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Levels of thermal stability in some glassy alloys of the Ge–Sb–Se system by differential scanning calorimetry

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Abstract

The thermal stability and crystallization of alloys in the Ge–Sb–Se system were studied by differential scanning calorimetry (DSC). A comparison of various simple quantitative methods to assess the level of stability of the glassy materials in the above-mentioned system is presented. All of these methods are based on characteristic temperatures, obtained by heating of the samples in non-isothermal regime, such as the glass transition temperature, T_g, the temperature at which crystallization begins, T_{in}, the temperature corresponding to the maximum crystallization rate, T_p, or the melting temperature, T_m. In this work, a parameter $K_r(T)$ is added to the stability criteria. The thermal stability of some ternary compounds of $Ge_xSb_{0.23-y}Se_{0.77-x+y}$ type has been evaluated experimentally and correlated with the activation energies of crystallization by this kinetic criterion and compared with those evaluated by other criteria.

Keywords: Amorphous materials; Liquid quenching; X-ray diffraction; Calorimetry; Thermal analysis

1. Introduction

Glassy alloys of chalcogen elements were the initial object of study because of their interesting semiconducting properties [1] and more recent importance in optical recording [2]. Recording materials must be stable in the amorphous state at low temperature and have a short crystallization time. Tellurium alloy films, in particular, are used as recording media as they have a low melting temperature and high absorption coefficient for the wavelengths of semiconducting lasers; promising materials with these characteristics have recently been studied [3,4]. Infrared transmitting glasses based on Ge–Sb–Se are technologically important because they are good transmitters of radiation in the 2–16 μm wavelength region. The applications include fabrication of optical components like IR lenses, windows and filters used in thermal imaging systems. They are less sensitive to the presence of impurities. The Ge–Sb–Se films result sensitive for the UV radiation, and exhibit mechanical, optical and structural changes [5,6]. Glass-forming regions in the Ge–Sb–Se system were studied by several authors [7–12]. Therefore, it is very important to know the glass stability and chemical durability of these materials. However, no simple way presently exists to formulate the correlation between the ideal composition and the stability of the glasses. With object to evaluate the level of stability of the vitreous alloys, different simple quantitative methods have been suggested. Most of these methods [13–17] are based on characteristic temperatures such as the glass transition temperature, T_g, the crystallization temperature, T_p, or the melting temperature, T_m. Some of them [18,19] are based on the reaction rate constant, K. Some of the others [20–22] are based on crystallization activation energy. These thermal parameters are easily and accurately obtained by differential scanning calorimetry (DSC) during the heating processes of glass samples. Dietzel introduced the first glass criterion, $\Delta T = T_{in} - T_g$ (T_{in} is the temperature at which crystallization begins), which is often an important parameter to evaluate the glass forming ability of the glasses. By the use of characteristic temperatures, Hruby developed the H_r criterion, $H_r = \Delta T/(T_m - T_p)$. On the basis of the H_r criterion, Saad and Poulain obtained two other criteria, weighted

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thermal stability H' and S criterion, $H' = \Delta T/T_g$, $S = (T_p - T_{in})\,\Delta T/T_g$, respectively.

In the present work, the above-mentioned criteria have been applied to the alloys $Ge_xSb_{0.23-y}Se_{0.77-x+y}$, where $x = y = 0.08$ (S1); $x = 0.13$, $y = 0$ (S2) and $x = 0.18$, $y = 0$ (S3), and it is found that the parameters ΔT, H_r, H' and S increase with decreasing germanium and antimony contents. Bearing in mind that the values of these parameters increase with increasing stability, it is possible to suggest that the lower the germanium and antimony of the alloy contents, the greater is its glass thermal stability [23]. In addition, a kinetic parameter, $K_r(T)$, with an Arrhenian temperature dependence, is introduced to the stability criteria. Decreasing values of the above parameter have been found for the alloys with decreasing germanium and antimony contents. This fact confirms that the S1 alloy is the most stable one.

