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**"Physical aging of the 62.5GeS<sub>2</sub>-12.5Sb<sub>2</sub>S<sub>3</sub>-25CsCl chalcogenide glass:  
assessing the mechanisms of equilibration and crystallization"**

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**Abstract**

The goal of this work is to provide an answer to the important scientific question: will a glass-forming liquid reach its equilibrium state or not before to crystallize during physical aging process, i.e. when it is maintained below its glass transition temperature? For this goal the physical aging process in a 62.5GeS<sub>2</sub>-12.5Sb<sub>2</sub>S<sub>3</sub>-25CsCl glass has been investigated for a long period (5 months) at 30°C below the glass transition temperature  $T_g$ . A crystallization was observed during this process, and was characterized through X-Ray Diffraction (XRD), Transmission Electron Microscopy (TEM) and Temperature Modulated Differential Scanning Calorimetry (MT-DSC) analyses. By evaluating the enthalpy loss related to the physical aging and by comparing this experimental quantity to the theoretical one, we have proved that this glass has reached its thermodynamic equilibrium state before crystallizing. Thus, this work evidences experimentally the ability for a glass former to crystallize under  $T_g$  after reaching its equilibrium state.

**Keywords:** Physical Aging, Crystallization, Chalcogenide glass.

## Introduction

Chalcogenide glasses are a centre of interest since many years now, due to their ability to transmit light from visible to far infrared range and their capacity to be easily shaped in different geometries, these advantages offering great potential in the development of new infrared cameras and optical fibres for the mid-infrared regions<sup>1,2</sup>. They also have an economic advantage because these glasses are cheaper than currently used single crystal germanium or ZnSe polycrystals.

Moreover, the non-equilibrium nature of these glasses is related to the structural relaxation occurring under the glass transition temperature <sup>3-6</sup>. Many studies have been recently reported to understand the glassy state nature and the associated physical aging, with a focus on polymeric materials <sup>7-9</sup> and few on chalcogenide glasses <sup>10,11</sup>. The recent studies on polymer materials highlighted the relaxation and crystal nucleation/growth of several samples once the equilibrium is reached <sup>7,12-15</sup>. The equilibrium state is reached when the relaxation enthalpy of the glass is equal to the maximum relaxation enthalpy as described in Figure 1 <sup>16</sup>. This maximum of enthalpy loss is noted  $\Delta H_{\infty}$  and can be estimated by the equation 1:

$$\Delta H_{\infty} = \Delta C_p (T_g - T_a) \quad [\text{equation 1}]$$

With  $\Delta C_p$  the difference between the heat capacities of the liquid and the glassy states at the glass transition temperature  $T_g$ , and  $T_a$  the aging temperature.

