Origin of photoelastic phenomena in Ge-Se network glasses

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The elastic properties of a series of Ge-Se glasses are measured during irradiation with sub-band-gap light using a laser-induced transient grating method. The elastic modulus is found to decrease prominently with increasing irradiation intensity. The process is found to be less prominent in glasses of high average coordination $\langle r \rangle$. Measured kinetics in the millisecond range are found to be too slow for a photoinduced electronic process and instead suggest a thermal origin. Infrared thermography is performed during irradiation to monitor temperature changes during photodarkening, photoexpansion, and photoelastic measurements. It is found that in the conditions of irradiation where photoelasticity is observed, all photostructural changes are directly associated with a change in temperature. COMSOL modeling of thermal flow through the sample closely reproduces the kinetics of photodarkening. Transient grating measurements as a function of temperature confirm that the change in elasticity during irradiation is essentially a thermally induced process. Currently available experimental evidence indicates that the photoelastic phenomena are not an optoelectronic process but rather the result of laser heating.

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I. INTRODUCTION

Spatial patterning and/or temporal modulation of elastic properties are key to the realization of acoustic and phononic structures for controlling the propagation of sound and elastic waves [1,2]. On-demand reversible creation of such patterns and modulations in solid substrates would permit the development of passive and/or active bulk or surface acoustic wave devices that could transform wireless communications and medical imaging [3,4]. A robust control of elastic constants through optical actuation would provide an ideal platform for practical implementation of such spatial patterns and/or temporal modulations. Within that context, chalcogenide glasses emerge as materials of interest due to their large photosensitivity under illumination with light wavelengths matching their band-gap energy [5–10]. In these glasses, photostructural effects manifest themselves through large changes in multiple physical properties, including density [5], refractive index [6], viscosity [7], absorption coefficient [8], or conductivity [9]. In addition, these phenomena are usually fully reversible upon light removal [7,9,10]. The ability to reversibly control the elastic constant through similar photostructural processes would therefore provide an invaluable tool for designing novel acoustic wave devices.

As proposed by He and Thorpe [11], the elastic moduli of chalcogenide glasses are determined by the density of covalent bonds in the amorphous network. In principle, the ability to locally break covalent bonds through photoexcitation of valence electrons [12] could be used to tune the bond density (and in turn the elastic constants) optically through targeted laser irradiation. Several research groups have investigated photoelastic processes in chalcogenide glasses [13,14]; however, the results they report are in disagreement. Tanaka *et al.* [13] measured the propagation of surface acoustic waves (SAW) in As_2S_3 films and observed a minute and slow photoelastic process in annealed samples irradiated with a mercury lamp. On the other hand Gump *et al.* [14] estimated the elastic constant of Ge-Se glasses from Brillouin scattering and observed a very large (∼50%) photoelastic effect under high-intensity irradiation with a focused laser beam at a wavelength of 647 nm. Gump *et al.* reported that the giant softening of Ge-Se glasses under irradiation with 647-nm laser light was predominantly athermal, with only 10% of the observed softening attributed to thermal effects. While Tanaka reported monotonic elasticity changes of amorphous As_2S_3 films, the timescale of the large and reversible changes in elasticity of Ge-Se under sub-band-gap irradiation was not investigated by Gump *et al.* In that later study, the 647-nm laser was both the probe and the source of the reported change. The near absence of photoelasticity in As_2S_3 glass compared to the large photoelastic response of Ge-Se glass raises the question as to the origin of the process since both glass types are known to be strongly photosensitive [7,8,15,16]. Further investigations are therefore needed to elucidate the origin of the photoelastic phenomenon.

In the present study we clarify the origin of the photoelastic process using the laser-induced transient grating (TG) method to independently measure the elastic modulus of a series of Ge-Se glasses under different conditions of irradiation and temperature. Photodarkening and photoexpansion are also measured in similar conditions to assess the extent of

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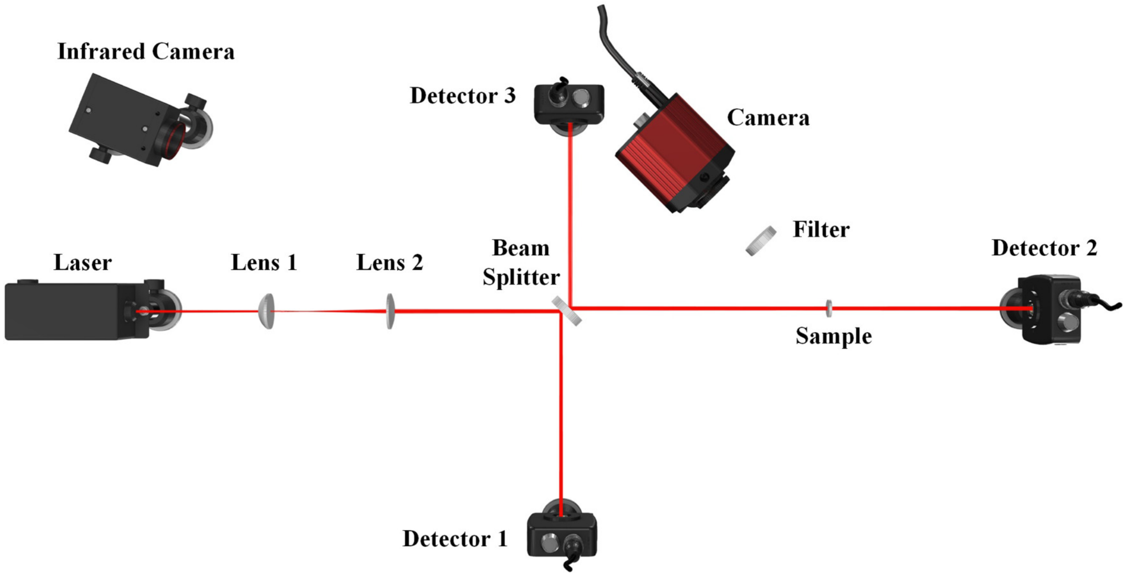

FIG. 1. Experimental setup for simultaneous measurements of transmission, reflection, photoexpansion, and surface temperature distribution of the Ge-Se glasses. A 2.5× beam expander made of lens 1 and lens 2 generates an incident beam dimeter of 2.1 mm. A spectral filter was applied in front of the camera to block the light of the laser wavelength.

photostructural changes. Furthermore, local changes in temperature are monitored simultaneously by infrared thermography. It is found that the origin of the change in elasticity is mainly of thermal origin and is not the result of photostructural processes. These results also draw attention to the potential thermal contribution of other photostructural changes such as photoexpansion and photodarkening upon high-intensity irradiation.

