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## **Physical aging of selenium glass: assessing the double mechanism of equilibration and the crystallization process**

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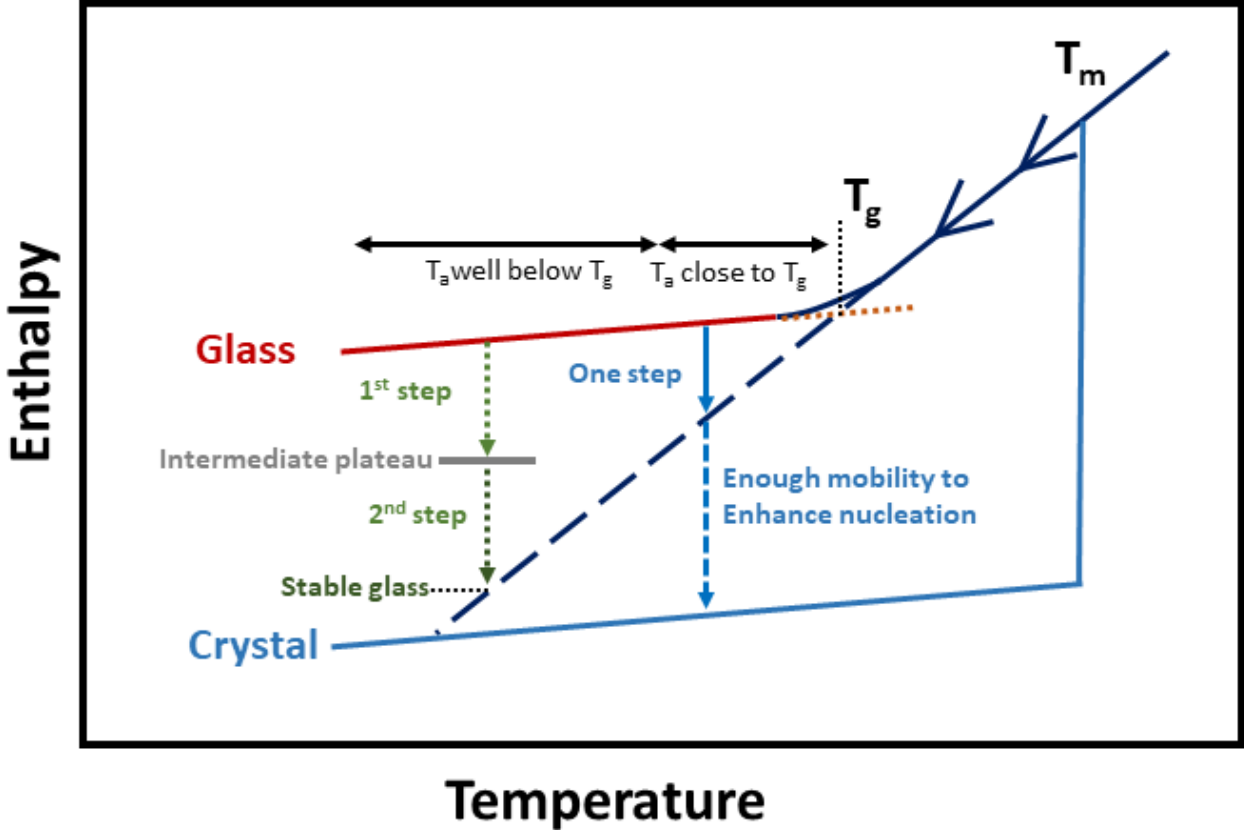
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### **Abstract**

This work focuses on the study of the physical aging of a selenium glass by differential scanning calorimetry (DSC) and fast scanning calorimetry (FSC). Aged samples of 30 and 40 years old at room temperature were analysed by classical DSC, and their enthalpies of recovery were calculated, showing that the glass has reached its thermodynamic equilibrium and is stable over time. The study of accelerated physical aging by using FSC on a rejuvenated sample allows reproducing the way by which this glass has reached its thermodynamic equilibrium at the laboratory time scale. We evidence that the glass reaches its equilibrium state in one or two steps, depending on the gap between the aging temperature and the glass transition temperature, resulting from the difference in the mechanisms governing the relaxation process. Furthermore, a second phenomenon is evidenced, consisting in the crystallization of the glass once the equilibrium has been reached for aging temperatures close to the glass transition temperature.

**Keywords:** Enthalpy of recovery, FSC, DSC, chalcogenide glass.

Graphical abstract:



## Introduction

Physical aging is a natural phenomenon undergone by the amorphous phase when it is maintained during a certain time below its glass transition temperature. The thermal signature of this physical phenomenon is more or less intense, depending on the aging duration and on the gap between the glass transition temperature  $T_g$  and the aging temperature  $T_a$ . Knowing this signature is a common procedure to reveal the thermal history and the thermal stability of a glass as mentioned in literature<sup>1</sup>. Furthermore, knowing the physical aging process is essential for predicting the time-dependent behaviour of glass-forming liquids. One of the main relevant parameters related to the physical aging is the enthalpy loss calculated by integrating the difference between aged and rejuvenated scans obtained by calorimetric investigations, and by using the following equation:

$$\Delta H(T_a, t_a) = \int_{T_1}^{T_2} [C_p^a(T) - C_p^r(T)] \cdot dT \quad (1)$$

Where  $C_p^a(T)$  and  $C_p^r(T)$  are the specific heat of aged and rejuvenated samples respectively, and  $T_1$  and  $T_2$  are arbitrary temperatures below and above the glass transition temperature  $T_g$ .

