Dynamic variations of the light-induced effects in a-Ge$_x$Se$_{100-x}$ films: experiment and simulation

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Abstract: Light-induced effects in a-Ge$_x$Se$_{100-x}$ chalcogenide glasses, i.e., photobleaching (PB), photodarkening (PD), and photoinduced structural transformations, have been investigated as a function of composition across the glass-forming region by an optical two-laser-beam technique, Raman analysis, and first-principles simulations. It was found that there is a critical concentration of Ge $x$ $=$ 30% that corresponds to the crossover from transient PB to the mixture of transient PD and metastable PB. At the microscopic level, this corresponds to the change in the photoexcitation process. At low-Ge concentration ($<$20%), it is governed by the lone pair (LP) excitation, which diminishes with an increase in Ge content, yielding Ge-Se bond breakage at $x$ $=$ 30%. Further, an increase in Ge concentration ($x$ $>$ 30%) favors breakage of the Ge-Ge bonds upon photoexcitation and formation of light-induced 3D nanostructures. The bond conversion process is verified by Raman analysis.

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References and links


1. Introduction

Photoinduced effects (PIEs) in chalcogenide glasses (ChG) have a long history of continuing interest due to the potential they hold for new, unexplored applications. As noted in a number of review articles referenced in [1], the underlying fundamental understanding of photoinduced phenomena is just as exciting and challenging for both experimentalists and theorists as their potential applications. PIEs arise from physical, chemical, electronic, or vibrational changes in a glass structure upon optical or x-ray excitation [2–6]. The observed diversity of PIEs can be ascribed to the unique electronic and atomic structures and lack of periodicity in ChG [7–12], as well as to a unique feature of the availability of states in the band gap associated with the lone pair (LP) electrons located at chalcogen atoms [7]. The combination of low coordination of the chalcogenide elements with the availability of the LP electrons on those elements allows structure reorganization with or without bond breaking [10,13]. The other feature of PIEs in chalcogenide glasses is their reversibility. It has been assigned to a unified bond-breaking mechanism, involving a combination of inter-molecular and intra-molecular bond scission or weakening [14].

Among photoinduced effects, photodarkening (PD) and photobleaching (PB) are of great interest due to the opportunity for their direct applications in optics and optoelectronics, including optical switching [15]. With respect to Ge-containing chalcogenide glasses, these two effects are largely structurally defined and their appearance is related predominantly to structural transformations [16,17]. Whereas PD has been widely studied and generally understood [1], the PB mechanism is still incompletely understood. There are two alternative models proposed: one model exploits the excitation-triggered, local structural reordering of homopolar bonds to heteropolar ones, and the second model links the effect to the photo-oxidation, i.e., Ge-O bond formation [1,18,19]. The latter effect is difficult to observe directly with available methods of structural analysis such as Raman spectroscopy because of the limited amount and low vibration intensity of the oxygen-containing bonds. For the oxide-containing compounds, the key methods used to investigate the structural changes are indirect, such as infrared (IR) spectroscopy. Tichy et al. [20,21], ascribe the increase in the amount of oxygen to a shift in IR spectra to smaller wavenumbers associated with an increase in local electronegativity. Controversial results about weight and thickness losses in obliquely deposited films are reported by Rajagopalan et al. [22] and Harshavardhan et al. [23], which the investigators relate to the formation of volatile, chalcogen-based oxides. Yet, they do not describe such effects for normally evaporated films. One presentation of the effect related to photo-oxidation suggests that the oxide film is situated on the surface, thus producing strain on the interface that induces states into the band gap [19]. However, bearing in mind the basic relations between structure and optical performance, this contradicts the general view that oxidation can be identified with bleaching of the glasses [24].

