

PHOTODARKENING RELAXATION IN AMORPHOUS As_2Se_3 FILMS DOPED WITH RARE-EARTH IONS

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The effect of rare-earth ions (Nd^{3+} , Sm^{3+} , Dy^{3+} , Ho^{3+} , Er^{3+} , and Pr^{3+}) in amorphous As_2Se_3 thin films on the photodarkening relaxation was investigated. The photodarkening amplitude depends on the kind and concentration of rare-earth dopant, as well as on the thickness of the sample and heat treatment. The photodarkening kinetics is described by a stretched exponential function with the dispersion parameter $0 < \alpha < 1.0$, which indicates high dispersion of the relaxation process in as-deposited and annealed chalcogenide films. The effect of impurities is manifested mainly through retardation of the photodarkening in doped samples, which leads to the increasing of the time constant of the process.

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1. Introduction

Special interest for the applications of chalcogenide glassy films is connected with doping of the glass by optically active rare-earth ions, which alter optical, photoelectrical and transport properties of the host material. The choice of rare-earth ions (Nd^{3+} , Sm^{3+} , Dy^{3+} , Ho^{3+} , Er^{3+} , and Pr^{3+}) is determined by the fact that these dopants are actually used in industrial applications in photonics and optical fiber telecommunication systems [1,2]. The films based on arsenic chalcogenides usually became darkened due to photostructural transformations under action of light from the region of fundamental optical absorption ($h\nu \geq E_g$). As the composition of a chalcogenide glass determines both the structural units and the mean coordination number of the amorphous solids [3], the effect of the composition in glassy systems As-Se and As-S on the level of photostructural transformations has been studied in detail [4,5]. At the same time little attention has been devoted to the influence on photodarkening of foreign impurity atoms introduced in the glass, although it was noted that the photodarkening is influenced by doping of amorphous chalcogenide films with Cu impurities [6]. Furthermore, recently we have demonstrated that Sn and Mn, and rare-earth ions (Sm^{3+} , Dy^{3+} , and Pr^{3+}) influenced the photodarkening relaxation in as-deposited and annealed amorphous AsSe and As_2Se_3 thin films [7,8]. There was established that doping of amorphous chalcogenide films by metals assists in stabilizing the glassy matrix with respect to light exposure and thermal treatment.

It was shown by X-ray diffraction measurements that the rare-earth ions (Dy^{3+} and Sm^{3+}) being introduced in glassy matrix determine the decrease of the quasi-distance ascribed to inter-layer spacing in the glassy network [9]. According to the "slip-motion" model [10,11] the metal impurities, which influence the structure of the glass matrix must be evidenced in the photodarkening process.

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In the papers [12-13] we have studied the persistent photoconductivity in As-Se amorphous films doped by tin, and the photoconductivity relaxation in the amorphous As-Se films doped by Sn, Mn, Sm and Dy.

In the present work we report the results of the study of the effect of rare-earth ions (Nd^{3+} , Sm^{3+} , Dy^{3+} , Ho^{3+} , Er^{3+} , and Pr^{3+}) on the photodarkening relaxation in conjunction with the results of the structural and thermal investigations (X-ray diffraction, and Temperature Modulated Differential Scanning Calorimetry (MDSC)).

2. Experimental

The glasses were synthesized from the elements of 6N (As, Se) purity by adding rare-earth oxides by the conventional technique. The rare-earth oxides were supplied by ALFA Aesar. Thin films of thickness from 0.3 to 6.3 μm were prepared by "flash" thermal evaporation in vacuum onto glass substrates held at $T_{\text{substr}}=100^\circ\text{C}$. The structure of the glassy As_2Se_3 bulk samples doped with various amount of rare-earth atoms was investigated by X-ray diffraction procedure, and MDSC technique. The measured X-ray diffraction curves have shown that all chalcogenide compositions are completely amorphous.

