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# COMPARATIVE ANALYSIS OF PHYSICAL AGEING KINETICS IN ARSENIC-SELENIDE GLASSES

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The compositional features of kinetics of enthalpy losses ΔH(t) caused by physical ageing in Se-rich chalcogenide glasses obeying chain-crossing structural model are analysed. The mechanism of natural physical ageing is explained by specificity of structural-topological complexes (ratio of hetero- and homopolar complexes) in the studied glasses.

**Key words:** chalcogenide glasses, physical ageing, diffential scanning calorimetry, structural fragments.

## Introduction

The physical ageing (PhA) is known to be an important phenomenon for amorphous solids, because it results in uncontrolled time drift of such their important exploitation properties as atomic density, elastic modulus, brittleness, permeability, strength, fracture energy, deformation, etc. [1]. Nevertheless, the microstructural characteristics of PhA have not been studied enough, known only some reports related to PhA in silicate glasses [2-4]. However, the silicate glasses (characterized by over-constrained networks) possess very slow relaxation kinetics at ambient conditions typically resulting in simple exponential law [4], which can be accepted only as a partial case for overall PhA kinetics.

From this point, the chalcogenide glasses (ChG) are more suitable objects for detailed examination of PhA kinetics, because they allow studying of almost complete picture of PhA at quite acceptable timescales ranging from a few days or even hours (in the case of very chalcogen-rich compositions) up to years or even decades (in case of chalcogen-depleted compositions) [5].

In general, the compositional variations in the ability to PhA are determined by a number of Lagrangian constraints per atom $n_c$ of ChG-forming networks built of fully-saturated covalent chemical bonds assuming their equivalence with movement stretching and bending limitations (mechanical constraints). Under this definition, the covalent bonding $Z$ can be described by mean number of covalent bonds per one atom of glass-forming network. The under-constrained networks possessing $Z < 2.4$ and smaller $n_c$, which are less than dimensionality of space $n_c < 3$, are subject to pronounced drift in their properties caused by thermodynamically-driven forces tending the system towards more favorable energetic state. In contrast, the over-constrained ($Z > 2.4$, $n_c > 3$) and optimally-constrained ($Z = 2.4$, $n_c = 3$) ChG do not age at normal conditions at all, demonstrating strong non-ageing ability.

In this paper, the kinetics peculiarities of natural PhA in under-constrained ChG of $As_{10}Se_{90}$ ($Z = 2.1$, $n_c = 2.25$), $As_{20}Se_{80}$ ($Z = 2.2$, $n_c = 2.5$) and $As_{30}Se_{70}$ ($Z = 2.3$, $n_c = 2.75$) glasses will be developed for this compositional row of glass formers taking into account their main structural features.

## Experimental

The $As_xSe_{100-x}$ ($x$ = 10, 20, 30) ChG were prepared by conventional melt quenching route in the evacuated quartz ampoules from a mixture of high purity precursors, as described elsewhere [5, 6].

Amorphous state and composition of the as-prepared ChG were controlled visually by a characteristic conch-like fracture, data of X-ray diffraction and X-ray photoelectron spectroscopy. Bulk samples in the form of thick (~3 mm) plates, prepared for differential scanning calorimetry (DSC) measurements, were used for the investigations. The DSC measurements were carried out using NETZSCH 404/3/F microcalorimeter pre-calibrated with a set of standard elements, the DSC traces being recorded in the ambient atmosphere with $q$ = 5 K/min heating rate. More detailed description of the measurements protocol can be found in [7].

## Results

The curve of time-dependent enthalpy losses $\Delta\underline{H}(t)$ in $As_{10}Se_{90}$ ChG associated with long-term PhA is presented on Fig. 1.

As it follows from Fig.1, the kinetic of PhA in $As_{10}Se_{90}$ ChG exhibits well-expressed four-steps character. The straightforward fitting of the experimental data describing enthalpy losses $\Delta H(t)$ in $As_{10}Se_{80}$ ChG during PhA with the stretched-exponential relaxation function [6] gives values of time constant $\tau \cong 663$ days and power index $\beta = 0.25$. Taking into account that this kinetics is characterized by hierarchically-constrained mixed serial-parallel relaxation, it was modelled by next equation [6]:

$$\Delta H_i(t)=\sum_{i=1}^{n}\theta(t-\Delta t_i)\left[a_i+b_i(1-\exp\left(-\frac{t-\Delta t_i}{\tau_i}\right)\right], \qquad (1)$$

where $\Theta(t-\Delta t_i)$ is Heaviside step function, whose value is accepted to be 0 for negative arguments ($t < \Delta t_i$) and 1 for positive ones ($t \geq \Delta t_i$), and n is number of steps in the relaxation kinetics.