The kinetic of PIEs are usually studied on short time intervals (e.g., fs, ns) because the response time is of the highest priority for practical applications. Thus far, the available data on the slow kinetics (seconds) are very limited and have not been reported in detail. Whereas previously, it was believed that with the increase of the illumination dose, the effect will not change its character—i.e., only photodarkening or photobleaching will occur if this is the way in which the photoinduced changes started. Recent studies demonstrate that the transition between these two effects becomes apparent with an increase of the exposure time. This demonstrates the dual role of light for occurrence of PIEs in ChG [25–27]. It also has
been found that light-induced effects are composition dependent and can transition from photodarkening to photobleaching with change from Ge-deficient to Ge-rich material [28]. It is important to note that, as the number of Ge atoms in a glass grows, its mean coordination number increases [29], giving rise, after passing the intermediate phase (IP), to evolution from a flexible ($x<20\%$) to a stress-rigid network ($x>30\%$) [30]. Whereas there are many studies related to the floppy phase of Ge-Se glasses, little research has been done on PIEs in rigid structures, including nearly stoichiometric composition GeSe$_2$.

In this paper, we provide fundamental insights into the origin of transient and metastable light-induced effects in a-Ge$_x$Se$_{100-x}$ systems across the glass-forming region, with a special emphasis on compositions characteristic of high-rigidity structures ($x\sim>30\%$). We use the two-laser-beam technique to investigate the crossover from transient PB to the mixture of both transient PD and metastable PB that occurs with a change in glass composition from close to intermediate phase to stress-rigid phase. Not rejecting the surface photo-oxidation process, we confirm with first-principles simulations that experimentally observed metastable PB in Ge-rich glasses ($x>30\%$) can be accounted for by photoinduced structural transformations. The validity of this assumption is confirmed with Raman analysis tracking the photo-structural changes.

2. Samples and methods

The study was performed on thin a-Ge$_x$Se$_{100-x}$ films deposited onto ITO-coated glass substrates by thermal evaporation from a previously synthesized ChG. Films were deposited using a Cressington 308R thermal evaporation system at a pressure of $10^{-6}$ mbar; a semi-Knudsen cell crucible was utilized to increase the homogeneity across the film. The previous studies have shown compositional and structural homogeneity in the films' depth [31]. The compositions of films were determined on five locations of each sample by Energy Dispersion X-ray Spectroscopy using a Hitachi S-3400N-II scanning electron microscope equipped with Oxford Instruments Energy + X-ray detector. It has been established that the pure Ge-Se films contain 29.2, 32.1, 39.5 atomic percent of Ge, with Se adding to 100 atomic percent for each particular composition. Film thickness ranged from 1.0 to 1.5 $\mu$m.

The photoinduced changes in the films were observed by the two-laser-beam technique [32]. For this technique, we used the following two lasers: (1) a low-intensity, 0.29mW/cm$^2$ probing laser diode of 655nm (above the absorption edge [28]) was used continuously to monitor changes in the transmission ($T$) and (2) a high-intensity 200mW/cm$^2$ pumping laser emitting light of 405nm was used to produce PD/PB effects. The pumping laser worked in an on/off regime with a period of 400s. Both beams were focused on the same area of the sample, with the pump completely overlapping probe light. As a result, relative changes in the transmission ($T/T_0$) as a function of time were collected.

We performed a subsequent Raman analysis on pre- and post-exposed samples in backscattering geometry in macro mode using a Horiba Jobin Yvon T64000 triple monochromator with a liquid-nitrogen-cooled, multichannel coupled charge device detector. The films were excited with the 441.6nm blue line from a He-Cd laser at a power of 25mW and with a circular area of ~0.2mm. To avoid photoinduced changes in the studied film by the laser light of the Raman system, we conducted measurements at liquid-nitrogen temperature and at a pressure of $10^{-5}$ Torr. Each Raman spectrum was collected over a period of 60 seconds. Each of the Raman spectra was normalized to the corner-sharing (CS) peak centered at 195cm$^{-1}$. Deconvolution of the Raman vibrational modes with a Gaussian shape distinguishes each of the modes. After fitting the areas under the individual peaks, integration of the bands centered at 195cm$^{-1}$ and 214cm$^{-1}$ revealed the fractional quantities of CS and edge-sharing (ES) structural units [33]. The accuracy of the fitting procedure is represented by the error bars on the respective graphs.
To understand the nature of the photoinduced structural development in the a-Ge$_x$Se$_{100-x}$ network, we applied first-principles simulations. We generated a model system of a-Se composed of 25 atoms. The required Ge content was achieved through replacement of some Se atoms with Ge, obeying the fourfold coordination of Ge. We used the WIEN2k package [34], with implementation of the Perdew-Burke-Ernzerhof parametrization of the generalized gradient approximation [35]. The periodic boundary conditions (infinite system) were applied to the model systems and the optimization procedure with finest optimization parameters performed for each a-Ge$_x$Se$_{100-x}$ composition. The optimization was carried out based on minimization of forces: the force tolerance of 0.5 mRyd/Bohr in combination with tight convergence limits of the energy 0.0001 Ryd, force 0.1 mRyd/Bohr and charge 0.001 e. The product of atomic-sphere radius and plane-wave cutoff in k-space was set to 7, while the Brillouin zone of a supercell was covered by the $4 \times 4 \times 4$ Monkhorst-Pack mesh. The energy-separating core and valence electrons were set to $-6.0$ Ryd. The photo-excitation was simulated through removal of an electron from the valence band. The delocalized nature of the hole left in the valence band tails was set to induce lattice relaxation of the immediate neighborhood. This allowed tracking of the photoinduced structural changes and revealed their effect on electronic properties. By returning the missing electron, the post-excitation regime was reestablished.

