

Photoinduced phenomena in chalcogenide glasses doped with metals

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ABSTRACT

In the present paper we have focus our study on relaxation of photodarkening in α -As₂Se₃ doped with Sn and rare-earth (RE) ions (Dy³⁺, Pr³⁺, Ho³⁺, Sm³⁺, Nd³⁺, Er³⁺). The relaxation process of photodarkening is described by a stretched exponential function with the dispersion parameter $0 < \alpha < 1.0$, and the time constant increasing with doping and heat treatment. On the basis of the structure-property correlation, the role of metal impurity in reformation of molecular cluster structure was studied with particular attention to retardation of relative "slip motion" of clusters by the impurity. The case of Sn in As₂Se₃ glass was probed by a local probe like ¹¹⁹Sn Mössbauer spectroscopy, and in conjunction with Temperature Differential Scanning Calorimetry (TMDSC) some aspects of the molecular glass structure were elucidate. Recommendation concerning the stabilization of the glass structure by metal impurity against photostructural transformation have been suggested, and which are very important for chalcogenide glasses doped with rare-earth ions as perspective materials for fibre optics amplifiers operating at the 1.3 μ m and 1.5 μ m telecommunication windows.

I. INTRODUCTION

The effect of light-induced photodarkening is characteristic of amorphous chalcogenides films and presents scientific as well as practical interests¹. The latter is mainly due to considerable changes in the optical absorption of the amorphous material associated with these photostructural transformations. The arsenic selenide amorphous films usually become darkened under action of light from the region of fundamental optical absorption ($h\nu \geq E_g$) and so-called photodarkening effect takes place. As the composition of a chalcogenide glass determines both the structural units and the mean coordination number of the amorphous solids², the effect of the composition in glassy systems As-Se and As-S on the degree of photostructural transformations has been studied in detail^{3,4}. At the same time, little attention has been devoted to the influence on photodarkening of foreign impurity atoms introduced in the glass. In the present paper the transmission spectra and the kinetics of photodarkening in amorphous As₂Se₃:Sn_x thin films ($0 \leq x \leq 5.0$ at %) and As₂Se₃ doped with rare-earth ions rare-earth (RE) ions (Nd³⁺, Sm³⁺, Dy³⁺, Ho³⁺, Er³⁺, and Pr³⁺) are presented. It was demonstrated that doping of As₂Se₃ with Sn and RE increase the optical absorption. The relaxation of optical transmission in the studied amorphous films is described by the stretched exponential function, and is explained in frame of the "slip-motion" model, which take into account the electronic effects and the molecular structure of the amorphous material. From X-ray diffraction measurements, it was find that, the interlayer spacing changes when the metal atoms are introduced in the glassy matrix, which reflects a loss of interlayer interactions. Losses of planarity of the layers naturally suppress the "slip motion" of the layers and which is reflected by quenching of photodarkening in metal-doped amorphous materials. The photodarkening relaxation are discussed in conjunction with the results of the structure investigations (X-ray diffraction, Mössbauer spectroscopy and Temperature Modulated Differential Scanning Calorimetry (MDSC)).

II. SAMPLE PREPARATION AND EXPERIMENTAL DETAILS

For Mössbauer spectroscopy experiments the starting materials for synthesizing the bulk glasses consisted of 99.999% As₂Se₃ from Cerac Inc., and isotopically enriched ¹¹⁹Sn in its elemental form. The enriched ¹¹⁹Sn was obtained

by hydrogen reduction of isotopically enriched (96%) SnO₂ purchased commercially. The reduced metal was purified by repeated melting to realize a shiny metallic bead that could be sliced with a sharp blade. The starting materials were sealed in evacuated (5·10⁻⁷ Torr) quartz ampoules in the desired ratio. The RE oxides which were adding in As₂Se₃ were supplied by ALFA Aesar. The materials were reacted at 930 °C for 48 hours in a rocking furnace. Melts were equilibrated at 50 °C above the liquidus for an hour, and then water quenched. Bulk glass samples containing 0.5÷7.0 atomic % of Sn in As₂Se₃ were synthesized. The structure of the glassy As₂Se₃ samples doped with various amounts of tin was investigated by X-ray diffraction procedure, Mössbauer spectroscopy, and TMDSC technique. Thin film samples of thickness $L=0.3\text{--}6.3\ \mu\text{m}$ were prepared by flash thermal evaporation in vacuum onto glass substrates held at $T_{\text{subs}}=100\ \text{°C}$.

