Journal of Thermal Analysis and Calorimetry, Vol. 79 (2005) 709–714

EFFECT OF THALLIUM ON THE CRYSTALLIZATION KINETICS OF THE CHALCOGENIDE GLASSES $GeSe_2$ AND $GeSe_4$

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The structure identification of the quenched compositions $GeSe_2$, $GeSe_4$, $GeSe_2Tl$ and $GeSe_4Tl$ has been confirmed by energy dispersive X-ray analysis (EDX), X-ray diffraction (XRD) and differential thermal analysis (DTA). The differential thermal analysis curves of the compositions under investigation were recorded at the heating rates 5, 10, 20, 30 and 50°C min^{-1}. Addition of thallium to $GeSe_2$ and $GeSe_4$ results in decreasing the glass transition temperature T_g, the crystallization temperature T_c and the melting temperature T_m. The effect of heating rates on the transition temperatures (T_g, T_c and T_m) was studied and the variation of the crystallization peak temperature T_p position was used to calculate the activation energy. The kinetic parameters of crystallization for the devitrification processes have been determined by three methods and discussed on the basis of Johnson–Mehl–Avrami model.

Keywords: *Ge–Se–Tl chalcogenide glasses, kinetics study of crystallization processes*

Introduction

It has been possible to identify two critical compositions in the IV–VI chalcogenide glassy system Ge_xSe_{1-x} by the anomalous variations of high-pressure electrical resistivity behavior. The first critical composition $GeSe_2$, the chemical threshold, refers to a stoichiometric composition. The second critical composition $GeSe_4$, identified recently as the mechanical percolation threshold, is connected with the structural rigidity of the material [1].

Addition of thallium to Ge–Se chalcogenide glasses is accompanied by a marked change in their structural and physical properties [2]. Investigation of the switching phenomenon in amorphous Ge–Se–Tl films has been carried out [3, 4], and there is a good agreement between the type of switching and the crystallization in chalcogenide glassy system [5, 6].

The kinetics of crystallization can be studied by different methods of thermal analysis [7–10]. Thermally activated transformations in the solid-state can be investigated by isothermal or non-isothermal experiments. A disadvantage of the isothermal regime is the impossibility of reaching a test temperature instantaneously and during the time which the system needs to stabilize, no measurements are possible, [11]. The crystallization process may be interpreted in terms of various theoretical kinetic models and the most successful empirical equation for crystallization of inorganic glasses in the Johnson–Mehl–Avrami (JMA) equation [12].

The aim of the paper is to investigate the effect of Tl addition on the crystallization kinetic parameters of the two critical glasses $GeSe_2$ and $GeSe_4$. Three different methods of analysis have been used to get the crystallization kinetic parameters from the same experimental data under non-isothermal condition.

Experimental

Bulk Ge–Se and Ge–Se–Tl glasses were prepared by the conventionel melt quenching technique [2,3]. The proper amounts required for preparing 10 g of the composition were weighed using an electrical sensitive balance of accuracy 10^{-4} g (Goansh ZP). The weighed materials were introduced into a cleaned silica ampoule, which was then evacuated to 10^{-5} Torr and sealed then placed in specially designed oscillatory furnace. The sample temprature was raised in steps. At first it was raised from room temperature to 250°C (about 30°C higher than *m.p.* of Se) and then kept constant for 2 h. Then temperature was raised in steps of 100 to 1000°C over a long period of time 13 h. Long duration of the synthesis and rocking of the melt were necessary for homogeneity of the composition. The ampoule was then rapidly quenched in ice water to obtain the sample in the glassy state.

The chemical composition under test was checked by energy dispersive X-ray (EDX) analysis using scanning electron microscope (Joel 5400). Full quantitative analysis results were obtained from the spectra by processing the data through ZAF correction program. The structure of $GeSe_2$, $GeSe_4$, $GeSe_2Tl$ and $GeSe_4Tl$ in powder form was investigated by X-ray diffractometer (XRD) type Phillips PM8203

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1388–6150/$20.00
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supplied with a copper target and Ni filter. The X-ray tube was operated at 40 kV and 25 mA. The diffraction patterns were recorded automatically with a scanning speed of 2° min^{-1} per minute and scanning angular range from 4 to 90°.