II. EXPERIMENT

A. Samples preparation and irradiation

Glasses from the Ge-Se system were selected for this study. The Ge-Se system offers a broad glass-forming range. This allows the synthesis of samples covering a wide range of bond density in the amorphous covalent network. Glasses of composition $Ge_{10}Se_{90}$, $Ge_{12.5}Se_{87.5}$, $Ge_{15}Se_{85}$, $Ge_{17.5}Se_{87.5}$, $Ge_{20}Se_{80}$, $Ge_{25}Se_{75}$, and $Ge_{30}Se_{70}$ (at. %) corresponding to an average coordination number $\langle r \rangle = 2.2, 2.25, 2.3, 2.35, 2.4, 2.45$, and 2.5, respectively, were synthesized from 5N high-purity elements using a high-vacuum technique previously described in detail [17]. After quenching and annealing 10 °C below the glass transition temperature T_g, the glass rods were sliced into disks of thickness 1–2 mm and polished on both sides with 0.05-μm alumina powder suspension. Samples were coated with a 400-nm-thick Al film on one side using physical vapor deposition for TG measurements and with a kapton film for thermography measurements. Samples used for photodarkening and photoexpansion measurements were left bare.

Photostructural effects were induced in the bulk of the Ge-Se glasses using a laser source of wavelength 810 nm corresponding to sub-band-gap energy for which all glasses have a low absorption coefficient $\alpha \approx 1\,\mathrm{cm}^{-1}$ (Fig. S1 of the Supplemental Material [18]). At this wavelength, all samples have >90% transmission (not including reflection). These conditions induce photoexcitation of valence electrons throughout the bulk of the glass such that the change in elasticity can be measured on the top surface while irradiating the back surface. Photodarkening, photoexpansion, and temperature changes were monitored simultaneously using the experimental setup described in Fig. 1. For photodarkening, the incident beam intensity was monitored using a beam splitter and detector 1, while the transmitted intensity and reflected intensity were measured on detector 2 and 3, respectively. Photoexpansion was monitored qualitatively using digital microscope imaging. Temperature was monitored using infrared thermography as described below.

B. Transient grating method

The TG method was used to provide an independent measure of elasticity during irradiation of Ge-Se samples. The TG method employs a picosecond pulsed laser for excitation (with a wavelength of 532 nm, pulse duration of 430 ps, and 1-kHz pulse repetition rate) and a continuous-wave laser as the probe (with a 514-nm wavelength and average power of 10 mW). The pulsed laser is split and recombined on the aluminum surface film by focusing to a 500-μm-diameter spot to produce a spatially periodic interference pattern [19,20] (Fig. 2).

Absorption of the laser light by the aluminum film induces rapid thermal expansion, which leads to the generation of a surface acoustic wave of wavelength λ_{ac} corresponding to the period of the interference pattern. The probe beam is focused at the center of the interference fringe pattern to a 300-μm-diameter spot and is diffracted by ripples induced by the surface acoustic wave. The diffracted probe light is superimposed with an attenuated reference beam and is directed to a fast silicon avalanche photodiode and recorded using a digital oscilloscope. The high-frequency oscillations in the temporal signal [Fig. 3(a)] are associated with

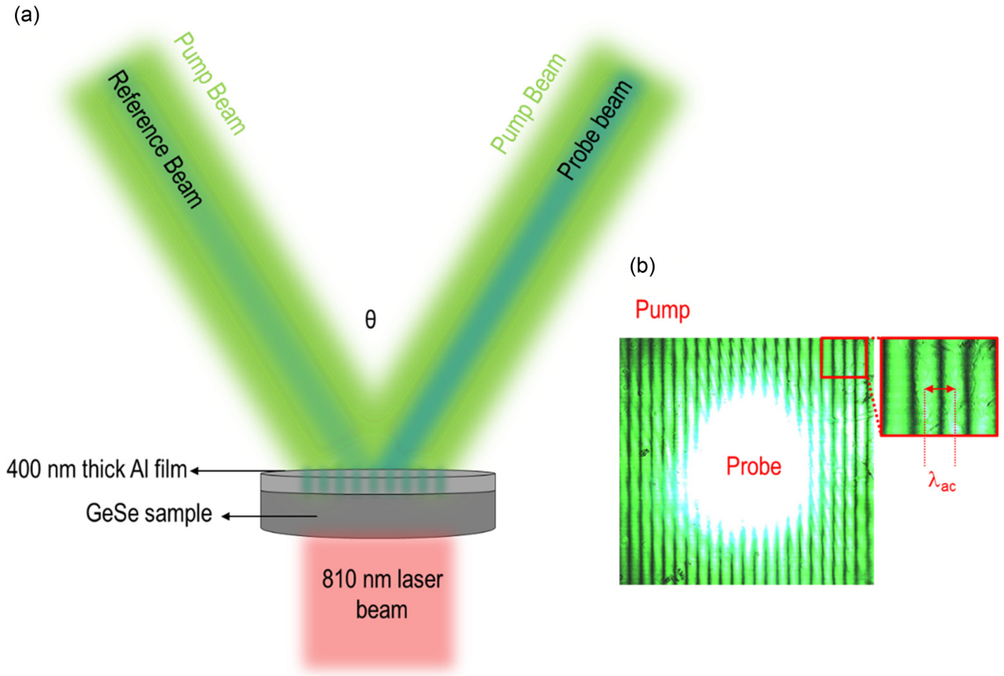

FIG. 2. (a) Schematic of the TG method used to measure change in elasticity during irradiation of Ge-Se glass. (b) Image of the interference fringe pattern created by the pump laser beams used to generate surface acoustic waves.

propagating surface acoustic waves, also referred to as Rayleigh waves. The Fourier spectrum of the acoustic oscillations in the temporal signal shows a single peak at the frequency of the Rayleigh wave [Fig. 3(b)]. This process is repeated for several acoustic wavelengths to produce a dispersion curve by changing the crossing angle θ between the incident excitation laser beams [Fig. 3(c)]. The slope of this curve corresponds to the Rayleigh wave speed v_R and yields