The Raman spectra of two As₂Se₃ thin films obtained by “flash” thermal deposition are compared to that of a bulk glass by Raman measurements. The experimental Raman spectra of thin films show that they are very close to that of bulk As₂Se₃.

To initiate photostructural transformations in thin film samples a He-Ne laser ($\lambda=0.63\ \mu\text{m}$, $W=10\ \text{mW}$) was used as a source of light exposure. The splitter was used to divide 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 of a part of the films in vacuum at $T_{\text{ann}}=100, 120, \text{ and } 150\ \text{°C}$ during one hour.

III. RESULTS AND DISCUSSION

3.1. X-ray diffraction patterns

It was established from the X-ray diffraction investigation that the position and intensity of the first sharp diffraction peak (FSDP) is changed as a result of doping of the As₂Se₃ glass by tin. The inter-configurationally inner distance calculated from the position of FSDP is 4.32 Å for pure As₂Se₃ glass and increases up to 4.547 Å for As₂Se₃+3.5 at.% Sn⁵. 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. The 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 As₂Se₃ layers allowing for a better packing at a smaller thickness. 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 cluster layers.

3.2. Mössbauer spectroscopy and Temperature Modulated Differential Scanning Calorimetry (TMDSC)

¹¹⁹Sn Mössbauer spectra of the glasses were taken⁶ in transmission geometry with a standard constant acceleration drive using an emitter of ^{119m}Sn in CaSnO₃. The 23.8 keV gamma-rays were detected with a thin NaI phosphor mounted on a photomultiplier tube. Spectra were accumulated at 78K using an exchange gas liquid helium Dewar. Our results reveal a single line at low ($0 < x < 3\%$) Sn alloying concentrations. At higher Sn concentrations ($3\% < x < 7\%$) one observes, in addition, a doublet feature in the line shapes. The observed doublet is assigned to quasi-octahedral SnSe.

Sn, Pr and Dy doped As₂Se₃ glass samples were also examined by MDSC technique. Samples were examined using a model 2920 MDSC unit from TA Instruments after a waiting time of 6 weeks. This permitted samples to relax. The typical operating conditions⁷ included a scan rate of 3 °C/min, 1 °C/100s modulation, and a sample size of 15 mgms encapsulated in hermetically sealed Al pans.

Glass transition temperatures T_g were obtained from the inflection point of the reversing heat flow. The maximum in T_g for As₂Se₃:Sn_x glasses (Fig.1) suggests that above the threshold additives no longer form part of the base structure, i.e., they nanoscale phase separate^{6,8}. The maximum in T_g suggests^{6,8} that above the threshold additives no longer form part of the base glass structure, i.e., they nanoscale phase separate (nsps). Such nsps effects already set in near As₂Se₃ base

glass ($x = 0$) as discussed elsewhere⁹. These effects are apparently delayed to higher x ($>5\%$) when Sn is doped in As_2Se_3 base glass. Mössbauer spectroscopy results show the presence of only the single line feature in the spectra at low x (<3 at. %). The isomer-shift of this line has been previously assigned^{6,10} to Sn that is tetrahedrally coordinated to 4 Se near-neighbors as in a $Sn(Se_{1/2})_4$ local structure. Apparently, introduction of Sn additive in As_2Se_3 base glass promotes growth of $Sn(Se_{1/2})_4$ units and leads the base glass to become As-rich. The latter can occur in one of two ways; either forming polymeric ethylenelike $As_2(Se_{1/2})_4$ units and/or monomeric As_4Se_4 cages based on the Realgar structure. It appears that in the base glass, the polymeric species are first nucleated slightly below $x < 0.4$, and monomeric ones thereafter ($x > 0.42$). The presence of the later, fragments the backbone progressively as $x > 0.42$, leading to reduction in T_g s.

T_g of the rare-earth doped glasses decrease as a function of doping concentration as shown in Fig. 1a and 1b. Addition of the rare-earth atoms deprives Se from the backbone and drives it As-rich and one expects T_g to decrease. The magnitude of the reduction 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) atoms are much bigger than As ($r_{cov}=1.20$ Å) and it is possible the additives segregate from the base network to form a separate nanophases.