In order to initiate photostructural transformations in thin film samples a He-Ne laser ($\lambda=0.63\text{ }\mu\text{m}$, $W=4$ and 10 mW) was used as a source of light exposure. The splitter was used for dividing the laser beam: one Si-photodetector was used for measuring the film transmittance, and another Si-photodetector was used for measuring the time stability of the laser intensity. The total transmittance of the film was currently measured during the exposure time with the aid of a registration module. The experimental set-up included a digital build-in PC-card for data acquisition PCI-1713A connected with the Si-photodetector. Special software was elaborated for automatic measurements. The relaxation curves were examined by computing fitting procedure using the stretched exponential presentation of the data: $T(t)/T(0)=A_0+A\exp[-(t-t_0)/\tau]^{(1-\alpha)}$, where t is the exposure time, τ is the apparent time constant, A characterizes the exponent amplitude, t_0 and A_0 are the initial coordinates, and α is the dispersion parameter ($0<\alpha<1$). The parameter $A=1-A_0$ characterizes the "steady-state" optical losses due to photodarkening. The thermal treating effect was examined by annealing some of the films in vacuum at $T_{\text{ann}}=120^\circ\text{C}$ during one hour. After the annealing the optical transmission relaxation under light exposure was recorded in the same manner.

3. Experimental results and discussion

3.1. Temperature modulated differential scanning calorimetry (TMDSC)

The metals Dy, Pr, Sm, Ho, Er and Nd enter the host glass as 3^+ ions, and, due to charge and large ion dimensions, induce deformations in the host matrix. From the X-ray investigation of the first diffraction peak (FSDP) in As_2Se_3 glasses doped with 0.5 at.% of Sn, Mn, Sm and Dy it was concluded [9] that disordered layers of the glass structure are locally distorted by insertion of the metal atoms that bond to selenium. A high covalency 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, of high electronegativity, produce a shift of the quasi-distance (calculated from the position of the first sharp diffraction peak) towards a lower value, i.e. rare-earth atoms play the role of network modifiers that smooth the disordered As_2Se_3 layers allowing for a better packing at a smaller thickness. The impurity therefore, 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 cluster layers.

Pr and Dy doped As_2Se_3 bulk glass samples were examined by TMDSC technique. TMDSC is a new thermal technique that can be used to get structural [7] information on As-Se glasses. In this case, the MDSC technique permitted to confirm if doping with rare earth atoms causes any significant change of the host network. Such changes could be: formation of rare-earth atom

centered nanophases, or incorporation of the rare earth atoms into host glass network. The MDSC results show that T_g 's of the doped glasses decrease and widths (W) of the glass transitions increase systematically as a function of doping concentration as shown in Fig. 1. The decrease of T_g in these non-stoichiometric glasses is not unexpected. Addition of the rare-earth atoms destroys the selenium-arsenic backbone and one expects T_g to decrease. The magnitude of the decrease is, however, surprisingly large, 20 °C upon alloying 0.5 at % of Pr which apparently saturates when the Pr content increases to 1 at. %. Both Pr ($r_{cov}=1.64$ Å) and Dy ($r_{cov}=1.60$ Å) are much bigger atoms than As ($r_{cov}=1.20$ Å) and it is possible the additives segregate from the base network to form separate nanophases. If the 3⁺ rare-earth additives would behave like As-atoms in As₂Se₃ base glass, the change in T_g would be minimal as shown by the data represented with triangles.

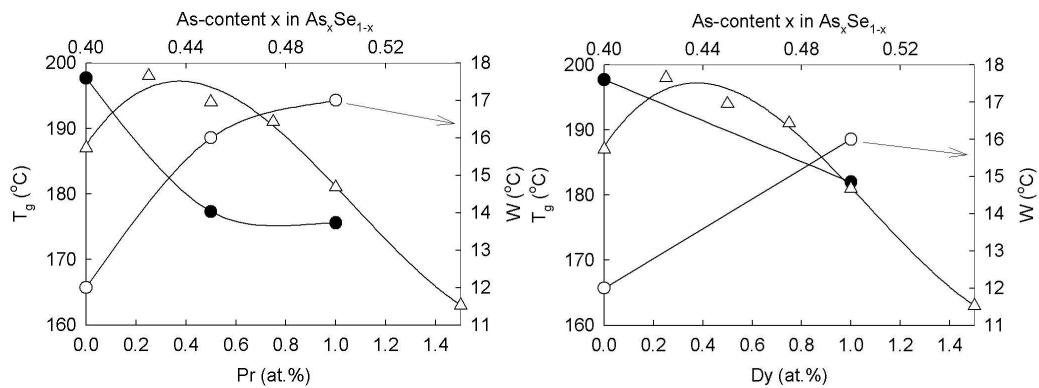


Fig. 1. T_g (●) and width (○) of T_g (noted W) as a function of doping concentration in (As₂Se₃)_{1-x}:RE_x glasses for RE=Pr (left panel) and RE=Dy (right panel). These parameters were deduced from the reversing heat flow using an MDSC model 2920 unit from TA instruments. Scan rate: 3 °C/min; Modulation: 1 °C/100s. The intrinsic variation of T_g in not-doped As_xSe_{1-x} is shown by Δ symbols.