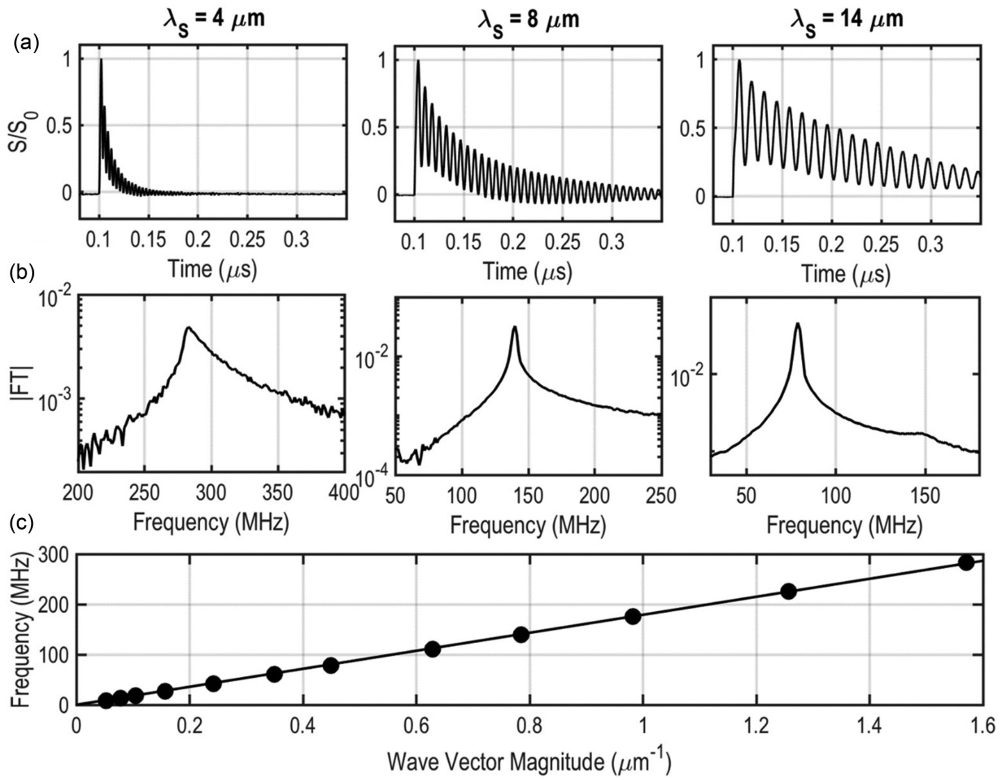

FIG. 3. (a) Surface wave oscillation measured in $GeSe_4$ at different SAW wavelength λ_s using the TG method. (b) The TG signal is Fourier transformed to identify the Rayleigh wave frequency. (c) A plot of frequency vs inverse wavelength yields the wave velocity in the material.

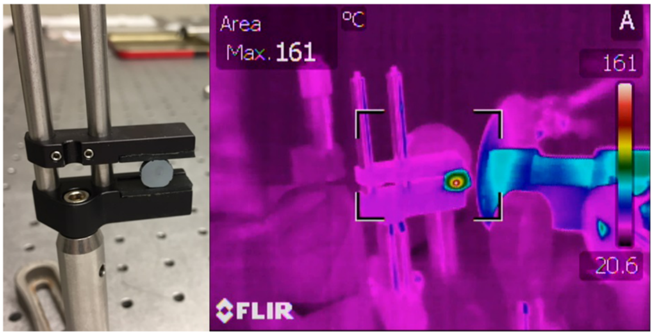

FIG. 4. (Left) Photo of a $GeSe_4$ chalcogenide glass disk mounted on a holder for simultaneous optical and thermal characterization. (Right) Infrared image corresponding to a frame of the movie recorded during irradiation. The temperature indicated corresponds to the maximum temperature of the irradiated spot located within the analysis frame.

the Rayleigh elastic modulus of the propagating medium (chalcogenide glass). We define the Rayleigh modulus M as a measure of the elastic modulus of the chalcogenide glass using the relation $M = \rho v_R^2$. It should be noted that the sound velocities measured this way agreed within ±10% with those reported in the literature [21,22] (Fig. S2 of the Supplemental Material [18]). The same measurement is then performed during back illumination of the chalcogenide glass sample with the 810-nm sub-band-gap laser source to quantify the photoelastic effect (Fig. 2). The spot size of the 810-nm laser was ~5 mm in diameter.

C. Thermography

The maximum temperature reached by the Ge-Se samples during irradiation was measured by thermal imaging using an FLIR T-300 IR camera with a 320 × 240-pixel resolution operating in the 8 to 13 micron range. Figure 4 shows an example of thermography image collected during irradiation of a $GeSe_4$ sample. The recorded temperature corresponds to the maximum temperature reached at the irradiation spot. Due to the low emissivity of bare chalcogenide glass, the front face of the samples was coated with a polyimide (kapton) film in order to maximize the measurement resolution. The emissivity of polyimide-coated Ge-Se samples was calibrated using a hot plate and a thermocouple from 20 to 90 °C. The emissivity value of the samples under test was tuned through the camera software until the temperature detected via IR camera was the same as the temperature of the hot plate. The temperature calibration curves collected for $GeSe_4$ and $GeSe_9$ using these emissivity values are shown in Fig. 5 and indicate an accuracy within ~1 °C. The calibrated emissivity of polyimide-coated Ge-Se samples was then used to monitor temperature during the photostructural experiments described in Fig. 1.

D. COMSOL simulations

Changes in temperature during irradiation of Ge-Se glasses were also modeled using the heat-transfer module in COMSOL MULTIPHYSICS software. The incident laser intensity profile was assumed to follow a Gaussian distribution. The absorbed energy was converted into thermal energy according to the absorption coefficient of the glass following the Beer-Lambert law. The differential form of the light intensity I is described as

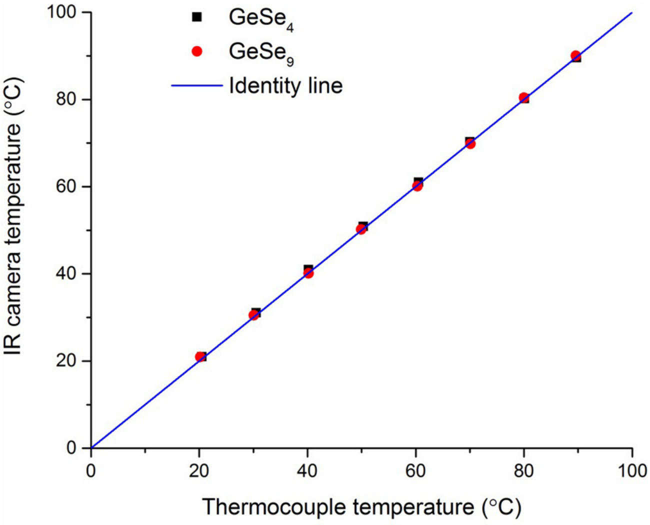

FIG. 5. Calibration curve showing the correlation between the temperatures measured by thermography and measured using a thermocouple for Ge-Se glasses coated with a polyimide film.

$$\frac{\partial I}{\partial z} = \alpha(T)I, \tag{1}$$

where z is the coordinate along the beam direction and $\alpha(T)$ is the temperature-dependent absorption coefficient of the sample measured as described in Sec. III C. The governing differential equation for temperature distribution within the sample is solved as follows:

$$\rho C_p \frac{\partial T}{\partial t} - \nabla(k\nabla T) = Q = \alpha(T)I, \tag{2}$$

where Q is the heat source term and equals the absorbed light, C_p is the heat capacity, ρ is the density, and k is the thermal conductivity. These two equations present a bidirectional coupled multiphysics problem that is well suited for modeling within the heat-transfer module of COMSOL MULTIPHYSICS using the parameters listed in Table I.