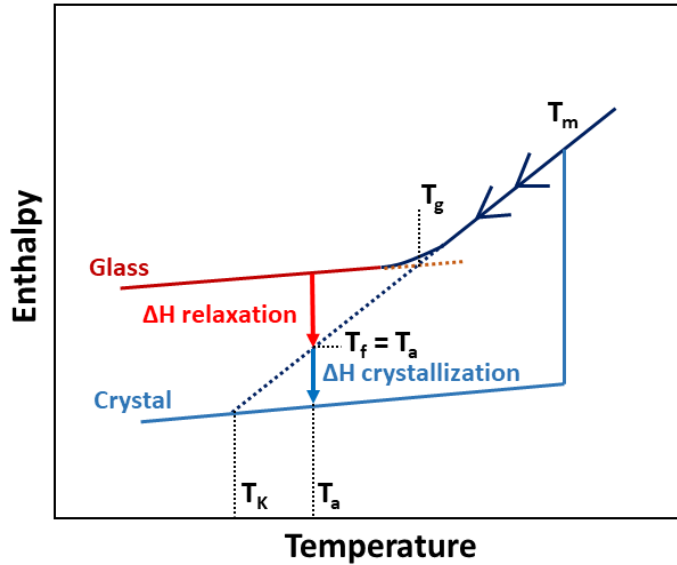


Figure. 1: Enthalpy of an initially liquid like state material as a function of temperature during cooling.  $T_m$ : melting temperature,  $T_g$ : glass transition temperature,  $T_a$ : aging temperature,  $T_K$ : Kauzmann temperature,  $T_f$ : fictive temperature,  $\Delta H$  relaxation: enthalpy loss during the aging process,  $\Delta H$  crystallization: enthalpy loss during the crystallization process occurring after reaching the equilibrium state.

Under the assumption that the thermodynamic equilibrium (corresponding to the extrapolated curve of the liquid like state presented by the blue dotted line in Figure 1) is reached for an infinite aging time (red arrow in Figure 1), the expected enthalpy loss noted  $\Delta H_\infty$  depends on  $T_a$ ,  $T_g$  and  $\Delta C_p$  at  $T_g$ , and can be estimated according to the following relation:

$$\Delta H_\infty = \Delta C_p \cdot (T_g - T_a) \quad (2)$$

One way for checking if a glass has reached its equilibrium state is to compare the experimental enthalpy loss calculated from equation (1), to the theoretical value estimated from equation (2). Another way is to estimate the fictive temperature  $T_f$ , concept introduced by Tool in 1931<sup>2</sup>, and defined as the temperature at which any property, related to the structural relaxation, is at the equilibrium state<sup>2</sup>.  $T_f$  is

calculated from the heating curves obtained by calorimetric investigations, and by using the “equal area rule” method<sup>3</sup> based on the following equation:

$$\int_{T_1}^{T_f} (C_{p,liquid} - C_{p,glass}) \cdot dT = \int_{T_1}^{T_2} (C_p(T) - C_{p,glass}) \cdot dT \quad (3)$$

Where  $T_f$  is the fictive temperature,  $C_{p,liquid}$  and  $C_{p,glass}$  are the specific heats in the liquid state and in the glassy state respectively,  $C_p$  is the specific heat at a given temperature, and  $T_1$  and  $T_2$  are arbitrary temperatures below and above the glass transition temperature.

According to this concept, the equilibrium state is reached when  $T_f$  is equal to  $T_a$ .

The way by which a glass reaches (or not) its equilibrium state after a very long aging time is still matter of debate in the scientific community<sup>4</sup>. Recently, it has been proven that this way is clearly dependent of the gap between  $T_g$  and  $T_a$  in different glass-forming liquids: polymer systems<sup>5-7</sup>, metallic glasses<sup>8</sup>, and chalcogenide glasses<sup>9-11</sup>. When  $T_a$  is close to  $T_g$ , the kinetics of the enthalpy of recovery occur in one step, whereas for  $T_a$  far from  $T_g$ , multiple steps appear in the kinetics of the enthalpy of recovery.

Recently, the use of the fast scanning calorimetry has generated many studies<sup>12-14</sup> concerning the fact that the physical aging can accelerate the ability to crystallize by forming nuclei after the reaching of the equilibrium state, as illustrated in Figure 1 by the blue arrow corresponding to the enthalpy loss related to the crystallization process. Indeed, this phenomenon well known from a theoretical point of view<sup>15</sup> is not easy to evidence experimentally because it appears after the complete structural relaxation. The use of the FSC has proven the possibility of reaching the equilibrium state in acceptable times on the experimental scale<sup>14,16-18</sup>.

The aim of this work is to investigate by classical DSC and FSC the kinetics of the physical aging (in one or two steps, ability to crystallize or not, etc.) in selenium glass, well known as an excellent glass former. Furthermore, this material is often used as a model glass according to the simplicity of its structure<sup>19-21</sup>. Investigations have been

performed on rejuvenated selenium glasses, but also on samples aged of 30 and 40 years.

