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Photoinduced fluidity and viscoelasticity in chalcogenide glasses

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Abstract

This work is an attempt to apply conventional mechanical testing to characterize the photoinduced viscoelastic behavior of chalcogenide glasses. Creep or relaxation-recovery experiments are usually performed to characterize the delayed elastic contribution to deformation, during thermally activated flow. In this paper, relaxation-recovery is used to characterize delayed elasticity under irradiation condition and to investigate the influence of the photon irradiation on the viscoelastic behavior. It is showed that thermally activated processes and photoinduced ones are decoupled. The viscoplastic deformation under irradiation is the sum of thermally activated and photoinduced

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processes. As soon as the irradiation ceases, chalcogenide glasses behave exactly as if they had never been irradiated. The photoinduced viscoelastic behavior seems to be solely due to transient photoinduced structural defects.

1 Introduction

Chalcogenide glasses exhibit a wide range of photoinduced phenomena, from photodarkening to photoinduced-amorphisation [1]. These phenomena have been extensively studied during the last decades [2, 3] because of their potential applications, especially in optics and optoelectronics. Most of the existing models interpret the photoinduced effects through the production of electron-hole pairs as the result of photoexcitation of chalcogenide lone pairs located at the top of the valence band [4, 5, 6]. The most spectacular photoinduced effect is probably the photoinduced fluidity, or "photofluidity", evidenced by Vonwiller [7] hundred years ago. A macroscopic and athermal photofluidity can only be produced by sub-bandgap light, corresponding to a low absorption, as it has been shown by Hisakuni and Tanaka [8, 9]. Photofluidity is considered as a keystone to understand various photo induced phenomena [10, 11]. Although some groups have started to investigate the phenomenon during the last 15 years [12, 13, 14, 15], only a limited number of studies were published on the subject, and the detailed mechanical behavior of glasses under irradiation remains poorly understood. Most of these studies are not focused on the mechanical behavior [13, 16] or at least just on the shear viscosity [8, 9, 14]. The analysis of the viscoelastic behavior, especially under shear stress, is a basis to understand the origin of photomechanical effects, such as photofluidity, photoexpansion or contraction [17]. Our understanding of the thermally activated

viscous flow and the kinetic fragility of glasses is not only based on viscosity measurements, but also on the analysis of the viscoelastic behavior, of the relaxation function or of the corresponding stretched exponent [18, 19, 20]. It is straightforward that similar analysis are required to understand photoinduced mechanical effects.

Glasses are viscoelastic bodies above, as well as below their glass transition temperature (T_g) , even if, below T_g , the characteristic time of this behavior becomes very high, actually so high that, at the human scale, glasses can be considered as pure elastic bodies. Nevertheless, when glasses have a large fictive temperature (T_f) , as a consequence of a rapid quenching, their viscosity is strongly lower than expected [21]. This is illustrated by the well-known TNM model [22] or the more recent MYEGA model [23]. Because of a high T_f , the viscous flow is exacerbated at short times even at temperatures well-below the T_g of the glass. Under irradiation, the fluidity of chalcogenide glasses is enhanced, so that this viscoelastic behavior becomes prominent at the laboratory time scale. A viscoelastic process has three components: the elastic part, the delayed elastic part and the inelastic part. Considering the Burger's model (Figure 1), the creep compliance is the sum of three components: an elastic $(J_e=1/\mu)$, an inelastic $(J_\eta=t/\eta)$ and a delayed elastic ($J_d=\frac{1}{\mu_d}\left(1-\exp\left(-\frac{t\,\mu_d}{\eta_d}\right)\right)$) [24], where μ is the shear modulus, η the shear viscosity, and μ_d and η_d the parameters of the delayed elastic contribution. This model yields the following expression for the creep compliance (J):

$$J(t) = J_e + J_d(t) + J_{\eta}(t) = \frac{1}{\mu} + \frac{1}{\mu_d} \left(1 - \exp\left(-\frac{t \,\mu_d}{\eta_d}\right) \right) + \frac{t}{\eta} \tag{1}$$

For an arbitrary loading history $\tau(t)$, the total shear strain (ϵ) is given by [25, 26]:

$$2\epsilon(t) = \gamma(t) = \int_{-\infty}^{t} J(t-s) \frac{\partial \tau(s)}{\partial s} ds$$
 (2)