DTA curves were obtained for each composition using a Shimadzu DTA-30 thermal analysis system. Different heating rates 5, 10, 20, 30, and 50°C min^{-1}. were used DTA measurements were calculated on each of the glasses to determine the thermodynamic aspects by consecutive thermal cycling covering the temperature range (T_g–T_m). Several measurements have been carried out on at least two different samples of the same composition to provide the accuracy and reproducibility measurements. The error in temperature is ≈±0.05°C.

Results and discussion

Structural identifications

The compositions $GeSe_2$, $GeSe_2Tl$, $GeSe_4$ and $GeSe_4Tl$ were checked using EDX spectroscopy. The EDX analysis indicates that there are no any other elements in the investigated compositions.

XRD patterns were recorded for the investigated compositions in powder form. The diffraction patterns for these compositions which are characterized by the absence of any diffraction lines, indicating the amorphous nature of the prepared compositions as shown in Fig. 1.

The scanning character of the DTA curves of the amorphous compositions $GeSe_2$, $GeSe_2Tl$ (Fig. 2) and $GeSe_4$, $GeSe_4Tl$ (Fig. 3) were recorded at the heating rates 5, 10, 20, 30 and 50°C min^{-1}. These curves are characterized by endothermic peak corresponding to the glass transition temperature T_g, one exothermic peak denoting the crystallization temperature T_c and one endothermic peak denoting the melting temperature T_m. Values of transition temperatures T_g, T_c and T_m are listed in Table 1. It is observed that T_g and T_m are almost independent of the heating rate α, while the crystallization exothermic point locations (begin–peak–end) changed markedly as the heating rate α was varied.

The data in this table show that the glass transition temperature T_g fluctuates around a mean value as α changes. This may be due to that the relaxation time of the glass transition process is small compared to the time allowed by the various heating rates. Consequently, one should not expect the heating rate to have a strong effect on the peak of T_g. The addition of Tl to Ge–Se system causes a decrease in T_g from 395 to 191°C for $GeSe_2$, $GeSe_2Tl$ compositions and from 165 to 132°C for $GeSe_4$, $GeSe_4Tl$ compositions at dif-

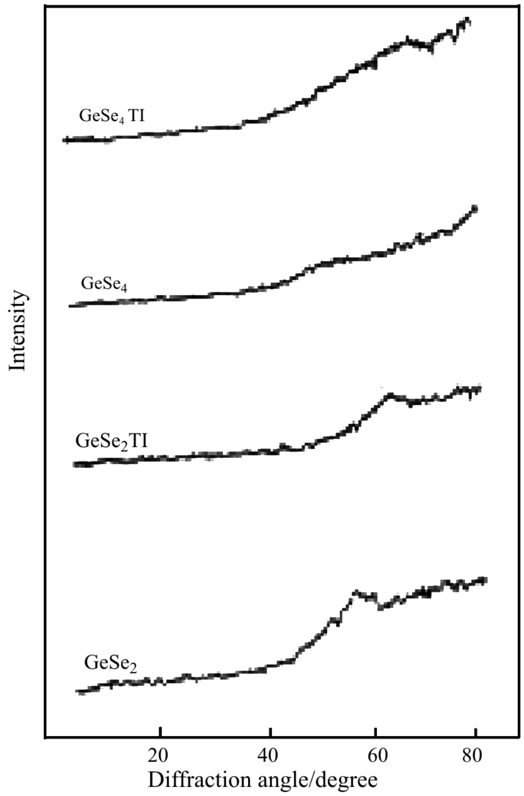

Fig. 1 The diffraction patterns X-ray of the chalcogenide glasses $GeSe_2$, $GeSe_2Tl$,$GeSe_4$ and $GeSe_4Tl$