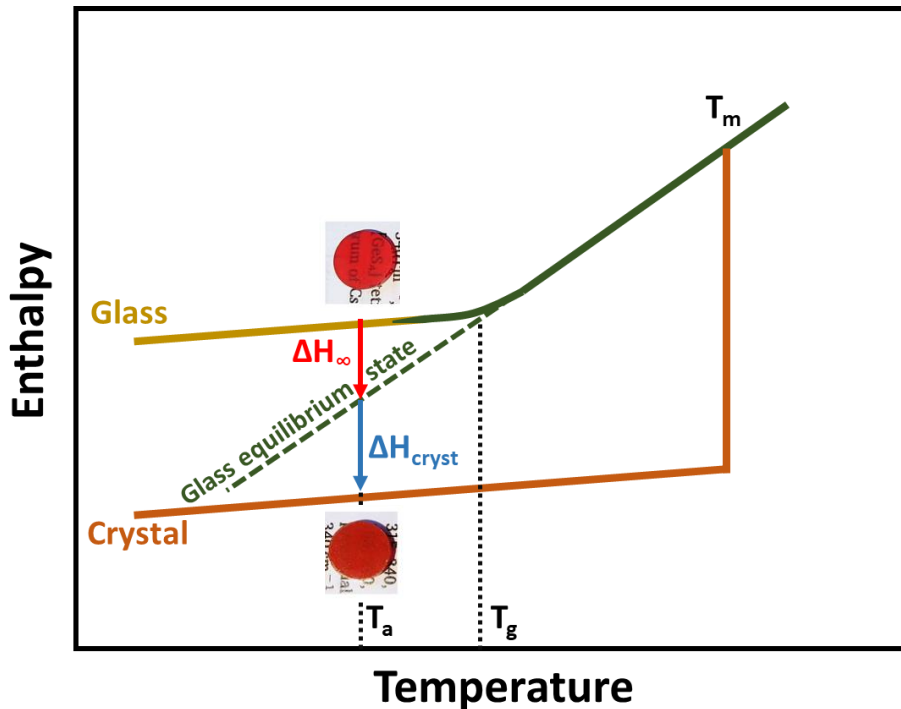


Figure 1: Enthalpy of an initially liquid state material as a function of temperature during physical aging at a temperature ( $T_a$ ) below the glass transition temperature  $T_g$ .

$\Delta H_\infty$  represents the maximum enthalpy loss when the glass has reached its equilibrium state corresponding to the extrapolated curve of the liquid like state.

$\Delta H_{cryst}$  represents the enthalpy loss if the glass crystallizes after reaching the equilibrium state (we may note that the crystal state is not reached in usual studies).

The two images are proposed to illustrate the transparency loss after the physical aging process for the glass studied in the present work. This loss is directly visible with eyes.

Our work focused on chalcogenide glass of the composition  $62.5\text{GeS}_2\text{-}12.5\text{Sb}_2\text{S}_3\text{-}25\text{CsCl}$ , which has proved its capability to produce glass-ceramics with controlled crystallization<sup>17-20</sup>. In a previous work [20], the authors had evidenced a glass transition temperature at the onset point of  $280^\circ\text{C}$ , and a crystallization peak with a maximum around  $478^\circ\text{C}$  during heating scans. Since physical aging can influence the material performances<sup>13,21,22</sup> it is important to study and give a better understanding of this phenomenon. Moreover, the way by which a glass reaches (or not) its equilibrium state after a certain aging time is still matter of debate in the scientific community<sup>16</sup>. Recently, it has been evidenced that this way is clearly dependent of the gap between

$T_g$  and  $T_a$  in different glass formers: polymeric systems <sup>23</sup>, metallic glasses <sup>24</sup>, and chalcogenide glasses <sup>25</sup>. The use of the fast-scanning calorimetry (FSC) has generated many recent studies <sup>7,26,27</sup> proving that the physical aging can accelerate the ability to crystallize by forming nuclei after reaching the equilibrium state. This phenomenon known from a theoretical point of view is difficult to evidence experimentally because it appears after the complete structural relaxation, but we highlighted it through the study of a selenium glass considered as an ideal glass former according to its simple structure<sup>28</sup>. This previous study highlighted that for aging temperature closed to  $T_g$ , the molecules constituting the glass have enough mobility to enhance the crystallization process after reaching the thermodynamic equilibrium. But in this last study, the highlight of the crystalline phase presence was not possible through XRD and TEM experiments because of the small quantity of crystals obtained by this way, and the own nature of the selenium, which sublimates under electron beam.

The challenge of this work is to investigate for the first time the physical aging process of a chalcogenide glass with a complex composition (62.5GeS<sub>2</sub>-12.5Sb<sub>2</sub>S<sub>3</sub>-25CsCl) presenting the ability of changing the optical transmission when a very small quantity of crystals is formed <sup>29</sup>, and to provide an answer to the important scientific question: will a glass-forming liquid reach its equilibrium state (extrapolated curve of the liquid like state) or not before to crystallize during a physical aging process?

## Experimental

The chalcogenide glass 62.5GeS<sub>2</sub>-12.5Sb<sub>2</sub>S<sub>3</sub>-25CsCl was synthesized using the melt-quenching technique, using high purity materials (5N Ge, Sb, S, Ga and 3N CsCl). The elements were weighted in a glove box and then introduced in a silica tube.

The preparation was evacuated down to 10<sup>-5</sup> Pa, sealed and heated in a rocking furnace at 850°C for 12h. The melt was homogenised and quenched in water at room temperature and placed in a furnace 10°C below  $T_g$  in order to avoid residual mechanical stress <sup>2,30,31</sup>.

