Crystallization of As_xSe_{1-x} from the glassy state ($0.005 < x < 0.03$)

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Abstract

The crystallization of As_xSe_{1-x} from the glassy state ($0.005 < x < 0.03$) is analyzed from calorimetric investigations. For each composition, the apparent activation energy for the crystallization reaction is determined with the Kissinger method. Upon increasing x, the apparent activation energy decreases. It is also found that the dependence of the inverse of the apparent activation energy for crystallization falls linearly with the reciprocal of the mean temperature used in the experiment. The latter result unambiguously indicates that the crystallization process for As_xSe_{1-x}, in the composition range investigated, is mainly controlled by the viscosity of the medium. Therefore, the crystallization reaction totally disappears when the amount of As atoms in the alloys reaches such a value capable of connecting enough Se chains to block their movement. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: As_xSe_{1-x}; Crystallization

1. Introduction

In chalcogenide-based glasses many systems exhibit, during the heating period, three consecutive transformations: glass transition ⇒ crystallization ⇒ melting. Nevertheless, it is also known that some of them do not respect this behaviour. This is the case of Ge–Se and As–Se systems, for which the crystallization cannot be obtained for compositions with greater than ≈ 4 at% of Ge [1] and ≈ 10 at% of As [1–3], respectively, but can re-appear for compositions close to $GeSe_2$ and As_2Se_3 [1–3]. This property is very important because, as pointed out by Quin et al. [4] and Lasocka et al. [5], the systems which show no crystallization reaction are of the threshold switching type while the others exhibit a memory-type behaviour.

In contrast to the stoichiometric composition As_2Se_3 and those close to it, the compositions with low As content received less attention. Thus, it is interesting to have more informations concerning the kinetics of crystallization of the As–Se system at such low As content. This is the goal of this work, in which new data concerning the kinetics of devitrification of As_xSe_{1-x} vitreous alloys are presented and compared with published results.

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2. Method

The values of the kinetic parameters were determined using Kissinger equation [6] given by

$$\ln\left(\frac{v}{T_{\mathrm{m}}^2}\right)$$
$$= -\frac{\Delta E}{RT_{\mathrm{m}}} + \left[\ln(K_0) + \ln\left(-\frac{R}{\Delta E}\left(\frac{\mathrm{d}F(\alpha)}{\mathrm{d}\alpha}\right)_{\alpha_{\mathrm{m}}}\right)\right], \quad (1)$$

where v is the heating rate, T_{m} the temperature for which the rate of transformation is maximum, ΔE the apparent activation energy, R the gas constant, K_0 a constant, α the rate of transformation and $F(\alpha)$ is the kinetic function of transformation. The classical Kissinger relationship is obtained if the term in brackets on the right-hand side of Eq. (1) is a constant. This is the case when the order reaction parameter (n) remains a constant during all the process investigated and when the reactions involved are described by an n-order Eyring equation. It was also shown that, this Kissinger equation remains valid either for heterogeneous or homogeneous nucleations [7]. In this last case, the apparent activation energy represents an average activation energy for the whole transformation which includes both the apparent nucleation and growth activation energies. Thus, the variations of $\ln(v/T_{\mathrm{m}}^2)$ with $1/T_{\mathrm{m}}$ will lead to the determination of an apparent activation energy. Because many results in the literature were obtained from this method, and to be able to compare our data with others, this is the method used to obtain our results.

3. Materials

Each sample of the expected composition was obtained from a mixture of both elements (99.999% purity) in a granular form. The mixture was introduced into a quartz ampoule and sealed in a vacuum of 10^{-3} Torr. Then, the ampoules were placed in a horizontally rotating oven and annealed at 1273 K during more than 10 h. Finally, they were water-quenched. The glass transition and crystallization temperatures were measured by differential scanning calorimetry (Perkin-Elmer DSC system 4) with different heating rates. Calibration of the cal-

orimeter was achieved for each heating rate from the measurements of the melting temperature of indium as a standard element. The vitreous nature of the sample was checked at room temperature by X-ray diffraction.