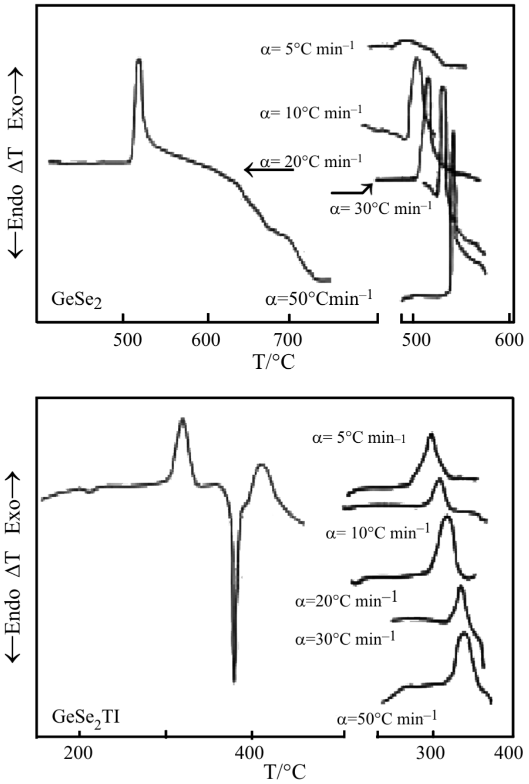

Fig. 2 DTA curves of the chalcogenide glasses $GeSe_2$ and $GeSe_2Tl$ measured at different heating rates

Table 1 The values of kinetic parameters under non-isothermal conditions of Ge–Se–T1 chalcogenide glasses

Composition	Rate α/°C min^{-1}	T_g/°C	T_c/°C			T_m/°C
			begin	peak T_p/°C	end	
GeSe$_2$	5	392	483	491	500	–
	10	–	491	500	530	691
	20	–	500	513	520	690
	30	399	525	532	552	705
	50	395	530	541	555	692
GeSe$_2$T1	5	186	275	306	315	370
	10	191	296	320	333	384
	20	191	293	327	337	381
	30	192	305	339	380	380
	50	193	310	348	363	380
GeSe$_4$T1	5	131	180	202	212	346
	10	134	200	210	222	350
	20	130	216	220	245	355
	30	130	210	227	350	356
	50	134	210	235	353	353

ferent heating rates. This may be attributed to the weak Tl–Tl bond strength [2] which has effect to decrease the viscosity of the melt, thereby decreasing the transition, crystallization and melting temperature. On the other hand, T_c shift to higher values as the heating rate α increases. Therefore, one can expect the heating rate α to have a strong effect on T_c and T_m. The profile (begin–peak–end) of the GeSe$_2$, GeSe$_2$Tl and GeSe$_4$Tl compositions depends on the heating rate. While, the composition GeSe$_4$ is not affected by the change of the heating rate α.

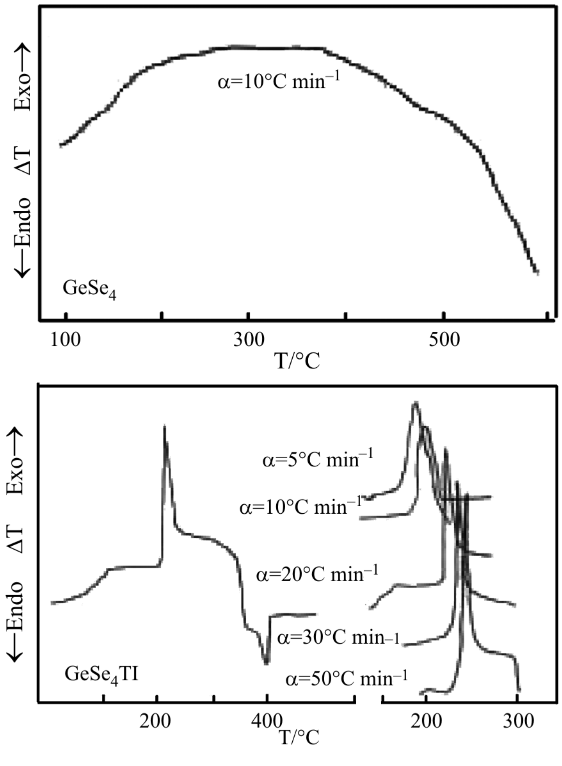

Fig. 3 DTA curves of the chalcogenide glasses GeSe$_4$ and GeSe$_4$Tl measured at different heating rates

The general trend is that the areas under the exothermic crystallization peaks become wider as the heating rate α increases. That is probably because a smaller amount of the sample material has been crystallized at lower values of α. Turbull [13] pointed out that, the resistance of liquids and glasses to nucleation implies something about their structure. Furthermore, the area under the crystalline peak becomes wider and shifts towards a higher temperature range with increasing α.