III. RESULTS

A. Laser-induced change in elasticity as a function of power and composition

The change in the elastic Rayleigh modulus of each Ge-Se glass was measured using the TG method during irradiation at increasing power. As shown in Fig. 6(a), the shift of the Rayleigh frequency was monitored while the 810-nm laser power was increased from 0 to 800 mW for each acoustic wavelength. As depicted in Fig. 6(b), the slope of the resulting dispersion curve decreases as a function of laser power, indicating a decrease in sound velocity with increasing power.

The measurements were repeated on glass compositions across the whole Ge-Se system and the corresponding change in Rayleigh elastic modulus was then calculated from the

TABLE I. Parameters used for the COMSOL MULTIPHYSICS simulation of temperature profiles during irradiation of Ge-Se glasses.

Material	Diameter (mm)	Thickness (mm)	Density (kg/m^3)	Heat capacity (J/kg/K)	Thermal conductivity (W/m/K)
$GeSe_4$	6.05	1.33	4329	300	0.2
$GeSe_9$	6.09	2.09	4355	330	0.2

density (which is assumed to be constant as a first approximation) for each glass as shown in Fig. 7. Glasses with increasing Ge contents have an increasing bond density as quantified by the average coordination number $\langle r\rangle$ defined as the product of the valence and atomic fraction of each atom in the glass [11]. The results shown in Fig. 7(a) indicate that highly reticulated glassy network with high bond density exhibit lower change in elasticity with increasing laser power. The correlation between $\langle r\rangle$ and the elasticity change is shown in Fig. 7(b) for a constant irradiation power of 280 mW. It is observed that the change in elastic modulus upon irradiation drops rapidly as the bond density increases in the glass. This behavior is consistent with the model of photoelasticity proposed by He and Thorpe [11] since a greater fraction of intact bonds would remain in the highly coordinated glasses despite a finite number of photoinduced bond excitation during irradiation, thereby dampening the change in elastic modulus. The observed trend may also be affected by the slight decrease in absorption coefficient with $\langle r\rangle$. However, it should also be noted that the glass transition temperature of Ge-Se glasses increases rapidly with $\langle r\rangle$ [23]; hence, any change in elasticity induced through thermal contributions would also be likely dampened at high $\langle r\rangle$ values.

B. Kinetics of laser-induced elastic change

Rapid changes of elastic properties would be a key requirement for achieving effective temporal modulation of the elastic modulus of elastic wave-supporting media and devices. Changes in elasticity induced by photoexcitation are expected to decay very rapidly as it is believed to be a purely electronic process. Excitation lifetimes are expected to be in the nanosecond range in amorphous semiconductors [24,25]. Hence, in order to determine whether the process exhibits rapid decay, a TG measurement was performed by modulating the intensity of the 810-nm laser beam using a diffraction-based reflective optical chopper to rapidly turn the irradiation on and off. The optical setup is described in Fig. 8(a) and illustrates how the successive TG measurements are performed during irradiation and shortly after irradiation is turned off. The results shown in Fig. 8(b) indicate that the elastic Rayleigh modulus shows no significant change when

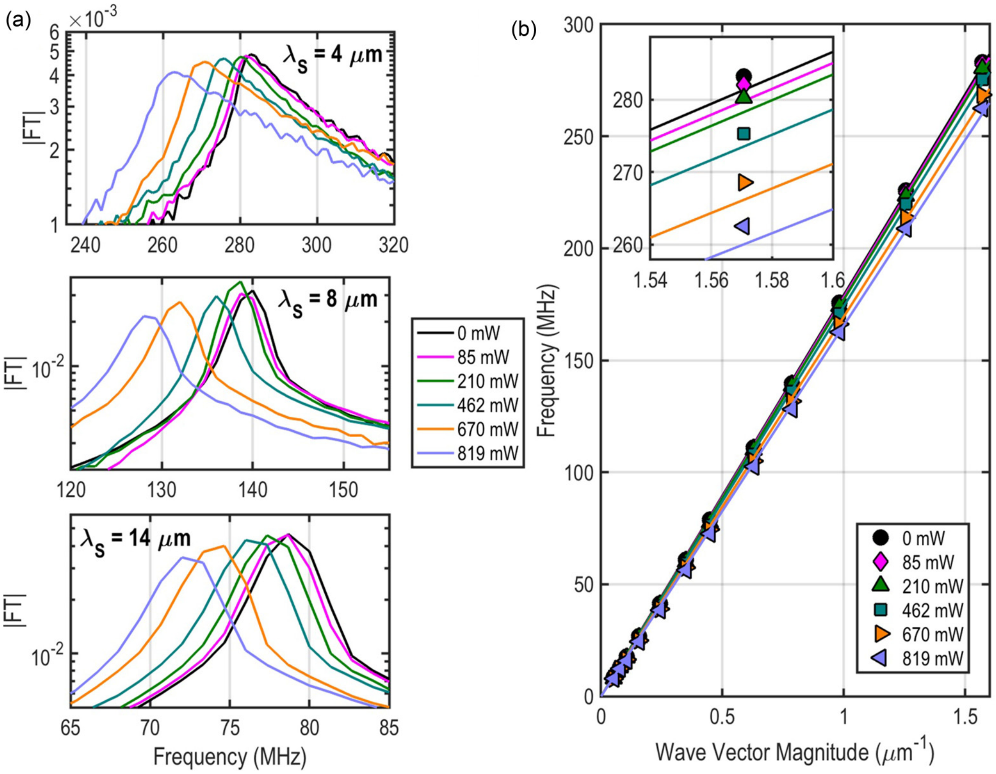

FIG. 6. TG measurement as a function of irradiation power in Ge-Se glass. (a) Shift in Rayleigh wave frequency with increasing irradiation power at different λ_s. (b) Dispersion curve showing the change in Rayleigh wave velocity (slope) as a function of irradiation power. The solid line denotes a linear best fit through the measured data points.