## Experimental

Amorphous selenium used in this work is a 40 years old glass (kept in a climatized room at 17°C) and rejuvenated (after measuring the enthalpy of recovery for a duration of 40 years). 40 years ago, this selenium glass was classically prepared by quenching from the melt. Let us note that a run has been performed ten years ago, i.e. on a selenium glass of 30 years old. The value of the enthalpy of recovery obtained for this sample (never published), will be reported in this paper. The selenium sample is in form of a small marble, and a complete marble is used for the DSC study. Let us precise that a part of this marble has been used for FSC analyses.

DSC experiments were performed on a Q100 from TA instrument coupled with a Refrigerated Cooling System (RCS). The experiments were conducted under an inert nitrogen flow of 50 mL/min and a heating rate of 10K/min. The DSC has been calibrated in temperature and energy using a standard of indium. All the experiments were performed with sample masses around 5mg inside aluminium pans. The reference and sample pans had identical masses within +/- 0,05mg to optimize the baseline.

FSC (Fast Scanning Calorimetry) experiments were performed on a power compensation twin-type chip based fast scanning calorimeter Flash 1 DSC from Mettler Toledo. Samples were cut from the bulk sample used for DSC analyses and deposited on a MultiSTAR UFS 1 MEMS chip sensors. The use of a Huber TC100 intra cooler allows cooling the sample down to -90°C and applying high cooling rates. The chamber is continuously flushed by 20mL/min nitrogen gas flow (avoiding water condensation)<sup>22</sup>. The FSC calibration consists in conditioning and corrections procedures. The conditioning checks the behavior of the sensor when heating it up to 400°C, also erasing potential history. Besides, a correction procedure compares the response of the thermocouples with the temperature of the resistances. As proposed in the literature<sup>17,23</sup>, the sample mass was estimated by comparing the heat flow step measured by FSC (at  $\beta_h = \beta_c = 1500\text{K/s}$ ) with the heat capacity step measured by

DSC (at  $\beta_h = \beta_c = 0$ , 17K/s) equal to 0,14 J/(g.K), considering that the heat capacity step is the same for both techniques. The sample mass found is around 20 +/- 5 ng. The glass transition temperature was extracted from the cooling scans, avoiding the thermal lag issues<sup>17</sup>, and is equal to 45°C for a rejuvenated selenium glass. As proposed by R. Pilar et al.<sup>14</sup>, the sample was heated up to 277°C to fully melt the glass in order to optimize the thermal contact.

In a first-time physical aging has been performed in-situ in the classical DSC by using the following protocol: the sample was heated up to 70°C to erase thermal history, then cooled down to the aging temperature  $T_a$  for aging times  $t_{ag}$ . The cooling rate was taken equal to the heating one, i.e. 10K/min. After the isothermal aging, the sample is cooled below  $T_a$ , at 10 K/min, and heated at the same rate above  $T_g$ , in regards to record the aged glass signal. The same thermal cycle is repeated to record the rejuvenated glass signal. The enthalpy of recovery is measured on normalized heat flow according to equation (1), by subtracting the rejuvenated glass signal to the aged one.

In a second time physical aging has been performed in-situ in the FSC by using the following protocol: sample was heated up to 150°C to erase the thermal history, then cooled down to the aging temperature  $T_a$  for aging times  $t_{ag}$  and finally cooled down to -50°C. The cooling rate is taken equal to the heating one i.e.  $\beta_c = 1500$ K/s. As performed with the classical DSC, the enthalpy of recovery is estimated according to equation (1), by subtracting the rejuvenated glass signal to the aged one.

## Results and discussions

Figure 2a shows the evolution of the normalized heat flow (normalized to the sample mass and the heating rate) as a function of temperature obtained by classical DSC for a selenium amorphous glass aged at 17°C for 10h, 300h and 40 years, in comparison with a rejuvenated sample. The glass transition temperature and the heat capacity step at this temperature have been estimated from the rejuvenated signal:  $T_g = 40^\circ\text{C}$  and  $\Delta C_p = 0,14$  J/(g.K). These values are in good agreement with the literature<sup>20,24</sup>, proving that the thermal signature of the glass is the same even after 40 years. This leads to assume that the glass is chemically stable. As classically



observed, the longer the ageing time, the greater the amplitude of the endothermic peak and the greater its shift to higher temperature.

