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Competitive photostructural effects in Ge-Se glass

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A detailed calorimetric study of photostructural changes in glasses of the Ge-Se system is presented. The photomodified structure corresponds to a distinct entropy state intermediate between a fully thermally relaxed glass and a fresh glass. This intermediate photoinduced structure appears to result from the competitive effects of photorelaxation (negative entropic contribution) and photoexpansion (positive entropic contribution) whose simultaneous contribution leads to an equilibrium state after extensive irradiation. The compositional dependence of photorelaxation and photoexpansion reveals that strong glass formers are resilient to photostructural change relative to fragile glass formers. This observation can be explained by the presence of fewer minima on the energy landscape of strong glass former, therefore not allowing the structure to sample many configurational states and resulting in lesser photostructural changes. A comparison of the power dependence and kinetics of photorelaxation, photoexpansion, and photodarkening during subbandgap irradiation suggest that the three effects are individual and distinct components of the overall photosensitive process.

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I. INTRODUCTION

In recent years, photosensitive processes in chalcogenide glass have attracted considerable interest due to a number of promising technological applications. This in turn is driving an effort to understand the complex fundamental mechanism underlying these effects. Applications of photosensitivity in amorphous chalcogenides are numerous and range from the processing of waveguide circuits,[1] diffraction elements,[2] and microlenses[3] to optical memories,[4] optoelectronic,[5] and optomechanical devices.[6] Photosensitive processes can be characterized by various effects such as photoexpansion,[7] photodarkening,[8] photorelaxation,[9] photoinduced anisotropy,[10] and fluidity;[11] however, it is recognized that all these effects originate from the light-induced formation of electron-hole pairs (excitons) that allow for bond rearrangement upon recombination. Photon absorption excites localized electrons from the chalcogen atom's lone pair state (located at the top of the valence band) leading to the formation of self-trapped excitons, also called valence alternation pairs (VAPs). These charged defects are relatively stable and allow for structural rearrangement as they decay.[12] This mechanism is thus purely optical in nature and is known to be fully athermal.[11,13] Photostructural change can be induced by either above or below bandgap light. Subbandgap light has a lower quantum efficiency and requires a laser source;[14] however, it is far more interesting for fundamental and technological purposes because it allows one to irradiate the bulk of the glass rather than to be limited to the surface. This permits to study bulk effects such as photorelaxation[9] and to easily produce advanced devices such as buried waveguides.[15] The effect of irradiation in the Urbach region has been extensively studied for the As_2S_3 composition due to the wide availability of He-Ne lasers. It is clear that all the photostructural effects mentioned above can be induced by the same subbandgap source.[16] Similarly, photodarkening, photoexpansion and photorelaxation were shown to happen simultaneously in Ge-Se glass exposed to light in the Urbach region.[13]

Very few studies have been directed at the compositional dependence of photoinduced effects in chalcogenide glass despite the well-known variation in structural characteristics associated with the average coordination number $\langle r \rangle$.[17] One difficulty arise from the fact that the bandgap and therefore the absorption coefficient varies with composition and that consequently a systematic study would require a tunable source in order to separate compositional effects from the effect of variation in absorbance. For example the variation in photodarkening observed at constant wavelength along the As-S system (Ref. 18) is likely due to the higher quantum efficiency associated with decreasing bandgap rather than with the increasing concentration of As-As bonds, as suggested. In contrast, photorelaxation effects induced with a tunable source at equivalent absorbance along the Ge-Se system show a very strong correlation with the average coordination number $\langle r \rangle$.[9] The observed behavior can be simply explained on the basis of structural arguments following the strong/fragile glass-former classification. The fragile floppy structures at low $\langle r \rangle$ number exhibit a large propensity for entropy relaxation as measured by modulated differential scanning calorimetry (MDSC), while the strong glass formers at $\langle r \rangle = 2.4$ experience almost no photorelaxation. Significant photorelaxation effects are therefore expected for any chalcogenide glass composition deviating from the $\langle r \rangle = 2.4$ optimal value defined by Phillips and Thorpe.[19,20] Photostructural relaxation is an inherent part of the mechanism of photosensitivity and should therefore be considered for applications capitalizing on photosensitivity such as optical microprocessing of photonic devices. Indeed, compositional variations in photoinduced grating efficiency have been observed in Ga-Ge-S glass[2] as well as variation in photoinduced fluidity in As-S fibers.[21] These variations could be explained in terms of photorelaxation phenomena. It should be noted here that annealing the glass near T_g only leads to minimal entropy release and does not preclude extensive photorelaxation during irradiation at room temperature; therefore, the relaxation effect during photoprocessing can-

