

X-ray sensing materials stability: influence of ambient storage temperature on essential thermal properties of undoped vitreous selenium

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Abstract. Amorphous selenium (a-Se) is currently used in x-ray image detectors as an x-ray photoconductor. Normally a-Se films used in device applications are fabricated by the evaporation of vitreous bulk material loaded into boats in a typical vacuum deposition system. The resistance against crystallization is an important factor in both film and bulk forms of a-Se. Previous work has indicated that the resistance to crystallization is surprisingly more pronounced around 35 °C [1]. In this work we have therefore examined the essential thermal properties of vitreous selenium (99.999%) samples that have been stored at different temperatures. The thermal characterization experiments involved a series of DSC (Differential Scanning Calorimetry) measurements in which have monitored the glass transition and melting endotherms, and the crystallization exotherm in heating-cooling-heating scans. In DSC experiments, a sample would be heated to a temperature above the melting temperature, equilibrated, then cooled at a fixed rate down to 20 °C, then equilibrated and finally scanned again under a heating schedule. The samples were isothermally stored at temperatures corresponding to 18, 35 and 55 °C. The thermal analysis results show that there are distinct differences in the thermal properties. We have examined the stability in terms of the difference in the crystallization onset temperature (T_c) and the onset of glass transition temperature (T_g). We also examined the Hruby coefficient (K_{gl}) of these samples, that is $K_{gl} = (T_c - T_g)/(T_m - T_c)$ where T_c is the crystallization onset temperature and T_m is the melting onset temperature. We have found K_{gl} to depend on the storage temperature. Surprisingly, we observed that the Hruby coefficient is actually larger at 35 °C compared to the values at 18 and 55 °C.

1. Introduction

Amorphous selenium (a-Se) is currently used in X-ray image detectors as an X-ray photoconductor [1]. Normally a-Se films used in device applications are fabricated by the evaporation of vitreous bulk material loaded into metal boats in a conventional vacuum deposition system. For reproducible a-Se based devices, it is highly desirable that the evaporated and deposited film material is fully vitreous; the



bulk material is usually vitreous a-Se pellets or shots prepared by melt quenching techniques. We therefore need to monitor the amorphous state of the starting bulk material during storage. The resistance against crystallization is an important factor in both film and bulk forms of a-Se. Previous work on Se photodarkening has indicated that an increased resistance to crystallization appears at around 35 °C [2, 3]. In fact, according to Reznik and coworkers, high-field avalanche rushing photodetector (HARP) video tubes provided the best operation at 35 °C, which avoid defect related blemishes in the image; these blemishes occurred during operation only at room temperature (RT) or below. It was also been found that only when Se-based film devices are kept close but below the glass temperature at 35°C, the photodarkening is totally reversible, whereas at RT there is a reversible and an irreversible component. The reversible photodarkening recovers after the cessation of photoexcitation whereas the irreversible part does not; the relaxation of these changes is characterized by different time constants. In this work we have examined the essential thermal properties of vitreous selenium (99.999%) bulk samples that have been stored at different temperatures without illumination, and discuss the results in term of possible structural and thermodynamic changes in these materials.

2. Experimental

We used pure a-Se (bulk granules of about 30-40 mg weight each) obtained from former Noranda Corporation, Canada, 20 years ago. The a-Se is rated as PR-grade (photoreceptor grade with purity 99.999%). The starting material was in the amorphous state with stable (aged) properties. We kept a large number of samples in a temperature controlled environment at 55 °C, 17.5 -18 °C and 35 °C for up to 5 months. The humidity was maintained constant at around 40% all the time, and measured by a Therminder device. The effect of water impurity on the crystallization of thin selenium film materials was studied by Legros et al.[4].

Differential scanning calorimetry (DSC) measurements were performed using TA Instruments DSC 2910 with an attached RCS (Refrigerating Cooling System) unit that allows heating and cooling. A piece of granule of the sample (about 20 mg in mass) was weighed and sealed in Al hermetic pan and then scanned under a schedule that has 3 scans: heating, cooling and heating again, i.e. an H-C-H schedule. The heating starts at 20 °C up to 250 °C, then cooling down to 20 °C and heating immediately starts again to 250 °C. The evaluation of thermal analysis results was performed by TA Instruments Universal Analysis (UA) software. Error bars are inside plots symbols.

