



# On the compositional diversity of physical aging kinetics in chalcogenide glasses



O. Shpotyuk<sup>a,b,\*</sup>, A. Kozdras<sup>c</sup>, V. Balitska<sup>d</sup>, R. Golovchak<sup>e</sup>

<sup>a</sup> Institute of Physics of Jan Dlugosz University of Czestochowa, 13/15, al. Armii Krajowej, Czestochowa 42201, Poland

<sup>b</sup> Vlokh Institute for Physical Optics, 5 Dragomanov Str., 79031 Lviv, Ukraine

<sup>c</sup> Institute of Mathematics and Physics, Department of Physics, Opole University of Technology, 75, Ozimska Str., Opole 45370, Poland

<sup>d</sup> Lviv State University of Vital Activity Safety, 35, Kleparivska Str., Lviv 79007, Ukraine

<sup>e</sup> Department of Physics and Astronomy, Austin Peay State University, Clarksville, TN 37044, USA

## ARTICLE INFO

### Article history:

Received 27 October 2015

Received in revised form 16 January 2016

Accepted 20 January 2016

Available online xxxx

### Keywords:

Chalcogenide glass

Aging

Kinetics

Enthalpy loss

## ABSTRACT

Compositional features of enthalpy losses  $\Delta H(t)$  caused by long-term physical aging at normal conditions are studied at the example of Se-rich chalcogenide glasses  $As_{20}Se_{80}$ ,  $As_{30}Se_{70}$  and  $Ge_5Se_{95}$  obeying “chain-crossing” structural model. The observed relaxation kinetics in general are described by a stretched exponential behavior, but can be also parameterized in terms of multi-step single exponential decays. Microstructural mechanism of natural physical aging in the studied glasses is explained by accepting their structural–topological specificity with a decisive role of preferential chemical environment around Se atoms. The characteristic time constants of aging are shown to increase in more topologically constrained structural fragments capable to relaxation. Independent relaxation stages originated from different chemical environments in  $As_{10}Se_{90}$  and  $Ge_5Se_{95}$  glasses allow observation of plateau-like behavior. However, plateaus are found to be smoothed in  $As_{20}Se_{80}$  glass because of overlap of different structural complexes responsible for relaxation.

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## 1. Introduction

Physical aging (PhA) is an important characteristic of all glassy-like solids, which are always obtained in technologically-frozen metastable state, that causes uncontrolled drift of their physical–chemical properties with time [1–3]. The PhA can be conveniently studied as enthalpy recovery ( $\Delta H$ ) with a differential scanning calorimetry (DSC) technique [4]. It was commonly accepted that PhA  $\Delta H(t)$  kinetics should be described in terms of a single time scale of equilibration when thermodynamic quantities approach equilibrium value of supercooled liquid at a particular aging temperature, following stretch-exponential behavior [5,6]. This was usually expressed as sigmoidal time dependence of fictive temperature  $T_f$  starting from the glass transition temperature  $T_g$  on quenching and approaching the aging temperature  $T_a$  with time. However, dramatic deviations from the extrapolated liquid-like behavior (when glass system reaches limiting  $T_f$  different from  $T_a$ ) reported in some glassy polymers [7,8] have led to a theory that equilibrium state of supercooled liquid cannot be attained for some glass-forming systems, e.g. residual excess of enthalpy  $\delta_H$  remains in these glasses and cannot be lost [9]. Discovery of plateaus in  $\Delta H(t)$  long-term kinetics of

chalcogenide glasses [10] and some polymers [11,12] has removed this discrepancy, testifying the existence of at least two equilibration mechanisms [12]. If one takes into account the existence of intermediate plateaus, then the observed non-zero  $\delta_H$  values can be explained by termination of the experiment just at the time when kinetics reached a first noticeable plateau (intermediate stage), while longer time-scale is needed to capture a full behavior. Direct evidence for two equilibration mechanisms in enthalpy recovery of several glassy organic polymers (polystyrene and polycarbonate) has been reported recently [7,11,12]. More than one plateau was reported for Se-rich glasses in  $\Delta H(t)$  dependence on  $\sim 20$  years' timescale of aging at room temperature [10]. So, we can ask reasonable questions:

What are the reasons/criteria to observe the plateaus in PhA kinetics?