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not be prevented by a simple thermal treatment of the glass.

While the effect of photorelaxation has been previously observed in various chalcogenide systems,[22–24] in this paper we investigate the thermodynamic characteristics of the photomodified glass structure and present a quantitative analysis in term of entropy state. The interplay between competitive photoactuated processes is also examined and the composition dependence of these processes is described.

II. EXPERIMENT

High purity glass samples were synthesized in three compositions along the Ge-Se system: $\mathrm{GeSe_9}$ $\langle r\rangle=2.2$, $\mathrm{Ge_3Se_{17}}$ $\langle r\rangle=2.3$, and $\mathrm{GeSe_4}$ $\langle r\rangle=2.4$. All samples were prepared under 10^{-6} Torr vacuum in silica ampoules previously cleaned with HF. The 6N purity starting elements were further purified *in situ* by sublimation and the sealed ampoule containing the appropriate ratio of elements were melted in a rocking furnace overnight. The glass samples were then quenched in air and annealed near T_g.

All irradiation experiments were performed with a Ti/sapphire tunable laser operating in the pulse mode with a repetition rate of 82 MHz and 100 fs pulse length. The absorption edge of each glass composition was measured with a UV-Vis spectrometer and the laser wavelength used for photostructural experiments was tuned accordingly so that each sample was irradiated at the same value of the absorption coefficient in the Urbach region. The laser power was tuned with a circular variable neutral density filter.

Photodarkening was measured by recording the change in transmission of an unfocused beam propagating through a 1 mm thick glass disk polished on both side. The transmitted intensity was recorded as a function of time with a silicon photodetector. In order to account for power fluctuations, the transmitted signal was scaled by a reference signal obtained from a second photodetector monitoring the initial laser output.

Photoexpansion was induced with an unfocused beam of diameter 1 mm incident perpendicularly to the polished surface of bulk glass samples. The surface expansion was measured with a Tencor P2 three-dimensional profilometer.

The extent of photorelaxation was measured with a modulated differential scanning calorimeter TA Q1000. The samples were scanned at 10 °C/min. The entropy and enthalpy variation were obtained by integrating the heat capacity curve of the irradiated sample and measuring the difference with a reference run obtained on the same sample scanned up and down at 10 °C/min.

III. RESULTS

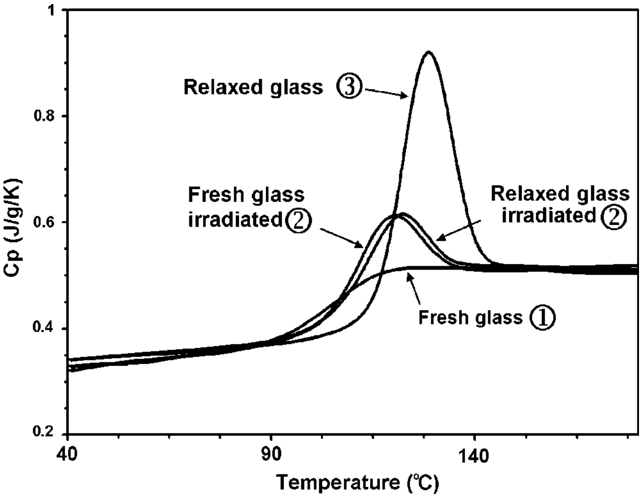

FIG. 1. MDSC trace of a thermally relaxed glass, a fresh glass, and the same two samples after extended laser irradiation in the Urbach region. The glass composition is $\mathrm{GeSe_9}$.

