Long-term ageing behaviour in Ge–Se glasses

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Abstract Effect of long-term physical ageing ($\sim$18–
21 years) in vitreous germanium selenides is studied using
differential scanning calorimetry method. It is compared
with short-term physical ageing observed in these glasses
earlier. Low compositional limit of the non-ageing ability
determined using old samples coincides with the onset of
reversibility window obtained using short-term aged sam-
ples of Ge–Se system by temperature modulated differen-
tial scanning calorimetry technique.

Introduction

The non-equilibrium metastable nature of glassy state
is a reason for all glasses obtained by conventional
melt-quenching technique to approach with time the equi-
librium structure of corresponded undercooled liquid, this
effect being known as physical ageing effect [1, 2]. The
kinetics of the related structural relaxation processes,
occurred during the transition of glass to a more energetically
favourable state, depends essentially on the departure of
ageing temperature (T_a) from a glass transition temperature
(T_g) slowing down significantly with (T_g-T_a) increase [2].
Thus, at normal conditions of storage, tens of years period
was needed to observe natural physical ageing effect in sil-
icate glasses [3, 4]. Since their T_g is much higher than T_g of
chalcogenide glasses (ChG) [1], we can expect physical
ageing effect to be recorded after few decades of natural
storage in all of the investigated Ge–Se ChG where it is
possible. Furthermore, time interval of 20–25 years has also
a practical meaning for the applications of these materials in
electronics and optoelectronics [5, 6]. Typical electronic
devices are used at normal conditions and their usual lifetime
is less than 20 years. So, it is quite important to have the
information on physical ageing processes taking place at
normal conditions during this period of time.

It was shown recently that natural physical ageing effect
in ChG consists of two components called short-term and
long-term physical ageing, respectively [7–9]. The dis-
tinction between these components is arbitrary (there are
no sharp time-constraints associated with each of them),
but they rely on different microstructural mechanisms. The
first one (short-term) is associated with straightening/
alignment of Se polymeric chains (can be alternatively
understood as transition from *cis-* to *trans-*conformations
of Se atoms in chain within a so-called double-well
potential) followed by shrinkage of surrounding network
[9]. This is a relatively fast process, which can be activated
at room temperatures. The other mechanism is associated
with prolonged overall shrinkage of under-constrained

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glass network (i.e. the number of constraints per atom, n_c, is less than 3), which can be accompanied by chemical bonds redistribution [10]. When polymeric Se chains (consisting of three Se or more Se atoms) are incorporated into a glass backbone, the fast shrinkage associated with alignment of Se chains initiates the overall shrinkage of under-constrained glass network [9]. When these Se_3 fragments are not present (e.g. $As_{30}Se_{70}$ composition) or they do not participate in the formation of glass backbone, the shrinkage occurs simply without the above short-term process provided the glass skeleton is under-constrained [10]. The latter process has slower kinetics and requires more time of natural storage to be detected experimentally.

Disregarding the long-term component of natural physical ageing has led some authors to a misleading conclusion on the non-ageing ability of some As-containing selenide glasses studied only few weeks after preparation [11–13]. In turn, this has led to inaccurate determination of the limits of reversibility windows (self-organized phase or intermediate phase) in As–Se and Ge–As–Se ChG, defined as the compositional range of ChG with optimally constrained ($n_c = 3$) networks and absence of physical ageing [11–14]. In particular, the onset of reversibility window had been observed at lower concentrations of As atoms (at 28 at.% of As), than predicted by the rigidity percolation theory [15]. Investigations on the ~20-years aged As_xSe_{100-x} glasses have removed this discrepancy showing that the onset of reversibility window for this ChG system coincides with the rigidity percolation point, determined at $x = 40$ ($As_{40}Se_{60}$ composition) in good agreement with Thorpe–Phillips percolation theory [8, 16].

For the case of Se-rich Ge–Se ChG, an unexpected behaviour was observed after ~15 years of natural storage expressed in a double-peak relaxation during differential scanning calorimetry (DSC) measurements [7]. However, the number of compositions was restricted by $Ge_{12}Se_{88}$ ChG [7], while the onset of reversibility window in this system is expected at $Ge_{20}Se_{80}$ composition [12, 14, 17].

In this article, we report the first results on very long natural physical ageing (up to ~20 years) in Ge–Se ChG compositions covered the onset point of expected reversibility window. The influence of preparation conditions on the ageing process is also discussed.