XRD measurements were performed on a Bruker diffractometer with a Co target ( $K = 1.79 \text{ \AA}$ ) equipped with a furnace. A step width of 0.04° was used for all the analyses with a scan speed of 1s in a  $\theta$ -2 $\theta$  mode, and the measurements were performed on powdered samples.

Unaged and aged materials were characterized by Transmission Electron Microscopy (TEM) on a JEOL ARM 200F microscope operated at 200kV. Bright field images and selected area electron diffraction (SAED) patterns were recorded with a parallel beam. Samples were prepared with a three-step procedure: (i) mechanical crushing of the glass in a mortar, (ii) dispersion of crushed pieces in ethanol and sonication, and (iii) deposition of a droplet on a TEM grid with a carbon film. TEM observations were carried out in the thinnest areas of fragments that were transparent to electrons. Additional data were collected in Scanning TEM (STEM) mode with a probe size of 0.2 nm and a convergence angle of 34 mrad. Images were recorded with both a bright field (BF) detector (collection angles 0-45 mrad) and a High-Angle Annular Dark-Field (HAADF) detector (collection angles 68-280 mrad).

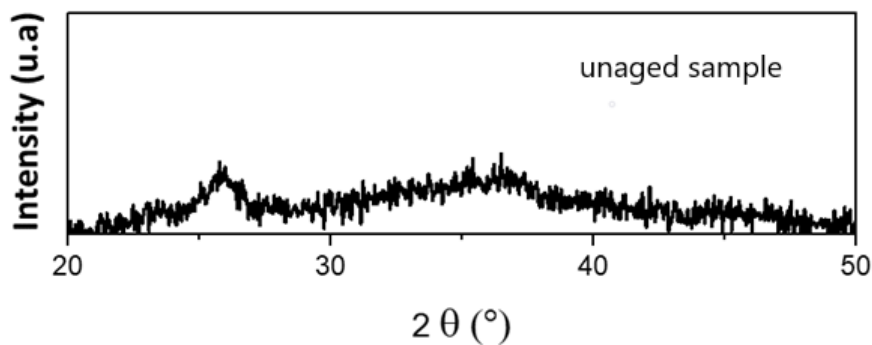
Modulated temperature differential scanning calorimetry (MT-DSC) experiments were performed with the Q100 apparatus from TA instrument. Temperature and energy were calibrated using indium as standard, and heat capacity using sapphire. All the experiments were performed with samples of about 5 mg inside aluminium pans under a 50mL/min nitrogen gas flow. The reference and sample pans had identical masses within +/- 0.05mg to optimize the baseline. The temperature modulation was performed with a heating rate of 5K/min, a modulation amplitude of  $\pm 0.796\text{K}$  and an oscillation period of 60s. This protocol called "heat-only mode" is the most accurate to analyse samples with an ability to crystallize during a heating ramp <sup>32</sup>.

The physical aging was performed during five months in a furnace at 250°C (under air), i.e. 30°C below the glass transition temperature<sup>29</sup>, on disk shape samples (diameter of 10 mm and thickness of 2 mm). These disk shape samples were directly cut from the ingot obtained inside the ampoule. After the aging time of 5 months, the samples were cooled down directly at room temperature. During a very long time in a ventilated furnace a very thin film (below 1 $\mu\text{m}$ ) of oxidation can be observed (irisation) that is then removed by a very slight polishing with alumina powder.

## Results and discussion

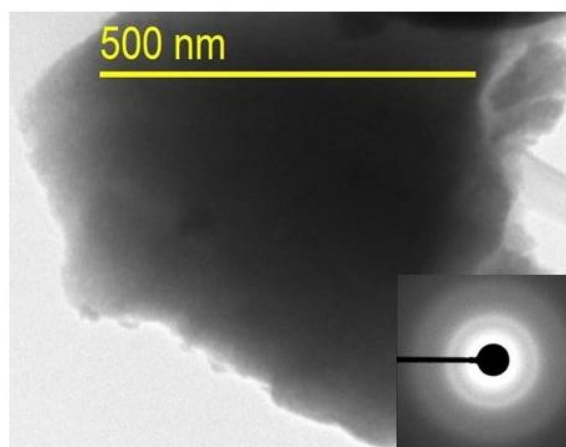
### a- Unaged sample

Before the aging process, the microstructure of the sample (unaged sample) was checked through XRD analysis and TEM with SAED patterns. As shown in Figure 2 the X-ray diffraction pattern corresponds to a fully amorphous sample.