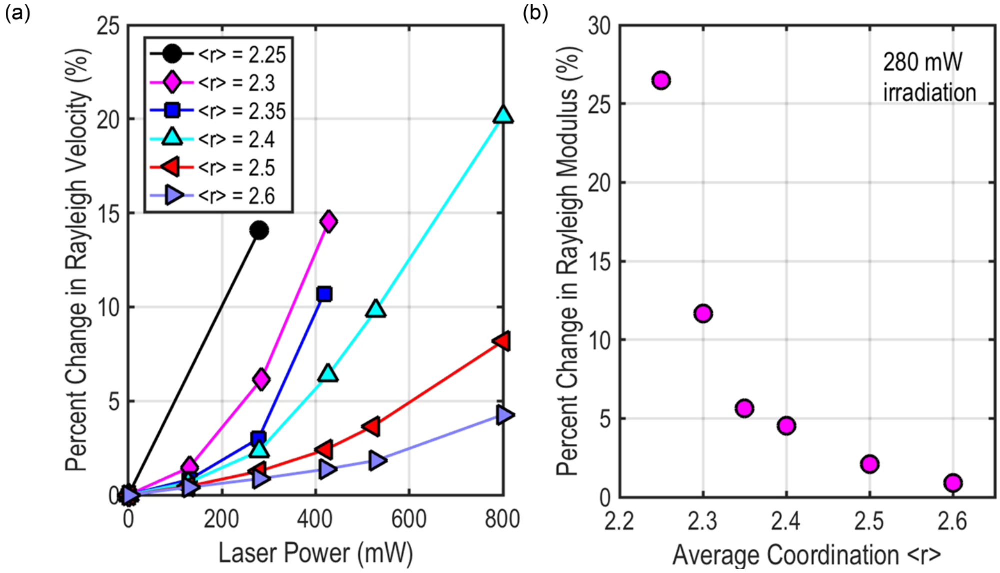

FIG. 7. Change in the Rayleigh elastic modulus with laser power for glasses across the Ge-Se system. (a) Percent change in Rayleigh wave velocity as a function of laser power for each glass composition. (b) Percent change in Rayleigh elastic modulus during irradiation with a power of 280 mW as a function of increasing bond density $\langle r \rangle$ in the glass.

the light is turned off after ∼0.1 ms. Further measurements with time delays of several milliseconds also showed minute changes. If the photoelastic process was only induced by electronic excitation, lifetimes in the range of nanoseconds would be expected, yet the observed lifetimes are more than four orders of magnitude longer. These results indicate that the light-induced elastic change observed by TG is too slow to be purely of electronic origin. This suggests that the change in elastic constant during irradiation could instead have a thermal origin.

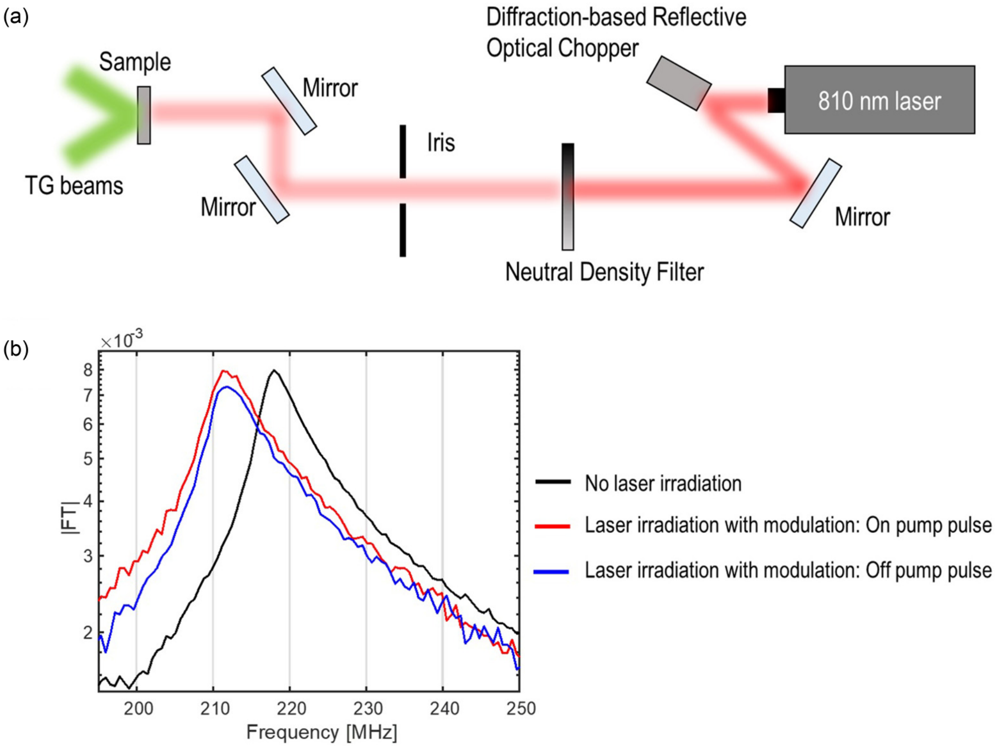

FIG. 8. TG measurement of elastic constant during rapid modulation of irradiation on and off using a diffraction-based optical chopper. (a) Optical setup. (b) Rayleigh wave frequency before irradiation (black line), during irradiation (red line), and 0.1 ms after turning off the irradiation (blue line).

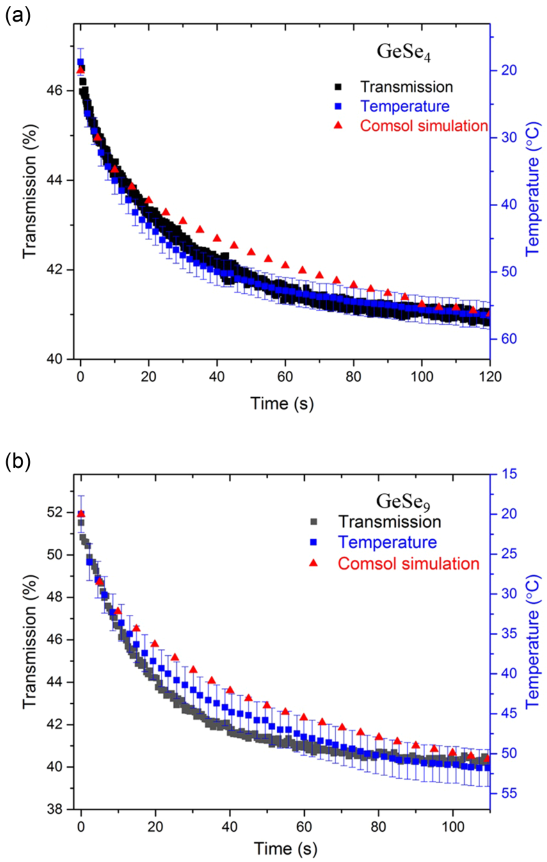

FIG. 9. Simultaneous change in transmission and temperature measured experimentally during laser irradiation with an intensity of 4.33 W/cm^2 in (a) GeSe$_4$ glass, and (b) GeSe$_9$ glass, compared with the corresponding change in transmission predicted by COMSOL simulation.