Figure 1 shows the typical heat capacity trace of a series of $\mathrm{GeSe_9}$ glasses in various state of relaxation. The fresh glass correspond to a reference sample with no thermal history which was first heated through the glass transition up and down at 10 °C/min and then immediately run and recorded. That way the sample did not anneal out any residual entropy and therefore correspond to the initial standard glass structure labeled ① in Fig. 2. The relaxed glass in Fig. 1 corresponds to a sample that has undergone thermal relaxation at room temperature for a period of eight years. This sample was stored in the lab at approximately 298 °C for that period of time. The temperature dependence of the structural relaxation time was determined for $\mathrm{GeSe_9}$ using the method developed by Moynihan.[25,26] In this method, the activation energy for structural relaxation is obtained form a series of measurements of the glass transition at different cooling rates and the relaxation time τ at various temperatures is predicted by assigning a value $\tau=200$ s at the glass transition temperature and extrapolating below T_g.[27] The value of τ estimated this way for $\mathrm{GeSe_9}$ at 298 °C is $\tau=5.5$ y. Assuming an exponential relaxation behavior, the glass will relaxed approximately 80% of its residual entropy after eight years. Hence, our sample did not reach the liquid-like equilibrium line, but rather corresponds to the entropy

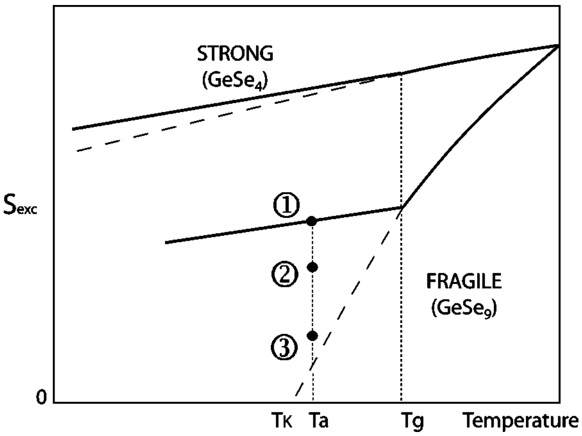

FIG. 2. Schematic representation of a Kauzmann plot for a fragile and strong glass showing the correlation between fragility and the rate of entropy loss upon supercooling below the melting point. The dashed line represent the extrapolation of the supercooled liquid entropy line below T_g. Points ①, ②, and ③ show different stages of thermally or photoinduced annealing at a temperature T_a. Fragile glass formers have a greater propensity for entropy relaxation.

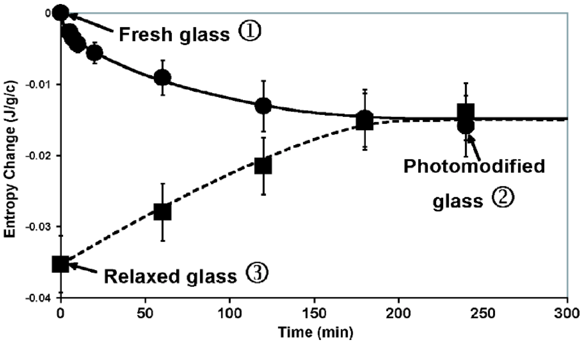

FIG. 3. Entropy variation of a bulk $GeSe_9$ glass during subband-gap irradiation. Squares indicate the effect of irradiation on a glass that has previously annealed out 80% of its residual entropy at room temperature. Circles indicate the effect of irradiation of a fresh glass containing a large amount of residual entropy.

state labeled ③ in Fig. 2. The large heat capacity overshoot observed in Fig. 1 corresponds to the glass regaining the residual entropy lost during annealing a room temperature.[27] The two intermediary heat capacity traces labeled ② in Fig. 1 correspond to glasses ① and ③ after extensive irradiation. This suggests that both glasses tend toward a common intermediary entropy state associated with the photomodified structure. This effect is further demonstrated in Fig. 3, which shows the evolution of glass entropy as a function of irradiation time for both the fresh glass and thermally relaxed glass. It is shown that both samples converge toward the same intermediary entropy state after long exposure to laser light in the Urbach edge. It should be noted here that the $GeSe_9$ composition was ideal for this study because of its low T_g (98 °C), which allows it to undergo extensive structural relaxation at room temperature in only a few years. In comparison, the relaxation time of Ge_3Se_{17} at room temperature is estimated at $\tau = 3 \times 10^3$ years.