*Figure 2: X-ray diffraction pattern of the unaged sample.*

Even if the X-ray diffraction highlights an amorphous sample, some nuclei can be already present without being detected by XRD analyses. TEM analyses were performed in order to confirm the amorphous state at the nano scale for the unaged sample. The results are presented in Figure 3.



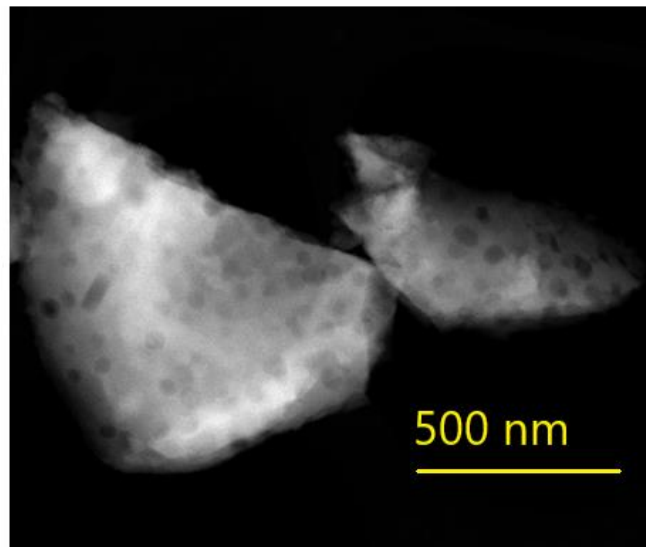
*Figure. 3: TEM bright field image on the unaged sample and corresponding SAED pattern (inset).*

The TEM image confirms the amorphous state of the unaged sample, with the absence of spot on the SAED pattern.

#### **b- Aged sample**

The sample was aged during five months in a furnace at 250°C, i.e. 30°C under the glass transition temperature. Once the aging is over, the transparency modification is directly evidenced and due to a partial crystallization of the glass <sup>20,29</sup> as shown in Figure 1 (see images).

The aged sample was also imaged by TEM experiments in order to observe the crystals formed during the physical aging. Figure 4 shows an HAADF-STEM image of the aged sample.



*Figure 4: HAADF-STEM image of the sample aged during 5 months at 250 °C. Dark discs correspond to partially or totally dissolved CsCl crystals.*

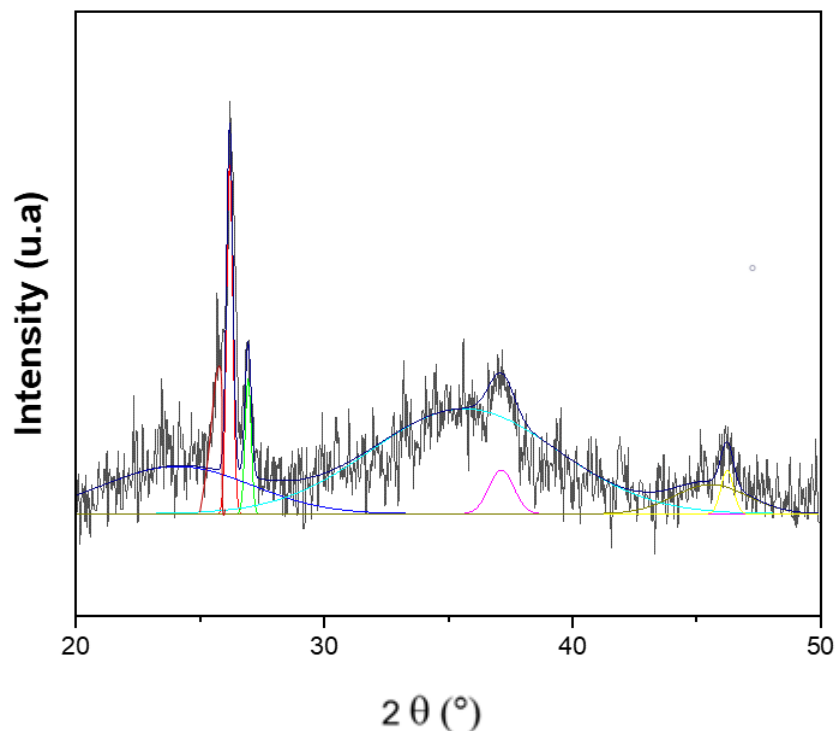
The TEM image in dark field contrast should exhibit bright spots corresponding to CsCl crystals, but, as explained in details in our previous work [29], the solvent used for the sample preparation dissolves partially or completely these crystals, and only holes (left by the dissolved crystals) or dark spots are observed.