How many plateaus can be observed, and why they are clear for some glasses and not for others?

By analyzing the available data, one can put forward a hypothesis that long-term PhA plateau in the enthalpy recovery is well observed experimentally for polymers with quite narrow distribution of molecular weights (like polystyrene and polycarbonate studied in [12]), while polymers with wide distribution of molecular weights demonstrate smoothed behavior [13]. To check this hypothesis, the full kinetics of PhA should be thoroughly studied with DSC for glasses with different distributions of molecular weights of constituent structural units, but simultaneously belonging to the same chemical family.

\* Corresponding author at: Institute of Physics of Jan Dlugosz University of Czestochowa, 13/15, al. Armii Krajowej, Czestochowa 42201, Poland.  
E-mail address: [olehshpotyuk@yahoo.com](mailto:olehshpotyuk@yahoo.com) (O. Shpotyuk).

To our opinion, the best model objects for such studies are the chalcogenide glasses (ChGs) of binary As/Ge–Se systems [14,15]. The Se-rich ChGs are characterized by relatively fast kinetics of PhA at room temperature in comparison to oxide glasses, for example, that allows studies of almost complete kinetics of natural PhA at accessible experimental timescales (ranging from a few hours to years) [4,16,17]. On the other hand, difference in molecular weight distribution can be achieved in these glasses by changing the connectivity between network-forming structural units. By changing chalcogen content in the sample, it is possible to change the number of mechanical constraints per atom  $n_c$ , which, in turn, will result in the formation of rigid molecular blocks of different molecular weights that will ultimately affect the relaxation behavior [18]. For ideal covalent networks of binary systems, the number of constraints per atom can be related to the average number of covalent bonds per atom ( $Z$ ), which is determined by chalcogen content (chemical composition) [4,18]. In respect to  $Z$ , the whole glass-forming region of ChG can be divided into three regions:  $Z < 2.4$ ,  $n_c < 3$  which corresponds to floppy under-constrained glasses;  $Z = 2.4$ ,  $n_c = 3$  associated with optimally-constrained rigid unstressed glasses; and  $Z > 2.4$ ,  $n_c > 3$  which is due to the over-constrained stressed rigid glasses. Significant PhA effect at room temperatures was recorded only for under-constrained floppy Se-rich glasses with  $Z < 2.4$  and  $n_c < 3$  [16,17]. The kinetics of enthalpy losses caused by a prolonged natural PhA (more than two decades) in these ChGs are found to have non-elementary character, showing multiple growing steps, the exact number and features of which being not well clear [10,19,20]. This multiple step-wise kinetics were assumed to be caused by mixed sequent/parallel hierarchy in the underlying relaxation events, which were directly dependent on the preferential chemical order in ChG. The latter was evidenced, in part, by chaotic analysis of time series applied to PhA kinetics in As–Se glasses [20], when embedding dimensions of reconstructed phase space appeared as a direct consequence of well-defined sequent stages in the growing kinetics of enthalpy losses  $\Delta H(t)$ .

In this work, the kinetics of natural PhA in glassy  $g\text{-Ge}_5\text{Se}_{95}$  ( $Z = 2.1$ ),  $g\text{-As}_{10}\text{Se}_{90}$  ( $Z = 2.1$ ),  $g\text{-As}_{20}\text{Se}_{80}$  ( $Z = 2.2$ ) and  $g\text{-As}_{30}\text{Se}_{70}$  ( $Z = 2.3$ ) are analyzed from the point of molecular weight distribution related to a number of proper structural network-forming units.