Figure 4 shows the typical profile of photoexpansion at the surface of a polished Ge-Se glass sample. The profile shown was induced in $GeSe_9$ with a 1 mm diameter beam at 780 nm and an intensity of 3.2 W/cm^2. The illuminated region is expanded convexly to a height of 20 μm and across a diameter around 1 mm equal to the beam size.

In order to probe a potential calorimetric signature associated with photoexpansion a thin slab of $GeSe_4$ was irradiated at a wavelength of 760 nm and subsequently analyzed with MDSC. The $GeSe_4$ composition is known to undergo almost no relaxation during illumination;[9] hence, it is expected that a eventual positive entropic contribution associated with photoexpansion could be detected in this glass. A slice of $GeSe_4$ 280 μm thick was irradiated throughout and expanded on both sides. The sample was approximately the size of the beam so that the bulk of the glass had undergone photoexpansion. Figure 5 shows the heat capacity trace of the exposed glass along with a reference run. The signals mostly superimpose and do not reveal a significant or conclusive change. The poor signal to noise ratio is due to the very small sample mass.

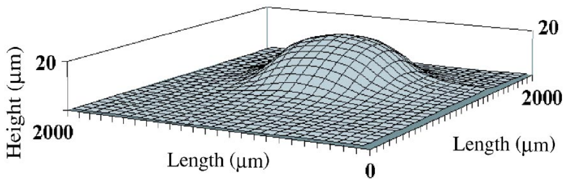

FIG. 4. Surface profile of a $GeSe_9$ glass after exposure to a 1 mm diameter laser beam. The beam is directed perpendicular to the polished glass surface. The laser wavelength is 780 nm and the intensity is 3.2 W/cm^2.

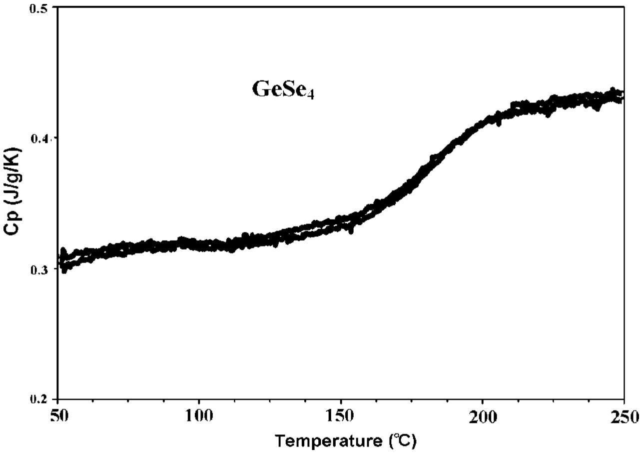

FIG. 5. MDSC trace of a 280 μm thick slab of $GeSe_4$ glass before and after irradiation with a laser beam of wavelength 760 nm and intensity 3.2 W/cm^2. The sample was cut to fit the beam size. The large noise ratio is due to the small sample mass.

Figure 6 compares the power dependence of photorelaxation, photoexpansion, and photodarkening in a $GeSe_9$ sample after a 10 min exposure to a beam of wavelength 780 nm. The extent of photorelaxation increases up to an intensity of 2.5 W/cm^2 and then decreases continuously for subsequent greater laser power. Figure 6(b) shows that the maximum in photorelaxation correlates with the onset of photoexpansion in the glass. Photoexpansion is virtually nonexistent after 10 min exposure up to an intensity of 2.2 W/cm^2 but then increases exponentially with higher power. In contrast, photodarkening appears to follow an almost linear dependence on laser power very distinct from the two other effects. Figure 6(b) also compares photoexpansion in the strong glass former $GeSe_4$ and the fragile glass former $GeSe_9$. It appears clearly that photoexpansion is lower at all laser intensity for the strong glass $GeSe_4$ associated with the optimally connected structure and average coordination $\langle r \rangle = 2.4$.