From the DSC thermograms, we obtained T_g , T_c and T_m . The stability S of these glasses was assessed using the relationship $S = T_c - T_g$. The measured glass transition, crystallization and melting temperatures were then used in the Hruby equation [5]. The Hruby parameter (K_{gl}) is a numerical measure of the glass-forming tendency and is given by

$$K_{gl} = \frac{T_c - T_g}{T_m - T_c}, \quad (1)$$

where T_c is the crystallization onset temperature, T_g is the glass transition onset temperature and T_m is the melting onset temperature.

3. Results and discussion

Based on previously published papers regarding the importance of 35 °C for a-Se, we started the temperature controlled environment experiments with the above storage temperature. As shown in figure 1, that glass transition temperature (T_g) does not change much after the initial first drop. However, the glass stability $S = T_c - T_g$ increases because of the higher glass crystallization temperature as is shown in figure 2. These results affect the Hruby parameter, which shows an increase with the storage time (figure 3). This is an indication that the material is becoming more stable after about one month of storage time, following which the pure a-Se material stability does not change significantly (DSC scans were performed periodically up to 5 months of storage time).

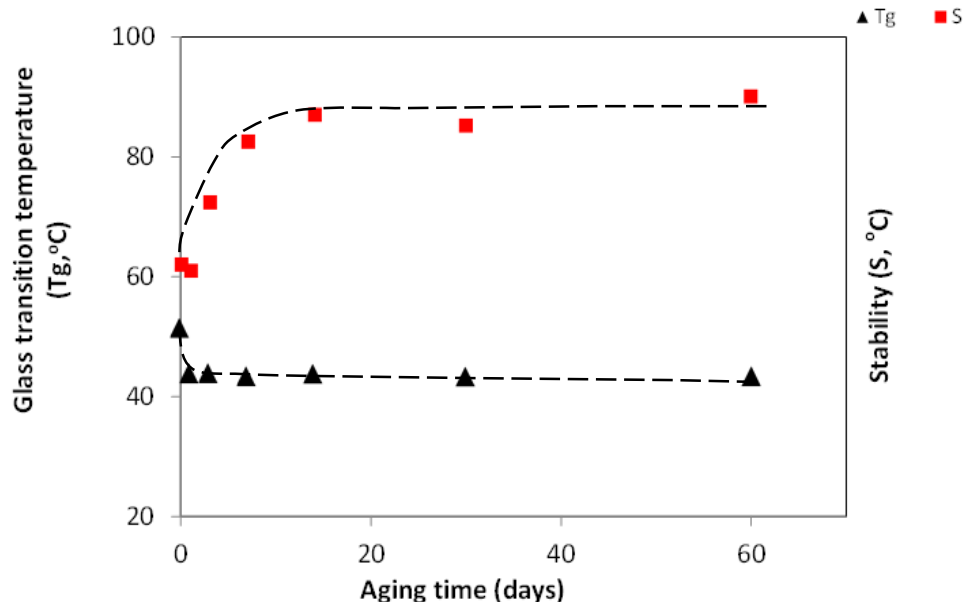


Figure 1. Glass transition temperature (T_g) and glass stability (S) of pure a-Se vs aging time when the storage temperature is kept constant at 35 °C in dark (dashed lines are guides to the eye only).

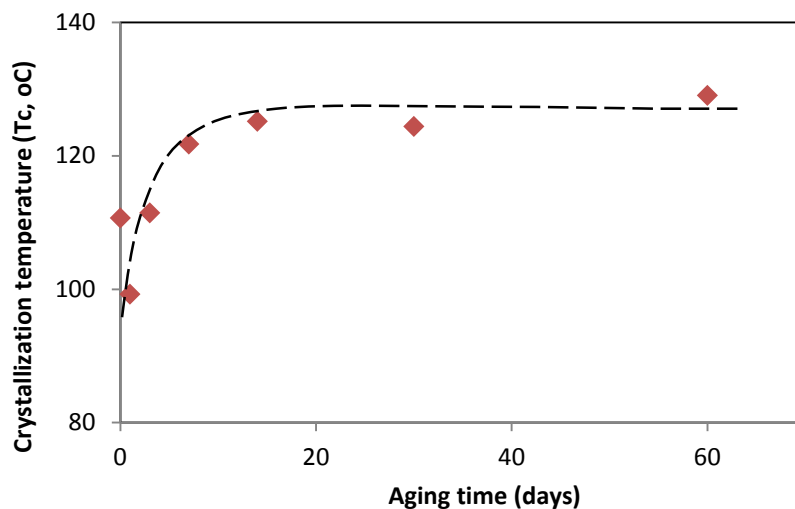


Figure 2. Crystallization onset temperature (T_c) of pure a-Se vs. aging time when the storage temperature is kept constant at 35 °C in the dark (the dashed line is a guide to eye).