4. Results

In Fig. 1 is displayed a typical enthalpic curve obtained during the heating period of an As_xSe_{1-x} vitreous alloy (in this figure $x = 1$ at%). At first, an endothermic reaction is observed at low temperature ($T_{\mathrm{g}} \approx 50°C$) corresponding to the glass transition phenomenon, second, an exothermic reaction of crystallization is observed at a higher temperature ($T_{\mathrm{c}} \approx 111°C$, onset temperature) and finally the endothermic reaction of melting appears ($T_{\mathrm{f}} \approx 215°C$). For compositions between 0 and 10 at% of As, all the enthalpic curves exhibit the same series of reactions [1]. As previously mentioned, for compositions with greater than 10 at% As, only the glass transition is observed, the ability to crystallize vanishes, and thus no melting reaction appears. For compositions with greater than 4 at%
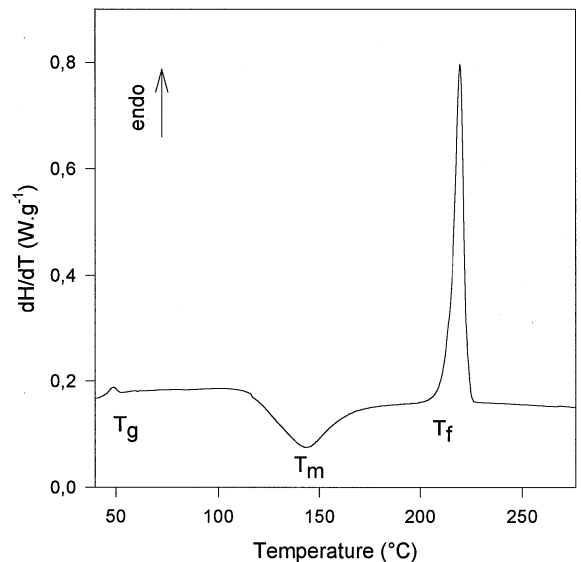

Fig. 1. Typical enthalpic curve obtained with the heating rate of 10°C/min on the $As_{0.01}Se_{0.99}$ vitreous alloy showing the glass transition, the devitrification and the melting reactions.

Table 1
Data collected from the enthalpic curves performed at 10°C/min on vitreous As_xSe_{1-x} ($0.03 \geqslant x \geqslant 0.005$)

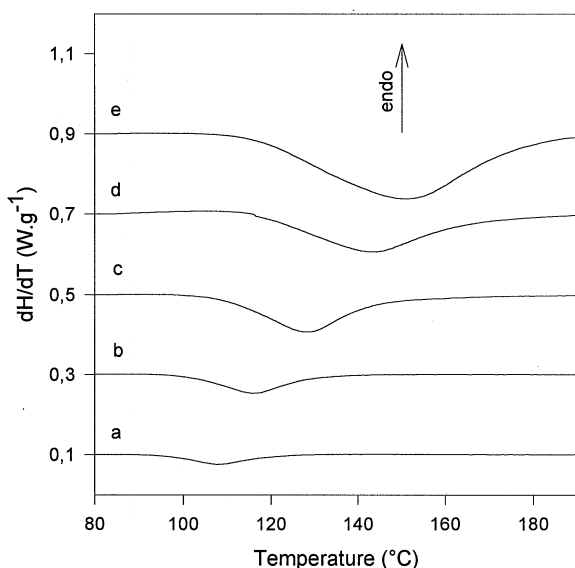|	$As_{0.005}Se_{0.995}$	$As_{0.01}Se_{0.99}$	$As_{0.02}Se_{0.98}$	$As_{0.03}Se_{0.97}$
T_g (onset) (°C)	45	47	50	57
T_c (onset) (°C)	111	117	119	127
ΔH_c (J/g)	56	50	56	
T_m (°C)	133	143	157	170
T_f (max) (°C)	220	219	217	217
T_f (onset) (°C)	215	213	211	211

Fig. 2. Variations with the heating rate of the exothermic peak of crystallization observed for $As_{0.01}Se_{0.99}$ alloy: (a) $v = 1$°C/min; (b) $v = 2$°C/min; (c) $v = 5$°C/min; (d) $v = 10$°C/min; (e) $v = 15$°C/min.

peratures at the extrema of the crystallization and melting peaks, obtained with a heating rate of 10°C/min, are reported in Table 1. The enthalpy of crystallization (ΔH_c) is also listed in Table 1.

