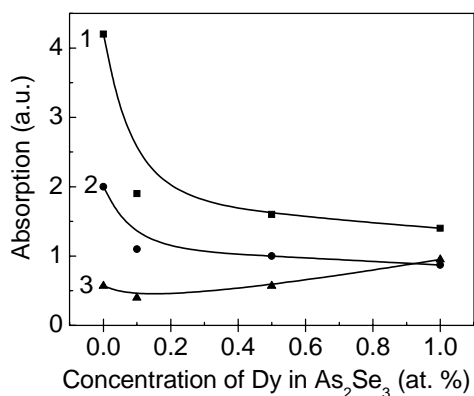


Fig. 9. The dependence of absorption of the composite films  $As_2Se_3$ :Dy/PVP on the concentration of rare-earth ions (Dy) in  $As_2Se_3$  glass at different wavelengths: 350 nm (1), 500 nm (2), and 700 nm (3).

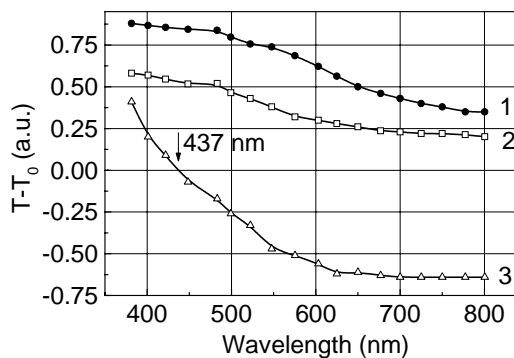


Fig. 10. The dependence of the decrement of transmittance ( $T-T_0$ ) for the composite films PVP/ $As_2Se_3$  (1), PVP/ $As_2Se_3+0.5$  at.% Dy (2), and PVP/ $As_2Se_3+1.0$  at.% Dy (3).

In our case, according to the obtained experimental results on the composite film structures  $As_2Se_3$ :PVP and  $As_2Se_3$ :PVP doped with Dy ions, the composites containing rare-earth ions exhibit

greater sensitivity to the light irradiation. This may be attributed to the local structure of rare-earth ion environment in the glass network dispersed in the polymer matrix.

As result from the Fig.9, the degree of absorption in the  $\text{As}_2\text{Se}_3:\text{Dy}/\text{PVP}$  composites depends also on the spectral range. Increasing of rare-earth ions in the composites leads to decreasing of the absorption (“bleaching”) (Fig.10). This effect was observed also in rare-earth doped Ga-La-S:Pr chalcogenide glasses [15]. The transition from “photodarkening” to “photobleaching” region take place around 437 nm, at the energies higher than the optical band gap of the amorphous  $\text{As}_2\text{Se}_3$ .

#### 4. Summary

New composites optoelectronic structures based on  $\text{As}_2\text{S}_3$  and  $\text{As}_2\text{Se}_3$  chalcogenide glass doped with rare-earth ions ( $\text{Pr}^{3+}$  and  $\text{Dy}^{3+}$ ) and polymers (PVA and PVP) were prepared and investigated. It was shown that adding of an inorganic semiconductor into the polymer increase the absorption and the new composites are sensitive to UV light irradiation. In the polymer/chalcogenide glass composite materials the “photodarkening” and “photobleaching” effects were observed. The investigated new composites are perspective for different photonic devices as well as for recording media with high resolution.

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