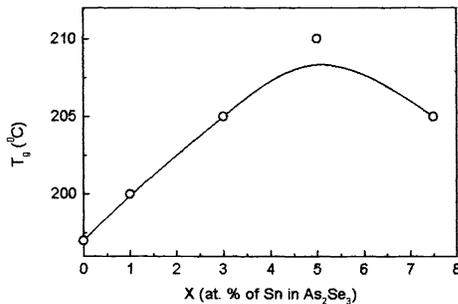


Fig.1a. Variation of T_g vs. Sn concentration in a glassy system $As_2Se_3:Sn_x$.

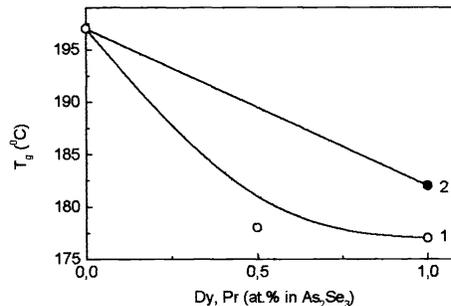


Fig.1b. T_g as a function of doping concentration in $(As_2Se_3)_{1-x}:RE_x$ glasses for RE=Pr (1) and RE=Dy (2).

3.4. Relaxation of photodarkening

The transmission spectra around the fundamental absorption edge measured for all thin film compositions before and after exposure were characteristic for amorphous chalcogenide films. A red shift of the absorption edge as well as the corresponding decrease of the transmission was clearly observed in agreement with the data published in literature. The photoinduced shift of the absorption edge after exposure decrease the transmission at a fixed wavelength by a factor of 15 to 30 %. The films doped with tin show about the same shift of the spectra though the starting transmission of these films is lower than that of undoped films.

Relaxation of the relative optical transmission $T(t)/T(0)$ of the amorphous $As_2Se_3:Sn_x$ and $As_2Se_3:RE$ thin films in dependence of the exposure time t for untreated films is shown in Fig.2a and 2b, respectively. At a constant light intensity, the presented dependences characterize the decay of the film optical transmittance with the increase of the dose of absorbed photons. From Fig.2a it is shown that even 0.5 at.% of tin impurity significantly reduces the photodarkening effect in as-deposited amorphous As_2Se_3 films.

The decrease of photodarkening is characteristic for amorphous As_2Se_3 films doped with tin amount up to 2.0 at.% Sn. For higher concentrations of tin the effect of reducing of photodarkening by impurity decreases. In annealed undoped and slightly doped (up to about 2 at. % Sn) amorphous As_2Se_3 films the photodarkening is rather weak while at higher impurity concentrations (4 and 5 at.% Sn) it becomes comparative to that in undoped unannealed films. It appears that for the glass composition up to 2.0 at.% Sn inclusive the heat treatment plays a stabilizing role against the photostructural transformations and only slightly affects the glass compositions with tin concentrations more than 2.0 at.%.

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. 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.2b) and annealed amorphous As_2Se_3 doped films.

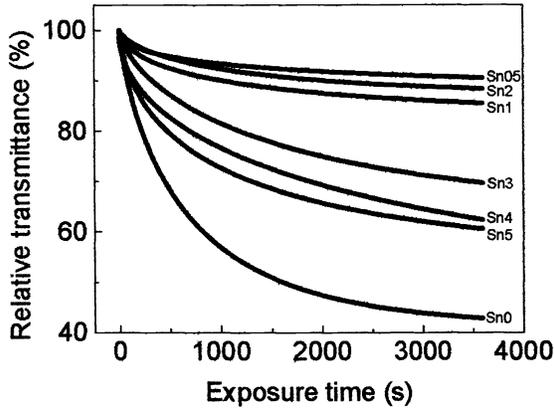


Fig.2a. Photodarkening kinetics of as-deposited $As_2Se_3:Sn_x$ films with exposure time. The figures against the curves denote the amount of Sn impurity introduced into the source material, in at.%.