A distribution of crystal size between 10 and 50 nm is observed, with an average value around 30 nm, suggesting that the crystal growth started just after the nucleation. The



hypothesis is that the nucleation rate is low (small driving force 30°C below the glass transition temperature) or the nucleation barrier is high, with a fast growth (high atomic mobility).

In order to estimate the crystallinity degree ( $X_c$ ) of the aged glass, two methods were used. The first one uses the XRD data, by calculating the ratio between the peak area associated to the crystalline part and the full area (which corresponds to amorphous and crystalline parts), as illustrated in Figure 5.



*Figure 5: X-ray diffraction pattern of a 5-month aged glass at 250°C with the different fits (highlighted with different colours) used to estimate the area of crystal (peaks) and amorphous parts (halo).*

The estimation for the crystallinity degree by XRD analysis is  $X_c = 10 \pm 2 \%$ . But this method is more qualitative than quantitative.

The second method is based on calorimetric analyses, and consists on comparing the heat capacity step value (noted  $\Delta C_p$ ) at the glass transition temperature taken at the middle point (noted  $T_{g \text{ mid}}$ ) :  $\Delta C_{p(T_{g \text{ mid}})} = C_{p, \text{liq}(T_{g \text{ mid}})} - C_{p, \text{glass}(T_{g \text{ mid}})}$ , between the unaged sample (the amorphous one) and the aged one. As already highlighted in our previous work<sup>29</sup> a cold crystallization phenomenon occurs in the glass transition range, and MT-

DSC analyses were needed in order to separate the contribution related to the heat capacity (shown in the “reversing signal” as the glass transition), to the contribution related to kinetic events (shown in the “non-reversing signal” as cold crystallization, structural relaxation, etc). The reversing signals corresponding to the unaged and aged samples were superimposed and shown in Figure 6.

