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Is the marginality of non-reversible heat flow in MDSC experiments a sufficient criterion for self-organization in network glass-formers?

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Physical ageing caused by 25-years natural storage is studied in glassy $\text{As}_{25}\text{S}_{75}$ by conventional DSC technique. The observed effect was recorded as a significant increase in the value of glass transition temperature and endothermic peak area in the vicinity of glass-to-supercooled liquid transition. This result testifies, that marginal values of non-reversible heat flow in temperature-modulated DSC (ΔH_{nr}), observed for *as-prepared* (or *short-term aged*) $\text{As}_x\text{S}_{100-x}$ samples within $22.5 < x < 29.5$ compositional range [Ping Chen et al 2008 Phys. Rev. B78 224208], can significantly increase after longer period of physical ageing. Owing to these and previous results on collapse of the reversibility window in

$\text{As}_x\text{Se}_{100-x}$ glasses after long-term physical ageing, we have concluded that marginality of non-reversible heat flow is not a sufficient criterion for express identification of the optimally-constrained self-organized phases in chalcogenide glasses. To make a conclusion on the marginality of ΔH_{nr} , the long-term component of physical ageing should be taken into account. A comparison between conventional or temperature-modulated DSC scans recorded for long-term aged and rejuvenated glass samples is considered as a suitable criterion for physical ageing in glasses and, therefore, for the possibility of their network to be optimally-constrained.

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1 Introduction Today, we can surely declare that no other class of materials has contributed to so many modern-day technologies as glasses, testifying on high importance of these disordered solids for human society [1,2]. Undoubtedly, the glasses will remain the high-tech materials, provided we can understand correlations between glass-forming ability, compositional trends in glass properties and glass structure.

A self-organization approach, developed on main principles of mean field theory and constraints counting algorithm, opens a conceptually new insight on this problem [3–6]. Assuming covalent bonds equivalent to Lagrangian constraints and their full saturation in glass network, the

glass structure is considered to be floppy or under-constrained if the average number of constraints per atom (n_c) is less than space dimensionality ($n_c < 3$), rigid and stressed or over-constrained if $n_c > 3$ and rigid but not stressed or optimally-constrained if $n_c = 3$ [4–10]. The Maxwell constraints counting algorithm predicts solitary transition from floppy to stressed-rigid network with increasing of its backbone connectivity (or n_c) by changing composition [7,8]. However, recently it was shown that this transition splits into two points [3]: second-order transition from floppy to unstressed-rigid and first-order transition from unstressed-rigid to stressed-rigid network. The stress-free intermediate phase having just $n_c = 3$ appears in

some range of compositions instead of a solitary point, because of self-organization of covalent networks [3]. Self-organization means that glass avoids creating over-constrained stressed regions, keeping $n_c = 3$ as long as possible unless there is no alternative [3,4]. Self-organized glasses, which belong to the intermediate-phase, are most attractive for device applications because they possess non-ageing ability. For comparison, the under-constrained glasses exhibit a pronounced drift in their physical-chemical properties caused by thermodynamically-driven forces in order to achieve more favorable thermodynamic state. This effect is known as physical ageing. Over-constrained glasses also age but the mechanism of related structural transformations, as well as their influence on physical-chemical properties of glasses, is not well-investigated up to now.

Covalent network glasses, such as chalcogenide glasses (ChG), can be considered as a convenient model object for understanding self-organization phenomenon, since their wide glass-formation regions allow one to obtain systematically under-, optimally- and over-constrained structures within defined glass-forming system by variation in chalcogen content only. Owing to high-coordinated atoms incorporated into glass backbone (such as As, Si or Ge), the ChG allow compositional domains where all underlying networks are optimally-constrained (alternatively, self-organized or self-adaptive), called also intermediate phases or reversibility windows [6].

During last decades, it was believed that marginality of non-reversible component of heat flow in temperature-modulated differential scanning calorimetry (MDSC) experiments provided a universal criterion for compositional demarcation of reversibility windows in ChG [6,9-13]. However, as it was shown recently at the example of binary As_xSe_{100-x} glass system [14], this criterion could not be used quite adequately to determine the reversibility window in terms of topologically self-organized networks with non-ageing ability. The recently repeated MDSC experiment with As-Se samples [13], which had been used eight years ago to establish the reversibility window in this binary ChG system within $29 \leq x \leq 37$ compositional range [9], have led, in fact, to the same conclusion. The compositional “narrowing” of reversibility window in As-Se system was observed in both cases after eight and twenty years of natural storage [13,14]. Indeed, to justify the possibility of rigidity transition in As_xSe_{100-x} ChG at $x < 40$ (the solitary transition is expected at $As_{40}Se_{60}$ composition), the existence of anomalous quasi-tetrahedral $Se=AsSe_3$ units ($x=28.5$) with double-bonded Se are usually assumed [9,11-13]. Despite these structural units are characterized by optimal number of Lagrangian constraints per atom ($n_c = 3.00$), they cannot be accepted as main building blocks for a backbone of As-based ChG obtained by conventional melt-quenching route [14-17]. Structural-chemical anomalies like double bonds need a close atomic packaging (the length of expected double bond seems to be 0.2 Å shorter than single covalent bond [15,18]), which is better satisfied

for phosphorous chalcogenides, or under extreme conditions (such as high pressures and temperatures, as it was shown by Borisova [15]).

