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# Crystallization kinetics of $Ge_{10}Sb_{30}Se_{60}$ glass

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## Abstract

The crystallization kinetics of bulk $Ge_{10}Sb_{30}Se_{60}$ glass has been studied by differential scanning calorimetry. The effective activation energy of crystallization has been evaluated on the basis of the Kissinger equation and the isoconversion cuts method. The empirical Šestak–Berggren model has been used for the description of DSC crystallization data as it provides the best fit to the experimental results. It has been found that the Johnson–Mehl–Avrami model could not be applied because of the influence of the nucleation process during crystallization. © 1998 Elsevier Science B.V.

*Keywords:* Chalcogenide glass; Crystallization; DSC; Kinetics

## 1. Introduction

Studies of the crystallization processes in chalcogenide glasses are of particular interest because they are connected with such important phenomena as memory type of switching, reversible optical recording, etc. Thermal analysis is a very useful tool for describing the crystallization kinetics as it is rapid and convenient. Usually, it is assumed that the heat flow, $\Phi$, evolved during the crystal growth can be expressed by the following kinetic equation [1]

$$\Phi = \Delta H A e^{-E/RT} f(\alpha) \tag{1}$$

where $\Delta H$ is the heat of crystallization, $A$ the pre-exponential factor and $E$ the effective activation energy for the crystallization process. It is possible to compute the activation energy using some known methods. In this work, we applied the isoconversional cuts [2] and Kissinger [3] methods for comparison. The function $f(\alpha)$ in Eq. (1) is an analytical expression describing the kinetic model of the studied process. We attempted to use the Johnson–Mehl–Avrami (JMA) model [4,5] in the first step

$$f(\alpha) = n(1-\alpha)[-\ln(1-\alpha)]^{1-1/n} \tag{2}$$

where $n$ is a kinetic exponent related to the dimensionality of the crystal growth. The degree of crystallization or conversion, $\alpha$, implies the volume of the crystalline part created during the crystallization process. In order to test the applicability of this model, generally the $z(\alpha)$ function is proposed [6]

$$z(\alpha) = \Phi T^2 \tag{3}$$

which can be easily obtained from the experimental DSC data on multiplying the measured heat flow by

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$T^2$. The maximum of the $z(\alpha)$ function $\alpha_p^\infty$ should be close to 0.632 [7]. If the value of $\alpha_p^\infty$ is considerably lower, the JMA model cannot be applied. According to our experience, the JMA model as a special case of the Šesták–Berggren (SB) equation, can seldom be used for the description of the crystallization kinetics of some chalcogenide glasses, owing to the basic assumption of applicability [8,9]. In the cases when the JMA model is not valid, the empirical SB model [10] should be used

$$f(\alpha) = \alpha^m(1-\alpha)^n \tag{4}$$

where the exponents $m$ and $n$ are related to the crystallization process mechanism. The detailed meaning of these two exponents is not clearly understood at present, with the exception of the fact that the value of $m$ should lie in the interval $0<m<1$ [11].

This work follows recent papers dealing with the studies of crystallization processes in chalcogenide glasses of the Ge–Sb–S [12–15] and Ge–Sb–Se [16–18] systems, which are important with a view to application purposes. A special attention has been turned to the Ge–Sb–Se glasses because of their good transmittance in the infrared region of 2–16 μm [16–18]. In particular, the physical and optical properties of the $Ge_{40-x}Sb_xSe_{60}$ family are studied in detail [19] but their crystallization data are limited. Our previous DSC investigations of the same family have shown that the crystallization peak is most clearly defined at the $Ge_{10}Sb_{30}Se_{60}$ composition. In the present paper, the crystallization kinetics and the evaluation of the activation energy of this type of glass is studied by using the non-isothermal method.

## 2. Experimental

The bulk glassy $Ge_{10}Sb_{30}Se_{60}$ composition was prepared by direct synthesis from elements of 5 N purity. Appropriate quantities from elements with a total weight of 6 g were sealed into a quartz ampoule, after evacuating to a vacuum of $10^{-3}$ Pa. It was heated at ~950°C in a rotary furnace for 24 h and the melt quenched in water.

A coarse powder of the glass being studied with similar particles size and with a weight of ca. 30 mg was encapsulated into aluminium capsules. The measurements were performed using the Mettler DSC 13E instrument controlled by a computer. The calorimeter was calibrated with indium, lead and tin standards. The calorimetric sensitivity $E$=1118.75 units per mW and $\tau_{lag}$=15 s were used for the measurements. The non-isothermal DSC curves were measured in the 303–673 K range, with heating rates $\beta$=5, 10, 15 and 20 K min$^{-1}$. All experimental data were performed using the TA-system software package.

For identifying the glass phases, the sample studied was annealed at ca. 300°C, which is close to the temperature of the crystallization peak, for 30 min. The X-ray diffraction analysis was carried out using an HZG-4 X-ray diffractometer (Freiberger Präzisionsmechanik, Germany) with Cu$K_\alpha$ radiation by a Ni filter.