## 2. Materials and methods

The ChG samples of  $\text{As}_{10}\text{Se}_{90}$ ,  $\text{As}_{20}\text{Se}_{80}$ ,  $\text{As}_{30}\text{Se}_{70}$  and  $\text{Ge}_5\text{Se}_{95}$  compositions were prepared in 1985 by conventional melt quenching route in evacuated quartz ampoules from a mixture of high purity (no worse than three nines) precursors, as described in details elsewhere [16,17]. The furnace was rocked to obtain the most homogeneous melt. Amorphous state and chemical composition of these ChGs was controlled visually by a characteristic conch-like fracture, data of X-ray diffractometry and X-ray photoelectron spectroscopy. Bulk samples of ~20 mg were used for DSC measurements.

DSC measurements were carried out using a NETZSCH 404/3/F microcalorimeter pre-calibrated with a set of standard elements, the DSC curves being recorded in the ambient atmosphere with  $q = 5$  K/min heating rate. This calibration procedure was repeated each time during routine kinetic measurements according to the developed protocol [10,16,17,19]. Three independent DSC measurements were performed in each case to confirm the reproducibility of the results. With all the precautions used, the enthalpy losses  $\Delta H(t)$  could be determined with  $\pm 0.2$  J/g accuracy, which includes measurement uncertainties and statistical error.

Before aging tests all samples were rejuvenated, e.g. heated ~50 K above the glass transition temperature  $T_g$  and cooled at  $q = 5$  K/min rate to the room temperature ( $T_a = 23$  °C). Then, the rejuvenated samples were stored in the dark at the same ambient conditions and repeatedly measured after certain time intervals (up to 6 years). Thus, the kinetic curves were detected in *backward-rejuvenation chronology*,

assuming that rejuvenated samples were quite close to as-prepared ones. Obviously, the difference in the area under DSC signal of aged and rejuvenated ChGs, calculated as shown in [10], is proportional to the enthalpy losses  $\Delta H(t)$ , this parameter being used to parameterize the PhA kinetics. The raw DSC patterns were processed with NETZSCH PC software package.

## 3. Results

Time-dependent enthalpy losses  $\Delta H(t)$  associated with long-term natural PhA in  $g\text{-As}_{10}\text{Se}_{90}$  are analyzed in details elsewhere [10,20], and in this paper we will use these results for a discussion on  $\Delta H(t)$  kinetics of  $\text{Ge}_5\text{Se}_{95}$ ,  $\text{As}_{20}\text{Se}_{80}$  and  $\text{As}_{30}\text{Se}_{70}$  glasses.

The kinetics of enthalpy recovery in  $g\text{-As}_{10}\text{Se}_{90}$  demonstrated well-expressed step-like behavior with at least 4 observable plateaus [20]. Similar multi-step-wise  $\Delta H(t)$  behavior is also characterized for PhA kinetics in  $g\text{-Ge}_5\text{Se}_{95}$  (Fig. 1), which in respect to the average coordination number  $Z$  is the full analog of  $g\text{-As}_{10}\text{Se}_{90}$  ( $Z = 2.1$ ). This kinetics exhibits two obvious steps followed by a third one, which corresponds to the close-to-saturation level of long-term PhA (Fig. 1). With increase in As concentration, the plateaus become less distinguished in  $g\text{-As}_{20}\text{Se}_{80}$  ( $Z = 2.2$ ) sample (Fig. 2), and again at least two steps can be resolved in  $\Delta H(t)$  kinetics of  $g\text{-As}_{30}\text{Se}_{70}$  ( $Z = 2.3$ ) sample (Fig. 3).