2. Theoretical background

The theoretical basis for interpreting DTA or DSC results is provided by the formal theory of transformation kinetics [24–28]. In its basic form, this theory describes the evolution with time, t, of the volume fraction crystallized, x, in terms of the nucleation frequency per unit volume, I_V, and the crystal growth rate, u, as

$$x = 1 - \exp\left\{-g\int_0^t I_V(\tau)\left[\int_\tau^t u(t')\mathrm{d}t'\right]^m \mathrm{d}\tau\right\} \qquad (1)$$

where m is an exponent related to the dimensionality of the crystal growth and the mode of transformation when the crystal growth rate is isotropic, an assumption which is in agreement with the experimental evidence, since in many transformations the reaction product grows approximately as spherical nodules [29]. Moreover, g is a geometric factor which depends on the dimensionality and shape of the crystal growth, and therefore its dimension equation can be expressed as

$$[g] = [L]^{3-m} \quad ([L]\ \text{is the length})$$

By assuming that the nucleation process takes place early in the transformation and the nucleation frequency is zero thereafter, case referred to as "site saturation" by Cahn [30], Eq. (1), becomes

$$x = 1 - \exp\left[-gN\left(\int_0^t u(t')\mathrm{d}t'\right)^m\right] = 1 - \exp\left(-gNI_1^n\right) \qquad (2)$$

where N is the number of pre-existing nuclei per unit volume and the growth integral is evaluated between 0 and t, since there is no nucleation period, $\tau = 0$.

Although, in general, the temperature dependence of the crystal growth rate is not Arrhenian when a broad range of temperature is considered [31]; however, over a sufficiently limited range of temperature (such as the range of crystallization peaks in DSC experiments), u may be described in a zeroth-order approximation by

$$u = u_0 \exp\left(-\frac{E}{RT}\right) \qquad (3)$$

where E is the effective activation energy for crystal growth and R is the ideal gas constant.

Taking the derivative of Eq. (2) with respect to time and substituting Eq. (3) in the resulting expression, the crystallization rate is obtained as

$$\frac{\mathrm{d}x}{\mathrm{d}t} = n(1-x)I_1^{n-1}gNu_0\exp\left(-\frac{E}{RT}\right) = nK(1-x)I_1^{n-1} \qquad (4)$$

K being the reaction rate constant.

The maximum crystallization rate is found by making $\mathrm{d}^2x/\mathrm{d}t^2 = 0$, thus obtaining the relationship

$$nK_p(I_1^n)|_p = \frac{\beta E(I_1)|_p}{RT_p^2} + (n-1)K_p \qquad (5)$$

in which $\beta = \mathrm{d}T/\mathrm{d}t$ is the heating rate for a non-isothermal process and the magnitude values which correspond to the maximum crystallization rate are denoted by subscript p.

By using the substitution $y' = E/RT'$ the integral I_1 can be evaluated [32] by the alternating series

$$S(y') = -e^{-y'}y'^{-2}\sum_{k=0}^{\infty}\frac{(-1)^k(k+1)!}{y'^k}$$

where it is possible to use only the first two terms, without making any appreciable error, and to obtain

$$I_1 = RT^2K(\beta E)^{-1}\left(1 - 2RTE^{-1}\right) \qquad (6)$$

if it is assumed that $T_0 \ll T$ (T_0 is the starting temperature), so that y_0 can be taken as infinity.

Substituting the last expression for I_1 into Eq. (5), one obtains the relationship

$$(I_1)\,|_p = \left[1 - 2RT_p(nE)^{-1}\right]^{1/n}$$

When this relationship is equated to Eq. (6), this gives

$$RT_p^2(\beta E)^{-1}K_0\exp\left[-E\left(RT_p\right)^{-1}\right] = \left[1 - 2RT_p(nE)^{-1}\right]^{1/n} \times \left(1 - 2RT_pE^{-1}\right)^{-1} \qquad (7)$$

or in a logarithmic form

$$\ln\left(\frac{T_p^2}{\beta}\right) + \ln\left(RK_0E^{-1}\right) - E\left(RT_p\right)^{-1} \approx 2RT_pE^{-1}\left(1 - n^{-2}\right) \qquad (8)$$

where the function $\ln(1 - z)$ with $z = 2RT_p(nE)^{-1}$ or $z = 2RT_pE^{-1}$ is expanded as a series and only the first term has been taken.