We compared these results above at storage temperature 35°C with the same pure a-Se bulk samples but kept at 55 °C and 17.5 °C - 18 °C of storage temperature. The T_g remains unchanged as a function of anneal time in all cases corresponding to the storage temperature of 17.5 °C-18°C and also at RT. At storage temperatures higher than the RT, or 35 °C and 55 °C, the T_g initially drops, which is about 7-8 °C, following which T_g becomes practically unchanged as shown in figure 4. Relaxation enthalpies follow the same tendency as well when the crystallization enthalpies do not change i.e. these particular enthalpies are independent of the storage time.

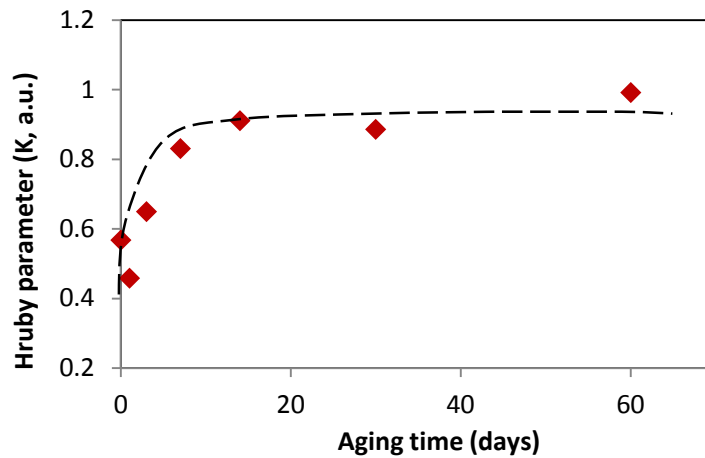


Figure 3. Hruby parameter (K_{gl}) of pure a-Se vs. aging time when the storage temperature is kept constant at 35 °C in the dark (the dashed line is a guide to the eye).

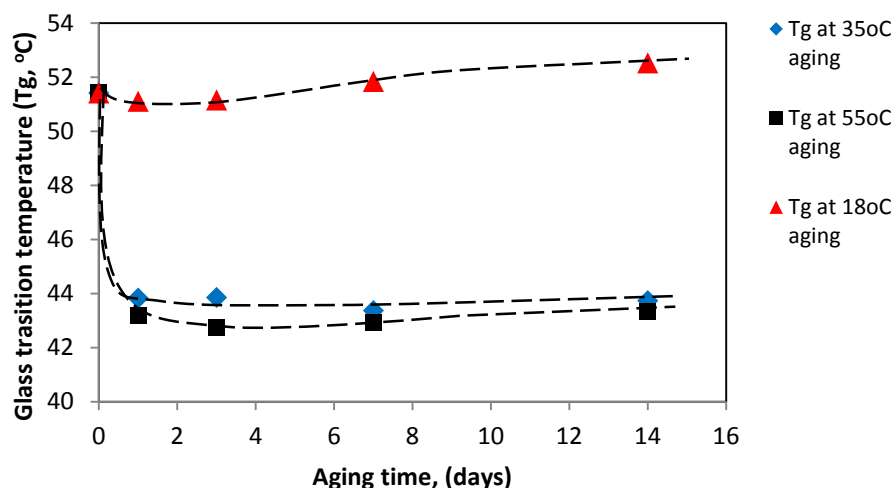


Figure 4. Glass transition temperature (T_g) of pure a-Se vs aging time when the storage temperature is kept at 35 °C, 55 °C and 17.5 °C in the dark (the dashed lines are guides to the eye).