The straightforward fitting of the experimental  $\Delta H(t)$  data with stretched exponential relaxation function [21,22]:

$$\Delta H(t) = \Delta H_\infty \left[ 1 - \exp\left(-\frac{t}{\tau}\right)^\beta \right], \quad (1)$$

where  $\Delta H_\infty$  is the maximal saturation value of enthalpy recovery achieved after fully completed PhA, gives the non-exponentiality index (fractional exponent)  $\beta \approx 0.30 \pm 0.05$  and time constants  $\tau \sim 10^3\text{--}10^5$  days depending on the composition. Remarkably, at the example of  $g\text{-As}_{10}\text{Se}_{90}$  it was shown [10,19] that time-dependent  $\Delta H(t)$  changes could be characterized by mixed serial kinetics, so that the overall process of PhA could be defined as a sum of several exponents:

$$\Delta H_i(t) = \sum_{i=1}^n \theta(t - \Delta t_i) \left[ a_i + b_i \left( 1 - \exp\left(-\frac{t - \Delta t_i}{\tau_i}\right) \right) \right], \quad (2)$$

where  $(t - \Delta t_i)$  is the Heaviside step function, whose value is 0 for  $t < \Delta t_i$  and 1 for  $t > \Delta t_i$ ;  $\Delta t_i$  is a so-called retardation time giving a time delay

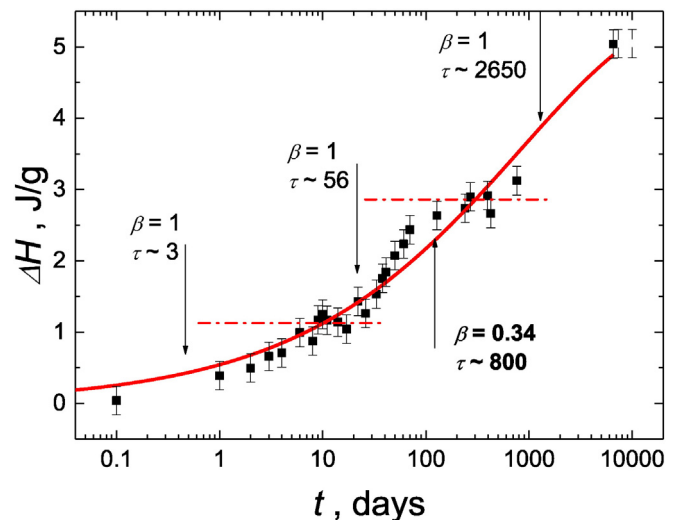


Fig. 1. Kinetics of enthalpy losses  $\Delta H(t)$  in  $g\text{-Ge}_5\text{Se}_{95}$  decomposed in three serial-subsequent single-exponential steps.

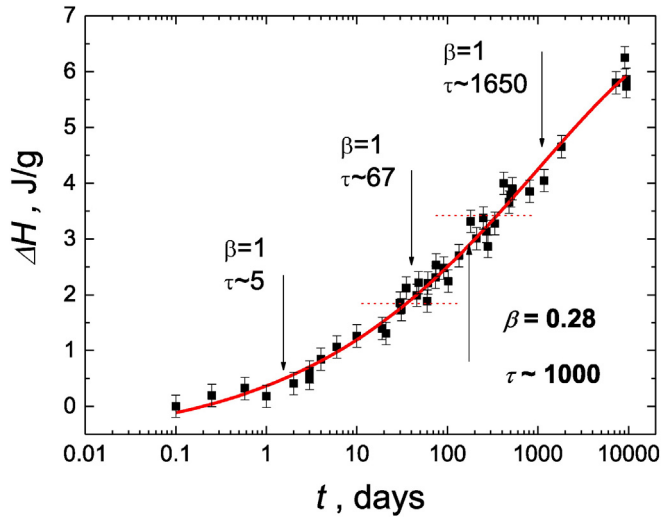


Fig. 2. Kinetics of enthalpy losses  $\Delta H(t)$  in  $g\text{-As}_{20}\text{Se}_{80}$  decomposed in three serial-subsequent single-exponential steps.

between neighboring sequent relaxation steps; and  $n$  is a number of steps in the relaxation kinetics.