3.2. Photodarkening relaxation

Photodarkening relaxation was measured during illumination of a series of samples of as-evaporated amorphous As₂Se₃, As₂Se₃:Dy_x, and As₂Se₃:Pr_x films doped with various impurities in various concentrations. The films differ by thickness (from 0.3 to 6.3 μm) and by position relative to the source of evaporation. The two rare-earth impurities (Dy and Pr) were added in concentration 0.1, 0.5 and 1.0 at. %. The effect of incident angle of evaporation was controlled by measuring three samples positioned just over the evaporator (center) and two one-centimeter steps aside (2-nd and 3-rd).

Fig. 2a and Fig. 2b show the dependence on concentration of photodarkening kinetics for As₂Se₃ thin films doped with Dy and Pr. Increasing of the rare-earth concentration reduces the photodarkening effect. The effect of film thickness seems to be, also, important. In Fig. 2b the increase of dopant concentration is directly related to the decrease of thickness. While in Fig. 2a the film doped by only 0.1 at.%Dy is the thinnest: 1.1 μm, and shows the highest relaxation curve (2) similar to the curve (4) measured on the thinnest film doped by Pr (1.2 μm). Nevertheless, in both cases (doping with Pr) the doping with RE elements leads to the increase of light transmittance during photodarkening, if compared to the transmittance of non-doped films.

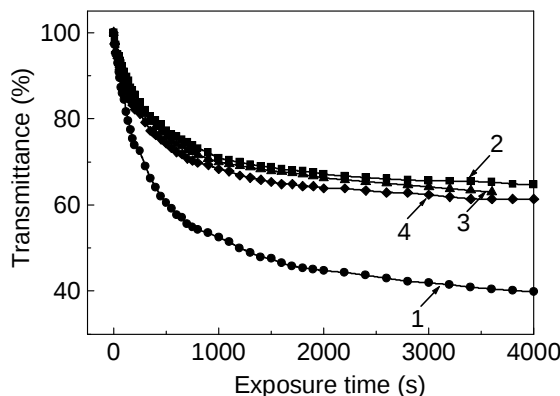


Fig. 2a. The relaxation curves of photodarkening for $\text{As}_2\text{Se}_3:\text{Dy}$ thin films: 1- As_2Se_3 ($L=6.25 \mu\text{m}$), 2- $\text{As}_2\text{Se}_3+0.1 \text{ at. \% Dy}$ ($L=1.1 \mu\text{m}$), 3- $\text{As}_2\text{Se}_3+0.5 \text{ at. \% Dy}$ ($L=2.25 \mu\text{m}$), 4- $\text{As}_2\text{Se}_3+1.0 \text{ at. \% Dy}$ ($L=1.9 \mu\text{m}$).

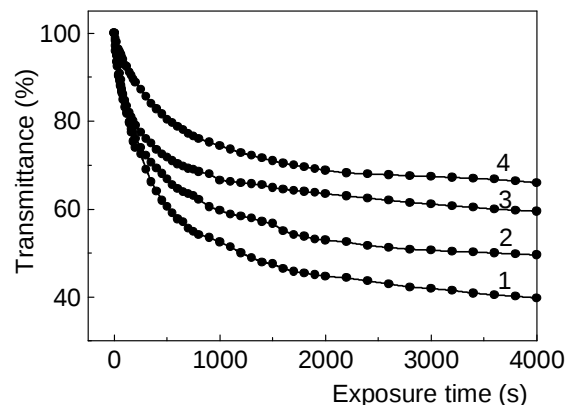


Fig. 2b. The relaxation curves of photodarkening for $\text{As}_2\text{Se}_3:\text{Pr}$ thin films: 1- As_2Se_3 ($L=6.25 \mu\text{m}$), 2- $\text{As}_2\text{Se}_3+0.1 \text{ at. \% Pr}$ ($L=2.1 \mu\text{m}$), 3- $\text{As}_2\text{Se}_3+0.5 \text{ at. \% Pr}$ ($L=1.5 \mu\text{m}$), 4- $\text{As}_2\text{Se}_3+1.0 \text{ at. \% Pr}$ ($L=1.2 \mu\text{m}$).