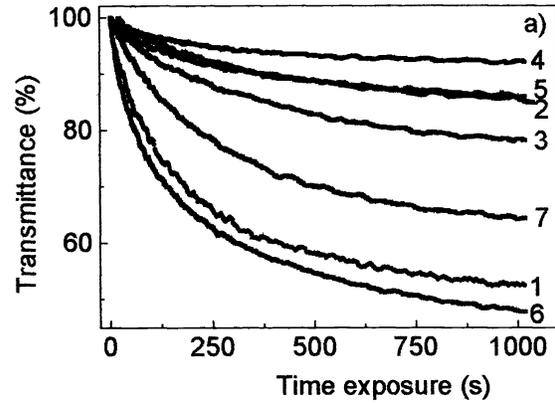


Fig.2b. Photodarkening kinetics of as-deposited (a) and annealed at $T_{ann}=120\text{ }^{\circ}\text{C}$ (b) $As_2S_3:Me$ samples: As_2Se_3 (1); $As_2S_3+0.5\text{ at.}\% \text{ Er}$ (2); $As_2S_3+0.5\text{ at.}\% \text{ Ho}$ (3); $As_2S_3+0.5\text{ at.}\% \text{ Nd}$ (4); $As_2S_3+0.5\text{ at.}\% \text{ Sm}$ (5); $As_2S_3+0.5\text{ at.}\% \text{ Dy}$ (6); $As_2S_3+0.5\text{ at.}\% \text{ Pr}$ (7).

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. Five parameters have been varied, A_0 and t_0 as the initial coordinates of the fitting curve, τ as the relaxation time constant, A as the photodarkening amplitude and α as the dispersion parameter ($0<\alpha<1$).

1. DISCUSSION OF THE RESULTS

3.1. Photodarkening relaxation

The photodarkening phenomenon 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 indicating the narrowing of the optical gap of the film at photodarkening, 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. Several models have been put forward to substantiate this broadening considering a particular individual atom as an initial object of photoexcitation^{3,4}. Recently, a novel model for photodarkening in $a-As_2Se(S)_3$ has been proposed^{1,11}, in which photoexcited charge carriers in extended states are considered as responsible for photodarkening. Unlike to the previous conceptions the new model takes into account the layered cluster structure of a chalcogenide glass. 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 (Fig.3a). This latter process alters interaction of lone-pair electrons between the layers leading to photodarkening effect. Earlier in his structural model proposed for explanation of photodarkening phenomena M.Popescu¹² has pointed out that distortion in the second and third coordination spheres should be taken into account as important factors.

The model of Shimakawa et al.^{1,11} 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 tin. The disappearance of photodarkening effect when a certain amount of the I-st group metal is added to $a-As_2Se_3$ may be referred to as an example¹³. The foreign metal atoms provide bridging between the layers and hence reduce the slip motion, thus hindering the photodarkening. We suggest that this consideration is applicable in the case of tin impurity in $a-As_2Se_3$, which represent a layered structure (Fig.3b), and sometimes-different molecular clusters¹⁴.

As was mentioned above to obtain a unified basis for comparison of the transmission relaxation $T(t)$ curves we used so called stretched exponential presentation (Eqn. (1) for the relaxation curves. As a background for Eqn. (1) two groups of mechanisms are usually considered¹⁵. 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 $4 \cdot 10^{-3}$). The parameters of the stretched exponent $A_0 A$, τ and α have been determined for all compositions of the untreated and annealed films.

The difference of the influence of tin impurity and that of annealing on photodarkening in As_2Se_3 films is illustrated in Fig.4a, which presents the relative transmittance decrement A in dependence on the impurity content in the films. The parameter $A=1-A_0$ characterizes the "steady-state" optical losses due to photodarkening. It is seen from the Fig.5a that the effect of Sn doping on the amplitude of photodarkening is strong at low doping levels up to 2 at. % Sn; with further growing of Sn content the effect becomes smaller and at about 4-5 at. % Sn it tends to the value characteristic for undoped films. The effect of annealing is much stronger for the undoped sample than for that doped with Sn. The time constant τ of the photodarkening process increases both in doped and thermally treated films comparative to that of the as-deposited film Fig.4b. This fact indicates that in these films the photodarkening process proceeds much slower than in untreated and undoped films.

