Role of rigidity and temperature in the kinetics of photodarkening in Ge\textsubscript{x}As\textsubscript{(45-x)}Se\textsubscript{55} thin films

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Abstract: We present insightful results on the kinetics of photodarkening (PD) in Ge\textsubscript{x}As\textsubscript{(45-x)}Se\textsubscript{55} glasses at the ambient and liquid helium temperatures when the network rigidity is increased by varying x from 0 to 16. We observe a many fold change in PD and its kinetics with decreasing network flexibility and temperature. Moreover, temporal evolution of PD shows a dramatic change with increasing x.

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References and links

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1. Introduction

Chalcogenide glasses show a remarkable change in their optical absorption, when irradiated with bandgap or sub bandgap light [1,2]. In most cases, light illumination results in photodarkening (PD), a substantial decrease in the optical bandgap and a concurrent change in refractive index [1]. PD is a well studied phenomenon over many years owing to its scientific and technological importance including potential for applications ranging from micro-lens fabrication to optical writing, photolithography, etc. [3–14]. A comprehensive understanding of PD is crucial for many of these applications.

It is believed that PD in chalcogenide glass thin films is mainly due to the presence of lone pair electrons at the valence band and the structural flexibility associated with the glassy network [1,15]. As a result, after the photo-excitation of electrons, lattice relaxation may occur at a defect site or somewhere else in the network structure leading to a decrease in the optical bandgap. The kinetics of PD have been explained using the photon assisted site switching model (PASS) [16,17], where a percolative growth of photon assisted site switched chalcogenide clusters of high energy states is predicted with the absorption of light. Consequently, structural flexibility of the network structure plays an important role in the kinetics of PD. Most previous studies on the kinetics of PD were conducted on good glass forming stochiometric compositions such as As$_2$S$_3$, As$_2$Se$_3$, for which the average coordination number is 2.4 [1,18,19]. The temperature of laser illumination is another important factor which may strongly influence the kinetics of PD [1]. Overall, the network rigidity and temperature make a noteworthy change in PD [15]. However, there are very few studies describing their influence on the kinetics of PD [1].

In this paper, we present new results on the kinetics of PD at the ambient and liquid helium temperatures, as the coordination number of Ge$_x$As$_{35-x}$Se$_{55}$ glassy system is increased from 2.45 to 2.61, by varying x from 0 to 16. Naturally, structural flexibility is expected to be higher for the glassy network which has a low average coordination number. In an attempt to explain the temporal evolution of PD, we measured the changes in absorption coefficient of the samples at a particular wavelength close to the optical bandgap.

2. Experimental details

The bulk samples of Ge$_x$As$_{35-x}$Se$_{55}$ glasses with x = 0, 5 and 16 are prepared by the melt quenching method starting with 99.99% pure As, Ge and Se powders. The cast samples are used as the source material for depositing thin films on a microscope glass slide substrate. We have prepared thin films of average thickness ~1.0 μm samples by thermal evaporation in a vacuum of about 1 × 10$^{-6}$ Torr. PD in these films is studied by a pump probe optical absorption method by using the experimental set up described previously [20]. In order to avoid any ambiguity in the kinetics related to the wavelength of the light, all the samples are irradiated with an above-bandgap light. We have chosen the wavelength of the pump beam as 532 nm (from a diode pumped solid state laser) for which the absorption coefficient of all the samples is much larger than 10$^6$ cm$^{-1}$.

The intensity of illumination was kept at 1 W/cm$^2$ for both the temperatures. The probe beam was a low intensity white light in the wavelength regime of 400-1200 nm and its transmission through the sample was measured using a Fourier Transform Infrared (FTIR) spectrometer (IFS66v/S). The pump beam was expanded considerably to encompass an area that was larger than the probe beam, so that a region of uniform light intensity was examined.
Fig. 1. Transmission spectra of Ge\textsubscript{x}As\textsubscript{45-x}Se\textsubscript{55} thin films with x = 0, 5 and 16, before and after illumination with 532 nm laser light at room and liquid He temperatures. The intensity of illumination was kept at 1W/cm\textsuperscript{2} for all samples at both the temperatures.

The two beams were directed such that they passed through the same spot on the sample. The spectra were collected with an interval of one minute from the time when the pump beam was switched on and continued until the PD was saturated. For low temperature measurement, we kept the sample inside an optical cryostat that was cooled down to the liquid helium temperature. The transmission spectra were recorded after stabilizing the temperature at 4.2K (~30 minute).