By applying this approach to three observed steps ( $i = 3$ ) in the enthalpy relaxation  $\Delta H(t)$  kinetics of  $g\text{-Ge}_5\text{Se}_{95}$  (Fig. 1), the PhA can be parameterized numerically as shown in Table 1. Although  $\Delta H(t)$  kinetics is smoother for  $g\text{-As}_{20}\text{Se}_{80}$ , one can obtain fitting parameters listed in Table 2 if approach (2) is applied assuming 3 steps in the kinetics as shown in Fig. 2. Finally, only two steps can be distinguished in  $\Delta H(t)$  of  $g\text{-As}_{30}\text{Se}_{70}$  ( $Z = 2.3$ ), in which parameters determined according to Eq. (2) are gathered in Table 3.

#### 4. Discussion

The observed values of  $\Delta H(t)$  and steps can be related to the completeness of PhA in each sample. The maximum enthalpy a glass can lose after an infinitely long PhA at  $T_a$  can be roughly estimated as

$$\Delta H_\infty \approx \Delta C_{p(T_g)} \cdot (T_g^c - T_a) \quad (3)$$

where  $\Delta C_{p(T_g)} = (C_{pl} - C_{pg})$  is measured at glass-to-supercooled liquid transition ( $C_{pl}$  and  $C_{pg}$  are the thermal capacities of supercooled liquid

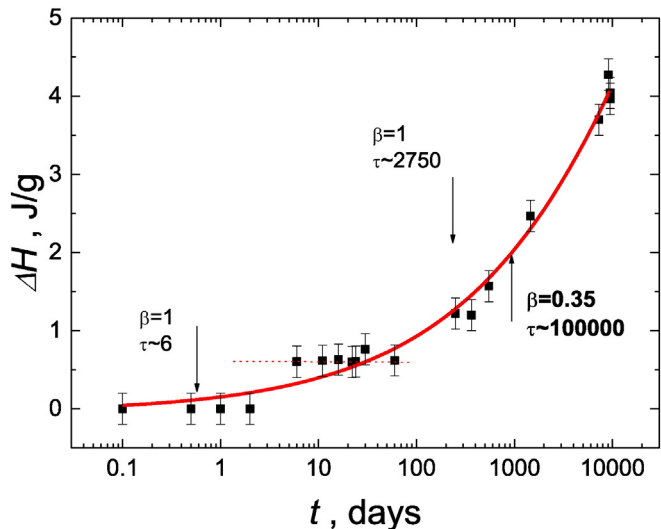


Fig. 3. Kinetics of enthalpy losses  $\Delta H(t)$  in  $g\text{-As}_{30}\text{Se}_{70}$  decomposed in two serial-subsequent single-exponential steps.

Table 1  
Fitting parameters in Eq. (2) describing three-step PhA kinetics in  $g\text{-Ge}_5\text{Se}_{95}$ .

Step # (duration in days)	Goodness of fitting $r^2$	$a_i$ , J/g	$b_i$ , J/g	$a_i + b_i$ , J/g	$\tau$ , days	$\Delta t_i$ , days
$i = 1$ ( $0 \div 10$ )	0.005	0	0.97	0.97	3	0
$i = 2$ ( $10 \div 1000$ )	0.022	0.97	1.92	2.89	56	8
$i = 3$ ( $>1000$ days)	0.017	2.89	2.27	5.16	2650	403

and glass, respectively), and  $T_g^c$  is the glass transition temperature obtained when glass is cooled through the transition region at a given rate (equal to the fictive temperature  $T_f$  of the rejuvenated glass determined by the Moynihan's method) [23].

The  $\Delta H_\infty$  parameters for the investigated ChG are calculated using experimental data on  $\Delta C_{p(T_g)}$  (Table 4). From the obtained results it can be concluded, that natural PhA in  $g\text{-As}_{10}\text{Se}_{90}$  is complete after two decades of aging [19], while  $g\text{-As}_{20}\text{Se}_{80}$  and  $g\text{-As}_{30}\text{Se}_{70}$  samples have aged only to ~55% and ~25% of their maximum  $\Delta H_\infty$  values, respectively, for the same period of time. So, more steps are possible in  $\Delta H(t)$  kinetics in these ChGs. Nevertheless, one should plan an experiment for at least decades to observe them at room temperature in the samples with low chalcogen content.