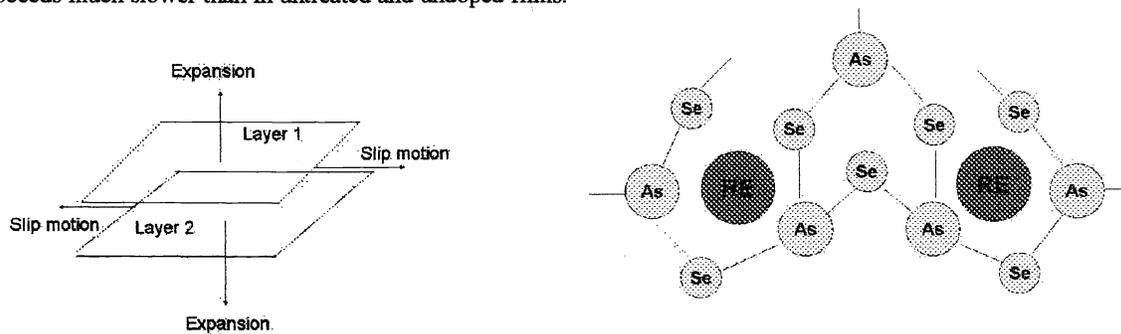


Fig.3a. Schematic illustration of the layers in a- As_2Se_3 . The arrows indicate the "slip motion" and the "expansion", respectively. Fig.3b. The structure model for α - As_2Se_3 doped with rare-earth ions.

The time constant is of the same order of magnitude in all these samples and has no any definite relation with the impurity concentration. This type of behavior is different from that observed in amorphous $AsSe:Sn$ films¹⁶, in which the time constant rapidly increased with the Sn content in the case of the annealed films. For all the examined the dispersion parameter α remains much less than unity films indicating the large degree of dispersion.

In the absence of tin the arsenic chalcogenide glass is formed of corrugated and disordered layer domains with some correlation between them. This correlation leads to a rather compact packing with low inter-configurational distance. When Sn is added then, due to the tetrahedral disposal of the sp^3 bonds with the chalcogen the dopant atom inserted in the network increases the thickness of the layered configuration as revealed by the significant shift of the FSDP towards lower angles. This insertion corresponds in fact to the introduction in the network of the structural units of the type $SnSe_2$. The effect is greater for higher dopant content but only up to a certain concentration, because further the separation of the reciprocally ordered configurations is interrupted by more and more interconnection between layers and a transition to three-dimensionally (3D) connected network follows. The transition is preceded by the appearance of structural units of the type $SnSe$. Then, the direct consequence of this transition will be reflected in the intensity of the FSDP which gradually disappears. For the glasses $As_2Se_3:Sn$ the transition towards 3D network seems to start very early (at ~ 2 at. % Sn) compared to the glasses $As_2S_3:Ge$, where the transition starts for more than 25 at. % Ge. The interruption of the two-dimensional structure and transition is probably due to a more ionic character of the Sn-Se bonds compared to Ge-Se bonds. The ionic component gives a higher structural mobility in the network and therefore a higher instability of the glass. Thus, we can expect that the tin impurity 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 structural layers and the character of their relative motion.

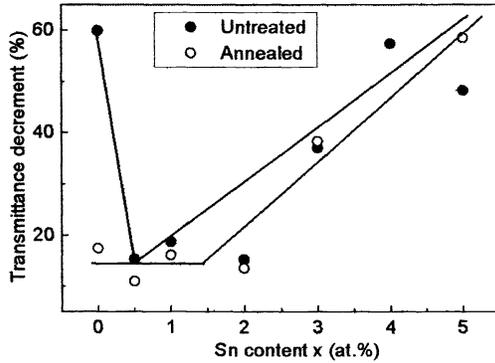


Fig. 4a. The dependence of the transmittance decrement on the tin contents in amorphous $As_2Se_3:Sn_x$ films

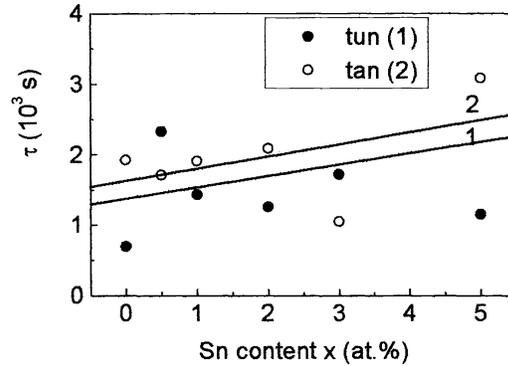


Fig. 4b. The dependence of the Constant time α on the tin contents in amorphous $As_2Se_3:Sn_x$ films

The central message from the Mössbauer spectroscopy result is that the group IV additive removes Se from the base glass to form tetrahedrally coordinated $Sn(Se_{1/2})_4$ local unit in the base glass. In the previous work⁷ on As_xSe_{1-x} binary glasses we suggest that the As-rich units nanoscale phase separate from the backbone of the glasses. The suggestion is based on the experimental fact that T_g of the glasses show a threshold behavior near $x=0.40$. By systematically adding more Sn in the stoichiometric glass, one could address the issue of how do the $Sn(Se_{1/2})_4$ local units connect in the base glass. This could be done by establishing the compositional dependence of the glass transition in glasses of the type- $[As_2Se_3]_{1-y}Sn_y$.