3. Experimental results

Data in Fig. 1 demonstrate that distinctly different photoinduced effects are observed for a-Ge$_x$Se$_{100-x}$ glasses depending on the compositional variation. The concentration of Ge $x \approx 30\%$ is found to be critical. Below this content, for $x = 29.2\%$, only a transient effect is present. Above this content, for $x = 32.1\%$ and $x = 39.5\%$, metastable effects emerge.

Thereby, when Ge$_{29.2}$Se$_{70.8}$ is illuminated with a pumping beam, its relative transmittance rapidly increases by 3% and saturates (Fig. 1(a)). During the follow up rest period, the effect disappears completely. Even on repeating on/off cycles, this tendency remains unchanged and exceptionally transient PB is seen.

When the critical concentration of Ge is exceeded, the mixture of the effects—transient photodarkening (during the pump period) and metastable photobleaching (during the rest period)—is observed (Fig. 1(b)). Moreover, the higher the Ge content, the more pronounced the magnitude of both the transient and metastable changes. In the case of Ge$_{32.1}$Se$_{67.9}$, a decrease in transmittance of 2.5% is observed upon light irradiation (Fig. 1(b), black circles). Once the film is allowed to rest, the quick rise of the film transparency that continues to increase gradually leads to a metastable PB effect. In subsequent “on/off” series, transient photodarkening is followed by build-up of metastable photobleaching, with enhanced amplitude of the PB during each next resting cycle. Consequently, at the end of the experiment, overall bleached film is produced with transparency of 1.5% above its initial level. Further, an identical trend of crossover from transient PD to metastable PB is seen for Ge$_{39.5}$Se$_{60.5}$ composition, with essentially much more pronounced magnitude of the effect (Fig. 1(b), blue triangles). Thus, overall metastable PB reaches $\sim 7\%$ over the initial level of transmittance for $x = 39.5\%$ Ge-Se compound.
The Raman spectra of the studied films expose the following five different regions, presenting the mode assignments of the structural units building the films: (1) Ge-Se corner-sharing (CS) clusters of GeSe₄ tetrahedra centered at 195 cm⁻¹; (2) edge-sharing (ES) clusters of GeSe₄ tetrahedra centered at 214 cm⁻¹; (3) a wider-frequency band centered at ~260 cm⁻¹ corresponding to the bond stretching in Se-Se chains and rings; (4) the band at 305 cm⁻¹ correlated to the asymmetrical stretching of ES bonds [33,36]; and (5) Ge-Ge homopolar ethane-like (ETH) structural units at 179 cm⁻¹. The intensities of the bands, as well as their exact positions vary depending on Ge concentration x [33,37]. Subsequent comparative Raman analysis of as-deposited with light-exposed films reveals the following: for Ge₃₂,₂Se₇₀,₈, only changes within the error in the ES:CS ratio are observed and the amount of the Se-Se and ETH-type bonding remains constant with development of the illumination time (Fig. 2(a)). There is a full consistency between the Raman spectra of virgin and light-illuminated spectra, showing no bond rearrangement and the experimental data (Fig. 1(a)), for which only transient PB has been seen on the optical transmission spectra as a function of time.