To obtain a unified approach for comparison, all relaxation curves were fitted to a stretched exponential function:

$$T(t)/T(0) = A_0 + A \exp[-(t-t_0)/\tau]^{1-\alpha}, \quad (1)$$

using standard computer least-square fitting procedure. This approach proved to be possible in our previous comparative study of photodarkening relaxation in As_2Se_3 films doped with Sn, Sm, Dy and Mn [7,14]. Five parameters have been varied, A_0 and t_0 as the initial co-ordinates of the fitting curve, τ as the relaxation time constant, A as the photodarkening amplitude and α as the dispersion parameter ($0 < \alpha < 1$).

For the obtained relaxation curves rather wide scattering of parameters is observed for samples of the same composition. For doped samples the reason for this dispersion may be that the concentration and distribution uniformity of impurity is not adequately preserved along the film at deposition. But the relaxation curves are significantly different in the case of non-doped As_2Se_3 as well (Fig. 3a). The main reason comes from the difference in thickness, particularly for the samples with submicrometer thickness. For these samples the effect of interference of light reflected at the front and the rear film boundaries significantly changes the amount of absorbed light leading to strong dependence of the photodarkening at a fixed laser wavelength on the film thickness [8].

Comparison of the parameters of the relaxation curves for samples deposited at different incident angles have shown that in the considered limits of distance from the center over the evaporator the greatest effect of photodarkening is observed for the central samples, in contrast to the results reported in the literature for obliquely deposited films [15]. Slight decrease of the photodarkening amplitude with the distance from the center is due to decreasing of the film thickness. This is true both for pure and doped As_2Se_3 films. We may conclude that no structure-caused position dependence is observed in our case.

It follows then that film thickness is the most important factor, which influences the photodarkening effect, for it depends on the amount of absorbed energy of light $I_A/I_0 = 1 - \exp(-kL)$, where k is the absorption coefficient and L is the film thickness. This amount is characterized by the amplitude A , determined from the fitting procedure. In Fig. 3b the values of the A parameter for all As_2Se_3 samples, pure and doped with Dy and Pr, are plotted in semilogarithmic co-ordinates $-\ln(1-A)$ vs. L . In ideal case this plot should give straight lines with the slope determined by the absorption coefficient k .

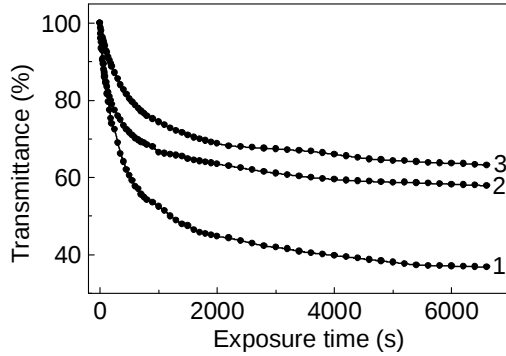


Fig. 3a. The relaxation curves of photodarkening for As_2Se_3 thin films. Thickness L , μm : 1-6,25; 2-1.5; 3-1.2.

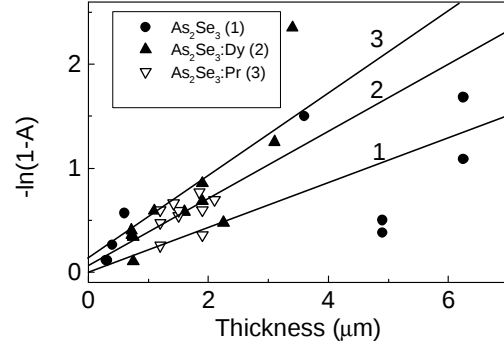


Fig. 3b. Semi logarithmic plot of photodarkening amplitude vs. film thickness ($-\ln(1-A)$ vs. L) for all As_2Se_3 samples, pure and doped with Dy and Pr.