IV. DISCUSSION

It was shown that glass-formers' fragility can be defined in thermodynamic terms as the rate at which the supercooled liquid loses entropy with decreasing temperature.[28] Fragile liquids lose entropy at a faster rate and reach the state of zero excess entropy at a Kauzmann temperature T_K closer to T_g relative to strong glass. The ratio T_g/T_K can then be used as a measure of fragility as it reflects the slope of the excess

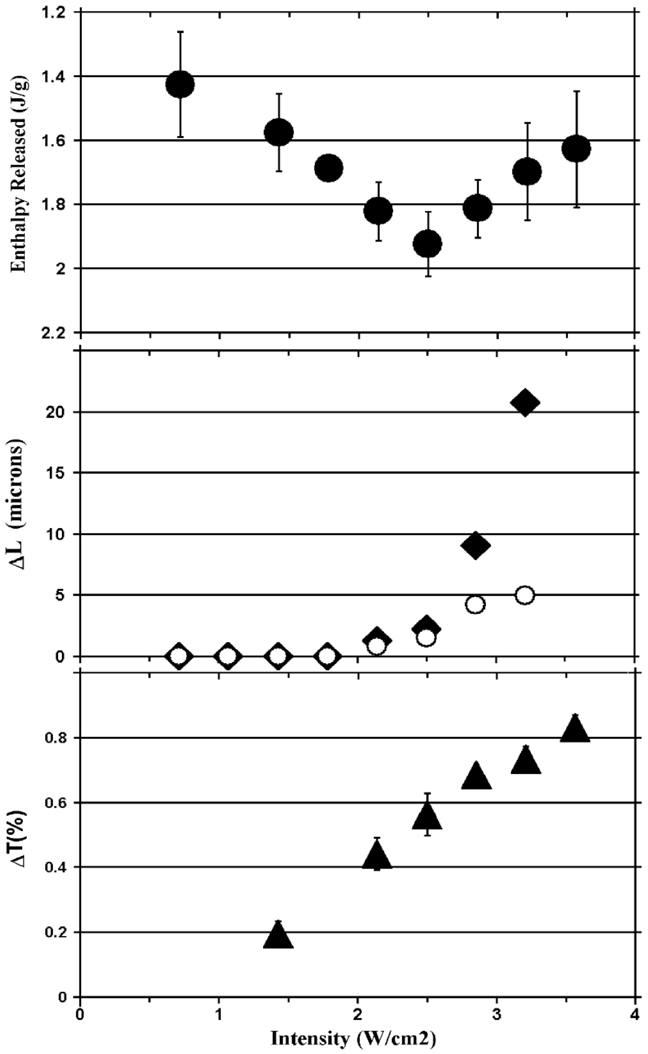

FIG. 6. Power dependence of (a) photorelaxation, (b) photoexpansion, and (c) photodarkening. The solid markers represent the effect of irradiation on the $GeSe_9$ glass composition and the open circles correspond to the $GeSe_4$ composition.