Note that Eq. (8) reduces to the Kissinger expression for the $n = 1$ case as one might have anticipated, since this corresponds to the homogeneous reaction case. Moreover, for most crystallization reactions the right-hand side (RHS) of Eq. (8) is generally negligible in comparison to the individual terms on the left-hand side for common heating rates ($\leq 100\,\mathrm{K\,min^{-1}}$). Thus, it can be seen that this method is appropriate for the analysis of not only homogeneous reactions but also heterogeneous reactions which are described by the Johnson-Mehl-Avrami equation in isothermal experiments. The approximation in Eq. (8) (RHS = 0) implies

$$\frac{\mathrm{d}\left[\ln\left(T_\mathrm{p}^2/\beta\right)\right]}{\mathrm{d}\left(1/T_\mathrm{p}\right)} = \frac{E}{R}$$

where the quoted approximation might introduce a 3% error in the value of E/R in the worst cases. (Typically, $n > 1$ and $E/RT_\mathrm{p} > 25$ suggest that the error introduced in E/R by setting the RHS of Eq. (8) to zero is considerably less than 1%). Eq. (8) also serves to determine the frequency factor, K_0, from the intercept of the $\ln(T_p^2/\beta)$ versus $1/T_\mathrm{p}$ plot. Eq. (4), which describes the time dependence of the reaction rate and Eq. (8), which allows for the simple extraction of the parameters E and K_0, form the basis for the analysis of constant heating-rate data.

In order to evaluate the thermal stability of glassy materials, Surinach et al. [18] introduced a $K(T_\mathrm{g})$ criterion, and Hu and Jiang [19] developed the $K(T_\mathrm{p})$ criterion, $K(T_\mathrm{g}) = K_0\exp(-E/RT_\mathrm{g})$ and $K(T_\mathrm{p}) = K_0\exp(-E/RT_\mathrm{p})$, respectively. Thus, the values of these two parameters indicate the tendency of glass to devitrify on heating. The larger their values, the greater is the tendency to devitrify. The formation of glass is a kinetic process. It is reasonable to assess the glass stability by a kinetic parameter, $K(T)$. The H_r parameter itself is a stability factor based on characteristic temperatures. Here a stability criterion is defined as $K_\mathrm{r}(T)$

$$K_\mathrm{r}(T) = K_0 \exp\left(-\frac{H_\mathrm{r}E}{RT}\right) \tag{9}$$

where T is any temperature between T_g and T_p. The theoretical background for the definition of the new parameter $K_\mathrm{r}(T)$ would be based on the analysis of the relation between the parameter $K(T)$ and $K_\mathrm{r}(T)$. Differentiating the expressions of both parameters results in

$$\mathrm{d}K_\mathrm{r} = H_\mathrm{r}EK_\mathrm{r}\left(RT^2\right)^{-1}\mathrm{d}T, \quad \mathrm{d}K = EK\left(RT^2\right)^{-1}\mathrm{d}T$$

and the relative variation in each parameter per Kelvin is

$$\frac{\Delta K_\mathrm{r}}{K_\mathrm{r}\Delta T} = \frac{H_\mathrm{r}E}{RT^2}, \quad \frac{\Delta K}{K\Delta T} = \frac{E}{RT^2}$$

It should be noted that the above-mentioned variation of the parameters $K_\mathrm{r}(T)$ is H_r times the variation in parameter $K(T)$, which could justify the accuracy of this new parameter.

Just like the $K(T)$ criteria, the smaller the values of $K_\mathrm{r}(T)$, the greater is the thermal stability of the glass. The obvious advantage of this method is that it can evaluate the glass stability over a broad temperature range other than that at one temperature such as T_g or T_p.

3. Experimental procedures

The alloys were prepared in bulk form by the standard melt-quenching method. High-purity (99.999%) germanium, antimony and selenium in appropriate atomic percent proportions were weighed (total 7 g per batch) into quartz glass ampoules. The contents were sealed under a vacuum of 10^{-2} Pa, heated to 1223 K for about 52 h turning at 1/3 rpm in order to ensure the homogeneity molten material and then quenched in water with ice, which supplied the necessary cooling rate