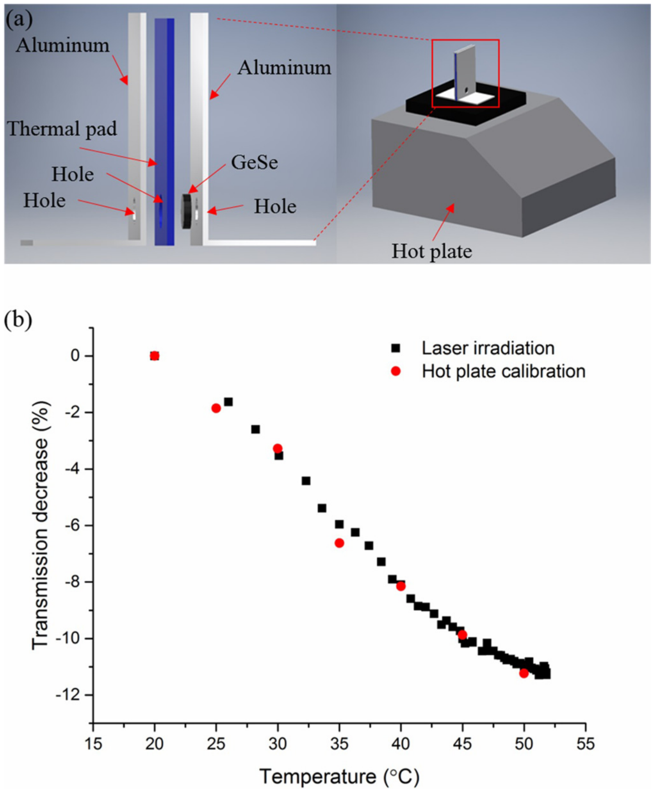

FIG. 10. (a) Experimental setup used to measure the change in transmission of Ge-Se glass disks as a function of temperature on a calibrated hot plate. (b) Decrease in transmission as a function of temperature for a GeSe$_9$ sample when the sample is heated on a hot plate compared to the change in transmission of the same sample with temperature measured by thermography under laser irradiation with an intensity of 4.33 W/cm^2.

C. Thermal characterization of photostructural changes in Ge-Se glass

Photostructural effects in Ge-Se glasses have been previously studied under low irradiation intensity and show the characteristics of athermal processes such as Bragg reflections at the irradiation wavelength [26]. But, while most photostructural effects in chalcogenide glasses are known to be athermal, the results of Sec. III B raise concern that a thermal contribution may be at play in the present case. Hence, in order to characterize a possible change in temperature during irradiation in similar conditions to the TG measurements and its contribution to photostructural changes, thermography was performed during irradiation using an infrared camera, simultaneously with measurements of transmission (photodarkening) and volume change (photoexpansion) as described in Sec. II.

D. Photodarkening

The results of simultaneous thermal and photodarkening measurements for GeSe$_4$ and GeSe$_9$ are shown in Figs. 9(a) and 9(b), respectively. Fig. 9 indicates that the change in transmission is concomitant with a temperature increase and that both phenomena follow an identical kinetic within measurement error. Changes in reflection during that measurement were negligible ($<0.1\%$) as shown in Fig. S3 of the Supplemental Material [18], thereby confirming that no surface damage occurred during the measurement and that the process involves a change in absorption coefficient rather than a large change in refractive index. The fact that the kinetics of the two processes shown in Fig. 9 nearly superimpose strongly suggests that the principal contribution to the photodarkening in these irradiation conditions may be thermal. Indeed, it is expected that the band gap of chalcogenide glasses reduces with increasing temperature, thereby leading to higher absorption [27].

In order to quantitatively confirm that the increases in absorption are consistent with an increase in temperature, the change in transmission was measured while heating the Ge-Se samples on a hot plate as shown in Fig. 10. The sample was sandwiched between two aluminum plates and imbedded in a thermally conductive layer to ensure homogeneous temperature distribution [Fig. 10(a)]. The results reported in Fig. 10(b) confirm that the transmission decreases nearly linearly with increasing temperature. The change in transmission induced by heating from the hot plate is then compared to the change in transmission induced by laser heating during the photodarkening experiment. The two changes in transmission closely overlap as shown in Fig. 10(b) for the GeSe$_9$ sample. The same behavior is observed for GeSe$_4$ glass as shown in

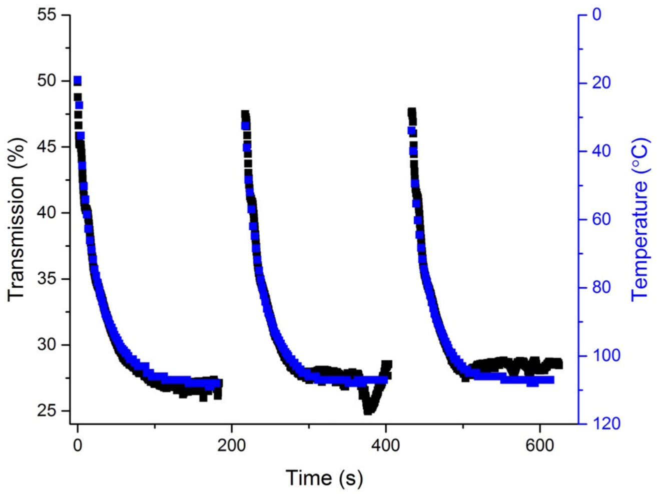

FIG. 11. Correlation between photodarkening recovery and temperature change over several cycles of light on and off in $GeSe_4$.

Fig. S4 of the Supplemental Material [18]. This confirms that the laser-induced change in transmission is quantitatively consistent with a change in temperature. Furthermore, the kinetic of laser-induced darkening was simulated with COMSOL using the temperature-dependent change in absorption derived from the hot-plate measurements. The results shown in Fig. 9 indicate that the thermal model reproduces well the experimental photodarkening data. Overall, these results unambiguously demonstrate that the darkening observed in Fig. 9 is mainly of thermal origin.

The correlation between laser heating and photodarkening was further investigated by measuring the kinetics of the two processes during dark recovery. Figure 11 shows the correlation between temperature and photodarkening when the light is turned off and the photodarkening recovers over time. The close match between temperature and transmission over multiple cycles further confirm the correlation between laser heating and photodarkening.

E. Photoexpansion

The change in volume commonly associated with photoexpansion was also monitored simultaneously with thermographic temperature measurements and photodarkening. Microscope images collected during the irradiation process are shown in Fig. 12(a) along with the temperature change and photodarkening for a $GeSe_9$ sample. A volume change in the region of irradiation becomes clearly visible when the