Experimental

The samples of vitreous Ge_xSe_{100-x} ($x = 2, 4, 8, 12$) were prepared in 1987 by melting a mixture of Ge and Se in a vacuum-sealed quartz tube heated at a temperature of 1,000 °C during 10 h. This was followed by a quench of the tube in water (Regime I). The samples were kept at an average room temperature ~21 years before present

calorimetric studies. The other samples of vitreous Ge_xSe_{100-x} ($x = 5, 8, 10, 20, 23, 25, 27$) were obtained in 1990. The mixture of high-purity precursors was melted in the evacuated quartz ampoules at 700 °C for Se-rich samples ($x < 10$) and at 900 °C for Ge-rich samples during 5 h in a rocking furnace. Then, the ingots were air-quenched from 630 to 650 °C to achieve a glassy state (Regime II). After synthesis, each of the samples was stored in the dark at natural conditions ~18 years before our calorimetric experiments. The amorphous state was controlled visually by a character conch-like fracture, data of X-ray diffraction and IR microscopy.

The DSC measurements were performed on NETZSCH 404/3/F microcalorimeter pre-calibrated with a set of standard elements, the DSC traces being recorded in the ambient atmosphere with 5 °C/min heating rate. Three independent DSC measurements were performed in each case to confirm the reproducibility of the obtained results. Standard rejuvenation procedure (heating of the aged samples ~50 °C above softening point, equilibrating of the obtained undercooled liquid and further its cooling with the rate >5 °C/min to the room temperature) was used to obtain glassy state close to the initial as-prepared one [7, 18].

Results and discussions

Differential scanning calorimetry traces for two decades aged Ge_xSe_{100-x} are shown in Fig. 1a. The rejuvenation procedure has led to the DSC traces shown in Fig. 1b, which can be considered as those corresponded to DSC traces of as-prepared Ge_xSe_{100-x} samples. Moreover, the DSC signals obtained after rejuvenation for Se-rich Ge–Se ChG are found to be consistent with those observed for the as-prepared samples [7, 18] and the values of $\Delta C_P(T_g)$ are found to be exactly the same. Thus, prolong natural storage does not cause any chemical ageing effects associated with oxidization, crystallization or other reactions able to modify the glass structure. As it is testified from visual inspection of Fig. 1, the strong endothermic peaks observed in the region of glass-to-undercooled liquid transition for long-term aged Ge_2Se_{88}, Ge_4Se_{96}, Ge_8Se_{92}, $Ge_{10}Se_{90}$ and $Ge_{12}Se_{88}$ (Fig. 1a) disappear after rejuvenation (Fig. 1b). So, we can conclude that these peaks originate from the enthalpy relaxation caused by two decades of natural storage being a signature of natural physical ageing effect. The areas A under the endothermic peaks are directly proportional to the enthalpy losses ΔH and their values will be used for further characterization of natural physical ageing effect.

Double peak relaxation was observed earlier for Ge_2Se_{98}, Ge_4Se_{96} and Ge_8Se_{92} compositions obtained according
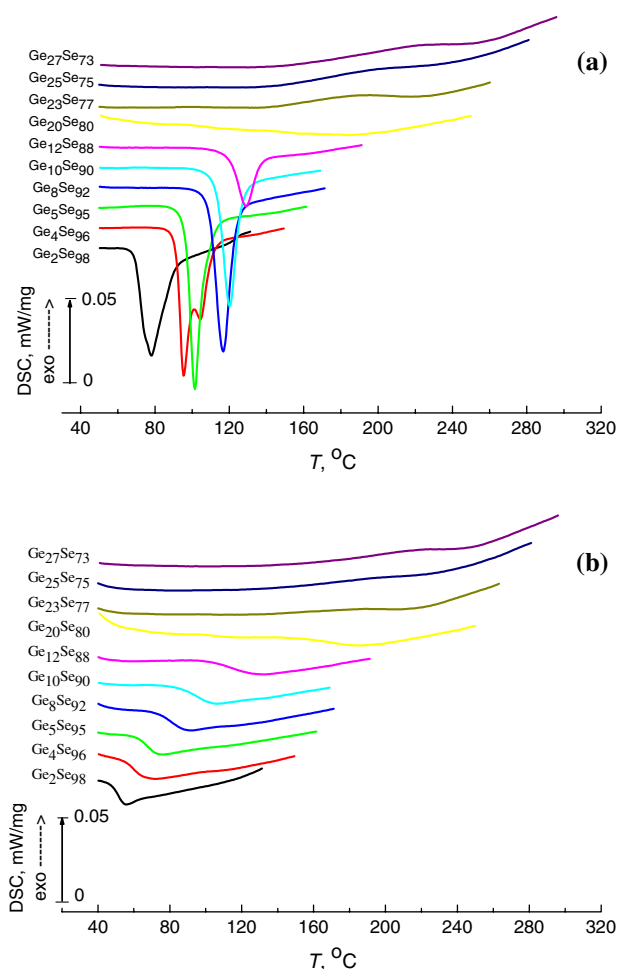
Fig. 1 DSC traces of vitreous Ge_xSe_{100-x} samples subjected to two decades of physical ageing (**a**) and subsequent rejuvenation procedure (**b**). The DSC traces of Ge_2Se_{98}, Ge_4Se_{96} and $Ge_{12}Se_{88}$ glasses are representatives of the samples obtained via Regime I, all the rest curves correspond to the samples synthesized according to Regime II