The activation energy for crystallization

The crystallization kinetics of amorphous alloys have been intensively studied using the classical Jonhnson–Mehl–Avrami (JMA) theoretical model in which the crystallized fraction χ can be described as function of time *t* according to the following formula:

$$\chi(t)=1-\exp[-(Kt)^{n}] \tag{1}$$

where *n* is the Avrami exponent, which depends on the mechanism of reaction and the dimensionality of the crystal growth [12]. *K* is defined as the reaction rate constant, which has on Arrhenian temperature dependence,

$$K = K_0 \exp\left(-\frac{E_c}{RT}\right) \tag{2}$$

where E_c is the activation energy for crystallization and K_0 is the frequency factor.

The crystallization process is generally well understood when the three kinetic parameters E_c, *n* and K_0 are known. Based on the aforementioned (JMA) model, different authors [8–10] have developed very diverse methods for calculating these parameters. In non-isothermal crystallization, the existence of a con-

Table 2 The values of activation energies obtained by different methods for the crystallization Ge–Se–T1 chalcogenide glasses

Compositions	Kissinger's method	Ozawa's method	Methods of Augis and Bennett	
	E_c/kJ mol^{-1}	E_c/kJ mol^{-1}	E_c/kJ mol^{-1}	K_0/s^{-1}
$GeSe_2$	190.0	190.45	210.05	$1.57\cdot10^{14}$
$GeSe_2T1$	152.3	144.87	145.03	$2.27\cdot10^{12}$
$GeSe_4T1$	138.5	119.24	111.30	$8.55\cdot10^{11}$

stant heating rate condition is assumed. The relation between the sample temperature and the heating rate α can be written in linear form

$$T=T_0+\alpha t \tag{3}$$

where T_0 is the initial temperature. The crystallization rate is obtained by taking the derivative of expression (1) with respect to time, bearing in mind that the reaction rate constant is a time function through its Arrhenius temperature dependence, resulting in

$$\dot{\chi}=nK^{n}t^{n-1}[1+at](1-\chi) \tag{4}$$

where $\dot{\chi}=\mathrm{d}\chi/\mathrm{d}t$ and $a=\alpha E_c/RT^2$.

Kissinger's method

According to Kissinger [14, 15], the term αt was neglected in comparison to unity when $(E_c/RT^2)<<1$, the second derivative $\ddot{\chi}=\mathrm{d}\dot{\chi}/\mathrm{d}t$ at the peak temperature is given by:

$$\ddot{\chi}=AnK(1-\chi)\left[\frac{\alpha E_c}{RT_p^2}-AnK\right] \tag{5}$$

where $A=[-\ln(1-\chi)]^{(n-1)/n}$. The peak temperature of crystallization T_p is identified as the temperature of maximum crystallization rate, i.e. the temperature at which $\ddot{\chi}=0$.

$$\frac{\alpha}{T_p^2}=C\exp\left(-\frac{E_c}{RT_p}\right) \tag{6}$$

where $C=(ARnK_0/E_c)$. Taking the logarithm of the above equation gives

$$\ln\left(\frac{\alpha}{T_p^2}\right)=\text{const.}-\frac{E_c}{RT_p} \tag{7}$$

Measurement of the variation of peak temperature with heating rate has been used to evaluate the activation energy of the reaction. Considering that the reaction order n remains constant through the greater part of the reaction, and so it was disregarded in the derivation. Accordingly, the activation energy of the crystallization E_c can be calculated from the shifts of the DTA exotherms, T_p with the heating rate. The shift in the exothermic peak temperature with change of the heating rate α observed in Figs 2, 3, are used to determine the effective activation energy of the crystallization.

Figure 4a shows a plot of $\ln(\alpha/T_p^2)$ *vs.* $(1/T_p)$ for the exotherms of Figs 2, 3 for $GeSe_2$, $GeSe_2Tl$ and $GeSe_4Tl$. A straight line was fitted to determine the effective activation energy E_c. The magnitude for the three compositions was as shown in Table 2.

