MOLECULAR STRUCTURE AND QUENCHING OF PHOTODARKENING IN As$_2$Se$_3$:Sn$_x$ AMORPHOUS FILMS

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Photodarkening relaxation under light exposure of a-As$_2$Se$_3$ amorphous films and doped with 0.5-5.0 at.% Sn were studied for their dependence on the concentration of impurities and thermal treatment. It was shown that both factors reduce photodarkening with the degree of reduction dependent on the concentration of impurity and temperature of heat treatment. The relaxation process of photodarkening is described by a stretched exponential with the dispersion parameter $0<\alpha<1.0$, and time constant increasing with tin concentration or thermal annealing. The case of Sn in As$_2$Se$_3$ glass was probed by a local probe like [119]Sn Mössbauer spectroscopy, and in conjunction with Temperature Modulated Differential Scanning Calorimetry (MDSC) some aspects of the molecular glass structure were elucidated. On the basis of the structure results and photodarkening ones the molecular origin of light-induced effects in Sn-doped As$_2$Se$_3$ was revealed.

1. Introduction

The effect of light-induced photodarkening is characteristic of amorphous chalcogenides films and presents scientific as well as practical interests [1]. 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 ($h\gamma \geq E_g$) 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 solids [2], 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, although it was noted that the photodarkening is influenced by doping of amorphous chalcogenide films with Cu impurities [5]. Furthermore, recently we have demonstrated that Sn and Mn, and rare earth foreign impurity atoms (Dy, Pr, Sm) influenced the photodarkening relaxation in as-deposited and annealed amorphous AsSe and As$_2$Se$_3$ thin films [6,7].

In the present paper we report the results of the study of the photodarkening relaxation in pure and separately doped with various amount of Sn (0.5 to 5.0 at.% Sn) amorphous As$_2$Se$_3$ thin films. Tin, which is prone to formation of tetrahedrally coordinated sites, affect the network of the host glass inducing changes in both short-range as well as medium range order. From the X-ray diffraction data, tin in arsenic chalcogenide glasses appears as a network former, which increases the effective thickness of the structural layers and the inter-layer distance [8]. The tin as a dopant also serve as a model probe atom to permit Mössbauer spectroscopy local structural characterization of the impurity in a chalcogenide glass [9,10].

The tin impurity significantly affect the edge absorption making the slope of its exponential part to decrease, widens the photoconductivity spectral interval and retards the recombination of photogenerated holes [11,12]. Furthermore, this particular fact that the metal impurities induced

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changes in photodarkening kinetics, presents special interest as regards the recent photodarkening model [1,13]. This model takes into account the layered cluster structure of a chalcogenide glass as well as the photoexcited charge carriers in extended states, which are responsible for photodarkening. As a result it was suggested that the foreign metal impurities in chalcogenide glasses induce changes in the intermediate ordering, which restrict mutual slip motion of the structure clusters.

2. Experimental results

2.1. Sample preparation & experimental details

For Mössbauer spectroscopy experiments the starting materials for synthesizing the bulk glasses consisted of 99.999% As_2Se_3 from Cerac Inc., and isotopically enriched [119]Sn in its elemental form. The enriched [119]Sn was obtained by hydrogen reduction of isotopically enriched (96%) SnO_2 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 ($5 \cdot 10^{-7}$ Torr) quartz ampules in the desired ratio. The materials were reacted at 930 ºC for 48 hours in a rocking furnace. Melts were equilibrated at 50 ºC above the liquidus for an hour, and then water quenched. Bulk glass samples containing 0.5÷7.0 atomic % of Sn in As_2Se_3 were synthesized. The structure of the glassy As_2Se_3 samples doped with various amounts of tin was investigated by X-ray diffraction procedure, Mössbauer spectroscopy, and MDSC technique.

Thin film samples of thickness L=0.3÷6.3 μm were prepared by flash thermal evaporation in vacuum onto glass substrates held at T_{subs}=100 ºC . To initiate photostructural transformations in thin film samples a He-Ne laser (λ=0.63 μm, W=4 and 10 mW) was used as a source of light exposure. The splitter was used for 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: $T(t)/T(0) = A_0+Aexp[-(t-t_0)/\tau]^{(1-\alpha)}$, 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_{ann}=100, 120, and 150 ºC during one hour. After the annealing the optical transmission relaxation under light exposure was registered in the same manner.

