Physical ageing in glassy As–Se induced by above-bandgap photoexposure

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Abstract

Physical ageing induced by above-bandgap photoexposure is studied in As–Se glasses using the differential scanning calorimetry technique. The kinetics of this effect are compared with those caused by natural storage in the dark. Acceleration of physical ageing processes is recorded for Se-rich glasses having more than three Se atoms in their chains.

Chalcogenide glasses (ChG) are distinguished by their high photosensitivity, which makes them prospective solid media for numerous applications in optoelectronics \cite{1–3}. So far, a significant number of publications is devoted to different effects induced by bandgap, sub-bandgap and above-bandgap light, and numerous models of photoinduced structural transformations are developed \cite{3–8}. At the same time, the too low penetration depth of bandgap and above-bandgap light (\(<\)0.1 \(\mu\)m) has led to the common opinion that only thin-film objects could be sensitive to this kind of photoexposure \cite{3,9}. A so-called opto-mechanical effect studied recently in thin ChG films \cite{5,6} speaks in a favour of this conclusion.

J.P. Larmagnac with co-authors \cite{10} were the first who pointed out an unexpected behaviour of pure Se under above-bandgap photoexposure. By studying the photo-dependence of sub-\(T_R\) relaxation in amorphous Se films of \(\sim6\) \(\mu\)m thickness using differential scanning calorimetry (DSC), they detected the largest increase in the relaxation rate for absorbed light with a 404 nm wavelength having very small penetration depth (\(<0.04\) \(\mu\)m). Owing to the apparent differences in film thickness and light penetration depth, the authors tried to explain the effect of above-bandgap photoexposure in the full volume of studied films, as testified by DSC, through further diffusion of photoinduced excitations in the form of over- and under-coordinated defects \cite{10}.

In the present paper, we report the first results on the influence of above-bandgap photoexposure on physical ageing in bulk As–Se ChG.

The ingots of vitreous \(\text{As}_x\text{Se}_{100-x}\) (\(x = 10, 20, 30\) and 40) were prepared by the conventional melt quenching route in evacuated quartz ampoules from a mixture of high purity precursors. The amorphous state and composition of the as-prepared ChG were controlled visually by a character conch-like fracture, data of X-ray diffraction and X-ray photoelectron spectroscopy. Bulk samples in the form of thick (\(\sim3\) mm) plates were prepared for DSC measurements.

One part of the as-prepared ChG samples was stored in the dark under room conditions; the other part was exposed with a continuous light using standard Ultra-Vitalux Osram 300 W lamp with a 350–600 nm band-pass filter under the same room conditions. Additionally, a special air-cooling system was used to prevent samples from heating during illumination. The temperature was controlled by thermocouples maintained at the free edges of the samples and no essential deviations from room temperature (\(T_R = 27 \pm 3^\circ\text{C}\)) were detected.
Physical ageing effects in ChG associated with slow structural relaxation towards thermodynamic equilibrium of undercooled liquid are relevant to all of the investigated ChG samples except As\textsubscript{40}Se\textsubscript{60} one \cite{11}, which is supposed to form a self-organized phase in terms of Phillips–Thorpe \cite{12}. So, the Se-rich ChG samples kept far below glass transition temperature ($T_g$) or subjected to different external influences lose their excess of configurational entropy, enthalpy or free volume (gained during melt quenching) to reach a more favourable thermodynamic state. This ageing behaviour is well revealed by the DSC technique through distinguishable changes in the glass transition region \cite{11,13}. A strong endothermic peak in the vicinity of $T_g$ appeared as a result of prolonged natural storage (natural physical ageing) \cite{11,13}, sub-bandgap photoexposure (photo-induced physical ageing) \cite{14,15} or maintenance in stationary high-energy radiation fields (radiation-induced physical ageing) \cite{16}, and was attributed to the enthalpy relaxation caused by these factors. The corresponding area $A$ under this endothermic peak in the DSC trace is directly proportional to enthalpy losses $\Delta H$: the greater $A$, the greater $\Delta H$; thus, the closer to equilibrium of undercooled liquid is glassy state \cite{17}. In further considerations, the $A$ value will be used as the main parameter to characterize physical ageing under above-bandgap photoexposure in the investigated ChG (the accompanying changes in $T_g$ values are beyond the scope of this paper).

It was shown recently, that bandgap and sub-bandgap photoexposures with $\sim$700–800 nm wavelength and a few W/cm$^2$ power of the as-prepared bulk Se-rich Ge-Se ChG caused an additional increase in $A$ values over those induced by natural storage \cite{15}. The observed effect was explained in terms of fragile-strong glass formers, and its athermal nature was emphasized \cite{18}.