In this work we examine the possibility to use marginality of non-reversible component of heat flow in MDSC experiments as a criterion for self-organization of another canonical ChG system, the binary As_xS_{100-x} glasses, which are claimed to have a wide reversibility window domain in $22.5 < x < 29.5$ range of compositions [11]. Conventional DSC measurements arranged in a normal real-time chronology conjugated with known rejuvenation procedure [19] will be used for these purposes.

2 Experimental Only $As_{25}S_{75}$ glass composition of binary As_xS_{100-x} system was tested by us. This composition is of a special interest, because it lays just in the middle of the predicted self-organized phase in this system [11], where all ChG are supposed not to undergo any structural relaxation associated with physical ageing.

The tested $As_{25}S_{75}$ glass samples were prepared near a quarter century ago by traditional melt-quenching technique [15] using high-purity initial ingredients. The ingots were air-quenched to a glassy state, which was controlled visually by a character conchoidal fracture, X-ray diffraction measurements and express electron-sonde microanalytical confirming glass composition.

After synthesis all samples were sealed in hermetic plastic bags and stored in the darkness under room conditions nearly 25 years before our calorimetric experiments. Owing to the above storage conditions and the value of glass transition temperature in this glass (~390 K in as-prepared state), the externally-activated processes are not expected to be significant during the storage. The vitreous state of the aged samples was checked again by conventional X-ray diffraction measurements showing typical pattern for glassy substances without any sharp reflexes character to crystalline inclusions. So, no phase separation or crystallization occurred in the considered samples during their prolonged storage. In addition, the composition and purity of the aged $As_{25}S_{75}$ glassy samples were checked by high-resolution x-ray photoelectron spectroscopy (Scienta ESCA-300) analysis.

The DSC measurements were performed using NETZSCH 404/3/F microcalorimeter pre-calibrated with a set of standard elements, the DSC curves being recorded in the ambient atmosphere with 5-15 K/min heating rates. Three independent DSC measurements were performed to confirm reproducibility of the obtained results. The glass transition temperature T_g was determined from DSC heating data in cross-point of tangents at the beginning of glass-to-supercooled liquid transition (a so-called “onset” T_g value), using Proteus[®] software. This program was also used to determine endothermic peak area A in the vicinity of glass transition. Statistical deviation of T_g for different measuring cycles did not exceed ± 0.3 °C, while error in peak area was about 2 %. To reach as-prepared state of the

investigated 25-years aged samples, the rejuvenation procedure involving heating above T_g and subsequent cooling [19] was performed just in the microcalorimeter chamber.

3 Results and discussion The effect of physical ageing is revealed in DSC curves of ChG as strong endothermic peak measured in the region of glass-to-supercooled liquid transition near T_g [19]. Besides the structural relaxation of glass network while going through the glass transition region, this peak also includes component connected with regaining of entropy lost during natural storage. The under-peak area A is directly proportional to the enthalpy losses ΔH and can be used as the reliable control parameter to quantify physical ageing effect. In fact, A value determined as shown in Fig. 1 can be roughly compared to the value of non-reversible heat flow component ΔH_{nr} in MDSC experiments. It means, that nonzero A value in DSC experiment corresponds to the nonzero value of non-reversible heat flow in MDSC experiment on the same glass sample.

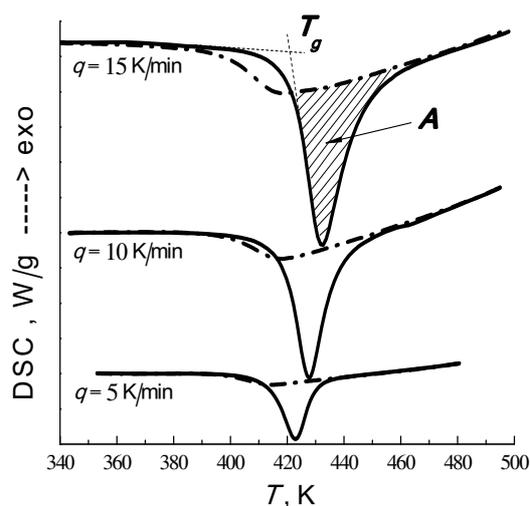


Figure 1 DSC curves of 25-years aged (solid) and rejuvenated (dash-dot) $As_{25}S_{75}$ glass at various heating rates q . Method for determination of A and T_g is shown for the case of $q = 15$ K/min.