From the X-ray diffraction investigations it was established that the position and intensity of the first sharp diffraction peak (FSDP) is changed as a result doping of the As_2Se_3 glass by tin. The inter-configurational inner distance calculated from the position of FSDP is 4.32 Å for the pure As_2Se_3 glass and increase up to 4.547 Å for As_2Se_3+3.5 at.% Sn, and thus representing an increase of about 5 % as compared to the pure glass [8].

Using the Möessbauer spectroscopy of a glass sample of As_2Se_3:([119]Sn) containing 1 wt % of [119]Sn, we have examined the local chemical environment of the Sn dopant in the As_2Se_3 base glass. [119]Sn spectra of the glasses were taken [14] in transmission geometry with a standard constant acceleration drive using an emitter of [119m]Sn in $CaSnO_3$. 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 samples also were examined MDSC technique. The typical operating conditions [15] included a scan rate of 3 ºC/min, 1 ºC/100s modulation, and a sample size of 15 mgms encapsulated in hermetically sealed Al pans. Glass transition temperatures were obtained from the inflexion point of the reversing heat flow. The non-reversing relaxation enthalpy was deduced from the non-reversing heat flow. The sum of these two heat flow terms represents the total heat flow. Conventional DSC measurements [15] would permit only the total heat flow term to be measured.

Fig.1 shows variations in $T_g(x)$ (top panel), the glass transition width $W(x)$ (middle panel), and the non-reversing heat $\Delta H_{nr}(x)$ (bottom panel) for Sn-doped As_2Se_3 glasses. In the top panel of Fig.1 we also compare variations in T_g of the Sn-doped As_2Se_3 glasses to those of As-doped ones. That comparison is rather revealing. One finds at low additive concentrations of either As or Sn, T_g of the base glass to increase with x, suggesting that that the base glass becomes more connected. However, as x approaches 2% of As or 5% of Sn, T_gs show a threshold behavior.
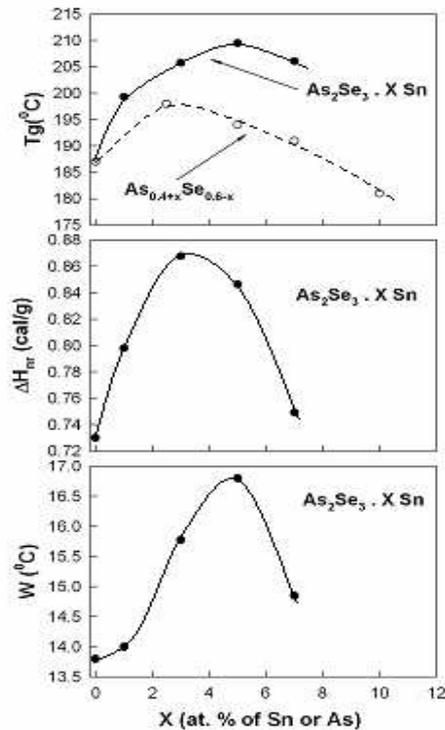
Fig. 1. Variations in $T_g(x)$ ($\bullet$) (top), $\Delta H_{nr}(x)$ (middle) and width $W(x)$ of $As_2Se_3Sn_x$ glasses terms as a function of x. $T_g(x)$ of As_xSe_{1-x} base glasses appears as ($\circ$). The smooth lines are just a guide to the eye.

The maximum in T_g suggests [14,16] 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 As_2Se_3 base glass (x = 0) as discussed elsewhere [17]. 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 [14,18] 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_gs (Fig.1)