to the Regime I [7, 18]. Similar effect was observed also during the present DSC experiment and it is shown in (Fig. 1a) at the example of Ge_2Se_{98} and Ge_4Se_{96} samples. These data indicate that the initial glass structure (frozen according to Regime I), which seems to be homogeneous before ageing, moves towards a heterogeneous one during the relaxation process associated with the physical ageing. The double-peak relaxation effect as a result of long-term physical ageing was not observed for all ChG obtained by Regime II (Fig. 1a). In particular, it was expected for Ge_5Se_{95} and Ge_8Se_{92} compositions, but not seen. As far as the melt temperature during synthesis in the case of Se-rich samples should not affect essentially the structure of undercooled liquid in Regimes I and II according to the results in [19], we can put forward a hypothesis that different behaviour during long-term physical ageing of corresponded glasses is related to a choice of quenching method. Rapid

quenching in water leads to the observation of double-peak relaxation effect, while the air-quenching does not. Regarding the structure of pure Se at the liquid state, it was observed some years ago [20] that the *cis/trans* chain conformation ratio in the glassy state depends on the quenching temperature. As a consequence, the number of Se_8 rings is more important when the quenching temperature is low, while the number of Se_n chains increases when the quenching temperature is high. It was also shown [21] that the dynamics of the molecular relaxation in the glass transition range was affected by this *cis/trans* chain conformation ratio. Finally, the latter work has also shown that the rejuvenation procedure used to restore the non-aged state of material or to erase the thermal history does not modify the initial *cis/trans* chain conformation ratio obtained during glass synthesis.

The compositional dependences of A values for aged and rejuvenated Ge_xSe_{100-x} samples are shown in Fig. 2. The corresponded values of the glass transition temperature (T_g), determined as the onset temperature of endothermic peak from DSC heating curves (5 °C/min), are shown in Table 1 for Se-rich samples. All ChG with $x < 20$ were affected by long-term physical ageing at natural conditions and those with $x \geq 20$ did not exhibit any essential changes under prolonged natural storage either in A and T_g values. It should be noted here, that most of the physical properties in Ge–Se glass system exhibit extrema in compositional dependencies at the point $x \approx 20$ [22, 23].

The obtained results agree well with the onset of reversibility window for Ge_xSe_{100-x} ChG ($x = 20$) determined by temperature-modulated DSC experiments for a few weeks/months aged samples [12, 14, 17]. So, compositional behaviour of short- and long-term components of physical ageing coincides in this system. Indeed, the onset of reversibility window directly corresponds to the
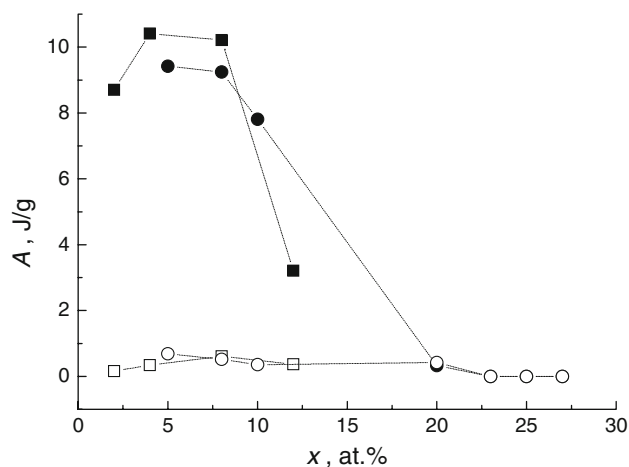
Fig. 2 Compositional dependences of the area A for two-decade aged (*solid symbols*) and rejuvenated (*open symbols*) vitreous Ge_xSe_{100-x} samples obtained using Regime I (*square*) and Regime II (*circles*). The *lines* are drawn as guide for the eyes