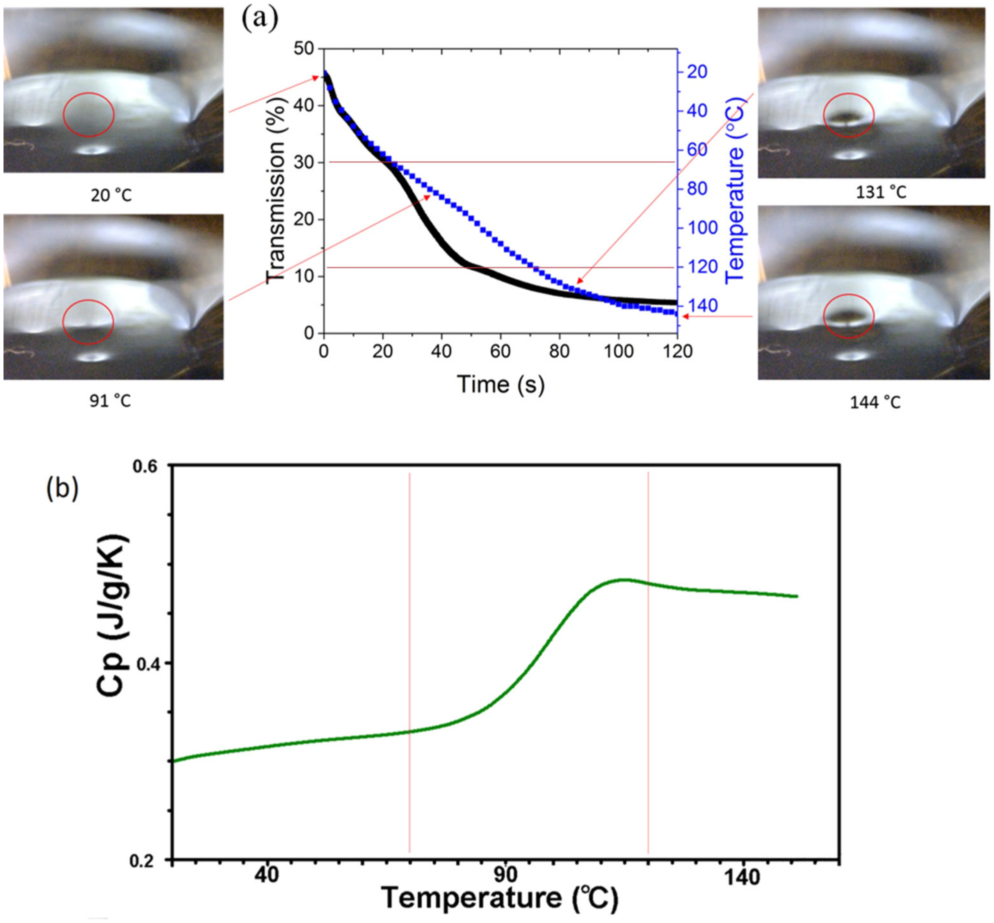

FIG. 12. (a) Correlation between photodarkening, temperature change, and photoexpansion monitored by optical microscopy during irradiation of a $GeSe_9$ glass with a power density of $9.15\,\mathrm{W/cm^2}$. (b) Specific-heat capacity C_p of $GeSe_9$ measured by DSC as a function of temperature in the glass transition range. The onset of photoexpansion correlates with the onset of the glass transition measured by DSC where the glass becomes a supercooled liquid.

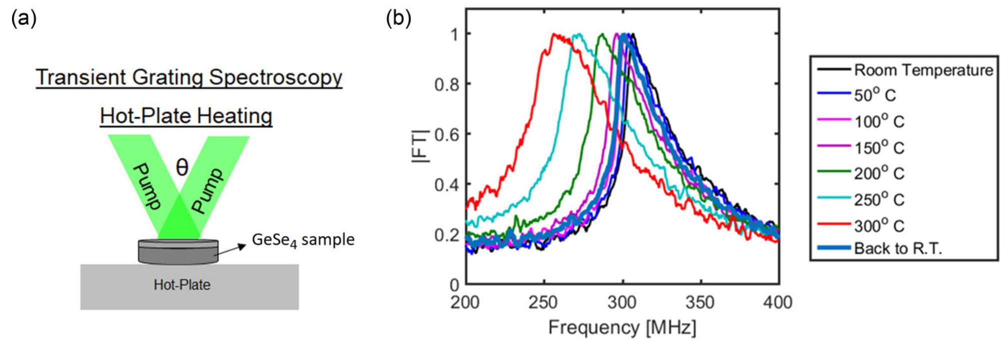

FIG. 13. TG measurement of elastic constant during temperature change on a hot plate. (a) Schematic of the experimental setup. (b) Rayleigh frequency shift with hot-plate temperature.

temperature reaches the onset of the glass transition region near 70 °C. The volume change becomes more prominent as the temperature increases across the glass transition as confirmed by the differential scanning calorimetry (DSC) measurement in Fig. 12(b). The surface profile measured by profilometry after photoexpansion exhibits a Gaussian shape with a diameter equal to that of the laser beam (Fig. S5 of the Supplemental Material [18]). As shown in Fig. 12(a), the change in surface profile also leads to a sudden drop in measured transmitted intensity most likely associated with a defocusing of the transmitted beam. The beam reflectivity exhibits a similar sudden drop due to the surface deformation as shown in Fig. S6 of the Supplemental Material [18] for a $GeSe_4$ sample. The systematic match between the onset of the glass transition and the onset of surface deformation in both glass compositions clearly indicates that the volume change observed in these conditions of irradiation is also of thermal origin. Finally, it should be pointed out that the Rayleigh velocity is inversely proportional to the density; hence, the observed expansion should in principle lead to an increase in Rayleigh velocity. Yet the results of Figs. 6 and 7 show a systematic decrease in Rayleigh velocity under irradiation. Hence, the small volume change during photoexpansion is expected to have minimal effect in comparison to the thermal contribution of reduction in the elastic modulus.

F. Thermal origin of photo-elastic change

Photodarkening and photoexpansion measurements as a function of temperature indicate that photostructural changes in Ge-Se appear to be thermally induced in the condition of irradiation where photoelastic change were previously observed. It is therefore expected that photoelastic effects may also have a large thermal component. In order to investigate the contribution of temperature to the photoelastic effect, the change in elasticity as a function of temperature was measured using TG on a $GeSe_4$ sample heated on a hot plate, as shown in the setup of Fig. 13(a). Thermally conductive tape was used as a contact layer between the $GeSe_4$ glass and the hot-plate heating surface. Figure 13(b) shows that the Rayleigh frequency shifts notably with increasing temperature. The corresponding change in Rayleigh speed is plotted as a function of temperature in Fig. 14.

In order to quantify the temperature change during measurement of the elastic constant induced by laser irradiation, infrared thermography measurements were performed on the $GeSe_4$ sample during the TG measurement under irradiation performed following the setup of Fig. 2. The results shown in Fig. 14 indicate a good correlation between the change in elasticity due to laser heating and hot-plate heating. Hence, in the same way as for photodarkening and photoexpansion, the change in elasticity due to irradiation can be ascribed to laser heating rather than an electronic process. This result is consistent with the slow kinetic observed in Sec. III B.