The results of the present work together with the slip-motion model of Shimakawa et al.^{1,11} may be used to estimate the behavior of 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 presence. Thermal treating 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. Because the tin tends to create directional bonds when are introduced in the host glass and especially during the annealing process some bridging bonds should appear between the layers. The structure of the glasses that contains tin impurity requires therefore some excess slip forces, i.e. leads to greater exposition doses and time constants. Furthermore, creation of clusters such as of $SnSe_2$ type may lower the density of the typical for AsSe lone-pair defects (i.e. D-centers) thus lowering the charge state of the layers and, finally, the photodarkening.

This effect is particularly important at high Sn contents in our case up to $x=2.0$ at.% Sn, when impurity approaches the dissolution limit and actually changes the number of structural units in the glass. In the untreated films, as it was pointed out earlier¹⁷, the changes in the structure after introducing Sn impurity occur first of all in the layers, that is why the slip mobility is retained, while the enlargement of the interlayer distance promotes the slip motion slightly decreasing the time constant of the process. The observed difference in the behavior of AsSe:Sn films and $As_2Se_3:Sn$ films may be attributed to non-stoichiometric character of AsSe in the structure of which there are numerous homopolar bonds.

The fact that the photodarkening kinetics may be described by a stretched exponential we may consider as indication of dispersion in kinetic mechanism, i.e. the time dependence of the process rate¹⁵. The data allow concluding that formation of 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 in the stage when the layer clusters are charged due to capture of charge carriers. Charge transport in chalcogenide glasses is known as highly dispersive due to wide distribution of capture times in multiple-trapping process¹⁸. For glasses like a- As_2Se_3 the

dispersive parameter α 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 α is increasing with addition of metal impurities indicates that the dispersion of the transport is decreased. This is in general accordance with both the stabilization of the structure and expected alteration of defect centers density.

It follows from the data for untreated films that introduction of RE impurities in a-As₂Se₃ 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. 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.5).

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. 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 As₂Se₃ (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 As₂Se₃ (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 results of the present work together with the slip-motion model of Shimakawa et al.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 presence. Thermal treating 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.

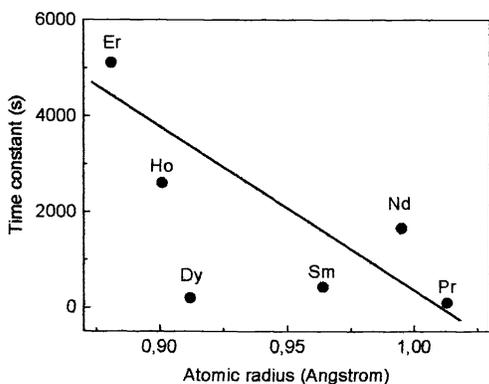


Fig.5a. The dependence of the time constant vs. atomic radius of the metal dopant.

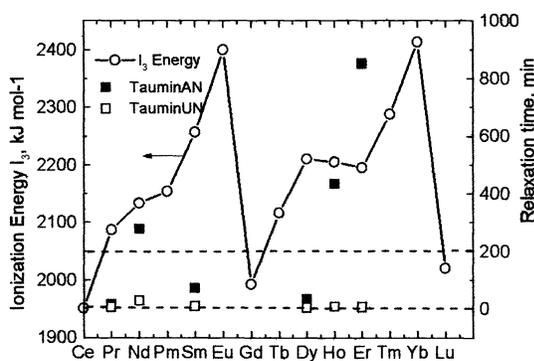


Fig.5b. The dependence of the relaxation time vs. 3-rd ionization energy of the rare-earth ions.

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 model¹¹ 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.

IV. SUMMARY

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 structural 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 suppressed the photodarkening. The relaxation of photodarkening kinetics for all compositions is described by 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. In frame of the "slip-motion" model, this dispersion may be naturally attributed to the multiple trapping of photoinduced holes¹¹. 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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