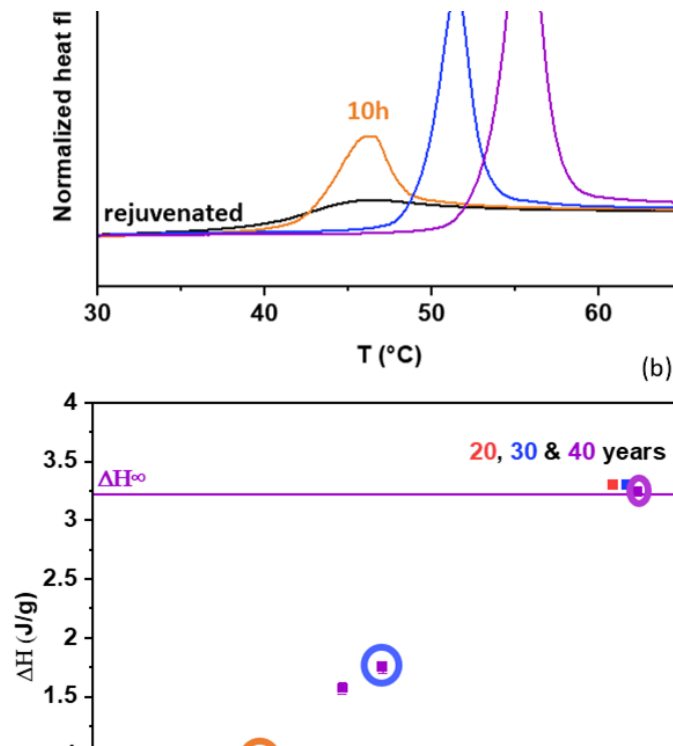


Figure. 2: (a) DSC curves obtained after aging time of 10h (orange), 300h (blue) and 40 years (purple) at 17°C and the rejuvenated signal (black). (b) Enthalpy of recovery  $\Delta H$  measured for selenium glasses aged of 20 (from ref <sup>25</sup>), 30 and 40 years and other aging duration (20min, 5h, 10h, 20h, 100h and 300h). The purple line represents the  $\Delta H^\infty$  value according to equation 1. The orange, blue and purple circles correspond to the  $\Delta H$  values measured for aging of 10h, 300h, and 40 years respectively.

Figure 2b shows the values of the enthalpy of recovery determined for different aging durations. We note that the enthalpy of recovery measured on the 40 years old selenium is equivalent to the one measured on the 20 and the 30 years old selenium, showing that the glass seems to have reached its equilibrium state. To check this, the enthalpies of recovery obtained for 20, 30 and 40 years old samples were compared to  $\Delta H^\infty$  corresponding to the theoretical enthalpy loss needed for a glass to reach its equilibrium state <sup>26</sup> and given by the equation (2) (see introduction).

By taking  $\Delta C_p = 0,14 \text{ J/(g.K)}$ ,  $T_g = 40^\circ\text{C}$  and  $T_a = 17^\circ\text{C}$  (temperature corresponding to the room temperature where the selenium has been stored during 40 years),  $\Delta H^\infty$  is equal to approximately  $3,2 \text{ J/g}$ . This value is similar to the one recorded for the long-time aged samples. Thus, we can conclude that selenium aged of 20, 30 or 40 years has reached its equilibrium state. Moreover, due to the consistence between this value of  $T_g$  and the one of the rejuvenated sample, we conclude that the selenium can be rejuvenated in order to obtain the thermal signature of the glass identical to the original one.

FSC analyses have been performed on rejuvenated selenium glass in order to compare with DSC analyses obtained on selenium glass having reached its equilibrium state. The first FSC experiments have been performed in order to investigate the aging temperature influence on the enthalpy of recovery measured for an aging duration of 10minutes.

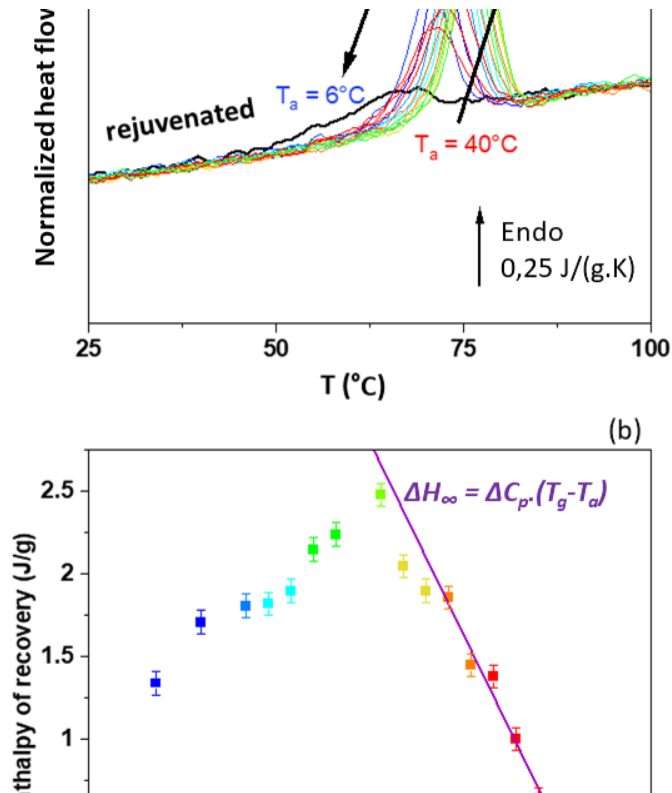


Figure 3: FSC experiments on amorphous selenium glass. (a) Normalized heat flow curves for 10 minutes aging at different temperatures  $T_a$  (from 40°C down to 6°C) and the rejuvenated signal in black. The curves are normalized to the sample mass and to the heating rate. (b) Enthalpy of recovery measured for each aging temperature. The purple line represents the theoretical  $\Delta H^\infty$  as a function of  $T_a$  for  $T_g = 45^\circ\text{C}$ .

