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EVALUATION OF CRYSTALLIZATION KINETICS BY MEANS OF DTA

M. D. BARÓ (a), N. CLAVAGUERA (b), S. BORDAS (a), M. T. CLAVAGUERA-MORA (c),
and J. CASAS-VÁZQUEZ (a)

Departamento de Termología, Universidad Autónoma de Barcelona, Bellaterra, Barcelona, (a)
Facultad de Física, Universidad de Barcelona, Avda Generalísimo, 647, Barcelona, (b)
Departamento de Física Fundamental, Universidad de Valladolid, Spain (c)

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The kinetics of bulk crystallization of $Se_{61.5}Ge_{15.4}Sb_{23.1}$ glasses was investigated from their thermal behaviour. In the thermal characterization of a glass the recrystallization temperature is highly dependent on both the rate of heating and the thermal history of the glass. Vitreous samples were prepared by quenching. From ratedependent curves it was found that the recrystallization process obeys first-order kinetics with an apparent activation enthalpy of 48 ± 5 kcal/mole. Further analysis allows determination of both the activation enthalpy, $H = 90 \pm 4$ kcal/mole, and the kinetic exponent of the Avrami equation, $n = 1.9 \pm 0.3$.

Kinetic investigations of crystallization of chalcogenide glasses are of interest for elucidating the nature of crystal growth and for research of semiconductive glassy materials with given properties. In particular, the glass-forming ability of binary germanium-selenium alloys is regulable within wide limits by incorporating a third element, such as Sb, as has been established since the work of Borisova and Pazin [1].

This paper reports on the kinetics of bulk crystallization of $Se_{61.5}Ge_{15.4}Sb_{23.1}$. We take this composition because, though it lies in the glass-forming region obtained from quenching of the melt in water [2], it is just outside the glass-forming region obtained for a constant cooling rate of 5°/min [3].

Experimental

Appropriate weighed amounts of the elements (Balzers 5N purity), introduced into a precleaned quartz tube, sealed in vacuum, were held at 1000° for 6 h, constantly agitated to make the melt homogeneous, and then quenched in water at room temperature. The amorphous state of the samples and their homogeneity were verified by X-ray diffraction and scanning electron microscope observations.

Thermal analysis was performed on 30 mg samples with a Mettler 2000 thermal analyser with constant rates r running from 1 to 25°/min, or on 200 mg samples with an STA 429 Netzsch thermal analyser. In all cases the DTA sample cell was filled for the initial run with material which had been ground into powder form. The reference material was corundum. During the run the sample chamber was ontinuously purged with 100 cc/min of dry Ar.

Results and discussion

Two typical successive curves obtained for $r = 5°/\text{min}$ are shown in Fig. 1. On heating, the glass transition at $T_g = 232°$ ideally takes the form of a step in the DTA trace, recrystallization results in an exothermic peak ($\Delta H_R = 560 \pm 50$ cal/mole), and melting yields an endothermic peak. On cooling, crystallization yields an exothermic peak, but with $\Delta H = 270 \pm 25$ cal/mole. This seems to indicate that, on cooling, crystallization is only partially achieved. This result may be explained by assuming that when the temperature has been lowered sufficiently to allow the formation of nuclei, the viscosity is already so high that it prevents growth of crystalline material.

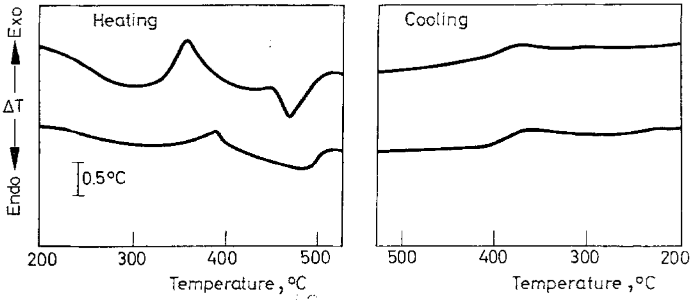

Fig. 1. Two successive DTA curves for a $Se_{61.5}Ge_{15.4}Sb_{23.1}$ glass

The onset of recrystallization is dependent upon the heating rate. This dependence was analysed through use of Uhlmann's treatment [4] in a preceding paper [5]. From this analysis the homogeneous nucleation rate