Fig. 2 displays the enthalpic curves performed at different heating rates on $As_{0.01}Se_{0.99}$ glass. Only the crystallization reaction is presented. In agreement with what is expected, the greater the heating rate the higher is the temperature for which the crystallization reaction appears. When the heating rate increases, the exothermic peak of crystallization appears on a larger and larger temperature domain. Whatever the heating rate, the peak shape is maintained, particularly the slow kinetic on the low-temperature side. The same results are obtained for the other compositions. Using the Kissinger method, the variations of $\ln(v/T_m^2)$ with $1/T_m$ are depicted in Fig. 3 which shows the expected linear variations for all the studied samples. From the slope and the intercept of these plots, we obtained the data reported in Table 2, in which other results collected from the literature are also reported.

5. Discussion

In Fig. 4, the results of this work on the variations of the apparent activation energy with the As content are reported. In the same figure, the published results on other binary systems (Se–Te, Se–Bi) are also displayed [13–17]. In this figure, solid lines are drawn through data points as a guide for the eye, while the grey area corresponds to the range of data which concern only pure Se [7]. When Te and Bi atoms are added to Se, we observe

As, the melting reaction appears before the end of the crystallization reaction. Thus, the peaks characterizing each reaction overlap. This is the reason for which, this study is limited from 0 to 3 at% of As. We have also to notice that only one glass transition and one devitrification reactions are observed. We never observed, as for instance in many Te-based alloys [8–11] and particularly on As_xTe_{1-x} [12], two glass transitions and/or two crystallization processes. The onset temperatures of the glass transition phenomenon, the crystallization and the melting reactions, as well as the tem-
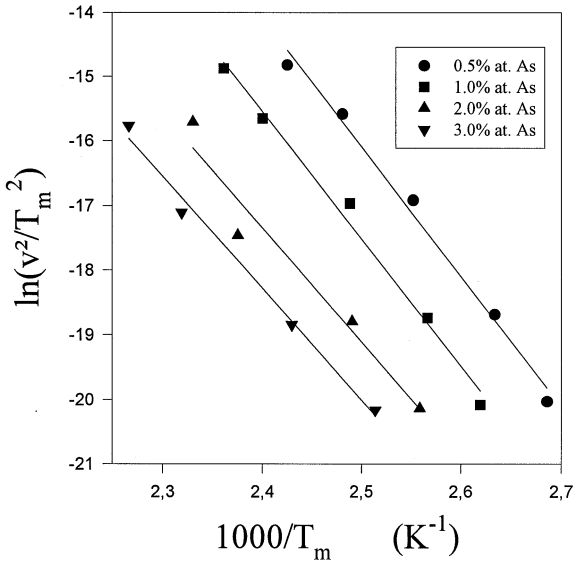
Fig. 3. Kissinger representation for the devitrification process for the As_xSe_{1-x} system ($0.03 \geqslant x \geqslant 0.005$).

Table 2
Values of the apparent activation energy obtained in this work on the As_xSe_{1-x} system and other values from the literature and concerning other binary Se-based alloys

Material	Kissinger (kJ/mol)			Ref.
Se	83.6			[7]
$Se_{1-x}As_x$				
0.005	80	DSC	Bulk	This work
0.01	79	DSC	Bulk	This work
0.02	73.2	DSC	Bulk	This work
0.03	71.3	DSC	Bulk	This work
$Se_{1-x}Bi_x$				
0.01	89.6 to 105 [1]	DTA	Thin film	[16]
0.005	100.2	DTA	Thin film	[15]
0.01	105	DTA	Thin film	[15]
0.015	112.7	DTA	Thin film	[15]
0.04	120.5	DTA	Thin film	[15]
0.05	113.7	DTA	Bulk	[13]
$Se_{1-x}Te_x$				
0.1	105	DSC	Bulk	[17]
0.15	110	DSC	Bulk	[17]
0.2	118	DSC	Bulk	[17]
0.25	125	DSC	Bulk	[17]

that the apparent activation energy increases with the amount of the added atoms. For As atoms the opposite behaviour is observed where the activation energy decreases as the As content increases. We have to point out that the use of other kinetic models to determine the value of the apparent activation energy for the crystallization process leads to some small change of the value of ΔE but not on the variations of ΔE with the content of As atoms [18].