Figure 3a represents the normalized heat flow evolution for aging of 10 minutes at different temperatures from  $T_a = 40^\circ\text{C}$  down to  $6^\circ\text{C}$ . We observe that the peak of the enthalpy of recovery is shifted to higher temperatures when  $T_a$  varies from  $40^\circ\text{C}$  down to  $26^\circ\text{C}$ , but the behavior is reversed for  $T_a$  varying from  $22^\circ\text{C}$  down to  $6^\circ\text{C}$ , i.e. when the gap between  $T_g$  and  $T_a$  is more and more important. This behavior has been already observed in literature<sup>27-29</sup>. We may note that the rejuvenated curve is perfectly superimposed to the others in both glass and liquid states, which is the expected calorimetric response when only physical aging occurs.

Figure 3b shows the evolution of the enthalpy of recovery corresponding to the results presented in figure 3a. The purple line marks the theoretical evolution of  $\Delta H^\infty$  as a function of aging temperature with  $\Delta C_p = 0,14 \text{ J/(g.K)}$  and  $T_g = 45^\circ\text{C}$ .  $T_g$  is different from DSC result due to the faster cooling rate<sup>30</sup>.

The values of the enthalpy of recovery highlight that the glass reaches the equilibrium state when the ten minutes aging is performed at temperatures higher than 30°C. Aging at temperatures between 6°C and 26°C highlight a second behavior with an enthalpy of recovery decreasing with the decrease of  $T_a$ . This behavior was first attributed to antagonist thermodynamic and kinetic effects on the structural relaxation, i.e., a competition between the driving force, which increases with reducing  $T_a$  (higher  $\Delta H^\infty$ ), and the molecular mobility, which decreases with decreasing  $T_a$ . Not long ago, Righetti et al.<sup>31</sup> interpreted the undercooling dependence of the recovery process in terms of relaxation mechanisms. For temperatures close to  $T_g$ , the structural relaxation is dominated by cooperative large-scale motions, whereas it is governed by small-scale localized rearrangements at higher undercooling.

The experimental results regarding the glass aged at 17°C for 30s up to 60 000s and at 35°C for 5s up to 3000s are presented in Figure 4a and 4b respectively. The corresponding evolutions of the enthalpy of recovery are presented in Figures 4c and 4d respectively.