$$I = \frac{N_v^0 kT}{3\pi a_0^3 \eta} \exp\left[-\frac{16\pi\sigma_g^3}{3(\Delta H_m)^2 RT_m T_r^3 (\Delta T_r)^2}\right]$$

and the crystal growth rate

$$u = \frac{fkT}{3\pi a_0^2 \eta}\left\{1 - \exp\left[-\frac{\Delta H_m \Delta T_r}{RT_m T_r}\right]\right\}$$

may be obtained. Here N_v^0 is the mean volume concentration of atoms, a_0 is the atomic diameter, η is the viscosity, σ_g is the molar free interface enthalpy between nucleus and liquid, ΔH_m is the molar enthalpy of fusion, T_m is the melting point, $T_r = T/T_m$ is the reduced temperature, $\Delta T_r = 1 - T_r$ is the reduced undercooling, and f is the fraction of sites at the crystal/liquid interface where atoms may be preferentially added or removed.

The temperature-dependences of I and u are plotted in Fig. 2, using the data of [5]. As shown in this Figure, I increases steeply with increasing undercooling up to a maximun of $\simeq 10^{16}$ cm^{-3}s^{-1} at 340° and then decreases with increasing undercooling; u decreases continuously, but at an increasing rate, with falling temperature, reflecting the dominant role played by the reducing rate of atomic diffusion.

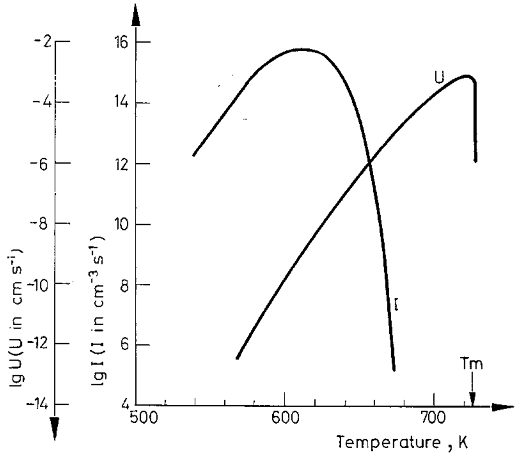

Fig. 2. Temperature-dependences of the nucleation rate I and crystal growth rate u

When the extent of recrystallization x is significant, the nucleation and crystal growth can be described by the following general kinetic equation:

$$x = 1 - \exp(-kt^{n})$$

where k is the rate constant given by

$$k = k_0 \exp - \frac{H}{RT}$$

From these two equations we have

$$\frac{dx}{dt} = k_0'(1 - x)\,[-\ln(1 - x)]^{m} \exp\left(-\frac{H}{nRT}\right) \quad \text{with } m = \frac{n-1}{n}$$

This last equation can serve as a good approximation for non-isothermal conditions [6]. In particular for $n = 1$ we have at the point of the maximun transformation rate

$$k_0 \exp - \frac{H}{RT_C} = \frac{Hr}{RT_C^2}$$

where r is the heating rate and T_C relates to the moment of the maximum transformation rate. Then a plot of $\ln(r/T_C^2)$ versus $1/T_C$ yields a straight line from which k_0 and H can be determined. Crystallization data from different heating rates are shown in Fig. 3.

We can also proceed without the assumption that $n = 1$, obtaining the following more general equation for the point of the maximum transformation rate

$$k_0' \exp - \left(\frac{H}{nRT_C} \right) \{[-[\ln(1 - x_C)]^m - m[-\ln(1 - x_c)]^{m-1}\} = \frac{Hr}{nRT_C^2}$$

where now x_C is the extent of recrystallization at $T = T_C$, and may depend on the heating rate. As in our case x_C does not vary significantly with the heating rate, we conclude from the data reported in Fig. 3 that $H/n = 48 \pm 5$ kcal/mole.