 γ is the local distortion due to the shear stress ($2\epsilon=\gamma$). The distortion being proportional to strain, let us use the terms "strain" instead of "distortion" in this paper. The total shear strain or the total distortion is also the sum of each viscoelastic part: $\gamma=\gamma_e+\gamma_d+\gamma_\eta$. Every strain component can be calculated individually, following the same procedure. The delayed elastic strain is obtained as:

$$2\epsilon_d(t) = \gamma_d(t) = \int_{-\infty}^t J_d(t-s) \, \frac{\partial \tau(s)}{\partial s} \, ds \tag{3}$$

Of course for a given stress: $\gamma_e(t) = \tau(t)/\mu$ and $\dot{\gamma}_\eta(t) = \tau(t)/\eta$. The recovery test allows for the identification of the delayed elastic strain component of the viscoelastic deformation. In this test, the stress is relieved at time $t > t_r$, after a loading period, up to t_r . As $\tau = 0$ for $t > t_r$, the elastic strain vanishes and the purely viscous component of the strain remains constant. The delayed elastic strain, at $t > t_r$, is provided by Eq.(3). The delay elastic component is the only one evolving during the recovery stage.

The purpose of this study is to make recovery tests on chalcogenide fibers submitted to different irradiation conditions and stress histories in order to analyze how irradiation contributes to their mechanical behavior.

2 Experimental procedure and results

The detail of the glass casting and fibers processing can be found in Ref.[15] and [27]. GeSe₉ fibers, 300 µm in diameter, 150 mm in length, have been first aged two months under irradiation, at room temperature ($20\pm0.5^{\circ}$ C, humidity: $60\pm3\%$). They reached their thermodynamic equilibrium, in the sense that viscosity is constant. Evidence of this is found in the fact that their relaxation function are unchanged over 2 months [15]: the photoinduced dynamic equilibrium is reached [5, 28], and the glass is supposed to be stable at a macroscopic scale. A fluorescent light Phillips MASTER TL-D 36W/840 was used as an irradiation source, illuminating with a low light intensity in the sub-bandgap range [15]. Then, the fibers have been stressed in torsion for the shear relaxation-recovery tests: one end of the fiber is fixed in its holder and the other end is submitted to a rotation with an angle α_0 [15]. An imposed constant strain $\gamma_0 = d\alpha_0/2L$ derives, where L is the fiber length and d its diameter. A constant shear strain γ_0 was applied, the same for all the fibers $(4.0\pm0.1\times10^{-3})$, up to $t=t_r$ and the stress was relieved at t_r . But three different irradiation conditions were used. Two fibers have been kept under irradiation conditions and mechanically relaxed during 63 days (t_r) , and when the stress was relieved for recovery, a first fiber (referred as to A) was kept under irradiation while a second one (referred as to B) recovered in the dark. A last fiber (referred as to C) was placed in the dark and mechanically relaxed 63 days, then the stress was relieved, and the fiber recovered, still in the dark. Therefore, fibers A and B underwent the same stress histories and the same irradiation conditions up to t_r while fibers B and C underwent the same irradiation conditions for $t \ge t_r$. The recovery kinetics were established by measuring the rotation kinetics of the

free ends of the fibers. The method used to measure each strain component during shear relaxation-recovery tests is described in Ref.[15]. The stress relaxation is fitted by $\tau(t)=\tau_0\ \varphi(t)$, with φ the shear relaxation function, and τ_0 the stress at t=0. Shear relaxation under irradiation (A and B: φ_{irr}) and in the dark (C: φ_{dark}) has been previously measured [15]. These shear relaxation functions can be fitted using two stretched exponential functions:

$$\varphi(t) = \begin{cases} \exp\left(-\left(\frac{t}{\tau_1}\right)^{b_1}\right) & \text{if } t < t_c \\ \exp\left(-\left(\frac{t}{\tau_2}\right)^{b_2}\right) & \text{if } t \ge t_c \end{cases}$$
(4)