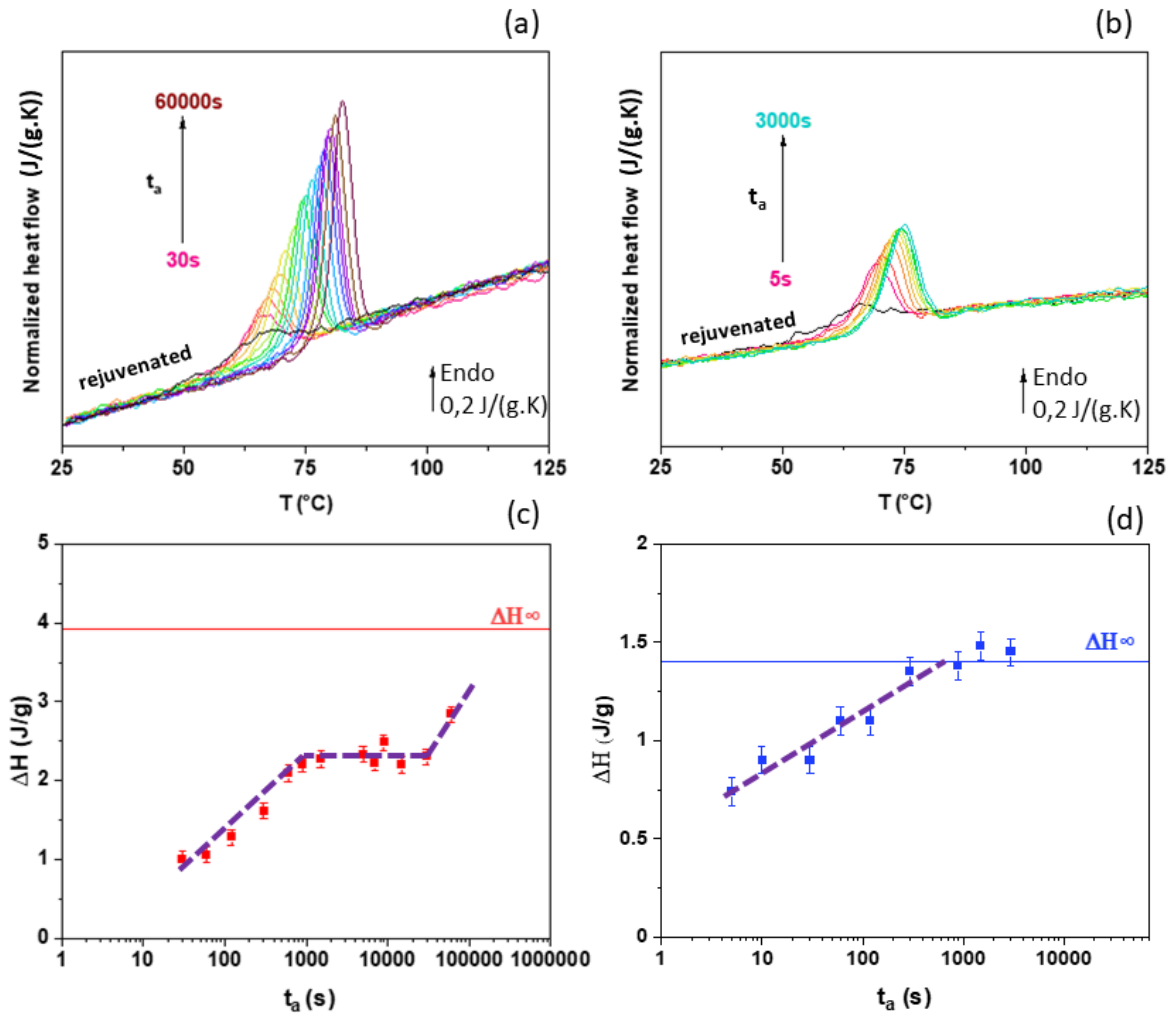


Figure 4: (top) Normalized heat flow curves obtained after aging on selenium glass at: (a) 17°C from 30s up to 60 000s and (b) 35°C from 5s up to 3000s. In both cases, the signal of the rejuvenated material is given in black. (bottom) Enthalpy of recovery vs. aging time for aging temperatures of (c) 17°C and (d) 35°C. The solid line represents the  $\Delta H^\infty$  value for these aging conditions. The dashed line is a guide for the eyes that marks the number of steps in the structural relaxation process.

One can notice that the structural relaxation proceeds in a one-step mechanism when the aging is performed at low undercooling ( $T_a = 35$  °C). On the other hand, at high undercooling ( $T_a = 17$  °C), a two-step evolution towards the equilibrium is observed. As already reported for polymers materials<sup>32</sup>, glassy glycerol<sup>33</sup> or other chalcogenide glasses<sup>9,34</sup>, for aging temperature well below  $T_g$ , the evolution of the enthalpy of recovery exhibits an intermediate plateau. Thus, the approach towards

the equilibrium is bimodal. This behavior is also observed for aging at 22°C and 24°C. We may note that the bimodal process for reaching the equilibrium state is only observed for aging temperature below  $T_a = 26^\circ\text{C}$ , i.e. the temperature corresponding to the highest enthalpy loss (see Figure 3b). This temperature range corresponds to the domain where the structural relaxation is governed by small-scale rearrangements (see Righetti et al.<sup>31</sup>). These results are in good agreement with the general interpretation of the double step recovery curves, i.e., the succession of localized then cooperative relaxation motions<sup>7</sup>. These results are also in good agreement with the literature, where the bimodal aspect is only observed for aging temperature far from  $T_g$ <sup>7,18</sup>. At the opposite, for aging temperatures close to  $T_g$  (31°C and 35°C in our case), a one-step behavior is obtained<sup>19,20</sup>. To summarize, the presence of multiple steps in the structural relaxation process results from the coexistence of different mechanisms with different time scale evolution.

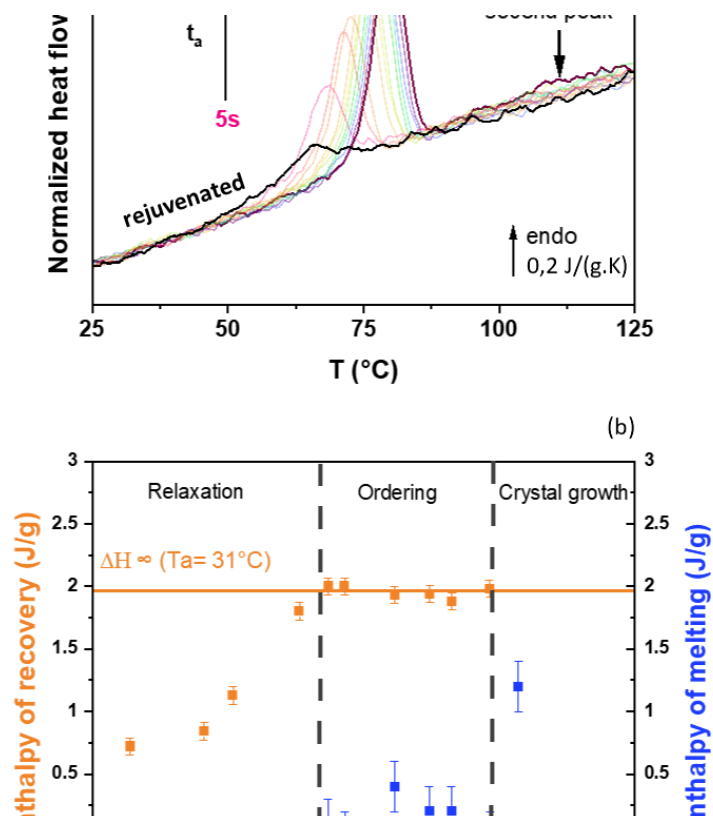


Figure 5: (a) Normalized heat flow curves for the sample aged at 31°C for different durations (from 5s up to 60 000s) with the rejuvenated signal in black. (b) Evolution of

*the enthalpy change for the enthalpy of recovery (in orange) and for the enthalpy of the second peak (in blue), three domains are indexed, corresponding to relaxation, ordering and crystal growth. The orange line represents the theoretical  $\Delta H^\infty$  value.*