Looking at the crystallization temperatures as shown in figures 4 it is clear that the only increase of crystallization onset temperatures is observed when the samples are kept at 35 °C; and are practically unchanged when the samples are stored at 17.5 °C – 18 °C and RT. The crystallization temperature shows a tendency to decrease at 55°C storage temperature.

Because the calculations of the glass stability and Hruby parameter (K_{gl}) are based on DSC results, it is expected that the only increase of these parameters will take place when the samples are stored at 35 °C as shown in figure 5 where it can be seen that at 17.5 °C – 18 °C, the crystallization temperature is almost unchanged but drops at 55 °C of storage temperature.

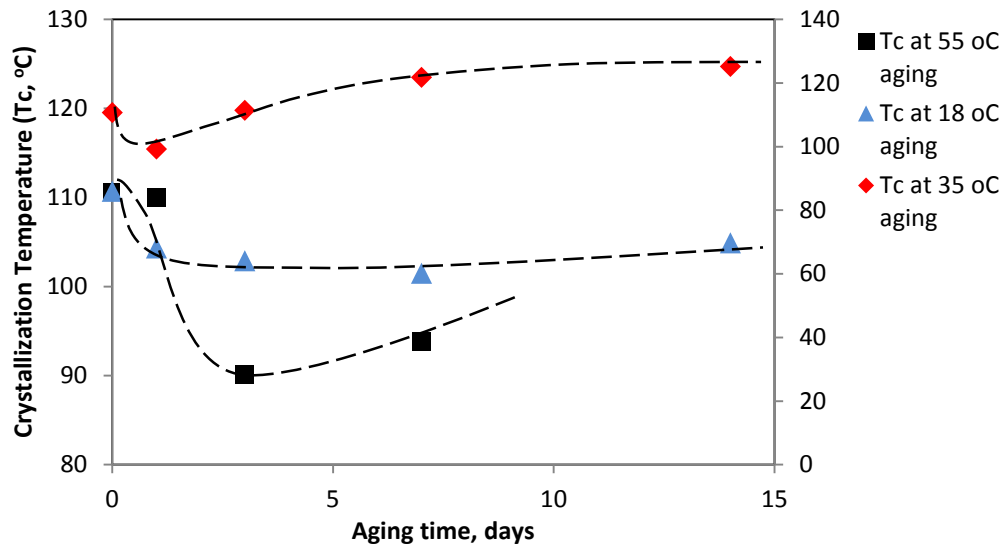


Figure 5. Crystallization onset temperatures (T_c) of pure a-Se vs. aging time when the storage temperature is kept at 35 °C, 55 °C and 17.5 °C – 18 °C in the dark (the dashed lines are guides to the eye).

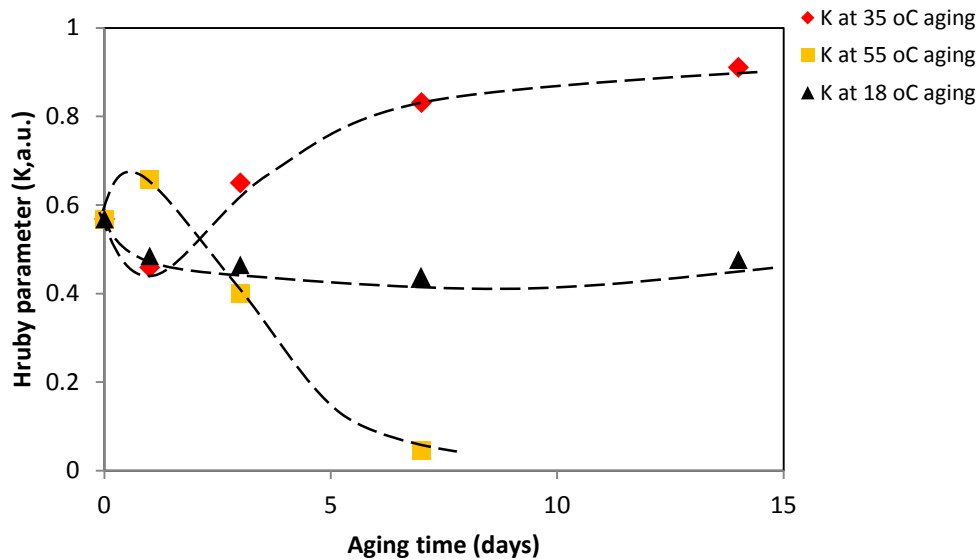


Figure 6. The Hruby parameter (K_{gl}) of pure a-Se vs. aging time when the storage temperature is kept at 35 °C, 55 °C and 17.5 °C – 18 °C in the dark (the dashed lines are guides to the eye).