The Raman results for the films with composition Ge₃₂,₁Se₆₇,₉ suggest marginal changes in the structural organization of this film as a result of the light interaction (Fig. 2(b)); this is in good agreement with the optically recorded data, implying weakly mixed PD and PB effects (Fig. 1(b), black circles).

In contrast, significant changes in Raman spectra are observed in Fig. 2(c) for post-exposed, as compared to pre-exposed, Ge₃₉,₅Se₆₀,₅ film. This can be related to the occurrence...
of a metastable PB that has been observed experimentally (Fig. 1(b), blue triangles). According to Raman analysis, the ES:CS ratio increases from 0.42 to 0.91. The concentration of ETH and Se-Se structures decreases from 9.8 to 7.9 and from 14.6 to 10.2, respectively. The increase in ES:CS ratio, together with simultaneous decrease in ETH and Se-Se structures, suggest that a large quantity of Ge-Ge bonds and corresponding Se-Se bonds are broken and converted (predominantly to ES tetrahedral units) as a result of relaxation in the post-light-exposed period. The reversibility of the PB effect also supports the hypothesis that its nature is mainly a function of structural reorganization and not of oxidation. Figure 3 presents the extracted data from the Raman spectra of the studied films, related to the quantitative evolution of the areal intensity of the structural units represented in the studied films.

4. Theoretical modeling and discussion

The following section deals with the structural interpretation of the physical properties of the a-Ge\textsubscript{x}Se\textsubscript{100-x} -class of glasses, with a focus on the implications of the compositional variation over the studied effects. We attempt to connect the experimentally observed light-induced transmittance changes (Fig. 1) with the structural transformations evident from Raman analysis (Fig. 2 and Fig. 3) and the first-principle simulations. Based on appearance of a metastable photoinduced effect in a-Ge\textsubscript{x}Se\textsubscript{100-x} films, this section is divided into two parts: films containing Ge below \(x = 30\%\) and films containing Ge above \(x = 30\%\). Following the classification suggested in Boolchand et al. [30], there is a threshold in the Raman signatures of the CS and ES units at around 31.5\% of Ge, above which nanoseparation or formation of a layered structure occurs. The latter releases stress arising from the high coordination of Ge in this concentration region.

4.1 a-Ge\textsubscript{x}Se\textsubscript{100-x} structural evolution up to 30\% of Ge content and respective light-induced effects

The photoinduced effects in a-Ge\textsubscript{x}Se\textsubscript{100-x} with Ge content \(x < 30\%\) range from photodarkening to photobleaching (Fig. 1(a)), [28,38]. The variety of these effects comes from the high flexibility of the glassy matrix due to the low (twofold) Se coordination, which becomes more and more restricted with an increase in Ge content. Boolchand et. al. demonstrated that 19.5\% concentration of Ge represents the limit of the floppy phase in the Ge-Se system [30]. The flexibility of high-Se-content glasses suggests that the photo-excitation follows the pathway well-known in a-Se—namely, it involves the lone pair electrons of Se atoms [13]. Because of the flexibility of this compositional region, one can expect photoinduced structural changes, e.g., flipping of the Se chains or inter-molecular reactions, changes of the van der Waals distances due to Coulomb interactions of photogenerated defects, and even crystallization of the Se content [1,28]. These effects can be superimposed and their
experimental identification can be difficult, but not impossible. In order to interpret our experimental results and reveal a mechanism of the photoinduced transformations, we first model the photoexcitation in the floppy part of the Ge-Se system with composition Ge$_{19}$Se$_{81}$. Because photocrystallization should be suppressed at $x = 19\%$ [28], we expect to observe only transient effects.

We present the structure of the modeled Ge$_{19}$Se$_{81}$ compound in Fig. 4(a). Apparent excess of Se atoms arranges into short elemental chains. With respect to Ge-containing bond types, the CS and ES tetrahedral units are found in the bonding pattern, with preference given to CS. The obtained bonding configurations are consistent with the Raman analysis [37]. At this high Se concentration, Ge atoms usually undergo $sp^3$ hybridization and bond to four Se neighboring atoms using two of the Se p-electrons (the other two p-electrons in Se are LP). In this manner, Ge is fourfold coordinated and Se is twofold coordinated in their most natural state. Except for stretching of one of the bonds at the fourfold Ge site to 2.8 Å (see details in Ref. 39), the average length of the Se-Ge bonds is 2.55 Å. The Se-Se bond length varies from 2.37 to 2.45 Å, which correlates well with the average bond length in a-Se [13]. Of course, due to the lack of order in the system, some under- or over-coordination of both Ge and Se atoms is possible that corresponds to their equilibrium defect condition.