## 3. Results and discussion

Fig. 1 presents typical DSC traces of glassy $Ge_{10}Sb_{30}Se_{60}$ measured at four different heating rates. As can be expected, the crystallization peak is shifted to higher temperature with increasing heating rate.

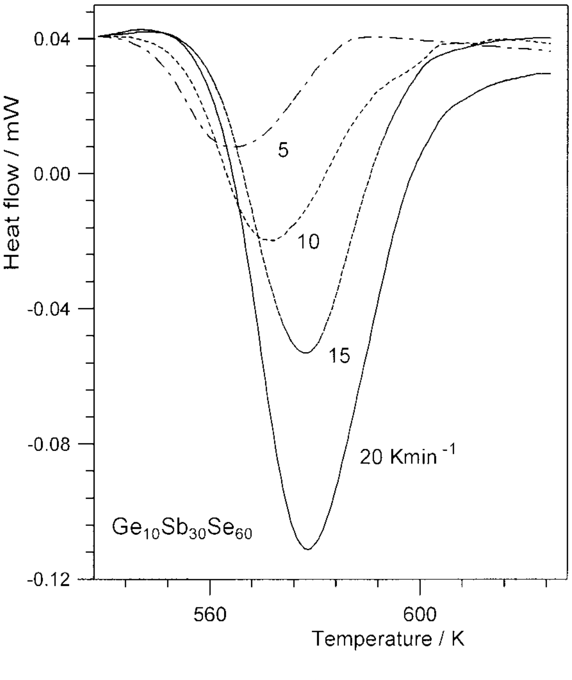

Fig. 1. DSC crystallization curves of $Sb_2Se_3$ in $Ge_{10}Sb_{30}Se_{60}$ glass measured at different heating rates, $\beta$, indicated by numbers.

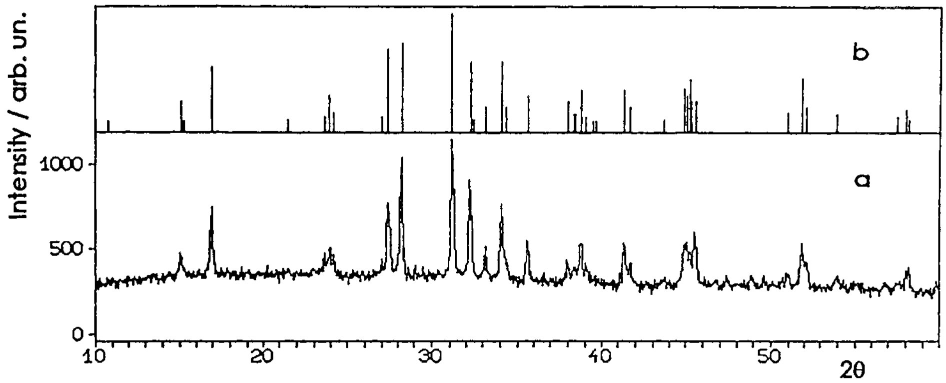

Fig. 2. (a) X-ray diffraction pattern of crystallized $Ge_{10}Sb_{30}Se_{60}$ sample. (b) The data for crystalline $Sb_2Se_3$ [19] are shown for comparison.

The X-ray diffraction data show that a $Sb_2Se_3$ phase crystallizes in this case (Fig. 2). The activation energy of the crystallization of $Sb_2Se_3$ from these four measurements is calculated and its variation with the degree of conversion $\alpha$ is shown in Fig. 3. The straight line corresponds to the value determined by the Kissinger method $E_{\mathrm{Kis}}=232.29\pm31.73$ kJ mol$^{-1}$. The activation energy calculated by the isoconversion cuts method (points in Fig. 3) is $E_{\mathrm{iso}}=234.40\pm49.02$ kJ mol$^{-1}$. The results are found to be in good agreement with those for the crystallization of $Sb_2Se_3$ in $Ge_{20}Sb_{20}Se_{60}$ [16]. This parameter represents complex processes involving nucleation and crystal growth but on the bases of this experiment it is impossible to distinguish or separate them.

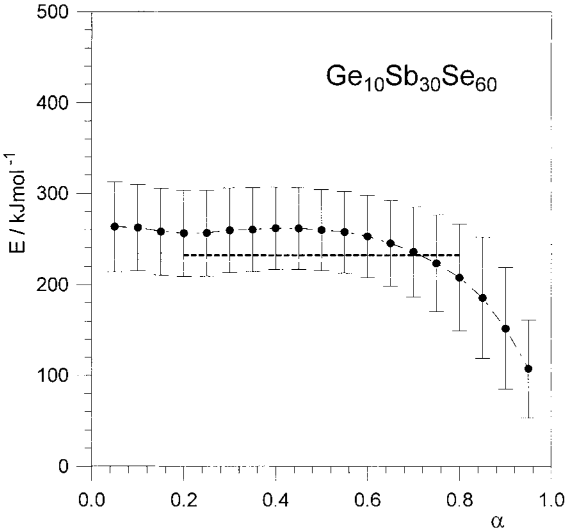

Fig. 3. Dependence of the activation energy $E$ on the degree of crystallization. The straight line is obtained by the Kissinger's method and the points are calculated by the method of isoconversional cuts. For the values and comparison see the text.