entropy variation with temperature. Due to the steep S_{exc} versus T slope associated with a fragile glass former, the corresponding glass builds up very large residual entropy when it is cooled down to room temperature far below T_g (Fig. 2). Because the relaxation time is an exponential function of the inverse temperature (Adam-Gibbs equation) the aging time for release of this residual entropy at ambient temperature is excessively long compared to laboratory time scale. However, when a glass undergoes athermal photoactuated fluidity at room temperature, the structural elements in the amorphous network gain enough degree of freedom to rearrange and release the residual entropy in a matter of minutes. The glass then tends toward the supercooled liquid equilibrium entropy line. This effect is known as photorelaxation or photoannealing. Our previous study[9] showed that the photoannealing effect is observed over a wide range of compositions and that its magnitude is consistent with the glass fragility. This study, however, raised the question of whether the glass can be photoannealed down to the supercooled liquid state or if the photoinduced structure corresponds to a distinct thermodynamic state. The answer to this question can be inferred from the results shown in Figs. 3 and 6. This series of experiment suggests that the photoinduced structure reaches an intermediary entropy state resulting from the competition between photorelaxation and photoexpansion. The competitive nature of photoexpansion and photorelaxation is particularly evident in Figs. 6(a) and 6(b). This experiment reveals that the photorelaxation efficiency drops sharply when the photoexpansion effect develops and becomes large, therefore indicating that there is a direct correlation between the two events. This apparent competitive effect implies that photoexpansion is associated with a positive entropy contribution in order to counter the photorelaxation effect. The entropic contribution of photoexpansion is indeed evidenced in Fig. 3. In this experiment, the irradiated glass had previously almost completely thermally relaxed and therefore released almost all of its residual entropy. In these conditions, the driving force for photorelaxation is null and the entropic contribution of photoexpansion can be observed independently. The irradiated glass now undergoes a gain in entropy instead of a loss and reaches an intermediary state identical to the one reached from above, i.e., by photoannealing a fresh glass. The equivalence of the thermodynamic state ② reached through photoexpansion of state ③ or photorelaxation of state ① suggests that the saturated photoinduced structural state corresponds to an equilibrium between photorelaxation and photoexpansion. In the experimental conditions of Fig. 3 ($GeSe_9$ irradiated with $2.85\ \mathrm{W/cm^2}$ at 780 nm), the equilibrium entropy state can be estimated at roughly 30% of the residual entropy in the initial glass. The fact that the entropy level of the photoinduced glass is a direct function of the light intensity supports the notion of a dynamic equilibrium between photoexcitation and thermodynamically driven but optically induced relaxation. This equilibrium can be seen as analogous to the dynamic equilibrium suggested by Fritzsche[29] for photoinduced fluidity. While the photoinduced fluidity provides structural degrees of freedom that allow for relaxation, it also induces photoexpansion, which acts as a competitive effect. Or, equivalently, the transition from a solid glass to a photoinduced fluid is associated with a structural volume expansion and an entropy increase, which is compensated by the entropy relaxation effect.

At this point it should be re-emphasized that the photoinduced volume expansion and entropy increase are not thermally induced and therefore do not vary in the cooperative way expected from equilibrium thermodynamics. This is a particularly striking fact in the case of photoexpansion induced in a thin slab of glass. A Ge_3Se_{17} sample polished to a thickness of $350\ \mu m$ and irradiated throughout perpendicular to its surface revealed photoexpansion of $7\ \mu m$ on the front face and $5\ \mu m$ on the back face. This corresponds to a 3.4% expansion of the sample thickness. Noting that the linear thermal expansion coefficient for Ge_3Se_{17} is $3 \times 10^{-5}/\mathrm{K}$,[30] the observed expansion would be associated with a 1130 K temperature increase if it were thermally induced. This temperature is above the melting point of any known Ge-Se crystalline phase, and it can therefore be safely concluded that the effect does not have a thermal origin.