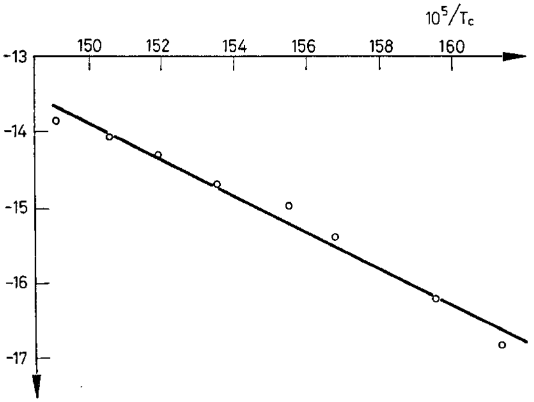

Fig. 3. Crystallization data from different heating rates

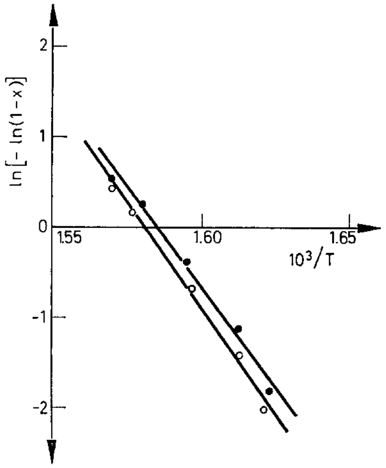

Fig. 4. Evaluation of the activation enthalpy H from kinetic data

In order to obtain the value of n, we proceed first to evaluate H by using the approximate relation [7]

$$\ln\left[-\ln(1-x)\right] \simeq \text{constant} - \frac{H}{RT}$$

to the recrystallization peak obtained with a heating rate of 5°/min (Fig. 1), assuming that the extent of recrystallization is proportional to the relevant area under the DTA peak. The kinetic data obtained for two different runs are plotted in Fig. 4. Least squares fitting gives $H = 90 \pm 4$ kcal/mole, and consequently we obtain $n = 1.9 \pm 0.3$. This result seems to indicate that the nucleation rate I is a decreasing function of time and that recrystallization is a diffusion-limited process [8].

References

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Résumé — Etude de la cinétique de la cristallisation dans la masse de verres $Se_{61.5}Ge_{15.4}Sb_{23.1}$ à partir de leur comportement thermique. La température de recristallisation dépend fortement tant de la vitesse de chauffage que de l'histoire thermique du verre. Des échantillons vitreux ont été préparés par refroidissement rapide. La recristallisation obéit à une cinétique du premier ordre, avec une enthalpie d'activation apparente de 48 ± 5 kcal·mol^{-1}. Une analyse ultérieure permet de déterminer l'enthalpie d'activation $H = 90 \pm 4$ kcal·mol^{-1} ainis que l'exposant cinétique $n = 1.9 \pm 0.3$ de l'équation d'Avrami.

Zusammenfassung — Die Kinetik der Massenkristallisation von Glas-Arten der Zusammensetzung $Se_{61.5}Ge_{15.4}Sb_{23.1}$ wurde an Hand ihres thermischen Verhaltens studiert. Bei der thermischen Charakterisireung von Glas hängt die Rekristallisationstemperatur stark sowohl von der Aufheizgeschwindigkeit als auch von der Wärmevorgeschichte des Glases ab. Glasige Proben wurden durch rasches Abkühlen hergestellt. Aus den geschwindigkeitsabhängigen Thermogrammen geht hervor, dass der Rekristallisierungsprozess der Kinetik erster Ordnung gehorcht, mit einer scheinbaren Aktivierungsenthalpie von 48 ± 5 kcal/mol. Die weitere Analyse ermöglicht die Bestimmung sowohl der Aktivierungsenthalpie $H = 90 \pm 4$ kcal/mol als auch des kinetischen Exponenten $n = 1.9 \pm 0.3$ der Avrami-Gleichung.

Резюме — Из термического поведения стекол $Se_{61.5}Ge_{15.4}Sb_{23.1}$ установлена кинетика их кристаллизации в массе. При термической характеристике стекла, температура рекристаллизации значительно зависит как от скорости нагрева, так и от термического происхождения стекла. Стеклообразные образцы были получены путем отжига. Из скоростнозависимых термограмм было получено, что процесс рекристаллизации подчиняется кинетике реакции первого порядка с кажущейся энтальпией активации 48 ± 5 ккал/моль. Дальнейший анализ позволил определить как энтальпию активации $H = 90 \pm 4$ ккал/моль, так и кинетическую экспоненту $n = 1.9 \pm 0.3$ уравнения Аврами.