A review of the results available in the literature which concerns this As–Se binary system leads to the following conclusions. In this range of As content, it was found that the kinematic viscosity in the liquid state exhibits a Se-type behaviour [19]. From dielectric and thermodynamic measurements it was also found that the shape of the capacitance relaxation function, associated with structural relaxation below T_g, is relatively insensitive to alloy composition although As addition to amorphous Se significantly slows the rate of structural relaxation [20]. From long-wave IR spectroscopy [21], it was observed that glasses of the As–Se system can be divided with respect to structures into four groups: $0 \leqslant x \leqslant 0.02$, $0.02 \leqslant x \leqslant 0.22$, $0.22 \leqslant x \leqslant 0.45$ and $0.45 \leqslant x$. In the first group, the arsenic

atoms cross-link a certain number of Se chains forming a branching polymeric structure. This reaction of As with Se in this concentration range leads to the formation of micro-inhomogeneous glasses. For the second group, as the As content increases, the bonds between Se atoms gradually disappear and a predominance of As–Se already present in the $As–Se_{3/2}$ trigonal pyramid is observed. Finally, from a study of the variations of the values of parameters characterizing the physical ageing kinetics with the As content, it was shown that a random incorporation of "As cells" (defined as a molecular species made of one As atom and the three connected Se atoms) modifies progressively the dimensionality of the medium up to $x = 0.08$ [22]. Thus, all the works performed on this Se-based chalcogenide alloyed with As atoms indicate that a small amount of As atoms only changes the connectivity of the medium. Thus, increasing the connectivity, increases the viscosity (or decreases the molecular mobility) and as a consequence, the values of T_g and T_c increase.

On the other hand, Kasap and Juhasz [7] in their study on pure Se and on Se-doped with differ-
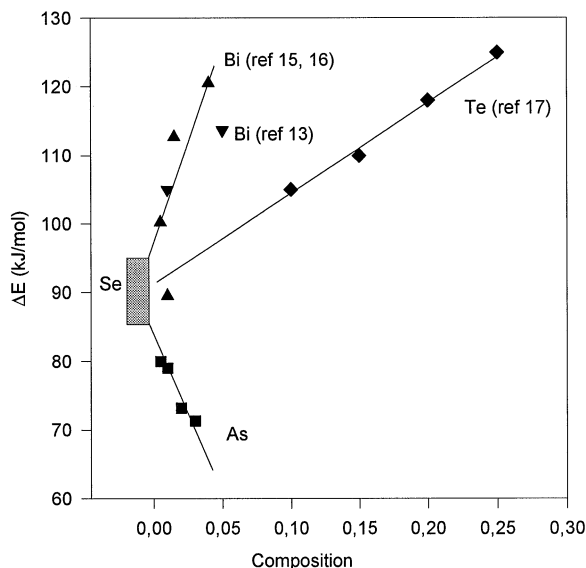
Fig. 4. Composition dependence of the apparent activation energy obtained from the Kissinger method for Se and different Se-based alloys. The solid lines are drawn through data points as a guide for the eye.
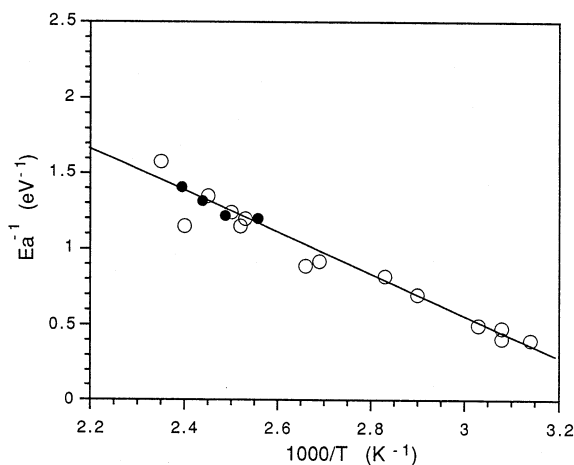

Fig. 5. Variations of the inverse of the apparent activation energy with the reciprocal of the mean temperature as proposed by Kasap and Juhasz [7]. Open circles are the Se and doped Se data of Kasap and Juhasz [7]. The straight line is the fit of the experimental data of Kasap and the full circles are the data obtained in this work.

ent elements (Te, As, Cl) have found that these elements at low concentration retard the crystallization (retard, indicates that for doped glasses, the reaction of crystallization appears at a higher temperature than those observed on the undoped glass). In the same work, it was shown that the inverse of the apparent activation energy for the crystallization (determined from the Kissinger method) as well as the inverse of the apparent activation energy for the physical ageing (concerning molecular movements around the glass transition temperature) fall nearly linearly with the reciprocal of the mean temperature used in the experiment. Thus, it was found that the variations of the apparent activation energy for both the physical ageing and the crystallization must obey the following relationship:

$$1/E_A = 1/E_0 - [T_0/E_0](1/\langle T \rangle), \qquad (2)$$

where E_A is the activation energy, $\langle T \rangle$ is the average temperature for particular experiments concerning T_g and T_c, E_0 and T_0 are the constants of the Vogel–Tammann–Fulcher equation for the

viscosity:

$$\eta = \eta_0 \exp\left[\frac{E_0}{k(T - T_0)}\right]. \qquad (3)$$

These results show that the added atoms retard the crystallization essentially by increasing the viscosity.