It is known that the mechanism of natural PhA in ChG is based on elementary relaxation acts of inner Se atoms within double-well potential (DWP) formed by the nearest chemical environment [4,24–26]. This process leads to the local alignment of Se-rich regions, which, in turn, creates prerequisite for the subsequent stage of PhA – the shrinkage of glass volume [24]. In Se-rich As(Ge)–Se glasses, three types of DWP for inner Se atoms are possible: –Se–Se– (A sites), =As(=Ge)–Se–Se– (B sites) and =As(=Ge)–Se–(=Ge)As= (C sites). According to the “chain crossing” model, which is supposed to be valid for all studied Se-rich glass compositions [4,27], the ratio of A:B sites in  $g\text{-As}_{10}\text{Se}_{90}$  is 67:33. The same ratio in  $g\text{-Ge}_5\text{Se}_{95}$  (B sites are associated now with =Ge–Se– complexes) having similar  $Z = 2.1$  is 79:21. In both of these ChGs concentration of A sites exceeds the concentration of B sites. The opposite trend is characterized for more rigid  $As_{20}Se_{80}$  ChG with  $Z = 2.2$ , where A:B ratio becomes 25:75 according to the “chain crossing” model formalism. At further  $Z$  increase, the A sites disappear and C sites appear instead, giving B:C ratio 71:29 for  $g\text{-As}_{30}\text{Se}_{70}$  with  $Z = 2.3$ . The C sites are optimally constrained with  $n_c = 3$  and, thus, do not participate in relaxation at room temperatures. Instead, they link  $AsSe_{3/2}$  pyramids into rigid clusters, leading to the increased effective molecular weight of relaxing units bridged by B sites.

Since –Se–Se– fragments (A sites) possess the lowest DWP barrier, they should determine the fastest initial stages of PhA in Se-rich ChG samples, sampling the whole network into kind of low-molecular weight relaxing units. Owing to the number of A sites (A:B ratio) in  $g\text{-As}_{10}\text{Se}_{90}$  and  $g\text{-Ge}_5\text{Se}_{95}$  samples and taking into account the length of Se chains predicted by the “chain crossing” model, we expect site A to relax almost independently of site B. Therefore, we speculate that plateaus at  $\Delta H \sim 1\text{--}2$  J/g with short time constants  $\tau$  (few-tens of days) observed in  $\Delta H(t)$  kinetics of these glasses (see Fig. 1 and [19]) are associated with relaxation mechanisms involving A sites.

At later stages of PhA in  $g\text{-As}_{10}\text{Se}_{90}$ ,  $g\text{-Ge}_5\text{Se}_{95}$  and in more rigid  $g\text{-As}_{20}\text{Se}_{80}$  (see Fig. 2), the role of B sites, possessing higher DWP barrier, increases. These B sites can be responsible for the delayed steps in the enthalpy recovery  $\Delta H(t)$  owing to a greater number of constraints per

Table 2  
Fitting parameters in Eq. (2) describing three-step PhA kinetics in  $g\text{-As}_{20}\text{Se}_{80}$ .

Step # (duration in days)	Goodness of fitting $r^2$	$a_i$ , J/g	$b_i$ , J/g	$a_i + b_i$ , J/g	$\tau$ , days	$\Delta t_i$ , days
$i = 1$ ( $0 \div 10$ )	0.093	0	1.4	1.4	5	0
$i = 2$ ( $10 \div 1000$ )	0.037	1.4	2.0	3.4	67	18
$i = 3$ ( $1000 \div 10,000$ )	0.048	3.4	2.7	6.1	1650	305