It is well known that the higher the Hruby parameter, the better is the glass forming tendency. This is also a way to estimate a given material's resistivity against crystallization. The higher is the difference between the glass onset crystallization temperature T_c and the glass transition temperature T_g , and the lower the difference between the melting onset temperature T_m and the crystallization onset temperature, T_c the material is considered to be more resistive to crystallization according to Hruby theory. There is a correlation between the glass forming ability, glass stability and materials resistance to crystallization. For a comparison of glass stability parameters, the reader is referred to the discussions given by Nascimento et al [6].

The DSC overlay thermograms presented at figures 7 and 8 show the evolution of crystallization upon cooling and heating for a-Se samples kept at 35 °C and 55 °C after 1 and 3 days of storage time i.e. at a temperature below but higher than the RT (35 °C) and at a temperature above the glass transition temperature of a-Se (55 °C). It is immediately clear that the DSC scan signatures are totally different. The crystallization enthalpy at cooling for samples kept at 35 °C decreases, i.e. the material becomes more resistive to crystallization. For samples that are kept at 55 °C, the crystallization enthalpy at cooling increases with storage time i.e. material is less resistive to crystallization.

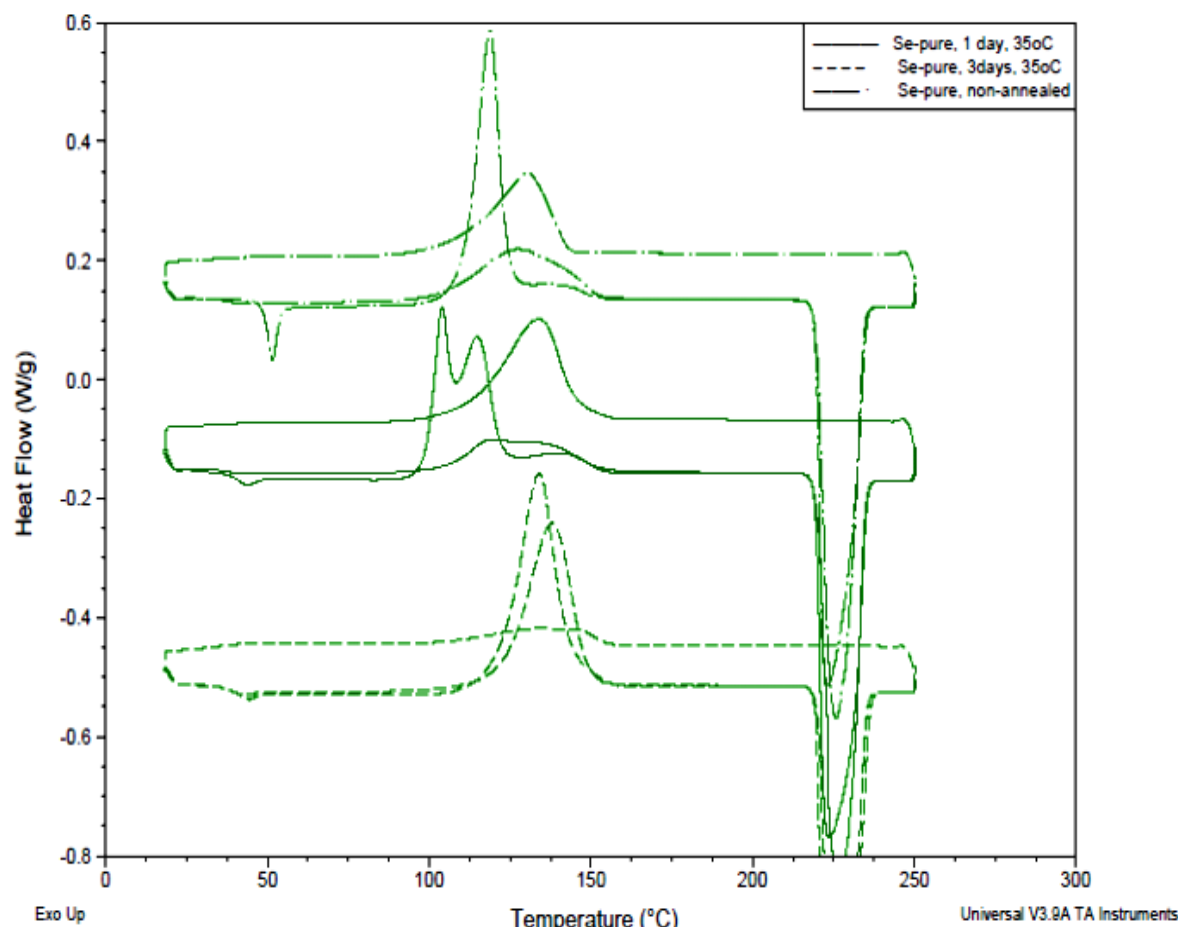


Figure 7. The evolution of DSC thermograms from H-C-H scans after the samples have been kept at 35 °C for different durations of storage (aging) time.

The type of behaviour of glass transformation properties of a-Se stored at different temperature can be explained by well-established models for enthalpy relaxation; and there are many previous works describing the phenomena of structural changes with storage time of amorphous materials including for a-Se. For example, in the earlier works of Stephens [7] reports on the viscosity and structural relaxation changes of a-Se vacuum evaporated films.

The thermal properties of pure a-Se such as the glass transition and crystallization depend on the synthesis and thermal history. Once quenched, the glass forms a network under stress, that is, the structure has a higher enthalpy than the extrapolated liquid or equilibrium enthalpy. The excess enthalpy is released through structural relaxation. The structural relaxation time that controls the rate of relaxation in the enthalpy depends on the temperature and also on the instantaneous enthalpy, (see for example reference [8]). For samples aged at 35 and 55 °C, there is an initial drop in T_g as can be seen in

figure 4. This is due to the fact that at these storage temperatures the equilibrium enthalpy is higher than that at the RT, and the structure also relaxes more quickly than at the RT. Thus, the observed T_g is lower for the sample aged at 35 °C and still lower for the sample aged at 55 °C.