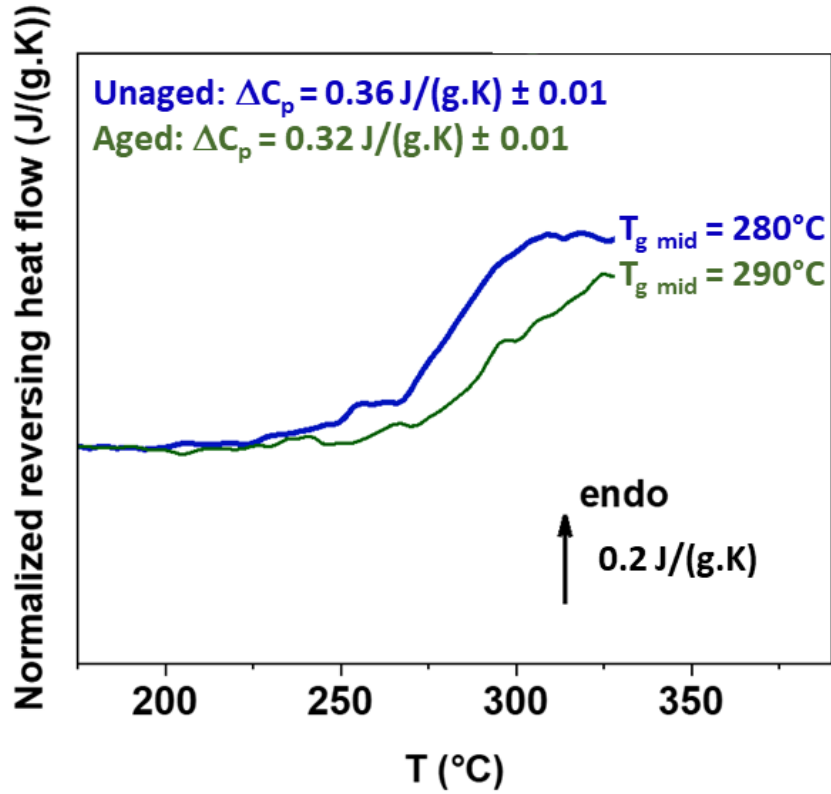


Figure 6: MT-DSC reversing heat flow signals of the unaged (amorphous) glass (blue curve) and the glass aged for 5 months at 250°C (green curve). The curves have been normalized to the sample mass.

As shown in Figure 6, the impact of the crystallization is clearly observed for the aged sample (green curve) with the  $\Delta C_p$  decrease from  $0.36 \pm 0.01 \text{ J/(g.K)}$  down to  $0.32 \pm 0.01 \text{ J/(g.K)}$ . It is well known that the heat capacity step at the glass transition temperature is proportional to the amorphous phase quantity. Thus, whatever the crystallization process, if  $X_c$  increases,  $\Delta C_p$  will decrease. Furthermore, the ratio between  $\Delta C_{p(\text{crystallized system})}$  and  $\Delta C_{p(\text{amorphous system})}$  is directly proportional to  $X_c$  :

$$X_c (\%) = \frac{\Delta C_{p(\text{crystallized})}}{\Delta C_{p(\text{amorphous})}} \cdot 100 \quad [\text{equation 2}]$$

According to the values obtained in this work, the crystallinity degree is around  $11 \pm 2$  %, which is in agreement with the crystallinity degree estimated from XRD analysis ( $X_{C,XRD} = 10 \pm 2$  %). Furthermore, the  $T_g$  increase from 280°C up to 290°C is also a marker of the presence of the crystalline phase. Indeed, the aging process usually implies a  $T_g$  decrease, but if a crystallization process occurs, the relaxation processes are constrained by the presence of crystals, and needs more energy to devitrify, implying an increase of the glass transition temperature.

As explained in the introduction, a glass maintained at a certain temperature below its glass transition temperature, will normally reach its equilibrium state corresponding to the extrapolated curve of the liquid-like state before starting a nucleation process. To confirm experimentally this theoretical scenario, the enthalpy loss of the aged glass should have reached (as a minimum) the  $\Delta H_\infty$  value (see equation 1). In our case this theoretical value is equal to 10 J/g by taking the values of  $T_g = 280^\circ\text{C}$ ,  $\Delta C_p = 0.36$  J/(g.K), and  $T_a = 250^\circ\text{C}$ .

As the physical aging process concerns only the amorphous phase, the calorimetric data were normalized to the amorphous fraction, i.e. 90% for the aged sample, in order to estimate the enthalpy loss in J/g. The Figure 7 presents the non-reversing heat flow signal associated to the aging process (and the cold crystallization starting around 275°C as shown in our previous work<sup>29</sup>) of the aged sample. The same curve but corresponding to the unaged sample was superimposed to highlight the difference in terms of calorimetric signature.