Figure 5a shows the evolution of the normalized heat flow curves obtained by FSC analysis on selenium aged at 31°C from 5s up to 60 000s. Beyond the recovery signature, we clearly observe a second peak appearing at higher temperature than the one related to the structural relaxation. Schick et al.<sup>14</sup> previously observed a broad peak at higher temperatures than the peak of the enthalpy of recovery. They attributed it to the melt of some nuclei, generated once the sample reached the equilibrium state. Figure 5b shows the evolution of the enthalpy of recovery and the enthalpy of melting (related to the second temperature peak). We observe first that the equilibrium is reached in one step after 500s aging. Then, a plateau corresponding to the value of  $\Delta H^\infty$  is reached. However, when the selenium is aged during 60 000s, a second endothermic peak appears implying an artificial increase of the enthalpy calculation. It is unlikely that this result is linked to the structural relaxation since the total enthalpy change exceeds  $\Delta H^\infty$ . Therefore, the most reasonable assumption is to relate it to a crystallization phenomenon occurring below the glass transition temperature, as evidenced by Schick et al.<sup>14</sup>. Thus, in our case we assume that when the equilibrium is reached, additional ordering proceeds, that progressively leads to crystal growth.

Another behavior has been obtained for selenium glass aged at  $T_a = 35^\circ\text{C}$  for aging times from 7000s up to 60 0000s, as shown in Figure 6a. A cold crystallization peak (circled in red) appears just after the peak of the enthalpy of recovery. The interpretation is slightly different there. The cold crystallization is the signature of the existence of nuclei that can grow into crystals above the glass transition. Figure 6b presents both evolutions of the enthalpy of recovery and the enthalpy of cold crystallization. The evolution towards the equilibrium is clearly observed in a first step, then the enthalpy of the cold crystallization peak starts increasing (this peak being exothermic, the value of this enthalpy is considered as negative), due to the enhanced nucleation. Similar to the crystal growth reported in Figure 5, we notice that the ordering process allowing the nucleation occurs consecutive to the structural

relaxation. In other terms, this suggests that the aged system has to achieve its equilibration to start crystallizing. These FSC results evidence the evolution from the steady state towards the crystalline state as schematized in Figure 1.

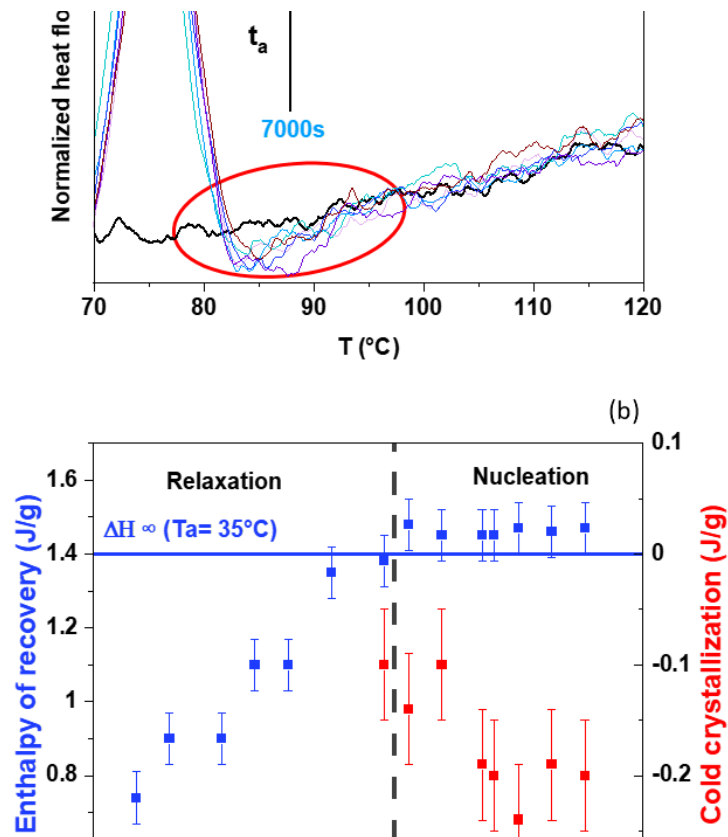


Figure 6: (a) Normalized heat flow curves for the sample aged at 35°C for different durations (from 7000s up to 60 000s) with the rejuvenated signal in black. (b) Evolution of the enthalpy of recovery (in blue) and for the enthalpy of cold crystallization peak (in red), domains indexed corresponds to relaxation and nucleation. The blue line represents the theoretical  $\Delta H^\infty$  value.

These results are in good agreement with those obtained for different polymeric materials<sup>12,13,15,35</sup> showing a crystallization process below  $T_g$ . For selenium glass, the crystallization following the reaching of the equilibrium is only possible for aging temperatures close to  $T_g$ , as evidenced in this work for  $T_a = 31^\circ\text{C}$  and  $35^\circ\text{C}$ , and also by the fact that no crystallization is observed for a selenium glass maintained at  $17^\circ\text{C}$  for a duration of 40 years. Thus, we can conclude that a selenium glass requires a minimum of energy to generate some nuclei when it is maintained far from  $T_g$ .