The average heat of crystallization, $\Delta H=-9.49\pm$ 0.45 J g$^{-1}$, is also calculated (Table 1). The scatter in the computed data (Fig. 4) is probably due to different and imperfect thermal contact of the coarse powdered sample with the aluminium capsule's bottom. The corresponding kinetic model is determined with the help of experimental DSC curves and a value of the activation energy is obtained. The $z(\alpha)$ function (Eq. (3)) is calculated and the results are listed in Table 1. It is obvious that the maximum $\alpha_p^\infty$ of the $z(\alpha)$ functions is significantly lower compared to 0.623 needed for the applicability of the JMA model [7]. Probably this is due to the fact that condition of saturation of sites is not fulfilled. Therefore, the SB model has to be used for the description of crystallization process of $Sb_2Se_3$ in $Ge_{10}Sb_{30}Se_{60}$ glass. The calculated parameters $m$ and $n$ are summarized in

Table 1
Parameters for the SB model ($E$=234 kJ mol$^{-1}$)

| $\beta$/K min$^{-1}$ | $\Delta H$/J g$^{-1}$ | $m$ | $n$ | ln A/s$^{-1}$ | $\alpha_p^\infty$ |
|---|---|---|---|---|---|
| 5 | −9.13 | 0.28 | 1.16 | 45.33 | 0.479 |
| 10 | −9.71 | 0.35 | 1.61 | 45.44 | 0.432 |
| 15 | −9.09 | 0.33 | 1.43 | 45.26 | 0.475 |
| 20 | −10.01 | 0.37 | 1.57 | 45.61 | 0.429 |
| Average: | −9.49 | 0.33 | 1.44 | 45.41 | 0.454 |
| S.D.: | ±0.45 | ±0.04 | ±0.20 | ±0.15 | ±0.027 |

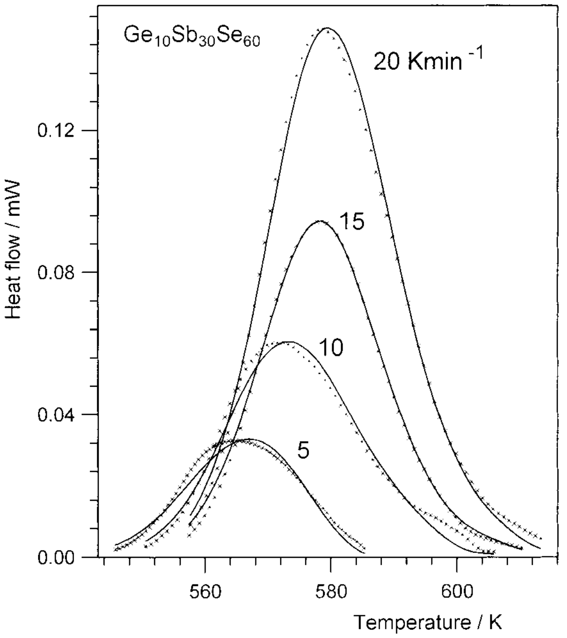

Fig. 4. Comparison of experimental data (· · ·) and calculated curves using the SB model (———).

Table 1. These kinetic exponents are related to the mechanism of the crystallization processes but their physical meaning is not yet known [11]. The SB model is taken as the basis for defining an accommodation function. From this point of view, the heterogeneous reactions are considered as simple homogeneous reactions and the SB accommodation function represents the degree of deviation from the ideal case. The comparison of experimental data (points) and calculated curves using the SB empirical model shows a relatively good agreement between them (Fig. 3).

## 4. Conclusion

From analysis using the Kissinger equation and the isoconversion cuts method, the effective activation energy of crystallization of $Ge_{10}Sb_{30}Se_{60}$ glass has been determined. Both the values ($E_{kis}$=232.29 and $E_{iso}$=234.40 kJ mol$^{-1}$) are in a good agreement. It has been found that, for the description of crystallization kinetics of $Sb_2Se_3$ in $Ge_{10}Sb_{30}Se_{60}$ coarse powder glass, the Šesták–Berggren empirical model must be applied. Since the values of $\alpha_p^\infty$ (0.429–0.479) are significantly lower compared to 0.623, the Johnson–Mehl–Avrami model cannot be used. This fact indicates that probably the condition of sites saturation was not fulfilled because of the influence of nucleation processes during the crystal growth.

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