Reporting our data (full circles) and those already reported by Kasap and Juhasz [7] (open circles), we obtain the variations presented in Fig. 5. In this figure, the straight line corresponds to the fit of the published experimental data of Kasap and Juhasz [7] concerning Se and Se-doped glasses. It is interesting to note that the same mathematical function fit our reported data of the $Se_{1-x}As_x$ vitreous alloys ($x < 0.03$). This result indicates that the crystallization of vitreous As–Se alloys is, as for pure and doped Se, controlled by the viscosity of the medium. From this point of view, the crystallization reaction vanishes when the amount of As atoms connects enough Se chains to block their ability to move.

This interpretation is confirmed by the analysis of the data concerning other Se-rich binary systems such as $Se_{1-x}Bi_x$ and $Se_{1-x}Te_x$. Reporting these
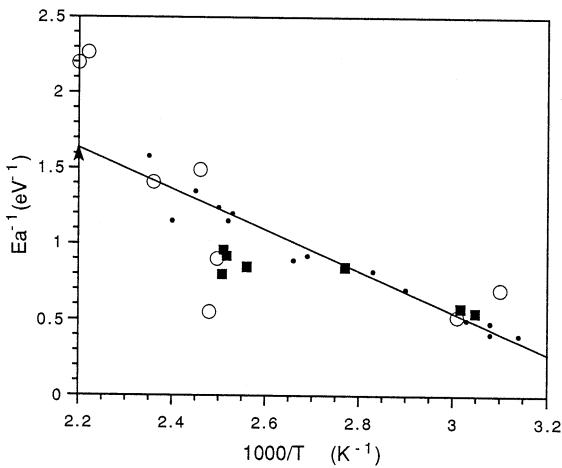
Fig. 6. Variations of the inverse of the apparent activation energy with the reciprocal of the mean temperature as proposed by Kasap and Juhasz [7]. Small full points are the Se and doped Se data of Kasap and Juhasz [7]. The straight line is the fit of the experimental data of Kasap and Juhasz, open circles are the data concerning the Se_xTe_{1-x} alloys and the full squares concern the Bi_xSe_{1-x} alloys.

data (full squares for Se–Bi and open circles for Se–Te) and those already studied by Kasap and Juhasz [7] (full circles), we obtain the variations presented in Fig. 6. In this figure, the straight line corresponds also to the fit of the reported experimental data [7]. It is clear that for $Se_{1-x}Te_x$ $(0.1 < x < 0.3)$ and $Se_{1-x}Bi_x$ $(0 < x < 0.04)$ vitreous alloys, that Eq. (2) does not fit these data. For these last systems, it is found that the viscous flow of the melt does not control the crystallization. This can be explained from the fact that, for Bi and Te atoms, the bonds engaged with Se are not necessarily covalent but can have a metallic character. Thus, all the added atoms included in the alloy do not necessarily respect the 8-N rule (the coordination of Bi is found to assume values between 3 and 4, while that of Te is found to lie between 2 and 3 depending on the experimental method used to prepare the samples [23–27]). This is the reason for which the crystallization is often observed as a multistage process in which the precipitation of Bi_2Se_3 or of Te is first observed. This is also the reason for which their glassy structures are often considered as demixed [28] or inhomogeneous

[29–31] and finally this is why these elements are considered as non-glass-formers [32].

6. Conclusions

Arsenic addition, in small amounts, to the selenium glassy matrix raises both the glass transition and crystallization temperatures. From the variations of the inverse of the apparent activation energy for the crystallization with the inverse of the temperature used in the experiments, it is concluded that the crystallization reaction for the investigated glasses is governed by the viscous flow of the medium. Thus, when the number of As atoms introduced in the alloy reaches a critical value, which is adequate to link enough Se chains, then the relative motion of these chains is blocked. This result indicates that the conclusions of Kasap and Juhasz [7] obtained on doped selenium remain valid even for higher concentration of the added elements provided that the type of bonds engaged are purely covalent.

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