Though strongly scattered, especially for thin films (as it was discussed above), the points show clear tendency to increase the ordinate with increasing the film thickness. Estimation of absorption coefficient from the slope of linear fit to the points gives a reasonable value of about $k=3 \times 10^3 \text{ cm}^{-1}$ for undoped As_2Se_3 . For As_2Se_3 doped with Pr and Dy slightly greater k values were obtained due to increase of impurity absorption. We may conclude that the observed variation of photodarkening amplitude for various samples is due mainly to the difference in film thickness, which regulates the amount of absorbed photons generating the photodarkening effect. Besides the thickness dependence of the position of optical absorption edge, the thickness dependence of the photodarkening in As_2Se_3 thin films was also explained by the strain induced by the lattice mismatch between the film and the substrate [16].

The effect of rare-earth (RE) metal impurity on the photodarkening process was studied in the same way, using thin film samples of undoped As_2Se_3 , and Pr, Dy, Ho, Er, Sm and Nd- doped As_2Se_3 with 0.5 at.% RE. As-deposited and annealed at $T=120^\circ\text{C}$ during 1 hour thin film samples of various composition were exposed to He-Ne ($P=10 \text{ mW}$) laser light and the optical transmission relaxation curves were recorded and analyzed with the above computer fitting procedure. The parameters A_0 , A , τ and α have been determined for all compositions of the untreated and annealed films. With exception of Dy, all studied RE added as 0.5 at.% of impurity significantly reduce the photodarkening effect in as-deposited (Fig. 4a) and annealed (Fig. 4b) amorphous As_2Se_3 doped films.

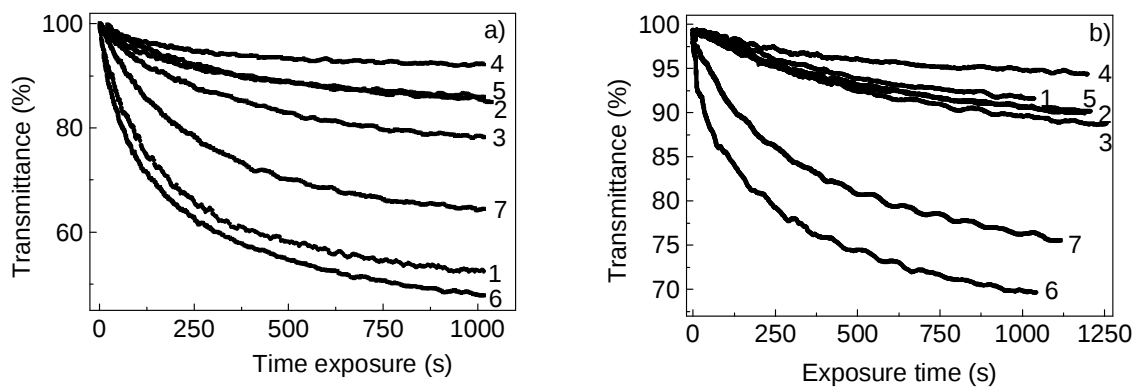


Fig. 4. Photodarkening kinetics of as-deposited $\text{As}_2\text{Se}_3\text{:Me}$ films with exposure time. As-deposited (a) and annealed at $T_{\text{ann}}=120^\circ\text{C}$ (b) samples: As_2S_3 (1); $\text{As}_2\text{S}_3+0.5 \text{ at.}\% \text{ Er}$ (2); $\text{As}_2\text{S}_3+0.5 \text{ at.}\% \text{ Ho}$ (3); $\text{As}_2\text{S}_3+0.5 \text{ at.}\% \text{ Nd}$ (4); $\text{As}_2\text{S}_3+0.5 \text{ at.}\% \text{ Sm}$ (5); $\text{As}_2\text{S}_3+0.5 \text{ at.}\% \text{ Dy}$ (6); $\text{As}_2\text{S}_3+0.5 \text{ at.}\% \text{ Pr}$ (7).

To obtain a unified basis for comparison of the transmission relaxation $T(t)$ curves we used the so called stretched exponential presentation for the relaxation curves in Fig. 4a and 4b in the form: $T(t)/T(0) = A_0 + A \exp[-(t-t_0)/\tau]^{(1-\alpha)}$, where t is the exposure time, τ is the apparent time constant, A characterizes the exponent amplitude, t_0 and A_0 are the initial coordinates, and α is the dispersion parameter ($0 < \alpha < 1$). As a background for the dependence $T(t)/T(0) = A_0 + A \exp[-(t-t_0)/\tau]^{(1-\alpha)}$, two groups of mechanisms are usually considered [17].