The results of the modelling with eq. (1) and the fitting parameters for four-step serial presentation of PhA in $As_{10}Se_{90}$ ChG are shown in Table 1.

The curve of time-dependent enthalpy losses ΔH(t) in $As_{20}Se_{80}$ ChG associated with long-term PhA is presented on Fig. 2.

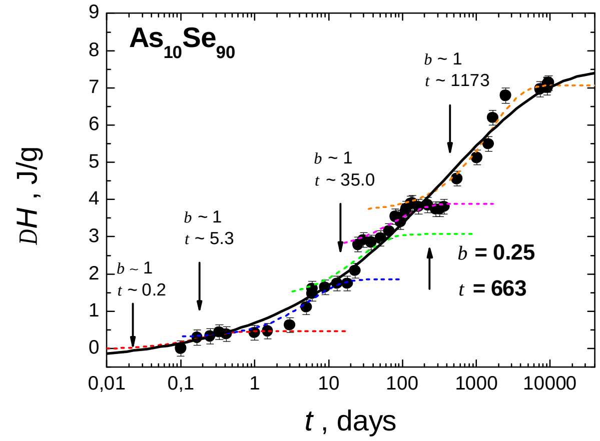

**Fig. 1.** Kinetics of ΔH(t) losses in $As_{10}Se_{90}$ ChG deconvoluted in four-steps serial single-exponential processes

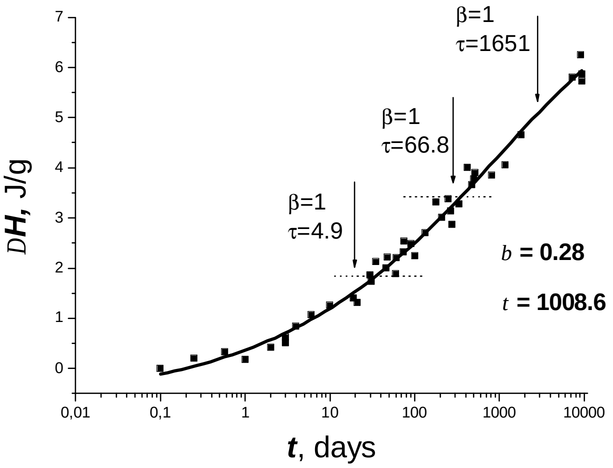

**Fig. 2.** Kinetics of ΔH(t) losses in $As_{20}Se_{80}$ ChG deconvoluted in three-steps serial single-exponential processes

**Table 1.** Fitting parameters describing PhA kinetics in As10Se90 ChG

| Step # (duration) | Fitting goodness $r^2$ | $a_i$, J/g | $b_i$, J/g | $a_i$+$b_i$, J/g | τ, days | $\Delta t_i$, days |
|---|---|---|---|---|---|---|
| $i$ = 1 (0÷1.5 days) | 0.008 | 0 | 0.46 | 0.46 | 0.2 | 0 |
| $i$ = 2 (1.5÷20 days) | 0.022 | 0.46 | 1.52 | 1.98 | 5.3 | 1.7 |
| $i$ = 3 (20÷365 days) | 0.038 | 1.98 | 1.82 | 3.80 | 35.0 | 16.5 |
| $i$ = 4 (365÷9500 days) | 0.034 | 3.80 | 3.27 | 7.07 | 1173 | 340 |

The kinetic of PhA in this $As_{20}Se_{80}$ ChG exhibits two-steps behaviour, the values of PhA is expected smallest as compared with the same in $As_{10}Se_{90}$ ones (number of constrains per atom $n_c$ = 2.5). The straightforward fitting of the experimental data describing enthalpy losses $\Delta H(t)$ in $As_{30}Se_{70}$ ChG during PhA with stretched-exponential relaxation function gives 1008.6 days and $\beta$ = 0.28. The results of the modelling with eq. (1) and the fitting parameters for three-step serial presentation of PhA in $As_{20}Se_{80}$ ChG are shown in Table 2.

