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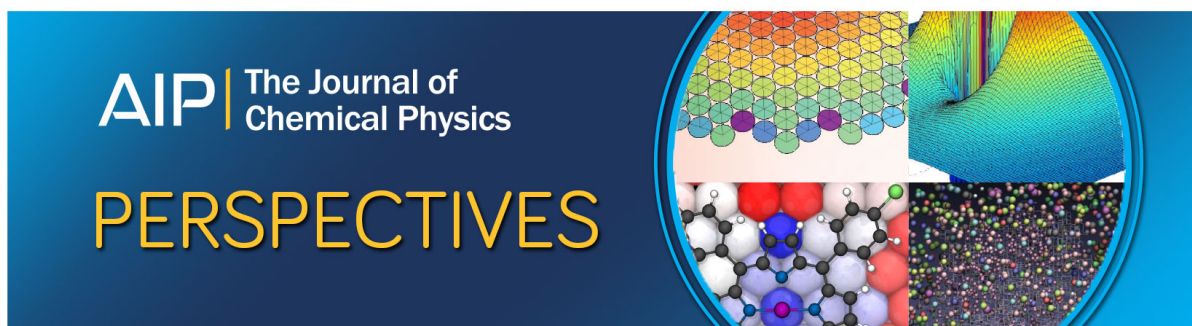
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Comment on “Molecular origin of aging of pure Se glass: Growth of inter-chain structural correlations, network compaction, and partial ordering” [J. Chem. Phys. 146, 224506 (2017)]

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Physical aging is known to be an important but still one of the most controversial problems in modern glass science,¹ remaining highly disputable even for such canonical glass-forming systems as floppy Se-based glasses.

Recently, Dash *et al.*² proposed the mechanism of physical aging in pure Se and Se-rich binary $\text{Ge}_x\text{Se}_{100-x}$ glasses ($x < 10$) based on decoupling of Se_8 crowns from a glass backbone. They performed modulated differential scanning calorimetry (MDSC) measurements on the samples aged for 4–8 months after preparation and observed a substantial narrowing of the width of glass transition W with time. In addition, these authors claimed “the existence of a new topological threshold” near $x = 3$ in the $\text{Ge}_x\text{Se}_{100-x}$ glass system (which corresponds to a mean coordination number of $r = 2.06$) using the maximum in the aging-induced increase of glass transition temperature T_g as a criterion.

However, some misinterpretations of the results in Ref. 2 may seriously mislead the glass scientific community and, thus, need to be carefully addressed.

First, the authors of Ref. 2 came to a conclusion that dramatic reduction in W due to physical aging has been totally missed by other researchers^{3,4} because of kinetic effects in conventional DSC at higher (≥ 10 °C/min) scan rates. In fact, in Ref. 3, the scan rate was 5 °C/min which is quite close to 3 °C/min used as a typical MDSC scan rate by Dash *et al.*² At such low scan rates (2–5 °C/min), the conclusions drawn from MDSC and conventional DSC would be quite similar, which has been convincingly proved at the example of As/Ge–Se glasses.^{3,5,6} The narrowing of glass transition range W as a result of physical aging or annealing was also observed previously in pure Se,⁷ a number of Se-based glasses,^{8,9} and even organic polymers.¹⁰ Moreover, in As–Se glasses, this narrowing was accompanied by changes in the asymmetry of non-reversing heat flow (ΔH_{nr}) measured at 2 °C/min scan rate after ~ 20 years of dark storage at room temperature.⁹ On the other side, if too low scan rate is used in MDSC measurements (like 0.3 °C/min, as used by Dash *et al.*² to capture the narrowing in T_g for vitreous Se), the sample spends too much time at near- T_g temperatures, resulting in a significant temperature-induced structural relaxation

(annealing) that combines with the competitive physical aging effect.

The central point in MDSC research of Dash *et al.*,² i.e., their claim on the new topological threshold near $x = 3$ in $\text{Ge}_x\text{Se}_{100-x}$ glasses, seems to be very controversial. Usually, T_g as defined from heating curves in MDSC/DSC experiments has no strong physical meaning, being just a transition point, which depends on numerous factors, such as heating rate, aging duration, time spent at near- T_g temperatures, etc.^{11,12} A better parameter describing a structural state of a glass is fictive temperature T_F ¹¹ which decreases and approaches aging temperature T_a upon aging.¹² If we are talking about the width of glass transition $W = T_g^{end} - T_g^{onset}$, we have to take into account more factors, such as thermal inertia of a system, linearity, and time of response of the calorimetric equipment.¹³ These parameters affect the apparent value of T_g^{end} and depend on the sample’s mass, thermal contact with crucible and thermocouple, speed of detection system, etc. Linear response conditions in MDSC can vary as a function of thermodynamic fragility of a glass too. Thus, the same conditions used for binary As/Ge selenides might not work for a glassy selenium sample due to a substantial difference in the fragility index. Even if one manages to exclude all these factors by a careful MDSC experiment, the non-linear nature of T_g aging kinetics cannot be ignored.¹⁴ Different regions can be distinguished in T_g aging kinetics of Se-rich glasses, as shown for $\text{As}_{10}\text{Se}_{90}$ glasses,¹⁴ which is equivalent to $\text{Ge}_5\text{Se}_{95}$ glasses in terms of network connectivity (both glasses have $r = 2.1$). In the beginning, T_g remains constant or even decreases slightly;¹⁴ then, after some threshold time t_{th} , the increase in T_g is clearly observed;¹⁴ it is correlated with the shrinkage of a glass backbone, as revealed by *in situ* positron annihilation lifetime measurements.¹⁵ The threshold time depends essentially on T_a , decreasing when T_a approaches T_g ; i.e., t_{th} is different for the glasses with different T_g aged at the same temperature. As a result, the isochronal aging-induced changes in T_g (especially as small as 2–4 °C)² cannot serve as a reliable signature of topological threshold in compositional dependence.