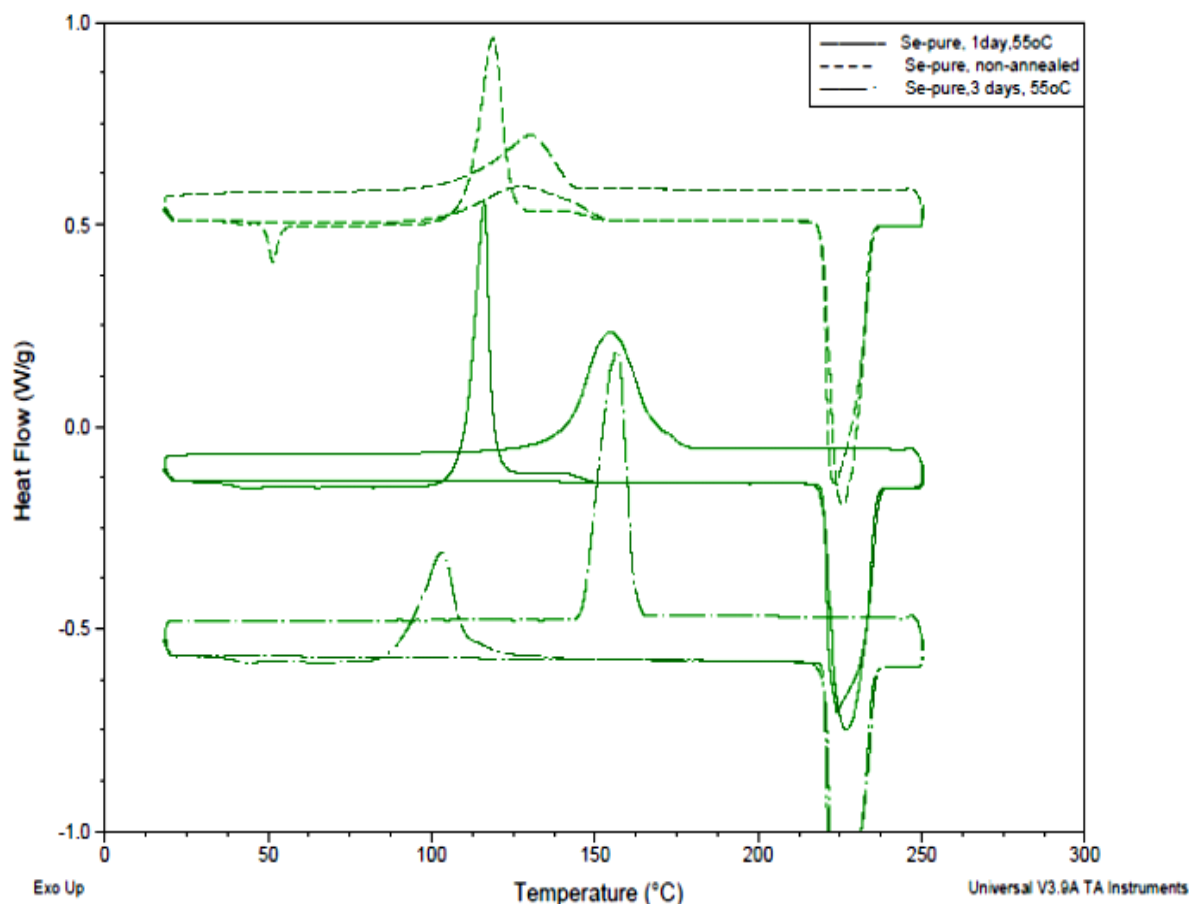


Figure 8. The evolution of DSC thermograms from H-C-H scans after the samples have been kept at 55 °C for different durations of storage (aging) time.

The most remarkable result in the present work is on the changes in the crystallization behavior. The crystallization process is a two-step process that has nucleation and growth. Either nucleation occurs first (heterogeneous nucleation) or continues during growth (homogeneous nucleation). Without an extensive detailed microscopic study, it is very difficult to separate the two processes. It would be reasonable to assume that in DSC experiments the crystallization onset temperature T_c probably corresponds to the onset of growth even though there may still be nucleation occurring at this time. Put differently, the onset marks a major nucleation and the start of growth. Further, the rate of crystal growth in a-Se is thermally activated without any unusual features (see, for example, ref [9]). Thus, based on the latter two assumptions, figure 5 indicates that the nucleation processes is suppressed at 35 °C. This is a very unusual result. Perhaps because the sample is very close to the glass transition temperature, the structure is too floppy to allow any large interfacial strains to build-up, that is, the floppy structure reduces the surface tension between the floppy glassy structure and the crystalline state. At 55 °C, the crystallization onset temperature is lower than that at the RT, because these high temperatures simply encourage nucleation and growth. We believe the key factor for understanding the higher resistance to crystallization at 35 °C must rely on the surface energy factor between the crystalline embryos and the floppy glass matrix. This view is in line with a recent conclusion on the examination of