![Fig. 4. (a) The Ge$_{19}$Se$_{81}$ structure possesses high amorphicity with almost uniform distribution of the atoms; (b) The Ge$_{28}$Se$_{72}$ system is distinguished by the well-defined layered structure and appearance of the Ge-Ge bond.](image)

The simulation reveals that photoexcitation in low-Ge content films is governed by the LP states of the Se atoms. Removal of an electron from the valence band occurs from the LP state, which enables a formation of the dynamic Se-Se bond (likewise in a-Se). The lone-pair-state missing electron is shifted deeper into the gap. It induces band gap shrinkage by around 0.05eV, which manifests itself in the transient PD component. With respect to the post-excitation regime, reappearance of the missing electron activates breakage of the light-induced bond and, therefore, the size of the band gap restores to its original value. Alternatively to the dynamic bond, any other Se-Se bond can be broken, which introduces an effect of the bond switching. Because the quantity of bonds before and after photoexcitation remains unchanged, the total energy of the Ge$_{19}$Se$_{81}$ compound is unaffected. The above suggests that the observed structural stability of the Ge$_{19}$Se$_{81}$ compound against photoexcitation may be linked to the well-known weak-aging property of the intermediate phase in a-Ge$_{x}$Se$_{100-x}$ glasses [30], because this composition is just at the compositional edge of the IP.

For the Ge$_{29.2}$Se$_{70.8}$ films referred to the stressed rigid phase, the transient PB, instead of PD, has been found (see Fig. 1(a)). The transient character of the light-induced effects suggests that this thin film still possesses properties typical for the IP. Because the Raman
analysis cannot recognize the difference between pre- and post-exposed samples (see Section 3), we modeled the photoexcitation in the Ge$_{28}$Se$_{72}$ system (Fig. 4(b)) to investigate the nature of the transient changes.

The Ge$_{28}$Se$_{72}$ system is characterized by a well-defined, three-dimensional structure due to an overall increase in cross-linking tendency. In addition to the CS and the increased amount of ES structural units, we observed formation of Ge-Ge ethane-like bonding configurations. The Ge$_{28}$Se$_{72}$ structural model suggests that Ge atoms create a skeleton of the layers surrounded by the Se atoms. The former gather into Se chains and form the outrigger raft structure, as proposed by Bridenbaugh and associates [40]. The length of the Ge-Ge bond is 2.63 Å, and the accompanying Se-Se bond is stretched to 2.80 Å, whereas the rest of the Se-Se bonds range in length from 2.35 to 2.55 Å. The length of the Ge-Se bonds randomly varies from 2.32 to 2.60 Å. This inhomogeneity is reflected in electronic properties by an ~0.02 eV increase in the size of the band gap (in comparison with the Ge$_{19}$Se$_{81}$ structure). The same trend is observed in data published by Micoulaut et al. [29].

The structural development in the Ge$_{28}$Se$_{72}$ system alters the excitation pathway. Instead of LP involvement, excitation causes breakage of the covalent Ge-Se bonds, preferably in the ES configuration. As a result, a dangling bond defect is formed at the Ge atom, whereas the Se atom reestablishes its normal valence to two. Remarkably, the defect state appears at the top of the valence band due to the partial saturation of the dangling bonds through the charge exchange with the available LP states. Therefore, the dangling bond is accommodated through the bond elongation in the immediate neighborhood—i.e., without much lattice perturbation. The size of the band gap remains almost unchanged, except that it increases slightly when the Ge-Se bond breaks next to the ETH configuration. In the post-excitation regime, the dangling bond attaches to any twofold Se atoms. The induced bond switching does not alter the homopolar/heteropolar bond ratio and therefore it has no effect on the total energy of the system or the size of the band gap. For this reason, no perceptible changes are seen in post-exposed samples on the Raman spectra for Ge$_{29.2}$Se$_{70.8}$ and Ge$_{32.1}$Se$_{67.9}$ in Fig. 2 and Fig. 3.