Ozawa's method

The activation energies of the crystallization processes have also been calculated based on the Ozawa's equation [16–18].

$$\ln\alpha=\text{const.}-1.052\frac{E_c}{RT_p} \tag{8}$$

The plot of lnα as a function of $1/T_p$ yields a straight line, the slope of which gives the activation energy E_c as shown in Fig. 4b for the investigated compositions. The values of E_c are given in Table 2.

Method of Augis and Bennett

Augis and Bennett [19] have developed an accurate method, which is based on substituting u for Kt in Eq. (4) as follows:

$$\dot{\chi}=nuu^{(n-1)}(1-\chi) \tag{9}$$

where

$$\dot{u}=\frac{\mathrm{d}u}{\mathrm{d}t}=u\left[\frac{1}{t}+a\right] \tag{10}$$

For $(E/RT)>>1$, the right hand bracket approaches its maximum limit and consequently u (at the peak)=1, or

$$u=(Kt)_p=K_0\exp-\frac{E_c}{RT_p}\frac{T_p-T_0}{\alpha}\cong1. \tag{11}$$

In a logarithmic form

$$\ln\frac{\alpha}{T_p-T_0}\cong-\frac{E_c}{RT_p}+\ln K_0. \tag{12}$$

Also the activation energy for crystallization can be deduced using Eq. (12). For the plots of $\ln[\alpha/(T_p-T_0)]$ *vs.* $1/T_p$ as shown in Fig. 4c. The values

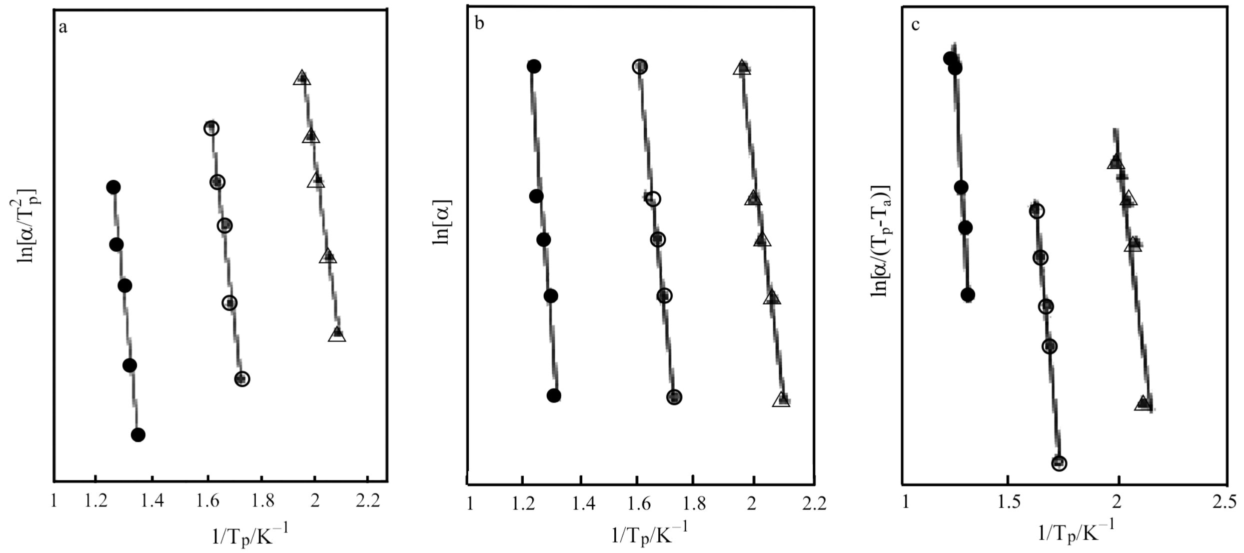

Fig. 4 a –ln[α / T_p^2] *vs.* 1/T_p plots for $GeSe_2$, $GeSe_2Tl$ and $GeSe_4Tl$ chalcogenide glasses; b – lnα] *vs.* 1/T_p plots for $GeSe_2$, $GeSe_2Tl$ and $GeSe_4Tl$ chalcogenide glasses; c – ln[α/(T_p–T_0)] *vs.* 1/T_p plots for $GeSe_2$, $GeSe_2Tl$ and $GeSe_4Tl$ chalcogenide glasses; ● – $GeSe_2$; ○ – GeS_2Tl; △ – $GeSe_4Tl$

of E_c and the frequency factor K_0 for the crystallization of amorphous $GeSe_2$, $GeSe_2Tl$ and $GeSe_4Tl$ have been calculated, and these values are given in Table 2.