3. Results and discussion

At first, we recorded the transmission spectra of as prepared thin films of a-Ge\textsubscript{x}As\textsubscript{45-x}Se\textsubscript{55} at 4.2K. Thereafter, we turned on the pump beam and recorded the spectrum until it showed no further change i.e. until the saturation of PD. All samples showed PD with illumination (Fig. 1), as the transmission spectrum of the samples moved to longer wavelengths. The change in transmission appears to begin immediately, grows gradually, and saturates.

To get detailed information about PD, we have defined the optical bandgap as the energy of photons where the value of absorption coefficient was \(10^4\) cm\textsuperscript{-1}. The initial bandgap values of the unexposed, as-prepared films of Ge0 (x = 0), Ge5 (x = 5) and Ge16 (x = 16) are
presented in Table 1. With light illumination, bandgap values show red shift and the strongest effect with $\Delta E_g = 90\text{meV}$ is shown by the sample Ge0.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Coordination number</th>
<th>As-prepared (eV)</th>
<th>Illuminated (eV)</th>
<th>$\Delta E_g$ (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{As}<em>{45}\text{Se}</em>{55}$</td>
<td>2.45</td>
<td>2.03</td>
<td>2.17</td>
<td>1.97 2.08 60 90</td>
</tr>
<tr>
<td>$\text{Ge}<em>{16}\text{As}</em>{40}\text{Se}_{55}$</td>
<td>2.50</td>
<td>1.99</td>
<td>2.14</td>
<td>1.97 2.09 20 50</td>
</tr>
<tr>
<td>$\text{Ge}<em>{16}\text{As}</em>{29}\text{Se}_{55}$</td>
<td>2.61</td>
<td>1.97</td>
<td>2.18</td>
<td>1.96 2.11 10 70</td>
</tr>
</tbody>
</table>

To compare the effect of temperature on PD, we conducted the experiment at room temperature for the same set of samples and their respective change in bandgap is given in Table 1. It is clear that PD shows a many fold increase with the decrease in temperature. For example, the change in magnitude of PD in the Ge16 sample is seven times more than its value at room temperature. The dramatic change in PD at the two temperatures can be explained on the basis of the rate equation [17]. Before illumination, let us assume that there exist $N_T$ absorption sites in the film. During illumination, rate of growth of the number of photodarkened sites (N) can be written as

$$\frac{dN}{dt} = K_p(N_T - N) - K_rN,$$

where $K_p$ is the rate at which initial sites are converted into photodarkened sites and $K_r$ is the rate at which photodarkened sites are converted back to the initial sites. At 4.2K, we assume that $K_p$ has a finite value, since it is mostly determined by the number of photons absorbed. When we increase the temperature, absorption coefficient increases and results in a larger $K_p$. However, on the other hand, $K_r$ is negligible at 4.2K due to minimal reversibility. Equation (1) suggests that at low temperatures, the fraction of PD sites is higher due to the small values of $K_r$. As we keep on increasing the temperature, $K_r$ will also tend to increase and the PD will decrease. Hence, at room temperature the magnitude of PD will always be lower than at 4.2K.

Having demonstrated the large temperature dependence of PD, let us consider its dependence on network flexibility. The parent glassy system for the present study is $\text{Ge}_0\text{As}_{45}\text{Se}_{55}$, which has an average coordination number ($\langle r \rangle$) of 2.45. This number increases to 2.61 with the addition of 16% Ge (see Table 1). For Ge0 sample with $\langle r \rangle = 2.45$ the red shift in bandgap energy, a quantitative measure of PD, at room temperature is 60meV. By comparison, for samples with higher $\langle r \rangle$ values, PD decreases drastically e.g. by a factor of six when $\langle r \rangle$ increases from 2.45 to 2.61. We have observed similar trends in PD also at 4.2K, however, Ge 16 shows more PD than Ge5 (see Table 1). To explain the observed trend, we consider the Ge atom, which acts as a bridge between the layered structures of As and S atoms, thereby reducing the overall structural flexibility. As a result, it is difficult for lattice relaxation to occur at a defect site or somewhere else in the network structure leading to a decrease in the optical bandgap.