4.2 a-Ge$_x$Se$_{100-x}$ network peculiarities for $x \geq 30\%$. Insights into the mechanism of the metastable changes

As was reported previously [27], when the Ge content is $x \geq 30\%$, the experimental data (see Fig. 1(b)) demonstrate a mixture of the transient PD and metastable PB effects. The Raman analysis provides some insight into the metastable changes: the homopolar bonds—i.e., ETH and Se-Se—are converted into the tetrahedral Ge-Se bonding (Fig. 3). However, the Raman results are not sufficient to gain an understanding about the origin of the transient PD and changes in the topology. To establish a complete picture of the photoinduced effects in the stressed-rigid networks, we model the Ge$_{36}$Se$_{64}$ system. Taking into account that the amplitudes of the transient PD and metastable PB grow with increasing Ge content (Fig. 1(b)), at a chosen concentration $x = 36\%$, we expect metastable changes to be well pronounced.

In the Ge$_{36}$Se$_{64}$ system, the tendency of Ge atoms to gather into the ETH bonds becomes more apparent (Fig. 5(a)). In addition, formation of a distorted rock salt structure is possible at this composition [41]. It has a quite different molecular origin because in this structure, the valence saturation is achieved through simple sigma-type bonding on the Ge site with the two p-electrons of Se. In this manner, the LP electrons of Se are involved in formation of a dative bond by which they orbit around both atoms, creating a negative charge around the Se atom. In such instances, both Ge and Se atoms appear as threefold coordinated because the length of the dative bond is the same (within a decimal) compared to the covalent bonds formation process. Subsequently, in this composition, Se sites give up lone pairs; i.e., Ge$_{36}$Se$_{64}$ possesses a deficiency of LP states.
Fig. 5. The photoinduced transition of the Ge_{36}Se_{64} system to more ordered state.
(a) Pre-excitation regime: the layered structure with weakly defined molecular cages;
(b) Post-excitation regime: clustering of the molecular cages into 3D nanostructures.

The photo-excitation applied to the model Ge_{36}Se_{64} system is found to induce breakage of
Ge-Ge chains and as a result, many dangling bonds at Ge atoms are generated. Because of
the deficiency of LP states at the Se atoms, the dangling bonds cannot be saturated.
Therefore, the defect states appear in the band gap causing a band gap shrinkage of ~0.2 eV
that manifests itself in the transient PD during light exposure (see Fig. 1(b)). The increase in
PD amplitude with growing Ge content is related to further suppression of the concentration
of Se lone pair states. With respect to the positions of atoms, the unsaturated dangling bonds
induce significant lattice perturbation due to displacement of the Ge atoms carrying the
dangling bond towards the Se atoms, which might share their electrons.

In the post-excitation regime, we observed an appearance of the newly formed
heteropolar CS and ES bonds and subsequently, a reduction in the homopolar ETH and Se-Se
bonds. The heteropolar bonds are assumed to be more energetically favored compared to the
homopolar ones [39]. The bond conversion induces ordering in structure defined by the
development of the dative bonds, with a pronounced effect of clustering into 3D
nanostructures (Fig. 5(b)). Due to clustering, the length of the Ge-Se bond deviates in shorter
range; it is 2.4–2.6 Å after excitation compared to 2.36–2.76 Å in the pre-exposed regime,
while the Se-Se bonds are stretched by approximately 10%. The photoinduced segregation
of clusters is reflected in the electronic properties by an increase in the band gap size of 0.22
eV. It is plausible to assume that the experimentally observed metastable PB effect (Fig.
1(b)) reflects the increase in the band gap size. The increase of the PB amplitude with Ge
content is related to the increase in concentration of the ETH bonds and the subsequent
growth of the conversion rate. The total energy of the pre-excited and post-excited structures
was found to be in the same range. Therefore, stability of the systems with respect to each
other suggests the existence of a potential barrier between them. Additionally, recent studies
by neutron scattering of GeSe_2 reported existence of two forms of ordering on the nanoscale
[42] and were later confirmed by wider region study of Ge-Se compositions by fluctuation
transmission electron microscopy (FTEM) [43]. Our simulations could not distinguish the
forms of ordering as depicted by these methods; however, the confirmation of ordering on a
short scale verifies the accuracy of our simulation.
The findings in our simulation of the photoinduced conversion of bonds completely agree with our Raman analysis (see Section 3). To the best of our knowledge, this is the first direct evidence of the conversion of homopolar to heteropolar bonds being responsible for the metastable PB in a-Ge$_x$Se$_{100-x}$ films. The only other previously reported direct evidence of the light-induced bond conversion was observed on ternary Ge-based glasses such as a-Ge$_x$As$_{35-x}$Se$_{65}$ [44].