**Table 2.** Fitting parameters in eq. (1) describing three-steps kinetics of PhA in $As_{20}Se_{80}$ ChG

| Step # (duration), days | Fitting goodness $r^2$ | $a_i$, J/g | $b_i$, J/g | $a_i+b_i$, J/g | $\tau$, days | $\Delta t_i$, days |
|---|---|---|---|---|---|---|
| $i$ = 1 (1÷20) | 0.0933 | 0 | 1.4 | 1.4 | 4.9 | 0 |
| $i$ = 2 (20÷335) | 0.03705 | 1.4 | 2.0 | 3.4 | 66.8 | 17.5 |
| $i$ = 3 (335÷10000) | 0.04821 | 3.4 | 2.7 | 6.1 | 1651.4 | 305 |

The curve of time-dependent enthalpy losses $\Delta H(t)$ in $As_{30}Se_{70}$ ChG associated with long-term PhA is presented on Fig. 3.

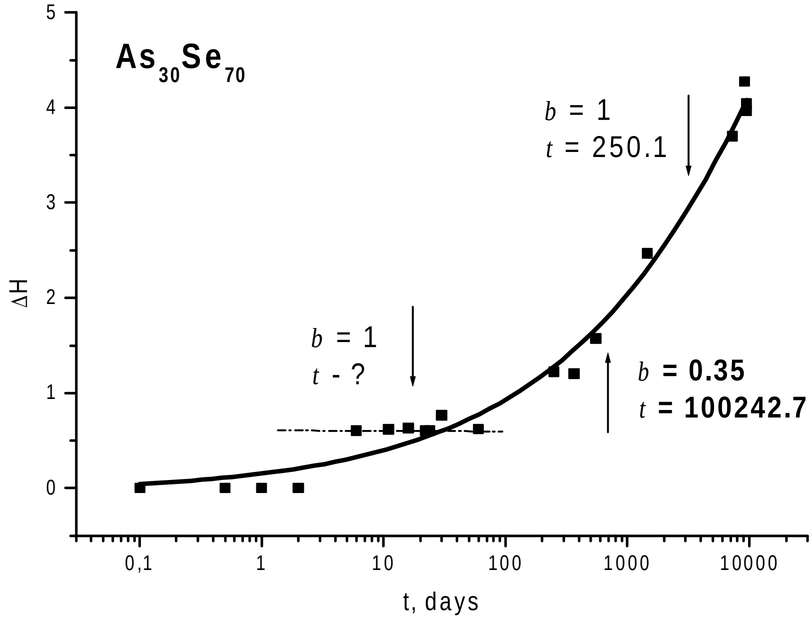

**Fig. 3.** Kinetics of PhA in $As_{30}Se_{70}$ ChG deconvoluted in two-steps serial single-exponential processes.

The kinetic of PhA in $As_{30}Se_{70}$ ChG exhibits two-steps behaviour, the values of PhA is expected smallest as compared with the same in $As_{10}Se_{90}$ and $As_{20}Se_{80}$ ones (the number of constrains per one atom $n_c$ = 2.75). The straightforward fitting of the experimental data describing enthalpy losses $\Delta H(t)$ in $As_{30}Se_{70}$ ChG during PhA with the stretched-exponential relaxation function gives $\tau \cong$ 100242.7 days and $\beta$ = 0.35. The results of the modelling with eq. (1) and the fitting parameters for two-steps serial presentation of PhA in $As_{30}Se_{70}$ ChG are gathered in Table 3.

**Table 3.** Fitting parameters in eq. (1) describing PhA kinetics in $As_{30}Se_{70}$ ChG.

| Step # (duration), days | Fitting goodness $r^2$ | $a_i$, J/g | $b_i$, J/g | $a_i+b_i$, J/g | $\tau$, days | $\Delta t_i$, days |
|---|---|---|---|---|---|---|
| $i$ = 1 (1÷300) | 0.022 | 0 | 0.7 | 0.7 | – | 0 |
| $i$ = 2 (300÷10000) | 0.0265 | 0.7 | 3.3 | 4 | 1398 | 250 |

## Disscusion

The mechanism of PhA in ChG is known to be based on elementary relaxation acts (twisting) of inner Se atoms within double-well potentials (DWP) associated with high flexibility of chalcogen chemical bonds [6–8].