**Table 3**  
Fitting parameters in Eq. (2) describing two-step PhA kinetics in  $g\text{-As}_{30}\text{Se}_{70}$ .

Step # (duration in days)	Goodness of fitting $r^2$	$a_i$ , J/g	$b_i$ , J/g	$a_i + b_i$ , J/g	$\tau$ , days	$\Delta t_i$ , days
$i = 1$ (0 ÷ 10)	0.011	0	0.7	0.7	6	0
$i = 2$ (1000 ÷ 10,000)	0.167	0.7	3.4	4.1	2750	300

atom  $n_c$  associated with them. Indeed, if  $-\text{Se}-\text{Se}-\text{Se}-$  fragments possess the smallest  $n_c = 2.00$  typical for “pure” Se chains, the B sites ( $=\text{As}-\text{Se}-\text{Se}-$  or  $=\text{Ge}-\text{Se}-\text{Se}-$ ) have  $n_c$  equal to 2.45 and 2.71, respectively. It means that time constants of steps in structural relaxation of  $g\text{-Ge}_5\text{Se}_{95}$  associated with B sites can be higher than in  $g\text{-As}_{10}\text{Se}_{90}$ , despite both glasses possess the same average coordination number  $Z = 2.10$ .

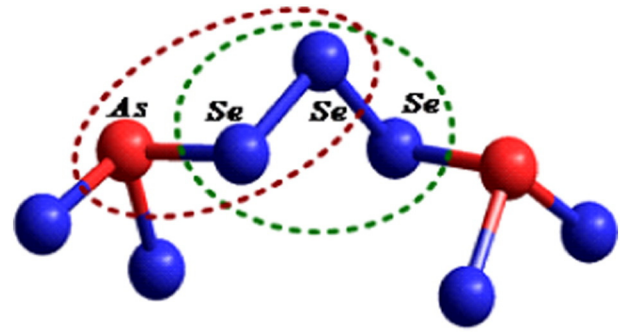
The most probably, the  $=\text{As}-\text{Se}-\text{Se}-$  fragments (B sites) are also responsible for slow enthalpy recovery in  $g\text{-As}_{30}\text{Se}_{70}$  (Fig. 3) with time constants  $\tau$  reaching thousands of days. Small deviations from the “chain crossing” model in the form of some non-zero concentration of  $-\text{Se}-\text{Se}-\text{Se}-$  fragments (A sites) in  $g\text{-As}_{30}\text{Se}_{70}$  [28,29] can be a reason for the first step in its  $\Delta H(t)$  kinetics (Fig. 3) with time constant  $\sim 6$  days. It is noteworthy that retardation times  $\Delta t_i$  in master Eq. (2) for most essential enthalpy steps of natural PhA associated with preferred relaxation of the same type of atomic environment around Se atoms are comparable in all ChG compositions (compare data in Tables 1–3 and [19]).

In real, the kinetics of natural PhA in ChG is more complicated, revealing a number of intermediate saturation plateaus and slight growing steps, leading to a wide scattering in the experimental points, which is especially well perceived for  $g\text{-As}_{20}\text{Se}_{80}$  (Fig. 2). It means that PhA cannot be simply defined only by independent relaxation of the above atomic sites (A, B and/or C) or their ratio. Indeed, when Se chain becomes short enough, the A sites overlap with B sites. It is illustrated in Fig. 4 by overlapping of  $=\text{As}-\text{Se}-\text{Se}-$  (B site, distinguished by red ellipse) and  $-\text{Se}-\text{Se}-\text{Se}-$  (A site, distinguished by green ellipse) parts of the same  $=\text{As}-\text{Se}-\text{Se}-\text{Se}-\text{As}=\text{}$  chain. Therefore, these sites cannot relax independently any more, leading to complicated coupling between relaxing structural units, and, thus, broadening their effective molecular weight distribution. Of course, this effect is most significant in the case of equivalent inputs from both these sites, so in ChG of  $\text{AsSe}_{4.5}$  composition ( $Z = 2.18$ ) [29]. We believe that it is one of the major reasons for the observation of smoothed  $\Delta H(t)$  kinetics in various polymer materials. The other factor, which should be mentioned here, is connected with temperature dependence of the constraints, which can be active/inactive below/above certain threshold temperature.