The parameters of the shear relaxation functions are described in the Table 1. The possible physical origin of such bimodal expression for the shear relaxation functions is still an open issue. As this bimodality is also evidenced in the dark, it is not connected to the spectrum of the light used to irradiate. Meanwhile Böhmer and Angell used such an equation to fit the relaxation function for pure a-Se in the dark [29]. They explained this bimodality by the existence of two main relaxation mechanisms, with different structural origins: Se-chains and Se-rings. The high stretched exponent (b), under irradiation $(b_1=0.59)$, for such a kinetically fragile glass indicates that the photoinduced relaxation is less cooperative than the relaxation in the dark. At this temperature, b<0.4 is expected in the dark, b=0.6 corresponds to T_g [19]. b_1 =0.5 measured here, in the dark, is not really connectable to the cooperativity, because the stretched exponent makes sense only if the glass is under equilibrium. The equation form of φ in Eq. 4, does not provide any analytical solution to Eq.(3), because stretched exponential functions have no Laplace transform [30]. It should be remembered that, in Eq.(3), J could be calculated

using φ and the following convolution equation [26]:

$$\frac{t}{\mu} = \int_0^t \varphi(s) J(t-s) ds = \int_0^t \varphi(t-s) J(s) ds \tag{5}$$

 φ_{irr} and φ_{dark} differ because of the photoinduced fluidity. Moreover, φ_{dark} is characterized by a significant lower relaxation time (defined as: $\int_0^{+\infty} \varphi(t) dt$ [26]). As a consequence, even if the strain was the same for all the relaxation tests, the stress history of fiber C strongly differs from those of fibers A & B. This is clearly illustrated by Figure 2: at $t=t_r$, the elastic strain instantaneously recovered is larger for fiber C than for fibers A and B. Moreover this strain is proportional to the stress $(\gamma_e(t_r)=\tau(t_r)/\mu)$.

Figure 3 presents the recovery of the delayed elastic strain for $t \geq t_r$ of fibers A, B and C. First, it highlights that fibers A and C, with permanent irradiation/dark conditions, recover with different kinetics and amplitudes, this being explained by their differences, both in terms of stress history $(\tau(t))$ and mechanical behavior (J(t)), this latter being influenced by light. From this figure, it also clearly appears that fiber B and fiber C recover exactly with the same kinetic. So, fiber B recovers exactly as if it has the same mechanical history than fiber C, and behaves exactly has if it has been never irradiated during relaxation. Fiber B has literally lost all the memory of the mechanical history produced by light, all the "photoinduced mechanical memory". The athermal nature of this photoinduced change has been demonstrated in Ref. [15]: the differences observed between the fiber in the dark and those under irradiation correspond to a temperature increase of 40°C (calculated from the viscosity difference, and the viscosity-temperature dependence of

the GeSe₉ glass [31]), but temperature measurements, with an infrared thermography camera (Thermacam FLIR Systems) showed no warming larger than 2°C. But, above all, the athermal nature of the process is evidenced by the recovery kinetic of fiber B: it exactly matches the recovery kinetic of fiber C. The recovery kinetic being only controlled by the stress history and the creep compliance (Eq. 3), a thermal effect would change the creep compliance, but not the stress history, so that fiber B would not behave exactly as fiber C.

3 Discussion

The Valence Alteration Pairs (VAPs) are defects described in chalcogenide glasses since decades [32], and used in a large number of models to explain photoinduced effects [3]. VAPs are present in significant number in chalcogenide glasses, but their density can be increased by irradiation, as explained by H. Fritzsche [5, 10]. When electron-hole pairs are excited, few of them do not radiate back to their initial ground state, but rather undergo non-radiative recombinations via metastable self-trapped exciton creations [4, 5]. This trapping occurs through a coordination change (VAPs creation). G.A.N. Conell has shown that VAPs have low energy barriers for diffusion and has described the mechanisms of their diffusion in the glass structure. In a glass, only a limited number of subsystem are in state allowing cooperative rearrangements involved in viscous flow. This is the basis of the well-known Adam-Gibbs model [33]: the viscosity is inversely proportional to the number of subsystems in a state permitting these rearrangements (i.e.: having low energy barrier for rearrangements). The photoinduced VAPs exactly correspond to

these subsystems: the irradiation increases their density and the viscosity is proportionally decreased. This is the reason why the fluidity (inverse of the viscosity) is proportional to the density of photons absorbed [15]. In such a scenario, thermally activated processes and photoinduced ones are decoupled, since photofluidity involves a very specific process. This specificity is highlighted by the low cooperativity of the relaxation processes under irradiation: the irradiation activates very specific processes with relaxation times lower than in the dark, but close to each other.