Second, all aging experiments were performed by Dash *et al.*² at room temperature, regardless of the distance from

T_g , which varies from ~ 40 °C for pure Se to about ~ 70 °C for $\text{Ge}_6\text{Se}_{94}$ glasses (see Fig. 4 in Ref. 2). However, the time constant of physical aging as well as the maximum enthalpy ΔH_{∞} , which the glass can lose during physical aging of infinite duration, depend essentially on the distance from T_g .^{12,16} Therefore, if one would like to compare correctly the changes in T_g and/or ΔH_{nr} caused by isochronal physical aging in glasses of different compositions (different contents of Ge in this particular case),² the total effect should be compared (when $\Delta H_{nr} = \Delta H_{\infty}$ or $T_F = T_a$) or performed at the same ($T_g - T_a$) or T_a/T_g for all glasses, as it was convincingly suggested elsewhere.^{14,16} Ideally, aging should be performed at the same non-equilibrium viscosity, which would correspond to very similar Maxwell relaxation times assuming that the shear modulus is similar (estimation of viscosity in the non-equilibrium range is not an easy task, though). Thus, it has been proven that the reversibility window in $\text{Ge}_x\text{Se}_{100-x}$ glasses (compositional domain where $\Delta H_{nr} \approx 0$ and glasses do not age) loses its physical meaning if the measurements are performed at the same ($T_g - T_a$) distance, being to a great extent an artifact of the MDSC experiment.¹⁶ In respect to this finding, the isochronal aging effects in $\text{Ge}_x\text{Se}_{100-x}$ glasses, recorded regardless of their T_g , cannot be simply compared neither in terms of W nor ΔH_{nr} .

Third, if Se_8 crowns are really decoupled from a glass backbone upon aging as suggested by Dash *et al.*,² the structure of aged $\text{Ge}_x\text{Se}_{100-x}$ glasses ($0 < x < 6$) should become more heterogeneous (even if one starts from highly homogeneous samples), consisting of two parts: (i) a Ge-rich rigid network with higher T_g and (ii) a flexible matrix with lower T_g built of Se_8 crown molecules. It seems quite reasonable that this scenario would result in broadening of W or even T_g bifurcation, as observed in some Se-rich Ge–Se glasses after very long physical aging.⁴ Nevertheless, this expectation is evidently in conflict with experimental observations on the narrowing of the T_g range in the aged glasses.^{2,9} Then, one needs to explain why the properties of the aged glass are determined by the only rigid newly formed Ge-rich network, but not a superposition of both Ge- and Se-rich parts. Moreover, calorimetric T_g for the as-milled amorphous Se predominantly built of polymeric Se_n -chains is higher than for the as-quenched Se composed of mixed Se_8 ring molecules and polymeric Se_n -chains,^{17–19} while an opposite trend in T_g is attributed by Dash *et al.*² to the effect of Se_8 crown molecules in Se-rich Ge–Se glasses. Additional argument comes from the fact, that formation of Se_8 crowns in supercooled liquid regime is thermodynamically favorable and irreversible process.^{20,21} If it occurred as a result of aging, then the rejuvenation procedure (heating of the glass just above T_g), which is known to completely erase the effect of physical aging,^{3,4,12} would become impossible. Even the structure of vitreous Se itself is a matter of ongoing discussions, pertaining to the controversies in the Se chains/rings ratio.²²

The evidence on possible decoupling of Se_8 crowns comes in Ref. 2 from the Raman lineshape analysis in the 200–260 cm^{-1} range, where three overlapped vibrational modes are considered.² The central mode at ~ 250 cm^{-1} (B) is associated with uncorrelated Se-chains, while the other two side modes at ~ 235 cm^{-1} (A) and ~ 260 cm^{-1} (C) are attributed to the correlated Se-chains and Se_8 molecules, respectively.²

Physical aging leads to the narrowing of this triad in both glassy Se and glassy $\text{Ge}_2\text{Se}_{98}$, accompanied by a small blue shift (~ 1 cm^{-1}),² which can be explained by a shrinkage of a glass backbone upon aging.¹² It is unclear, however, why the authors of Ref. 2 use a blue shift for A and B modes, but a red shift (~ 2 cm^{-1}) for the mode C position during the fitting procedure. Of course, one would obtain greater moiety of the C mode in the envelope of the fitted curve if two peaks are brought closer together (see Fig. 11 in Ref. 2). However, it is shown in a number of publications^{18,23,24} that the sensitivity of Raman frequencies is rather weak even to the changes in the chemical environment. So, to obtain a physically sound difference between the fits in the Raman spectra of aged and non-aged samples, one needs to fix the positions of A–C modes (or at least, apply the same blue shift to all these modes) during the fitting procedure. If just this constraint is satisfied, the opposite trend in mode C intensity would be evidently noticed in Fig. 11 of Ref. 2, which changes their conclusion on decoupling of Se_8 crowns from the $\text{Ge}_x\text{Se}_{100-x}$ glass structure to the opposite! The aforementioned controversies call for more thorough structural investigations on the mechanism of physical aging in Ge–Se glasses.

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