So, we can speculate that necessary condition to observe distinguished plateau-like behavior in the PhA kinetics is the possibility of independent structural relaxation of one type of relaxing units (equivalent to narrow distribution of molecular weights in organic polymers [11,30,31]) at a time, with distinct time constants  $\tau$  acceptable for experimental observations. Such condition is fulfilled in  $g\text{-As}_{10}\text{Se}_{90}$  and  $g\text{-Ge}_5\text{Se}_{95}$ , where chain-like  $-\text{Se}-\text{Se}-\text{Se}-$  fragments (A sites) can relax almost independently from  $=\text{As}-\text{Se}-\text{Se}-$  ( $=\text{Ge}-\text{Se}-\text{Se}-$ ) ones (B sites) owing to long Se chains allowed by a composition. In  $g\text{-As}_{20}\text{Se}_{80}$ , A sites are significantly overlapped with B sites (Fig. 4), so that they cannot relax independently any more. This leads to a complicated scenario of structural relaxation (equivalent to a broadening of molecular weight distribution) and smashes step-wise behavior in the enthalpy recovery  $\Delta H(t)$  at more

**Table 4**  
Thermodynamic parameters describing completeness of natural PhA in ChG.

ChG composition (Z)	$\Delta C_{p(Tg)}$ , J/gK	$T_F$ , K	$\Delta H_{\infty}$ , J/g
$g\text{-As}_{10}\text{Se}_{90}$ ( $Z = 2.10$ )	0.12	350	6.7
$g\text{-As}_{20}\text{Se}_{80}$ ( $Z = 2.20$ )	0.14	372	10.8
$g\text{-As}_{30}\text{Se}_{70}$ ( $Z = 2.30$ )	0.15	397	15.3
$g\text{-Ge}_5\text{Se}_{95}$ ( $Z = 2.10$ )	0.14	344	6.9



**Fig. 4.** Schematic illustration of bridge-like  $=\text{As}-\text{Se}-\text{Se}-\text{Se}-\text{As}=\text{}$  structural unit (red circles are used for 3-fold coordinated As atoms and blue circles stand for 2-fold coordinated Se atoms) as geometrically-optimized with ab initio quantum chemical calculations with RHF/6-311G\* basis set [29].

prolonged PhA durations. The same result is expected for multinary ChG systems, possessing a large variety of different chemical environments (multichemical environment such as in  $\text{As}-\text{Ge}-\text{Se}$  glass) and short chalcogen chains.

## 5. Conclusions

Kinetics of enthalpy losses  $\Delta H(t)$  caused by natural PhA in Se-rich ChG exhibits a well-expressed step-wise character only if the composition allows more or less independent relaxation of different relaxing units, which time constants differ enough to be resolved experimentally. Significant length of Se chains (such as in  $g\text{-As}_{10}\text{Se}_{90}$  and  $g\text{-Ge}_5\text{Se}_{95}$ ) allowed to distinguish the plateau-like behavior associated with quick-relaxing  $-\text{Se}-\text{Se}-\text{Se}-$  chemical environment at the early stages of PhA and further plateaus caused mainly by more slowly relaxing  $=\text{As}(=\text{Ge})-\text{Se}-\text{Se}-$  environment. The plateaus are found to be smoothed in the ChG possessing essential overlap between different structural fragments capable to relax, such as  $-\text{Se}-\text{Se}-\text{Se}-$  and  $=\text{As}-\text{Se}-\text{Se}-$  sites in  $g\text{-As}_{20}\text{Se}_{80}$ .

On the basis of these results, we conclude that the existence of differently relaxing structural units with narrow molecular weight distributions (molecular fragment for ChG can be defined here as independently relaxing structural unit, such as pyramids, tetrahedral, A, B, C sites or their agglomeration if the units are rigidly joint together) should lead to the observable plateaus in  $\Delta H(t)$  kinetics, while broadening of molecular weight distributions or their strong overlap should cause smooth scattered pattern in  $\Delta H(t)$  kinetics.

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