Similar behaviour is observed for the investigated Se-rich As–Se ChG under the influence of above-bandgap photoexposure (Fig. 1). It is shown that physical ageing processes in ChG samples with $x=10$ and $x=20$ are significantly accelerated by photoexposure, those for $x=30$ are slightly modified, while bulk properties of ChG with $x=40$ are insensitive to above-bandgap photoexposure. The kinetics of enthalpy losses (represented by $A$ values) are shown in Fig. 2(a) and compared with the enthalpy losses caused by the storage of as-prepared samples in the dark at $T_R$ and at $T_A=40^\circ$C. It is clearly seen that in the case of As\textsubscript{10}Se\textsubscript{90} samples, thermal annealing at $T_A$ is insufficient to achieve the value of enthalpy changes produced by photoexposure. On the other hand, the enthalpy losses at $T_A$ for As\textsubscript{30}Se\textsubscript{70} ChG are greater than those induced by above-bandgap photoexposure (Fig. 2(a)). These data additionally testify the athermal character of produced changes.

Since essential heating components are excluded from our consideration, the pure physical ageing under above-bandgap photoexposure at near-room temperature can be found as the difference between enthalpies lost during dark storage and under photoexposure, represented in Fig. 2(b) through $A_{\text{dark}}$.
Fig. 2. Kinetics of enthalpy losses $\Delta H \sim A$ (a), induced by storage in the dark at $T_R$ (black), in the dark at $T = 40^\circ C$ (grey) and under above-bandgap light illumination at $T_R$ (white); the difference between white and black curves (b). The lines are drawn as guide for the eyes.

and $A_{\text{light}}$, respectively. The compositional behaviour of this effect fully coincides with compositional trends in short-term natural physical ageing in As–Se ChG treated in terms of mean-field constraints theory [19] and “chains crossing model” [20]. This similarity allows us to assume that the general coincidence in the corresponding microstructural mechanism is responsible for the observed structural relaxation. So, we suppose that elementary relaxations within $n_{\geq 3}$ chains (the number $n$ of Se atoms in chain here is considered as the number of Se atoms between two As atoms) followed by shrinkage of under-constrained network, as it is described for the case of natural physical ageing [21], are produced by the above-bandgap photoexposure. These elementary relaxations in bulk As–Se ChG with $x < 30$ are associated with the twisting of the inner Se atoms within Se–Se–Se fragments [11,21]. This process can be described in terms of a double-well potential diagram [22] associated with high flexibility of chalcogen–chalcogen bonds [17]. The only difference consists in the initiating factors. During natural storage, the elementary relaxations of Se atoms within the double-well potential have a fluctuating nature. Randomly started at different sites in a sample bulk, they initiate the further shrinkage of a glass network due to the contraction of the free volume released during twisting (or straightening of Se polymeric chains [21]) processes. In the case under consideration, electron–hole pairs are intensively generated in the surface layers of the sample by above-bandgap light facilitating the above structural relaxation mechanism. Because of the continuing photoexposure and strong electron–phonon coupling proper to ChG [23], the photoperturbation leads to the appearance of additional elastic strains in the surface part of the sample. In the transient under-illumination conditions, this stress relaxes into a sample depth, like it happens in the surface-modified Se-rich fibres [24,25] propagating the physical ageing effect. In such a way, the changes produced by above-bandgap photoexposure near the surface of the samples stretch into their depth producing a measurable effect for DSC technique.

According to the “chains crossing model” [20], the Se$_n$ chains with $n \geq 3$ fully disappear in As–Se ChG after As$_{25}$Se$_{75}$ composition. This leads to The vanishing of elementary relaxations of the inner Se atoms, which are considered as precedents for a fast shrinkage of a glass matrix [11,16]. Only the slow shrinkage of under-constrained glass network (all ChG with $x < 40$ are accepted to be under-constrained in full correspondence with [11]) is possible for ChG compositions with $25 < x < 40$. However, this kind of shrinkage needs a long time period of natural storage to be detected experimentally, comparable with tens of years as it was testified recently [11]. This is also a reason for the negligible ageing produced in As$_{30}$Se$_{70}$ ChG by above-bandgap photoexposure at room temperature (see Fig. 2).

**Conclusion**

A physical ageing effect induced by above-bandgap photoexposure is recorded for Se-rich bulk ChG by the conventional DSC technique. It is associated with the acceleration of physical ageing processes occurring in these materials at room temperature. The mechanism of the observed photoinduced enthalpy losses is assumed to be connected with dissipation into the bulk of elastic strains produced at the surface layers of the sample by light excitations.

**References**