IV. DISCUSSION

A. Photoelasticity in chalcogenide glasses

The results of Sec. III lead to the conclusion that the photoelastic effect in chalcogenide glasses is primarily of thermal origin and is not an optically induced electronic process. To be precise, the laser irradiation does induce excitation of valence electrons but this process results in energy transfer through phonon coupling and heat creation rather than a change in elasticity due to bond breaking. It is informative to compare the conditions of irradiation of the present study with that of

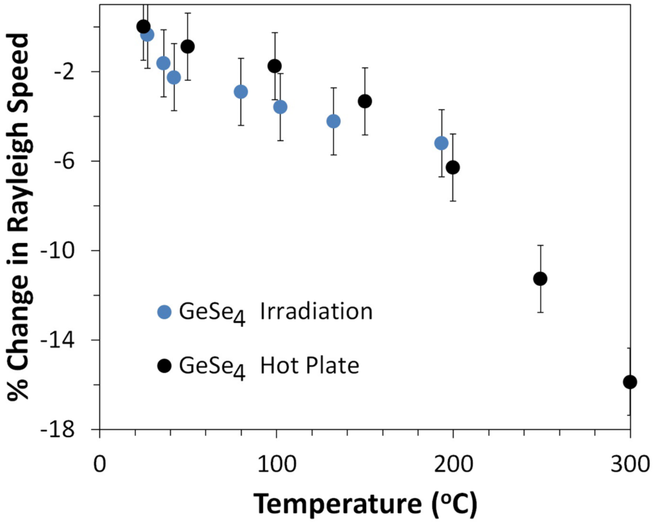

FIG. 14. Percent change in Rayleigh wave velocity of $GeSe_4$ during temperature change when the sample is heated on a hot plate compared to the change in Rayleigh wave velocity of the same sample during change in temperature measured by thermography under laser irradiation. The similarity in trend confirms that the laser-induced change in elasticity has a thermal origin.

previous reports of photoelasticity in the literature. Previous measurements by Gump *et al.* [14]. were performed with a 647-nm laser beam focused to a 50-μm spot size with a power of 1 to 6 mW on the same glass series as the present study. These conditions correspond to an intensity of 50 to 300 $\mathrm{W/cm^2}$ with an absorption of $\sim$100% (Fig. S1 of the Supplemental Material [18]) compared to 9.15 $\mathrm{W/cm^2}$ and an absorption $<$10% in the present study. In other words, the energy deposition rate of Gump *et al.* is at least two orders of magnitude larger than the rate which melts both glasses in this study. This clearly indicates that the measurements of Gump *et al.* are performed on the liquid rather than the glassy state. The process is therefore clearly not an optically induced one and must be mostly of thermal origin.

In comparison, Tanaka *et al.* [13]. observed a minute and slow decrease in sound velocity during long-term irradiation of an annealed glass with a low-intensity mercury lamp. The small effect observed here is fully consistent with photoinduced relaxation. The effect of photorelaxation in chalcogenide glasses has been extensively investigated both in terms of volume and enthalpy relaxation [16,28,29]. It is indeed expected that low-intensity irradiation will lead to contraction even in an annealed glass, due to the high fictive temperature of the glass relative to the irradiation temperature [29]. When provided with enough structural degrees of freedom the glass will evolve towards thermal equilibrium, in this case towards a higher density. This in turn would lead to a decrease in sound velocity. This process is small and slow, consistent with the change observed by Tanaka *et al.* [13]. This further supports the conclusion that photoelasticity is not an optically induced electronic process, but rather the result of thermal changes ancillary to laser irradiation. This work demonstrates that there is no experimental evidence that irradiation of chalcogenide glasses can lead to an athermal change in elasticity. The term photoelasticity rather appears to be a misnomer since it is not associated with a light-induced process.

B. Thermal effects during photostructural changes

While the present study shows that photoelasticity results from heating, there is ample and unambiguous evidence that most photostructural changes in chalcogenide glasses are not thermally induced but are indeed optically induced. For example, irradiation of glass flakes [30] and films [10] leads to reversible expansion or contraction in the direction of the light polarization. Hence, photoexpansion is undeniably a photoinduced effect and it is also known to be more pronounced at lower temperature contrary to expectations if it were thermally induced [5]. Similarly, irradiation of bulk glass or films with monochromatic light leads to the inscription of a periodic index pattern creating a Bragg reflector at the irradiation wavelength [31,32]. Hence, photorefraction is also undeniably a photoinduced effect and it is also known to be polarization dependent [33]. Finally, sub-band-gap irradiation of glass fibers and flakes [7] leads to a decrease in viscosity that is more pronounced with decreasing temperature. The photofluidity process can also be observed at room temperature under fluorescent bulb exposure [15]. Hence, photofluidity is also unambiguously a light-induced effect.

But, while there is much evidence that photostructural changes in chalcogenide glasses are athermal, the results of Sec. III B should raise awareness of the potential for a significant thermal contribution when high-intensity irradiation is used to induce effects such as photodarkening and photoexpansion. For example, structural changes observed in Ge-Se glasses irradiated with fully absorbed laser light at wavelength 514 nm and power of 24 W/cm [2] are most likely the result of thermal effects rather than photostructural changes [34]. Similarly, surface grating formation on As-S glasses using fully absorbed laser light at wavelength 514 nm and power of 200 $\mathrm{W/cm^2}$ is likely to be associated with thermal effects rather than photodarkening [35]. Even polarization-dependent effects such as optical field-induced mass transport [36] may be largely aided by thermal effects. Indeed, these effects are not observed at low power but become prominent when powers up to 110 W/cm [2] of fully absorbed laser light (514 nm) are used to irradiate As_2S_3 films. Considering that the glass transition temperature of As_2S_3 ($T_g \sim 200$ °C) is comparable to that of GeSe4 ($T_g \sim 160$ °C) from the present study, it is likely that the As_2S_3 glass has reached a temperature above its T_g and that thermally induced fluidity provides the necessary degrees of freedom to induce a measurable response to the optical torque. Hence, the process likely results from a combination of thermal and optical effects.

V. CONCLUSION

Photostructural changes in chalcogenide glasses have received much attention over the last 40 y due to their fundamental and technological interest. A very rich set of effects have been reported including scalar and vector changes. These processes have important technological implications from lithography to optical microfabrication of photonic devices. Optically induced changes in elasticity are also of much interest for the development of new bulk and surface acoustic wave devices that can be either spatially patterned or activated via rapid temporal modulation. However, it is found that the photoelastic process previously reported in chalcogenide glasses does not originate from photoinduced electronic excitation but is rather a thermally induced process with slow kinetics that is not compatible as a temporal modulator with acoustic frequencies used in solid-state acoustic devices. In contrast, the thermally induced change in elasticity is compatible with slow on-demand patterning of acoustic devices. Infrared thermography performed in the course of photodarkening and photoexpansion measurements also emphasize the potential contribution of thermal effect towards photostructural changes. The fine balance between structural changes associated with photoexcitation and the resulting heat dissipation should be carefully considered when interpreting photostructural effects under high-intensity irradiation.

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