The first one includes diffusion-controlled processes with random distribution of transport parameters in a disordered glass. The second group combines the relaxation hierarchy of several successive steps with a distribution of relaxation times. Approximation of the experimental decays with the aid of a standard computer fitting procedure proved to be attainable for all curves (χ^2 better than 4×10^{-3}). The parameters of the stretched exponent A_0 , A , τ and α have been determined for all compositions of the untreated and annealed films (for $t_0=0$) (Table 1).

Table 1. The parameters of the stretched exponential obtained by fitting the experimental points and calculated curves for $\text{As}_2\text{Se}_3\text{:Me}$ samples.

As-deposited $\text{As}_2\text{Se}_3\text{:Me}$ Films				
Composition	A_0 , %	A , %	τ , s	α
As_2Se_3	49.9	79.0	126	0.43
$\text{As}_2\text{Se}_3+0.5$ at.% Er	82.9	18.6	3894	0.28
$\text{As}_2\text{Se}_3+0.5$ at.% Ho	73.7	28.4	4878	0.28
$\text{As}_2\text{Se}_3+0.5$ at.% Nd	81.9	24.1	17412	0.73
$\text{As}_2\text{Se}_3+0.5$ at.% Sm	81.0	21.2	553	0.45
$\text{As}_2\text{Se}_3+0.5$ at.% Dy	35.5	81.7	227	0.59
$\text{As}_2\text{Se}_3+0.5$ at.% Pr	59.6	46.0	340	0.27
Annealed at $T_{\text{ann}}=120$ °C during 60 min $\text{As}_2\text{Se}_3\text{:Me}$ Films				
Composition	A_0 , %	A , %	τ , s	α
As_2Se_3	33.9	74.6	38121	0.61
$\text{As}_2\text{Se}_3+0.5$ at.% Er	34.5	74.6	51124	0.67
$\text{As}_2\text{Se}_3+0.5$ at.% Ho	35.6	77.4	26003	0.67
$\text{As}_2\text{Se}_3+0.5$ at.% Nd	51.1	97.4	16573	0.91
$\text{As}_2\text{Se}_3+0.5$ at.% Sm	72.0	29.9	4310	0.50
$\text{As}_2\text{Se}_3+0.5$ at.% Dy	34.4	81.3	1980	0.75
$\text{As}_2\text{Se}_3+0.5$ at.% Pr				

It follows from the data for untreated films that introduction of RE impurities in a- As_2Se_3 reduces the relaxation time constant and increases dispersion. The parameter α was found to be less than unity and to lie between 0.32 and 0.71 for untreated films (Fig. 5a). The variation of the kinetic parameter τ of the stretched exponential is most interesting as it reflects the changes in the process rate in dependence of the sort of impurity atom. The time constant τ of the photodarkening process is much stronger dependent on the sort of impurity, increasing in the impurity series Dy-Pr-Sm-Er-Ho-Nd, for as-deposited, and particularly after annealing of the samples, and depend on the atomic radius of the rare-earth ion (Fig. 5a).

The values of the time constant τ for untreated and thermally annealed films are plotted in Fig. 5b along with the 3rd ionization energy values (I_3) of ions in Lanthanide series. The overall trend across the series for the latter is to increase because of increase in nuclear charge across the f -electrons block. However, between f^7 and f^8 at Gd there is a break due to step in exchange energy [18]. It is clearly seen from Fig. 5b that for as-deposited RE-doped films the time constant of the photodarkening process remains about the same as in undoped As_2Se_3 (lower dashed line) and is only slightly dependent on the species. After annealing the process rate becomes strongly species dependent, with the time constant varying in correlation with the ionization energy I_3 . Though the time constant τ is increased due to annealing in all the samples, including undoped As_2Se_3 (upper dashed line), this increasing is different for various species and correlates with the behavior of the I_3 .

This fact suggests that chemical activity of RE impurity in the host chalcogenide glass is enhanced by annealing.

