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ON THE COMPOSITIONAL TREND OF
PHOTODARKENING $\text{Ge}_x\text{Se}_{1-x}$

Antonín VIDOUREK, Ladislav TICHÝ and Radim ŠVEJKA
Joint Laboratory of Solid State Chemistry
of Academy of Sciences of the Czech Republic and University of Pardubice

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Glassy $\text{Ge}_x\text{Se}_{1-x}$ samples were prepared from 5N purity elements. The expansion coefficient (α_p) and optical transmission of virgin and illuminated samples (halogen lamp at room temperature) have been studied. The extreme values of photodarkening are shifted into Se-rich region, somewhere close to $x = 0.2$. All the dependences (relative changes of Urbach edge slope, atomic volume (V_m) and expansion coefficient (α_p) in the temperature range from 40 to 80 °C versus atomic fraction of Ge) indicate an extreme around $x \approx 0.2$ in the region of the Philips threshold, where the mean coordination number of pseudoatom is: $\langle \text{CN} \rangle = 2.4$.

Introduction

Photoinduced phenomena in amorphous chalcogenides have been of interest for a long time, see e.g. Ref.¹. Among discussed properties of amorphous chalcogenides a compositional trend in absorption edge shift (photodarkening) in $\text{Ge}_x\text{Se}_{1-x}$ glasses has been discussed recently². The maximum of photodarkening was supposed to be close to GeSe_2 and the lattice dynamical aspects have been applied to the explanation of the reversible photodarkening

in amorphous chalcogenides². However, from more recent results³ it follows that for amorphous thin films of $\text{Ge}_x\text{Se}_{1-x}$ prepared by thermal evaporation the maximum of photodarkening is not close to GeSe_2 , but it is shifted to Se-rich region. For example, the photodarkening (in meV) $\Delta E_g(x) = E_g(x, \text{virgin}) - E_g(x, \text{illuminated})$, where $E_g(x)$ is the optical gap, has been found to be: $\Delta E_g(0.4) = 0$; $\Delta E_g(0.33) = 26.5$; $\Delta E_g(0.3) = 26$; $\Delta E_g(0.25) = 39$; $\Delta E_g(0.15) = 10$; $\Delta E_g(0) = 0$ for the thin films studied³. The discrepancy in compositional trends of photodarkening in bulk and thin film samples of $\text{Ge}_x\text{Se}_{1-x}$ could be due to some differences in the structure and physical properties of thin films and bulk glasses, but it could also reflect the well known uncertainty in estimation of the optical gap of bulk glasses.¹⁾

In this communication we report our preliminary experimental results concerning photodarkening in glassy $\text{Ge}_x\text{Se}_{1-x}$ samples monitored by measurements of the photoinduced changes of the Urbach edge slope.

Experimental

Glassy $\text{Ge}_x\text{Se}_{1-x}$ samples with $x = 0.1, 0.15, 0.2, 0.25, 0.3, 0.33, 0.4$ were prepared from 5N purity elements in the way described in Ref.⁵. The bulk samples were annealed to glass-transition temperature (T_g) in order to relax the material. From prepared bulk samples plan parallel samples of thickness varying from 0.1 to 0.3 mm were made for optical measurements (final polishing was always done with a suspension of Al_2O_3 powder in water free alcohol). The optical transmission of virgin and illuminated samples was measured using a Perkin Elmer Lambda 12 spectrophotometer. The sample was illuminated with a halogen lamp (at room temperature) equipped with an infrared-cut filter for time $t = 60$ min. The values of absorption coefficient (K) were calculated from the relation

$$K = \frac{1}{d} \ln \left[\frac{(1 - R)^2 + [(1 - R)^4 + 4R^2 T^2]^{1/2}}{2T} \right]$$

where d is the sample thickness, R and T are reflectivity and transmission, respectively. The values of Urbach edge slope (σ) were calculated from $\ln K$ vs. $h\omega$ dependence. At least 40 experimental points were taken into calculation. We also measured the thermal expansion of the glasses prepared. It is well

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We note that optical gap for thin films is usually calculated from the Tauc plot⁴. In the case of bulk glasses E_{03} or E_{04} are taken as a measure of the optical gap, i.e., energy corresponding to the value of absorption coefficient $K = 10^3$ or 10^4 cm^{-1} since we measure the Urbach edge region and hence: $K \sim \exp(h\omega/\sigma)$, where σ is the Urbach edge slope. Consequently, any change in σ affects the E_{03} or E_{04} value.

known that the expansion coefficient (α_p) is dependent on the thermal history of a glass. Hence, the samples for α_p measurements were firstly heated to the temperature $T = T_g - 20$ (heating rate: 5 K/min). At this temperature the samples were annealed for $t = 60$ min and afterwards they were cooled down to room temperature at a cooling rate of 5K/min. Samples "formed" in this way were used for the α_p measurements. The samples "forming" and α_p measurements were made using a very precise dilatometer TMA CX 03R (see e.g. Ref.⁶) at the heating rate 5 K/min and probe loading 100 mN.