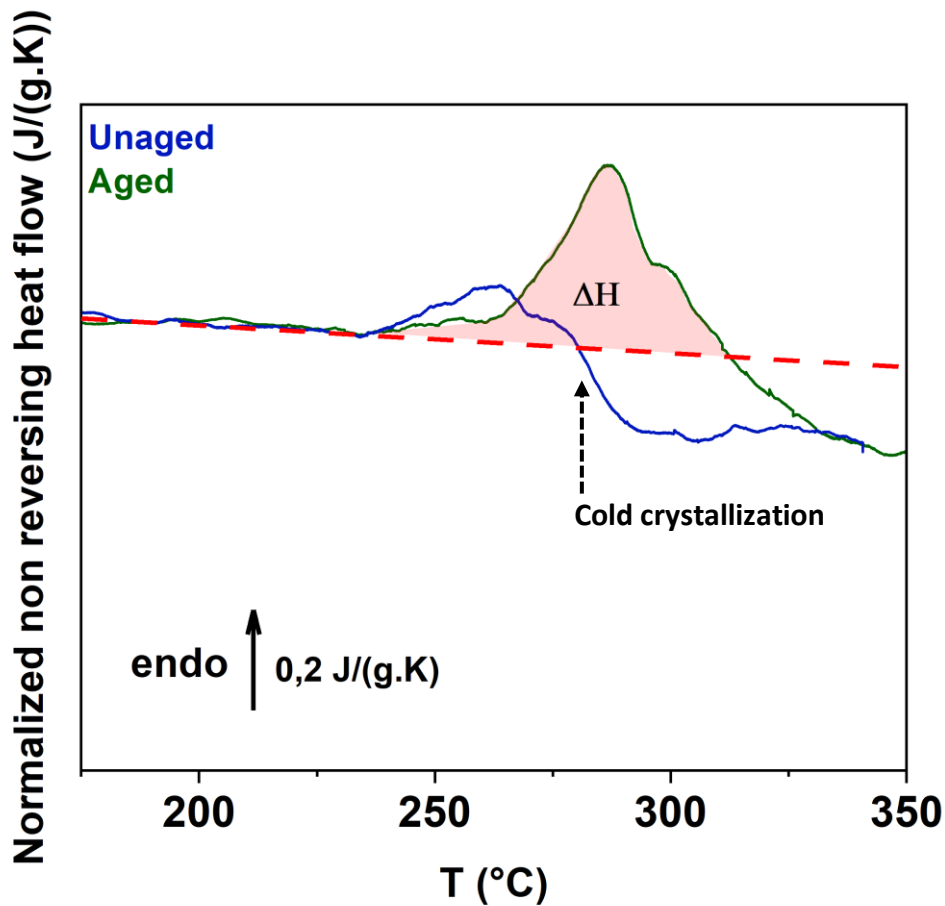


Figure 7: MT-DSC non-reversing heat flow signals of the aged and unaged glasses. The area in red corresponds to the enthalpy loss related to the aging process. The curve corresponding to the aged sample was normalized to the amorphous fraction, i.e. 90%.

The enthalpy loss related to the aging process is measured from the green curve presented in Figure 7 (red area), and is equal to  $\Delta H = 11 \pm 0.2$  J/g.  $\Delta H$  value being very close to  $\Delta H_{\infty} = 10$  J/g, this MT-DSC experiment confirms that the amorphous phase of the aged glass has reached its equilibrium state. Thus, this experimental work is in good agreement with the theory exposed in the introduction part, i.e. a glass can crystallize under its glass transition temperature once its thermodynamic equilibrium state is reached.

## Conclusions

The goal of this work was to provide an answer to the important scientific question: will a glass-forming liquid reach its equilibrium state or not before to crystallize during a physical aging process? For this goal, this physical phenomenon has been investigated for the first time in the 62.5GeS<sub>2</sub>-12.5Sb<sub>2</sub>S<sub>3</sub>-25CsCl glass for a very long period (5 months) at 30°C below the glass transition temperature  $T_g$ . XRD and TEM analyses on the unaged sample confirm the fully amorphous state of this sample. The sample aged 30°C below the glass transition temperature during 5 months has lost its transparency as expected for this specific glass when a certain crystallinity degree is reached. This loss is visible directly with eyes but in order to quantify the crystallinity degree ( $X_c$ ), data obtained by XRD and MT-DSC analyses were analysed and  $X_c$  is estimated around 10%. In order to confirm or not if the chalcogenide glass composition 62.5GeS<sub>2</sub>-12.5Sb<sub>2</sub>S<sub>3</sub>-25CsCl exhibits the expected theoretical behaviour, i.e. a nucleation/growth can be observed only once the aged glass has reached its equilibrium states, the enthalpy loss related to the aging of 5 months is measured by MT-DSC experiments. The value obtained experimentally was found very close to the theoretical one, which corresponds to the enthalpy loss if the glass has reached its thermodynamic equilibrium state. Thus, this new and original experimental work is in good agreement with the theory proposed by the scientific community defending the possibility for a fully amorphous glass to crystallize below its glass transition temperature if it has reached its equilibrium state.

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