Table 1 Changes in the glass transition temperatures (T_g) of Se-rich Ge$_x$Se$_{100-x}$ glasses caused by two decades of natural storage

Glass composition	Regime	T_g (°C aged)	T_g (°C rejuvenated)	ΔT_g (°C)
Ge$_2$Se$_{98}$	I	69.3[a]	47.5	21.8
Ge$_4$Se$_{96}$	I	91.5[a]	55.3	36.2
Ge$_5$Se$_{95}$	II	96.3	61.9	34.4
Ge$_8$Se$_{92}$	I	109.0[a]	73.1	35.9
Ge$_8$Se$_{92}$	II	108.1	73.4	34.7
Ge$_{10}$Se$_{90}$	II	112.9	83.6	29.3
Ge$_{12}$Se$_{88}$	I	119.6	101.1	18.5

T_g values are determined as the onset temperatures of endothermic peaks from DSC heating curves (5 °C/min) with the ±0.5 °C accuracy

[a] Means onset temperature for the first peak of double-peak relaxation behaviour in DSC trace

rigidity transition point (Ge$_{20}$Se$_{80}$ composition with average coordination number $Z = 2.4$), which should be the first point with $n_c = 3$ (note, that long-term component of physical ageing is possible only when $n_c < 3$) according to "chains crossing model" formalism [9, 10, 24]. The Ge$_{20}$Se$_{80}$ composition should be also the first composition with lack of –Se–Se–Se– fragments, which should consist of Se–Se bond-shared tetrahedra only according to the above-mentioned model. So, short-term component of physical ageing ideally should be also restricted by this composition. In other words, the percolation of structural units with $n_c = 3$ in Ge–Se glass backbone and disappearing of elementary Se$_3$ chains should take place at the same compositional point leading to coincidence in the compositional ranges of short- and long-term components of physical ageing.

However, a lot of experimental data speak in a favour of existence of –Se–Se–Se– fragments up to Ge$_{30}$Se$_{70}$ composition [25–27]. Thus, a significant deviation from "chains crossing model" towards "outrigger raft model" is expected for Ge$_x$Se$_{100-x}$ glasses with $x > 15$ [25, 28, 29]. According to this model, the network of such ChG exhibits a tendency to form a structure character to high-temperature crystalline form of GeSe$_2$ [29]. The extra Se atoms form Se-rich regions depending on the composition and do not participate in the network connectivity [25]. These regions can exhibit the straightening/alignment process, but without followed up shrinkage of the whole network, since they are not included into this network (contrary to "chains crossing model" statements) and are restricted by more rigid surroundings. Thus, in the case of "outrigger raft model", the onset point of reversibility window occurs when the percolation of structural units with $n_c = 3$ takes place and the elementary Se$_3$ chains do not participate in the connectivity of glass backbone.

Owing to a great number of experimental data showing the extrema in compositional dependences of most physical properties around $x \approx 20$ [22, 23], we can expect this situation happens roughly at Ge$_{20}$Se$_{80}$ composition with $Z = 2.4$.