As it follows from above experimental results, the PhA in the studied ChG exhibits well-expressed step-wise character, showing some kinds of plateaus and steep regions. The increasing of As content leads to decreasing of PhA in full accordance to increased $n_c$ values (from 2.25 for $As_{10}Se_{90}$ to 2.5 for $As_{20}Se_{80}$ and 2.75 for $As_{30}Se_{70}$ ChG). Moreover, with increasing of As content, the values of power index in the stretched-exponential relaxation function increases (from 0.25 for $As_{10}Se_{90}$ to 0.28 for $As_{20}Se_{80}$ and 0.36 for $As_{30}Se_{70}$ ChG). This means, obviously, decrease in the dispersivity of the system, so the number of steps in the PhA kinetics decreases too (from 4 for $As_{10}Se_{90}$ to 3 for $As_{20}Se_{80}$ and 2 in $As_{30}Se_{70}$ ChG).

These features can be well explained by accepting main structural signatures of the studied ChG.

Thus, in $As_{10}Se_{90}$ ChG, the Se atoms created -Se-Se-Se- ($n_c$ = 2.0) and =As-Se-Se- ($n_c$ = 2.45) fragments taken in 67:33 ratio, while in $As_{20}Se_{80}$ this ratio become 25:75. In contrast, in $As_{30}Se_{70}$ ChG, the intermediate surroundings of Se atoms significantly changes: -Se-Se-Se- chains disappear, and new =As-Se-As= ($n_c$ = 3) environment is formed instead (the radio between =As-Se-Se- and =As-Se-As= fragments reaches 29:71). Under such conditions, three possible DWP can be assumed for central Se atoms in the studied $As_xSe_{100-x}$ (x = 10, 20, 30) ChG owing to their immediate surroundings, namely -Se-Se-Se-, =As-Se-Se- and =As-Se-As= fragments with differ heights of energetic barriers.

As known, the -Se-Se-Se- fragments possess the smallest height of energetic barrier, while the =As-Se-As= fragments are characterized by the largest barrier. The -Se-Se-Se- fragments relax on the initial stages of PhA with time constant $\tau$ ~4.9 days, and =As-Se-As= fragments relax at the final stage of PhA with time constant $\tau \sim 1200 \div 1600$ days (see Tables 1-3), although (according to serial-parallel specific of PhA) the relaxation of all structural fragments occurs on each stage.

Since the content of -Se-Se-Se- structural fragments in $As_{20}Se_{80}$ ChG (25 %) is less that in $As_{10}Se_{90}$ (67 %) [5], the initial two steps in $As_{20}Se_{80}$ glasses arise very quickly. Therefore, its separate distinction is not possible under such condition (see Fig. 2), and, consequently, the first and second steps cooperate giving the smallest $\tau$. In $As_{30}Se_{70}$ ChG, the homoatomic –Se-Se-Se- fragments are absent at all, and initial stage of relaxation are caused mainly by shrinkage of =As-Se-Se- fragments, producing only two steps in the relaxation kinetics. The retardation times $\Delta t_i$ remain on the same order for all studied ChG (Table 1–3).

## Conclusion

It was shown that kinetics of enthalpy losses $\Delta H(t)$ caused by prolonged storage of $As_xSe_{100-x}$ in a dark at room temperature during more than two decades, exhibits a well-expressed step-wise character, showing some kinds of plateaus and steep regions. The microstructural mechanism of natural physical ageing explains well the observed stretch-exponential behavior in relaxation kinetics in terms of hierarchically-constrained mixed serial-parallel relaxation events having different atomic precursors. This kinetics can be decomposed into elementary components, each of them being single exponential. It was established that amplitude of PhA, as well as time constant determined by content of structural fragments with different values of $n_c$.

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# ПОРІВНЯЛЬНИЙ АНАЛІЗ КІНЕТИКИ ФІЗИЧНОГО СТАРІННЯ В АРСЕН-СЕЛЕНОВИХ СТЕКЛАХ

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Проаналізовано особливості кінетики втрат ентальпії ΔH(t) в процесі фізичного старіння в Se-збагачених халькогенідних стеклах у межах ланцюгово-пов’язаної структурної моделі. Механізм природного фізичного старіння пояснено особливостями структурно-топологічнимих комплексів (співвідношенням гетеро- і гомополярних фрагментів) досліджуваних стекол.

**Ключові слова:** халькогенідні стекла, фізичне старіння, диференціальна скануюча спектроскопія, структурні фрагменти.