After understanding the large difference between the magnitudes of PD at the two very different temperatures and as a function of rigidity of the glassy network, it is of interest to discuss its kinetics. Figure 2 shows the temporal evolution of the change in absorption coefficient for the wavelength at which the transmission is 30% before any illumination by the pump beam. A careful analysis of Fig. 2 shows that upon room temperature illumination, a change in absorption appears almost instantaneously, grows gradually, and saturates within a few minutes. On the other hand, prolonged illumination of more than an hour is not sufficient to saturate PD at 4.2K. By assuming time-dispersive reactions, i.e. $K_p = At^{\beta-1}$ and $K_r = Bt^{\beta-1}$, the changes in absorption coefficient ($\Delta \alpha$) can be written as
\[ \Delta \alpha = \Delta \alpha_0 \left[ 1 - \exp \left\{ \left( \frac{t}{\tau} \right)^\beta \right\} \right], \] (2)

where \( t, \Delta \alpha, \beta \) and \( \tau \) are the illumination time, saturated change in absorption coefficient, dispersion parameter (0< \( \beta \) <1) and the effective time constant, respectively. The effective time constant \( \tau \) in Eq. (2) can be calculated using the following equation

\[ \tau = \left( \beta / A + B \right)^{1/\beta}, \] (3)

where \( A \) and \( B \) are the temperature and intensity dependent constants in \( K_p \) and \( K_r \) respectively. First we analyze the kinetics of PD shown by Ge0 samples. The experimental data at both the temperatures fit very well to the stretched exponential function described by Eq. (2) (Fig. 2). Further, we find that \( \tau \) shows a significant increase (from 450 to 3700 seconds) when illumination temperature is reduced to 4.2K. An analysis of the experimental data for the Ge5 and Ge16 samples also shows a decreasing trend of the effective time constant with increasing temperature. It should be noted that the PASS model takes into account “percolation-like” effective medium theory after getting the solution of Eq. (1) [i.e., Eq. (2)].

It is known that if the difference in \( \alpha \) for initial and after illumination is not very large, \( \Delta \alpha \) is almost proportional to \( \Delta N \). Then we may continue with Eq. (2) in our analysis [21]. The effective time constant values of Ge5 and Ge16 calculated using Eq. (2) are presented in Table 2. The large increase in \( \tau \) with decrease in temperature can be understood by analyzing Eq. (3). At 4.2K, \( A \) has a finite value and since the recovery rates are quite negligible at this temperature, we can assume \( B = 0 \). However, as the temperature increases, the cumulative increase in \( A \) and \( B \) values eventually results in lower values of \( \tau \). Similarly, using Eq. (2), we can find saturated number of transformed sites \( N_s \), which is equal to \( \Delta N_\tau / (A + B) \). Since the value of \( B = 0 \) at low temperature, \( N_s \) will be higher at 4.2K and is nearly equal to \( N_T \). However, as temperature increases, \( N_s \) will decrease due to the cumulative increase in \( A \) and \( B \) values. Further, if we consider the saturated change in absorption coefficient (\( \Delta \alpha_s \)), the low temperature values are much larger than their respective room temperature values and can be easily inferred from \( N_s \).

\( \Delta \alpha \) value of the parent glassy system Ge_{19}As_{55}Se_{35} at both temperatures is bigger than its corresponding values for the samples containing Ge (see Table 2). The large decrease in \( \Delta \alpha \) with Ge addition can be understood by considering the fact that Ge acts as a bridging atom in the layered structure and thereby increases the rigidity of the glassy network. As a result, \( N_T \) will decrease. However, it is difficult to estimate the changes in \( B \), but we can assume that the value of \( A \) decreases since the increase in rigidity will decrease the promotion reaction. The experimental observation of the kinetics of PD for all the three samples demonstrates that the rigidity plays an important role in determining the dynamics and can be effectively utilized to tailor PD by the suitable modification of composition.
Fig. 2. Variation of absorption coefficient with time for the wavelength, which has an initial transmittance of 0.3 before illumination. Hollow circles represent the experimental data and the red line indicating the theoretical fit using Eq. 2.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Δα (cm⁻¹)</th>
<th>τ (Seconds)</th>
<th>β</th>
</tr>
</thead>
<tbody>
<tr>
<td>As₄Se₅5</td>
<td>7000</td>
<td>2500</td>
<td>3700</td>
</tr>
<tr>
<td>Ge₅As₄Se₅5</td>
<td>3800</td>
<td>854</td>
<td>1600</td>
</tr>
<tr>
<td>Ge₁₀As₁₀Se₅₅</td>
<td>5000</td>
<td>560</td>
<td>1900</td>
</tr>
</tbody>
</table>

4. Conclusions

In conclusion, we have observed a dramatic influence of temperature and network rigidity on PD and its kinetics. The samples with low average coordination number show the strongest PD, however the kinetics are much slower. Similarly, PD effects are very much stronger and slower at low temperatures. The present results show that the PD can be easily controlled and tailored by manipulating the forward and recovery rate constants in the kinetics equations, which may find potential applications in designing photo sensitive/insensitive chalcogenide glasses. The temporal evolution of PD shows a large change in GeₓAs₄5ₓSe₅₅ samples, when x is increased from 0 to 16.

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