From this table, it is observed that the values of the activation energies obtained by using the three methods are approximately of the same order for each composition. The addition of Tl to Ge–Se system decreases the stability of the amorphous phase, so the activation energy of crystallization E_c is less than that of Ge–Se. This leads to concluding that the addition of Tl enhances the crystallization of Ge–Se. The decreases in the activation energy may be explained by considering the structural change in the samples due to addition of Tl. A similar trend has been observed in previous work for As_2Se_3 doped with Tl [20] and the same methods used to calculate the activation energy for different compositions [21, 22].

Conclusions

Crystallization kinetics of the chalcogenide $GeSe_2$, $GeSe_4$, $GeSe_2Tl$ and $GeSe_4Tl$ glasses have been successfully determined under non-isothermal experiment using three different methods. It is found that the addition of Tl will decrease T_g by about 51 and 19% for $GeSe_2$ and $GeSe_4$, respectively, and the crystallization activation energy E_c decreases by about 26% for $GeSe_2$, while in case of the only composition $GeSe_4$ it was not effected by the change of heating rates. Such a decrease in activation energy may be attributed to the increase in chemical disorder and a change in the microstructure.

References

1 S. Asokan, M. V. M. Prassad, G. Parathasarathy and E. S. R. Gopal, Phys. Rev. Lett., 62 (1989) 808.
2 M. F. Kotkata, H. T. El-Shair, M. A. Afifi and M. M. Abdel-Aziz, J. Phys. D: Appl. Phys., 27 (1994) 623.
3 M. F. Kotkata, M. A. Afifi, H. H. Labib, N. A. Hegab and M. M. Abdel- Aziz, J. Thin Solid Films, 240 (1994) 143.
4 M. A. Afifi, M. M. Abdel- Aziz, H. H. Labib and E. G. El-Metwally, Vacuum, 61 (2001) 45.
5 G. B. Thomas, A. F. Fratand and J. R. Bonsell, Phil. Mag., 26 (1972)1261.
6 M. Lasocka and H. Matypia, J. Non-Cryst. Solids, 14 (1974) 41.
7 A. H. Moharram and M. Abu El-Oyoun, J. Phys. D: Appl. Phys., 33 (2000) 700.
8 R. A. Ligero, J. Vazquez, P. Villares and R. Jimenez-Garay, Thermochim. Acta, 162 (1990) 427.
9 J. Vazquez, C. Wagner, P. Villares and R. Jimenez-Garay, J. Non-Cryst. Solids, 235–237 (1998) 548.
10 Y. Q. Gao and W. Wang, J. Non-Cryst. Solids, 81 (1986) 129.
11 M. J. Strink and A. M. Zahra, Thermochim. Acta, 298 (1997) 179.
12 H. Yinnon and D. R. Uhlmann, J. Non-Cryst. Solids, 54 (1983) 253.
13 D. Turbull, J. Phys. Chem., 66 (1962) 609.
14 H. E. Kissinger, Anal. Chem., 29 (1957) 1702.
15 R. L. Takhor, in: Advances in Nucleation and Crystallization of Glasses, American Ceramic Society, Columbus 1972, p. 166.
16 J. J. Zhang, R. F. Wang and H. M. Liu, J. Therm. Anal. Cal., 66 (2001) 431
17 T. Ozawa, J. Thermal Anal., 2 (1970) 301.
18 N. Sbirrazzuoli, I. Vincent, J. Bouillard and L. Elegant, J. Therm. Anal. Cal., 56 (1999) 783.

19 J. A. Augis and J. E. Bennett, J. Thermal Anal., 13 (1978) 283.
20 M. F. Kotkata, M. M. Radwan, M. H. El-Fouly and S. A. Fayek, J. Mater. Sci., 25 (1990) 2107.
21 A. A. Abou-Shely, Physica B, 325 (2003) 372.
22 C. Pacurariu, M. Lita, I. Lazau, D.Tita and G. Kovács, J. Therm. Anal. Cal., 72 (2003) 811.

Received: June 15, 2004
In revised form: June 30, 2004