The DSC curves obtained for 25 years aged and rejuvenated $As_{25}S_{75}$ glass samples at different heating rates q are shown in Fig. 1. The well-expressed endothermic peak in the vicinity of T_g testifies that this glass, which belongs to the middle of reversibility window as determined by MDSC [11], loses a part of its enthalpy/entropy excess (attained in as-prepared state) in a result of 25-years natural storage. The difference in A and glass transition temperature T_g values for rejuvenated and 25-years aged samples ($\Delta A \sim 9$ J/g and $\Delta T_g \sim 25$ K at $q = 15$ K/min heating rate) gives an evidence for significant structural rearrangements during physical ageing. On the other hand, the values of

heat capacity changes $\Delta C_P(T_g)$ during glass-to-supercooled liquid transition are found to be exactly the same for aged and rejuvenated samples giving evidence that prolong natural storage does not cause any chemical ageing effects associated with oxidization, crystallization or other reactions able to modify the glass structure. So, we can conclude in strong accordance to the above results that non-reversible component of heat flow in MDSC experiment will be not marginal for this particular composition after long period of physical ageing. Existence of long-term physical ageing (nonzero ΔA value) in glassy As_xS_{100-x} contradicts strongly to the previous conclusion on a possible reversibility window in glassy As_xS_{100-x} system identified with MDSC technique within $22.5 < x < 29.5$ range of compositions [11]. It means that marginal values of non-reversible heat flow recorded for short-term aged glasses is not an appropriate criterion to determine the limits of reversibility window in these materials, *because its value has a time-dependent kinetics*. In general, enthalpy losses ΔH follow a sigmoidal time dependence as hypothetically shown in Fig. 2, which depends on the choice of ageing temperature T_a in respect to T_g [14,19]. Thus, for some glass compositions with fast component of natural physical ageing (for example, with lower T_g) a significant non-reversible component of heat flow can be detected within short experimental timescale, while for glass compositions with more extended kinetics (higher T_g) the marginal value of this component just after synthesis (or short-term periods of physical ageing) can lead to misleading conclusions. Longer periods of storage depending on the specific kinetics of the glass composition are needed to conclude the existence of an ageing process.

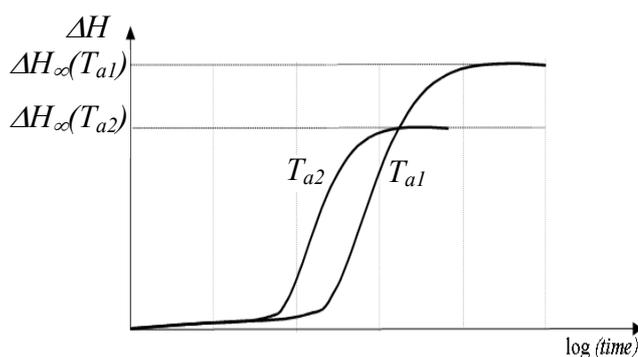


Figure 2 Schematic of expected variation of the energy lost during physical ageing at two different temperatures $T_{a1} < T_{a2} < T_g$.

So, despite its advantage in simultaneous measurements of both reversible ΔH_r and non-reversible ΔH_{nr} heat flow components, the MDSC technique cannot be strictly accepted as quite reliable tool for express identification of optimally-constrained phase in ChG. Indeed, ΔH_{nr} value depends on a lot of factors: conditions of MDSC experiment (heating ramp and temperature modulation param-

eters), quenching rate used during glass preparation, phase composition of glass, its thermal prehistory and, finally, includes a component connected with regaining of the entropy lost during physical ageing [14]. It also depicts the average cooperative rearranging region size distribution during transition from glassy to supercooled liquid state [20]. Thus, its relevance to the connectivity of glass backbone and self-organization phenomenon is not simple, especially in the case of such thermally-inert solid systems as melt-quenched bulk ChG. The observed compositional features in ΔH_{nr} (such as shoulders, plateaus, valleys, flattening regions etc.) [11] can be rather explained by some changes in the structure of glass-forming units corresponding to different heat-flow-absorption networks, like departing of S_8 rings from a covalent network in S-rich glasses ($x < 25$), etc.

Owing to the above consideration, all the boundaries of reversibility windows in ChG (at least As-based), determined using as-prepared or short-term aged samples and marginality of ΔH_{nr} values as a criterion, should be reconsidered. Possibility for long-term kinetics of physical ageing should be taken into account. Moreover, the correlation between self-organization phenomenon and ΔH_{nr} has to be demonstrated more rigorously.

4 Conclusions Strong physical ageing effect, revealed through an increase in glass transition temperature and endothermic peak area in the vicinity of glass-to-supercooled liquid transition, is recorded in $As_{25}S_{75}$ glass subjected to long-term natural storage over 25 years. So, the marginality of non-reversible heat flow in express-MDSC experiments is not an appropriate criterion for identification of the boundaries of reversibility window in these ChG in sense of self-organized phase and non-ageing ability. Owing to the previous results on the collapse of intermediate phase in long-term aged As_xSe_{100-x} glasses, the above conclusion can be generalized for all chalcogenide glasses. We suggest, that DSC experiments (regardless temperature-modulated or conventional) performed in a real-time scale chronology from earliest stages of as-prepared (rejuvenated) up to long-term aged state can be used for the quantitative measure of physical ageing and, thus, correct determination of the boundaries of reversibility windows in ChG.

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