We now examine the sharp composition dependence observed for the photostructural changes. The effects described above are particularly large and easy to observed in fragile glasses but are, in contrast, very small in strong glasses. Figure 6(b) shows that photoexpansion becomes very large for the fragile $GeSe_9$ composition, while it is comparatively more than four times smaller for the strong composition $GeSe_4$. Moreover, the calorimetric signature of photoexpansion is so small in $GeSe_4$ that it could not be positively detected within the resolution limit of the MDSC on a thin slab sample (Fig. 5). It appears that strong glass compositions are resistant to photostructural alteration in a similar way as they are resistant to thermal degradation,[31,32] i.e., strong glasses display very small change in heat capacity as they pass through the glass transition while in contrast fragile compositions display a large jump in heat capacity when they become fluid.[31,33] Large changes in heat capacity are associated with the glass ability to undergo extensive structural rearrangements. This correlation between the photoexcited state and thermally excited state is also supported by the similarity between the structure of a-Se under photoexcitation and that of liquid selenium observed by extended x-ray absorption fine structure analysis.[34] It then seems justifiable to describe the composition dependence of photostructural change in terms of potential energy hypersurface by analogy to the composition-dependence description of thermally induced structural changes.[35,36] Amorphous chalcogenide structures lend themselves to this theoretical treatment because the number of minima on the potential energy surface correlates with the number of covalent bond and angular constraints and consequently with the average coordination number $\langle r \rangle$ and fragility. Within this formalism, photoinduced fragile fluids have high density of configurational states and can explore a rich energy landscape. This results in a larger rate of change of configurational entropy S_c for a given degree of excitation. This allow for the photoinduced entropy increase from state ③ to state ② in Fig. 2 as well as the large photoexpansion shown in Fig. 6(b). On the other end of the fragility spectrum, the strong composition $GeSe_4$ is associated with an energy landscape having very few minima and therefore very few configurational states to sample. Consequently, under equivalent photoexcitation, the strong glass produces very small structural changes. In other words, the photoelectronic excitation process, which produces transient bonds,[34] and electron spin resonance active[37] and VAP defects[38] in the glass structure, only leads to a net change if the photoexcited structural units can undergo rearrangement into a different configuration before they decay back to stable structural states. The three-dimensionally connected networks of strong glasses are very resilient to such rearrangement (fewer minima to explore) and therefore undergo small photoinduced changes. Hence, the structural implications associated with the fragility classification of glass-forming liquids seem to be applicable to describe photoinduced phenomena.

Finally, we examine the difference in power dependence between the three photostructural effects illustrated in Figs. 6(a)–6(c). It appears clearly that photoexpansion, photodarkening, and photorelaxation have distinct power dependence. Photodarkening increase linearly with power, while photoexpansion has an exponential dependence and photorelaxation displays a maximum at around $2.5\ \mathrm{mW/cm^2}$. Moreover, these three effects were also shown to follow distinct kinetics under subbandgap irradiation. Tanaka demonstrated that As_2S_3 irradiated with a 2.0 eV He-Ne laser showed one order of magnitude difference in kinetic between photodarkening and photoexpansion.[39] Additionally, Schardt *et al.* reported almost two orders of magnitude difference in kinetics between photodarkening and photorelaxation in $GeSe_9$.[13] It should be noted here that the present work and Ref. 13 report the *in situ* photodarkening[40] while Tanaka reports the permanent photodarkening.[39] Nevertheless, the large differences in both power dependence and kinetic of the three photoinduced effects clearly demonstrate that they do not arise from the same photostructural event and that the mechanisms leading to these phenomena are distinct. While the origin of all photostructural change is understood to be the photoexcitation of localized lone pair states, the structural event that follows appear to be quite complex and also to depend on the properties of the glass structure. However, since all the effects appear to happen simultaneously, they must each represent a contribution to the overall mechanism and consequently, a measure of each effect can be seen as a probe of different steps or contributions to the full mechanism. Hence, a simultaneous probing of each photoinduced effect should provide a powerful means of improving our general understanding of photostructural changes.

V. CONCLUSION

A detailed calorimetric study of photosensitivity in Ge-Se glass reveals that the photomodified glass structure corresponds to an intermediary entropy state that can be reached either by introducing entropy in a fully relaxed glass or decreasing the residual entropy of a fresh glass. This state appears to be the result of an equilibrium between competitive contribution from the photorelaxation and photoexpansion effects. It is shown that optimally interconnected structures such as that of the strong glassformer $GeSe_4$ undergo minimal photostructural change. This compositional trend is observed for photorelaxation and photoexpansion, but is expected to be followed by any photoactuated phenomenon that involves significant structural rearrangement. Such resistance of strong glass networks to photostructural deformation is reminiscent of their resistance to thermal degradation and can be explained on the basis of the number of energy minima associated with configurational states available on the potential energy hypersurface. It is also shown that various photostructural effects have distinct power dependence as well as distinct kinetics. This suggest that the observed effects correspond to individual component of the overall photosensitive process. It might then be possible to enhance particular effects through kinetic or compositional selectivity and optimize the optical processing methods that capitalize on photostructural changes such as holographic recording or waveguide direct writing.

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