5. Conclusion

Light-induced effects have been investigated by optical and structural analysis and first-principles simulation in the a-Ge$_x$Se$_{100-x}$ chalcogenides as a function of composition across the glass-forming region, with a special emphasis on high-rigidity transition ($x\sim>30\%$). By means of the two-laser-beam technique, the critical concentration of Ge $x=30\%$ was found, reflected in the crossover from transient PB to the mixture of transient PD and metastable PB; this can be linked to the transition from the close-to-intermediate phase to the stress-rigid phase. To provide better insights into the nature of PIEs, we utilized atomistic models to examine photo-excitation and relaxation mechanisms in correlation with local order and topology. The topology analysis of a-Ge$_x$Se$_{100-x}$ demonstrated an evolution from homogeneous flexible phase to a layered structure inherent to the stress-rigid phase. The successive study of the excitation mechanism and subsequent light-induced alteration in topology suggests that Ge:Se ratio, rather than network rigidity, plays a decisive role in the manifestation of PIEs. According to our investigation, alteration in the photoinduced effects is governed by availability of the lone pair states at the Se atoms that are sensitive to the Ge:Se ratio. However, it does not correlate strictly with the boundaries of the phase transition ($x=19.5\%, 26\%, 31.5%$ [30]). The secondary role of network rigidity has also been found in a recent study of PIEs in the ternary Ge-containing glasses [44]. The results of that study support our findings.

At low-Ge content ($x<20\%$), the photoexcitation mechanism follows that in a-Se, it involves the lone pair electrons and induces the defect states in the band gap, giving rise to the PD [13]. As Ge concentration grows, the number of LP decreases, reaching the critical limit at $x=30\%$. At this point, the excitation starts to cause Ge-Se bond breakage, thus forming the dangling bonds. These dangling bonds tend to saturate available LP states, resulting in the transient PB (Fig. 1(a)). At the same time, this bond switching does not cause changes in the homopolar/heteropolar bond ratio, which was also confirmed by Raman analysis performed on pre- and post- exposed Ge$_{29.2}$Se$_{70.8}$ samples, where no detectable changes were observed (Figs. 2(a), 3). As Ge content exceeds 30\%, nucleation of the Ge atoms into ETH-like structures along with the lone pair deficiency start to favor the breakage of the Ge-Ge bonds during photo-excitation. The simulations indicated that the unsaturated dangling bonds generate defect states in the band gap, which is responsible for the transient PD in both Ge$_{32.1}$Se$_{67.9}$ and Ge$_{39.5}$Se$_{60.5}$ (see Fig. 1(b)), which also induces significant lattice perturbation. In the post-excitation period, the latter is found to trigger a conversion of the homopolar to heteropolar bonds that is directly verified by the Raman analysis (Fig. 3), i.e., an increase in the edge-sharing to corner-sharing ratio with a simultaneous decrease in ETH and Se-Se. Ultimately, the bond conversion activates transition to the more ordered structure, whose main feature is a clustering effect into the 3D nanostructures. It increases the band gap, which can be linked to the experimentally observed metastable PB effect, which becomes more and more pronounced in a post-excitation period with each successive light exposure. However, to validate the changes in the band gap as the result of formation of light-induced 3D nanostructures, further investigation is required and can be done by absorption spectroscopy methods. We anticipate that the light-induced clustering that we established in this study is the underlying mechanism responsible for the phase-change memory phenomena in the Ge$_{50}$Se$_{50}$ films [45].
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