photocrystallization of a-Se films, where the authors have concluded that "the observed growth rate between 260 and 302 K is driven by local strain, and that relaxation of this strain near T_g suppresses crystal growth until thermally assisted processes accelerate the photo-crystallization at higher temperatures [10].

4. Conclusions

Samples of pure aged amorphous Se were stored at temperatures below the RT at 17.5 °C – 18 °C, at temperature below T_g at 35 °C but higher than the RT and at 55 °C, which is above the glass transition of a-Se. Thermal analysis performed by DSC and the examination of the glass stability and Hruby parameters of these samples reveal the following results:

- (a) Samples of aged pure a-Se stored at a temperature of 35 °C but below the glass transition temperature T_g are more resistive to crystallization. These samples possess higher glass stability (S) and Hruby parameter (K_{gl}) than the other samples, because the crystallization onset temperature T_c increases during the first two weeks of storage time and then stabilizes henceforth
- (b) Samples of a-Se stored at temperatures below the RT at 17.5 °C – 18 °C, exhibit properties that do not change with the time.
- (c) Samples of a-Se stored at temperatures above the T_g at 55 °C exhibit a decreased glass stability because the crystallization temperature T_c decreases, i.e. there is a reduction in the glass stability and the Hruby parameter of these samples.
- (d) DSC glass transformation results, changes in glass stability and Hruby parameter of a-Se are discussed and explained in terms of structural relaxation of amorphous materials.

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