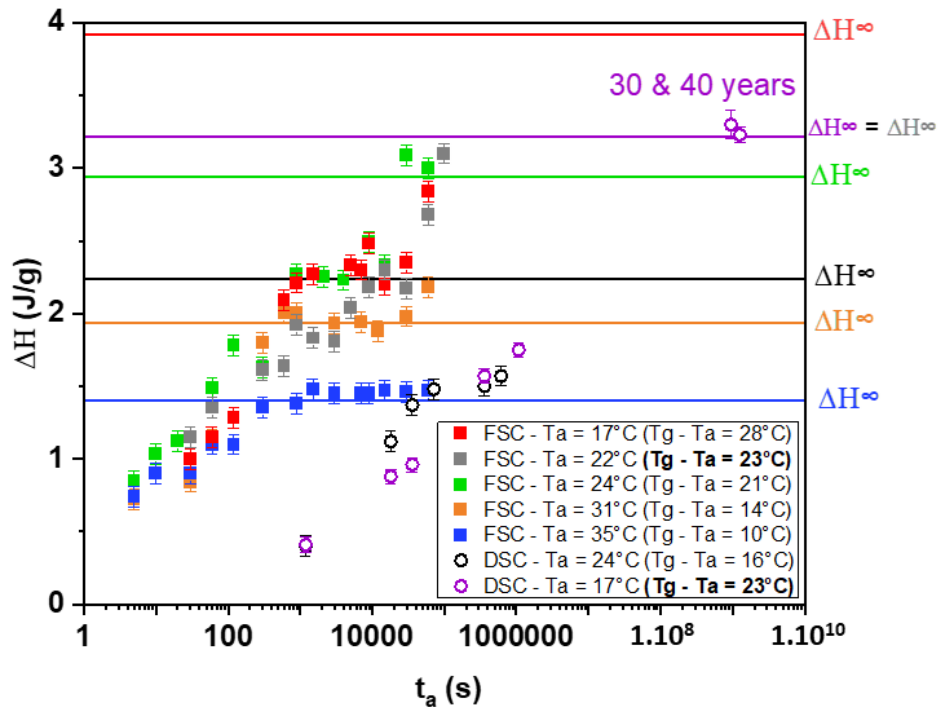


Figure 7: Evolution of the enthalpy loss with time: Comparison between classical DSC (circles) and FSC (squares) analyses performed on selenium glass aged at different aging temperatures (FSC: 17°C, 22°C, 24°C, 31°C, 35°C. DSC: 17°C, 24°C). The solid lines represent  $\Delta H^\infty$  values for each aging condition. For aging performed at 22°C by FSC (grey squares) and at 17°C by DSC (purple circles) the quantity ( $T_g - T_a$ ) is equivalent and equal to 23°C.

Figure 7 summarizes all the aging experiments performed by classical DSC and FSC. In all cases, the aging performed with FSC occur faster than those performed with a classical DSC, allowing to reach the equilibrium state at the laboratory time scale. The obtained data can be compared in terms of aging temperature or distance to the equilibrium. For example, the purple line indicates the  $\Delta H^\infty$  value associated with the aging at 17°C by DSC and 22°C by FSC, i.e. an identical  $\Delta H^\infty$  value in order to compare both kinetics. For an equivalent distance to the equilibrium, the fact that the physical aging is accelerated by FSC is clearly evidenced. However, one could still interpret this result as the consequence of higher molecular mobility when performing aging at a temperature which is 5 °C higher in FSC. To assess this question, we can compare the results obtained when aging in both FSC and DSC is

performed at 17 °C. Obviously, the aging kinetic in FSC is still faster (about less than ten days vs. more than ten years). Therefore, there is an additional effect that leads to an acceleration of the structural relaxation when performing aging experiments in FSC. This behavior is associated with the difference in the surface/volume ratio between samples analyzed by both techniques. In a 20ng sample (typical FSC sample mass) the surface/volume ratio is superior to the one of classic bulk samples analyzed by standard DSC. This induces a faster diffusion of the free volume hole to the surface <sup>17,36</sup>. Such effect is comparable to reported confinement effects of the glass <sup>7</sup>, that was also observed on polymer films <sup>37,38</sup> or nanocomposite <sup>39,40</sup>.

Furthermore, we note that the intermediate plateau observed for aging at 17°C, 22°C and 24°C is always detected for the same  $\Delta H$  value, i.e. around 2,2 J/g. Our hypothesis is that this value might correspond to a state where the system exhibits a minimum of Gibbs free energy <sup>41</sup>.

## Conclusions

selenium glass is a model material for studying the complex behaviors related to the structural relaxation occurring during aging. The enthalpy losses measured for glasses aged of 30 and 40 years at room temperature, allows to conclude on a stable glass once the equilibrium is reached from aging temperature well below the glass transition temperature. The fact that aging experiments performed by FSC imply the same  $\Delta H^\infty$  value than those obtained for selenium glasses naturally aged during 30 and 40 years at room temperature highlights that FSC measures are well representative of the bulk glass. Furthermore, FSC experiments highlight the bimodal approach of the structural relaxation towards the equilibrium state, for different aging temperatures far from  $T_g$ . Finally, for aging performed closed to the glass transition temperature, FSC analyses allow to observe the crystallization phenomenon generated once the sample reached the equilibrium state. This phenomenon, thermally activated, is possible only if the aging process is performed not so far of the

glass transition temperature. Indeed, despite an aging of 40 years at room temperature, a selenium glass remains fully amorphous.

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