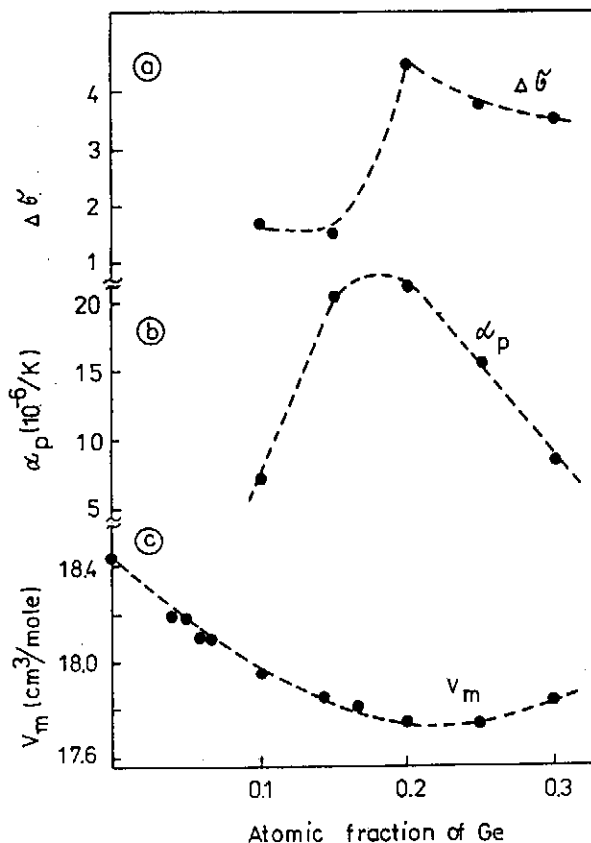


Fig. 1 a) Compositional trend in photoinduced relative change of the Urbach edge slope in Ge_xSe_{1-x} glasses. We note that for $x = 0.33$ and $x = 0.4$, not shown here, the photoinduced relative changes of Urbach edge slope are within experimental error.
 b) Compositional trend in expansion coefficient in the temperature region of 40 - 80 °C for Ge_xSe_{1-x} glasses.
 c) Compositional trend in the mean atomic volume (V_m) for Ge_xSe_{1-x} glasses. Except for the value for $x = 0$, all the other V_m values are taken from⁸. In all cases the dashed curves are a guide for eyes only

Results and Discussion

In Fig. 1a the relative change of the Urbach edge slope ($\Delta\sigma$) induced by illumination of studied samples is plotted versus atomic fraction of Ge. The quantity $\Delta\sigma$ is defined by the relation

$$\Delta\sigma = 100 \frac{\sigma_i - \sigma_v}{\sigma_v}$$

where σ_i and σ_v mean the Urbach edge slope of illuminated (i) and virgin (v) sample, respectively. For readers' convenience in Fig. 1b the plot of expansion coefficient versus atomic fraction of Ge is shown and finally in Fig. 1c a plot of the mean atomic valume (V_m) versus atomic fraction of Ge is displayed. All the dependences indicate an extreme around $x \sim 0.2$, i.e. in the region of the Phillips threshold (PT)⁷, where the mean coordination number of pseudoatom is: $\langle\text{CN}\rangle = 2.4$. Assuming that the change in $\Delta\sigma$ can be taken as a measure of photodarkening of our bulk glasses, the compositional trend of photodarkening is shifted into Se-rich region, close to PT, like in the case of amorphous thin films. This result can indicate that network rigidity plays some role in photodarkening.

According to Phillips⁷ in the covalent network a topological threshold appears when the system is mechanically stable, i.e. it appears at such chemical composition where the number of constraints per pseudoatom is equal to the number of available degrees of freedom ($N_d = 3$). We speculate that in the region of PT ($\langle\text{CN}\rangle = 2.4$, $x = 0.2$ in our case), if the material is excited, the excitation is conserved due to a mechanical stability of the network surrounding the excited place. In the region where $\langle\text{CN}\rangle < 2.4$, i.e. in our case for $x < 0.2$, the network starts to be underconstrained (soft) the material is perhaps more easily excited than in the former case. However, the excitation is probably not so much stable since the network is rather flexible and only by a decrease of the temperature of illumination the excitation could be conserved since the relaxation back to a ground state could be suppressed. In the region where $\langle\text{CN}\rangle > 2.4$, i.e. in our case for $x > 0.2$, the network starts to be overconstrained (rigid), it is not easy to realise an excited state and perhaps higher intensity of excitation light is necessary (or at least longer illumination time is needed) to reach an excited state. However, once the excited state is reached, it could be stable since the relaxation is suppressed in the rigid network surrounding an excited area.

We conclude that the compositional trends in photodarkening of the bulk Ge-Se glasses and thin Ge-Se amorphous films are roughly similar. The extreme values of photodarkening (a shift of the optical gap in the case of thin films and a relative change of the Urbach edge slope in the case of bulk glasses) are shifted into Se-rich region, somewhere close to $x = 0.2$. It is possible that the mechanical stability of the network can enhance the photodarkening since photoinduced perturbation of the structure could be relatively easily realized and,

simultaneously, such a perturbation could be rather well conserved due to mechanical stability of the network.

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