The results of Fig.1 also reveal that at higher additive concentrations(x>3%) of Sn, the additive no longer goes in the base glass. The reduction of T_g s at x>5% of Sn, and the concomitant appearance of non-tetrahedral Sn site is suggestive of the following picture. The isomer shift and quadupole splitting of site B compare well with those of crystalline SnSe [14]. The crystallographic phase is isomorphic to GeSe, and consists of a layered structure in which cations possess a distorted rocksalt configuration with 3 short and 3 long Sn-Se bonds. Thus, it appears that an SnSe-like nanophase nucleates in the glasses at x>5% Sn, and lowers the global connectivity of the backbone that is reflected in the reduction of T_g, $W(x)$ and ΔH_{nr}.(Fig.1). These physical quantities are

controlled by the majority phase, i.e., the backbone of the glasses. With increasing Sn concentration, nanocrystalline-SnSe phase appears in the glasses and rapidly leaches the tetrahedral Sn alloyed in the backbone. Incorporation of the oversized Sn in the As_2Se_3 layers stresses them and at some point the solubility limit (x~4%) is reached. Thereafter, the additive acquires a more compact quasi-octahedral local structure and nanoscale phase separates [17].

2.2. 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. All As_2Se_3:Sn_x films underwent typical photodarkening under illumination. 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 decreese 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 thin films in dependence of the exposure time t for untreated and annealed films is shown in Fig.2a and Fig.2b, respectively.
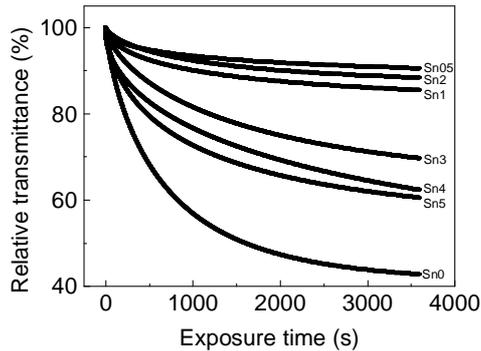
Fig. 2a. Photodarkening kinetics of as-deposited As_2Se_3:Sn_x films with exposure time. The figures against the curves denote the amount of Sn impurity introduced into the source material, in at.%.
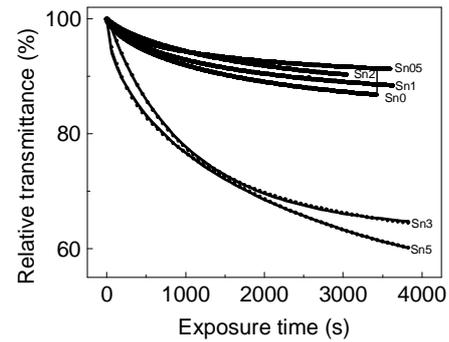
Fig. 2b. Photodarkening kinetics of annealed at T=100 °C As_2Se_3:Sn_x films with exposure time. The figures against the curves denote the amount of Sn impurity introduced into the source material, in at.%.

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 fotodarkening effect in as-deposed 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 phodarkening 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.%. To obtain a unified basis for comparison of the transmission relaxation $T(t)$ curves we used so called stretched exponential presentation for the relaxation curves in Fig.2a and Fig.2b in the form:

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

Here 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 $(0 < \alpha < 1)$.

For the obtained relaxation curves rather wide scatter 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. 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 [7].

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-pare 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 photoexcitiation [3,4]. Recently, a novel model for photodarkening in a-$As_2Se(S)_3$ has been proposed [1,13], 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. 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.Popescu [19] 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. [3,4] 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 phodarkening effect when a certain amount of the I-st group metal is added to a-As_2Se_3 may be referred to as an example [5]. 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.

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 in Fig.2a and Fig.2b. As a background for Eqn. (1) two groups of mechanisms are usually considered [20]. 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 (for $t_0=0$).

The difference of the influence of tin impurity and that of annealing on photodarkening in As_2Se_3 films is illustrated in Fig.3a, 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.3a 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. 3b. This fact indicates that in these films the photodarkening process proceeds much slower than in untreated and undoped films. 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 films [12], 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.
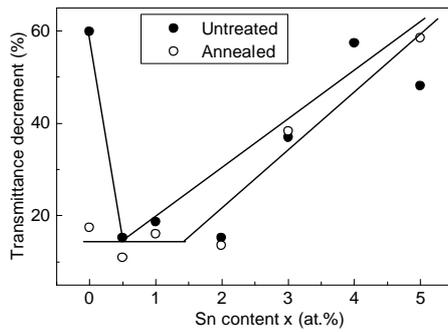
Fig. 3a. The dependence of the transmittance decrement on the tin contents in amorphous As_2Se_3:Sn_x films.
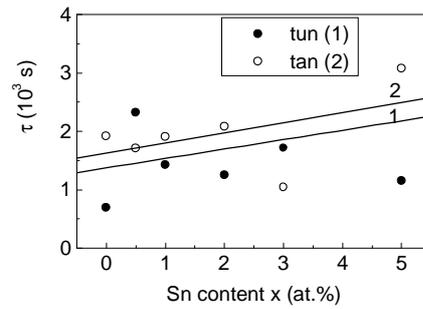
Fig. 3b. The dependence of the Constant time α on the tin contents in amorphous As_2Se_3:Sn_x Films.