In contrast to As–Se ChG, the type of connection between main structural units of Ge–Se ChG (GeSe$_4$ tetrahedra) plays an important role for constraints counting after $x > 20$. Depending on their interconnection: corner-sharing (CS), edge-sharing (ES) or face-sharing (FS) including connection through Se–Se bridges, we can theoretically obtain structural fragments with $n_c = 3$ up to $x = 28.5$ composition. So, it is quite reasonable that long-term natural physical ageing effects are not observed in the investigated Ge$_{20}$Se$_{80}$, Ge$_{23}$Se$_{77}$, Ge$_{25}$Se$_{75}$ and Ge$_{27}$Se$_{73}$ ChG (Figs. 1, 2). The x value where the network of Ge$_x$Se$_{100-x}$ glasses becomes over-constrained ($n_c > 3$) makes an upper limit of the reversibility window and indicates a starting point for the phase-separation-related processes of ageing, which demand higher temperatures of storage to be observed experimentally. The upper limit of reversibility window is fully determined by the possibility to form optimally constrained clusters in order to avoid the stresses arising from the cross-linking elements, as well as by the crystallization ability of a glass. We believe, it is not precisely defined and presumably depends on the glass preparation conditions and/or thermal prehistory of the samples. Moreover, it is a high probability that conventional method of Ge–Se ChG preparation causes reversibility window (in a sense of optimally constrained network with $n_c = 3$) to be very narrow with the upper limit close to a point at $x \approx 21$–23, since no structural signature of intermediate phase was found in Ge$_x$Se$_{100-x}$ glass system recently [26, 30]. It should be noted, that molar volume exhibits a broad minimum in $20 < x < 25$ compositional range [22] meaning that decreased number of floppy Se modes in glass structures above $x \approx 25$ results in the formation of mechanically more stressed network with a greater content of free volume available for relaxation. So, the upper limit of reversibility window ($20 \leq x < 26$) as observed by temperature-modulated DSC experiments [12, 14, 17] could be also attributed to a stress relaxation of this network. All the described compositional features of short- and long-term physical ageing can be summarized in Fig. 3.

Conclusions

Long-term physical ageing in Ge$_x$Se$_{100-x}$ leads to the increase in endothermic peak area A near glass transition region and glass transition temperature T_g. This effect is strongly dependent on the glass composition, being well

Fig. 3 Schematic diagram of the compositional features of physical ageing in Ge–Se ChG
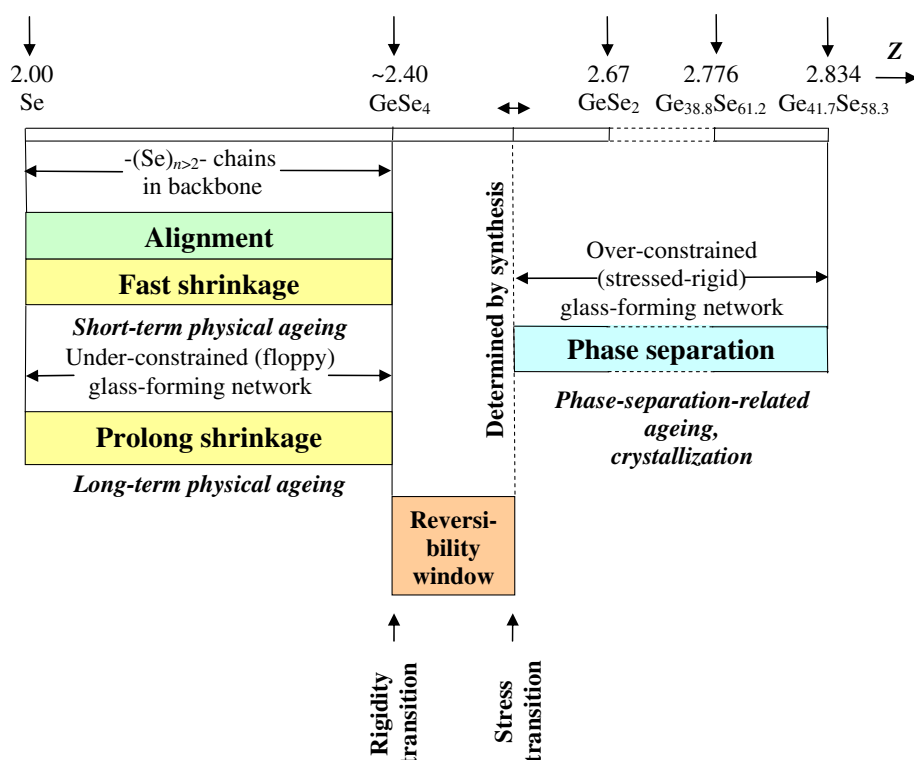
expressed only in Se-rich ChG with $x < 20$. The onset point of the reversibility window determined by temperature-modulated DSC experiments for a few weeks/months aged samples at $x \approx 20$ is roughly confirmed by studying the two decades old samples. This fact is explained by the coincidence in compositional behaviour of short- and long-term components of physical ageing. The existence of double-peak relaxation phenomenon in Se-rich samples is assumed to be connected with rapid quenching of ChG during synthesis procedure, which makes different *cis/trans* chain conformation ratio in the glassy state.

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