Fibers A & B are kept under irradiation all along the relaxation test. According to this, the mechanical histories of fibers A and B can be decomposed as a sum of thermally activated and photoinduced processes, this latter being mainly due to light-induced VAPs. As soon as the irradiation ceases, light-induced VAPs vanish because de-trapping instantaneously occurs. The transient aspect of VAPs is supported by the instantaneous and reversible changes observed during photodarkening for the same glass composition [34] or for an other Ge-Se glass [35]. Even if the recombinaison of such defects induces some local bond re-arrangements [5], since the density of light-induced VAPs is very low at such intensity, the glass network is not so much affected at a macroscopic level. It explains why no structural changes can be detected after irradiation, in the medium range order, at low intensities [14]. Then, when fiber B is placed in the dark, only the thermally activated changes remain, and it behaves exactly as if it has never been irradiated. All the photoinduced changes instantaneously recover when the irradiation ceases, so that they do not contribute anymore to the viscoelastic behavior.

These results support the idea that irradiation do not enhance thermally activated processes, it promotes new processes. These processes are supposed to be mainly VAPs diffusions, or at least correlated to transient bond breaking around chalcogen atoms. It also implies that photofluidity, or more generally the photoinduced viscoelastic behavior, is mainly due to transient defects in the structure and not to permanent photoinduced changes, since the "photoinduced mechanical memory" is instantaneously lost when the irradiation ceases. Therefore, any permanent structural changes occurring during photoinduced viscous flow are more probably the consequences of flow than the cause. Any changes observed by Raman spectroscopy during photoinduced deformation in chalcogenide classes [16] rather reveal the consequence of the photoinduced viscous deformation than the reason why it becomes possible: the VAPs creations. Any model for photofluidity, based on "knots" (wrong homopolar bond) release in the structure [9, 16] can not explain the instantaneous increase of viscosity when irradiation ceases [9]. If these knots can break within few femtoseconds and decrease the viscosity, they can not all reform instantaneously when the irradiation ceases and instantaneously increases the viscosity. These models can not explain the recovery kinetics observed in this study and the fact that the viscoelastic behavior changes as soon as the irradiation ceases. Moreover, such models founded on homopolar bond breaking, also used to explain other photoinduced changes [36], can not explain the photofluidity in pure a-Se [14] without involving other processes, while photofluidity dependence to irradiation seems to be universal [15]. They are also not able to explain why various photoinduced effects are prominent in chalcogenide rich Ge_xSe_{1-x} and $Ge_xAs_xSe_{1-2x}$ glasses [15, 37, 38]. A model based only on the diffusion of VAPs is consistent with this latter observation. It can also explain why photoinduced fluidity is more prominent in As-based than in Ge-based glasses [15], because pnictogen atoms can be involved in VAPs, while four-fold germanium can not [32].

4 Conclusion

Photoinduced effects can persist or not after irradiation depending on whether the effects are due to transient, recoverable or permanent changes [35]. Viscoelastic bodies, after being stressed, deform only according to their mechanical history: they recover. If the memory of this mechanical history could be perturbed, without stressing the sample, the deformation behavior would change. The instantaneous change of the viscoelastic behavior, observed when the irradiation ceases, strongly suggests that the photofluidity is mainly due to transient changes occurring through metastable self-trapping. Above all, it suggests that the processes responsible of photoinduced viscous flow are strongly decorrelated to those responsible of the thermally activated viscous flow.

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Condition	τ_1 (days)	b_1	τ_2 (days)	b_2	$t_c = 17 \text{ (days)}$
irradiation - φ_{irr} -	16.8	0.59	16.5	0.35	17
dark - φ_{dark} -	321	0.50	1160	0.31	39

Table 1: Parameters of the shear relaxation functions.

Figure 1: Burger's model, made of 3 components: elastic (spring), delayed elastic (parallel spring and dashpot) and inelastic (dashpot). The corresponding compliance are denoted J_e , J_d and J_{η} .

Figure 2: Evolution of the total strain during the relaxation-recovery tests (lines are guides for the eyes). When $0 \le t \le t_r$ (relaxation test), the strain is imposed as constant (γ_0) and the stress relaxes. At $t=t_r$ the stress is relieved, the elastic strain instantaneously recovers. The elastic strain recovered is proportional to the non-relaxed stress: $\gamma_e(t_r) = \tau(t_r)/\mu$. At $t>t_r$, the delayed elasticity recovers. When $t\to +\infty$, only the inelastic strain remains.

Figure 3: Evolution of the delayed elastic strain recovered at $t > t_r$, for fibers A, B and C. The delayed elastic strain (γ_d) is normalized by the strain imposed during the relaxation test (γ_0) .