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 work [15] 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 [1,13] 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 lover 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 earlier [7], 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 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 rate [22]. The data allow concluding that formation of photoinduced absorption is limited by a dispersive process with the exponent $\alpha \cong 0.5$. 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 process [21]. 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.

At it was shown above alloying 1.0 at.% of Sn in As_2Se_3 glass qualititatively quenches photodarkening. Clearly, alloying traces of Sn must alter not merely the local structure but the medium range structure of the alloyed network as well. We suggest that Sn inserts between the (12-membered (As_6Se_6) ring containing) layers characteristic of the orpiment structure (often used to model the base glass). The idea is supported generally by our Mössbauer and MDSC measurements. The metal dopant goes in tetrahedrally at low x, and increases the connectedness of the base glass as reflected in the 15 ºC rise of T_g. Here we must remember that Sn (1.8) has a lower Pauling electronegativity [22] than As (2.0), and for that reason will remove Se away from the later driving the base glass As-richer. For these reasons one would expect T_g to increase both on account of the fact that the coordination number of Sn (of 4) exceeds that of As (of 3) and also because the As-As bonds form in polymeric ethylene-like $As_2(Se_{1/2})_4$ units apparently form part of the backbone. A parallel behavior is observed in base As_xSe_{1-x} glasses in the $0.38<x<0.42$ range. Presence of $Sn(Se_{1/2})_4$ units in the backbone suppresses the formation of monomeric As_4Se_4 units in the glasses. The latter apparently contribute to reduction [17] of T_g of base As_xSe_{1-x} glasses at $x>0.44$ for example.

Alternatively, it is likely that Sn goes largely in the layers and buckles them, since Sn possesses a larger (1.40 Å) covalent radius than As (1.20 Å). The Sn-Se bond strength (47.4 kcal/mole) exceeds [22] that of As-Se one (41.7 kcal/mole). The enhanced intralayer interactions come at the expense of reduced interlayer ones. Furthermore, from x-ray diffraction measurements was found that the interlayer spacing increases by 6% (on an average) upon alloying Sn in As_2Se_3. The increased inter-layer spacing reflects a loss of inter-layer interactions. The buckling or loss of planarity of the layers would naturally suppress the slip motion of the layers that is thought to contribute to photodarkening as suggested by Shimakawa and collaborators [13].

The reduction in optical gap of As_2Se_3 glass upon alloying Sn, most likely, results from a broadening of the valence band. The top of the valence band in these glasses has contribution from Se lone-pair electrons [23]. The lone pair band broadens because of a pressure effect. The size mismatch produced by doping Sn in the layers produces stresses that are primarily localized on the bridging Se atoms, the most forgiving and flexible connections (coordination number of 2) in the backbone. This is akin to applying an external pressure. And as shown [24] by R.Zallen the band-gap of crystalline As_2Se_3, indeed, decreases upon applying an external pressure. The same physical mechanism occurs in the glass with chemical doping serving to clamp the Se local environments.

3. Summary

New experimental results based on optical absorption edge studies, Mössbauer spectroscopy and MDSC have been obtained. These findings provide new ideas to understand the molecular origin of photodarkening suppression in Sn-doped As_2Se_3 glass. It was shown that tin 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 increased inter-layer spacing reflects a loss of inter-layer interactions. The buckling or loss of planarity of the layers suppresses the slip motion of the layers. The main feature of the photodarkening effect in the samples under study is that the tin impurities and heat treatment suppressed the photodarkening. We expect these ideas to extend to other layered chalcogenide glasses.

Acknowledgement

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