The photodarkening phenomena in chalcogenide glass films under illumination has no plain explanation up to now in spite of detailed investigation and a series of models advanced for interpretation of it. The red shift of the absorption edge on photodarkening indicates the narrowing of the optical gap of the chalcogenide 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. To analyze our experimental results we have used the novel approach for photodarkening phenomenon in a-As₂Se(S)₃ [10,11], 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 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 metals under study. The foreign metal atoms provide bridging between the layers and hence reduce the slip motion, thus suppressing the photodarkening.

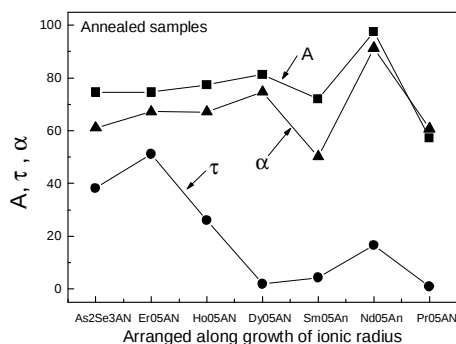


Fig. 5a. The dependence of the parameters of the strength exponential A , τ , and α on the atomic radius of rare-earth ions for annealed samples.

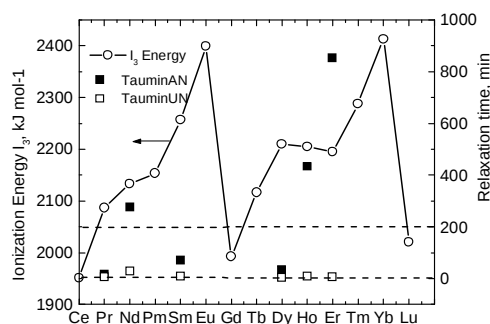


Fig. 5b. The dependence of the relaxation time τ vs. 3-rd ionization energy I_3 of the rare-earth ions.

The results of the present work together with the slip-motion model of Shimakawa et al [10,11] may be used to estimate the behavior of RE and tin impurity in the photodarkening process. It is seen from the experiment that the effect of impurity is manifested mainly through retardation of the photodarkening process due to impurity. Thermal annealing is also known as an important factor to act upon the structure of an amorphous solid and to transfer the energy necessary for reconstruction and removal of constraints. The time constant of the process in undoped films is several times increased after doping and annealing. This fact clearly indicates the strong retardation of the slip motion of the structure layers due to presence of impurity.

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 presence of metal impurities strongly enhances the annealing effect in comparison with the undoped film. The rate of the process is obviously correlated with the chemical activity of the dopant. The difference in the photodarkening time constant for the untreated and annealed films grows with increasing impurity content. In the context of the model [10,11] this fact clearly indicates the strong retardation of the slip motion of the layers due to presence of the impurity. 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.

4. Summary

As₂Se₃ thin films and doped with rare-earth (Nd³⁺, Sm³⁺, Ho³⁺, Dy³⁺, Er³⁺ and Pr³⁺) ions were prepared and investigated. For structural characterization of the prepared chalcogenide glasses

the X-ray diffraction, and MDSC technique were used. The comparative study of the effect of metal impurity on the photodarkening kinetics is obscured by strong influence of the film thickness on the amplitude of photodarkening. This influence results from the exponential dependence of the absorbed light energy on film thickness and leads to significant scatter of photodarkening amplitude due to slight thickness difference. The dependence of the effect on the deposition angle in the studied angle interval is insignificant and is reduced to the film thickness dependence as well.

It was shown that tin and rare-earth impurities strongly affect the network of the host glass inducing changes in both short-range as well as medium-range order. In particular they exert significant influence on the atom-scale structural configurations (quasi layers) and the character of their relative motion. The main feature of the photodarkening effect in the samples under study is that the metal impurities and heat treatment suppress the photodarkening. The relaxation of photodarkening kinetics for all compositions is described by a stretched exponential function. 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 $0 < \alpha < 1.0$. In our case it is the dispersive character of hole transport that may cause the dispersive character of the relaxation after photogeneration kinetics. The fact that α increases with the addition of metal impurities indicates that the dispersion of the transport increase. In the frame of the "slip-motion" model this dispersion may be naturally attributed to the multiple trapping of photoinduced holes [19,20]. The strong effect of metal additives on the photodarkening kinetics, especially on its response to thermal treatment is in agreement with the "slip-motion" model. Doping of amorphous chalcogenide films by metals assist in stabilising the glassy matrix with respect to light exposure and thermal treatment.

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