Table 1
Characteristic parameters of the alloys S1, S2 and S3

Alloy	β (K min^{-1})	T_g (K)	T_in (K)	T_p (K)	T_m (K)	ΔT (K)	H_r	H'	S (K)
S1	2	416.0	507.0	529.0	585.0	91.0	1.625	0.219	4.813
	4	420.1	514.0	537.4	595.0	93.9	1.630	0.224	5.230
	8	424.2	521.0	547.5	606.5	96.8	1.641	0.228	6.047
	16	429.0	528.5	557.5	617.6	99.5	1.656	0.232	6.726
	32	430.8	531.9	560.6	621.6	101.1	1.657	0.235	6.735
	64	433.8	539.2	572.8	636.0	105.4	1.668	0.243	8.164
S2	2	518.1	564.0	581.1	629.1	45.9	0.956	0.089	1.515
	4	524.0	571.1	588.0	637.0	47.1	0.961	0.090	1.519
	8	529.6	578.8	597.6	648.6	49.2	0.965	0.093	1.747
	16	535.9	586.2	607.7	659.7	50.3	0.967	0.094	2.018
	32	542.0	593.5	618.3	671.3	51.5	0.972	0.095	2.356
	64	548.1	601.9	631.3	686.3	53.8	0.978	0.098	2.886
S3	2	585.0	615.0	634.6	677.6	30.0	0.698	0.051	1.005
	4	590.4	623.2	641.9	688.5	32.8	0.704	0.056	1.039
	8	595.7	630.9	652.1	701.8	35.2	0.708	0.059	1.253
	16	601.1	638.8	659.7	712.7	37.7	0.711	0.063	1.311
	32	606.5	646.7	670.9	727.0	40.2	0.717	0.066	1.604
	64	612.0	654.7	686.1	745.2	42.7	0.723	0.070	2.191

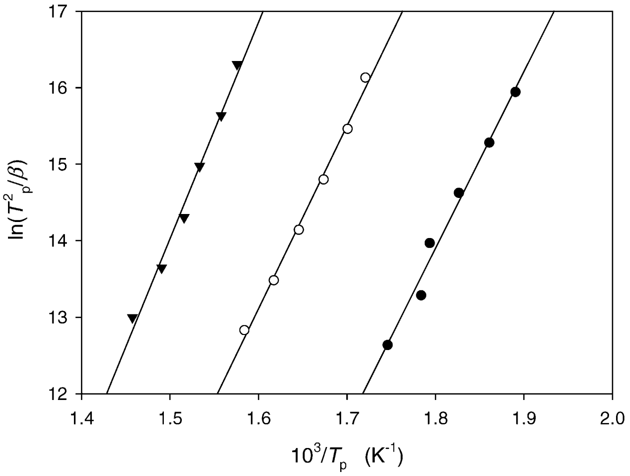

Fig. 1. Plots of $\ln(T_p^2/\beta)$ versus $1/T_p$ and straight regression lines for the three glassy alloys, S1 (●), S2 (○) and S3 (▲).

for obtaining the glass. The amorphous state of the material was checked through a diffractometric X-ray scan, in a Siemens D500 diffractometer. The homogeneity and composition of the samples were verified through scanning electron microscopy (SEM) in a Jeol, scanning microscope JSM-820. The calorimetric measurements were carried out in a Perkin-Elmer DSC7 differential scanning calorimeter with an accuracy of ±0.1 K. A constant 60 ml min^{-1} flow of nitrogen was maintained in order to provide a constant thermal blanket within the DSC cell, thus eliminating thermal gradients and ensuring the validity of the applied calibration standard from sample to sample. Moreover, the nitrogen purge allows to expel the gases emitted by the reaction, which are highly corrosive to the sensory equipment installed in the DSC furnace. Temperature and energy calibrations of the instrument were performed using the well known melting temperatures and melting enthalpies of high-purity indium and zinc supplied with the instrument. For non-isothermal experiments, glass samples weighing about 10 mg were sealed in aluminium pans and scanned at room temperature through their T_g at different heating rates 2, 4, 8, 16, 32 and 64 K min^{-1}, by using an empty aluminium pan as reference. The glass transition temperature was considered as a temperature corresponding to the inflection point of the lambda-like trace on the DSC scan.

4. Results and discussion

The characteristic temperatures from DSC scans are given in Table 1. The thermal stability of the three alloys studied can be estimated by using the characteristic temperatures T_g, T_{in}, T_p, and T_m. The existing stability-criterion parameters based on these characteristic temperatures are also listed in Table 1.

To obtain the kinetic parameters of crystallization, Eq. (8) is applied. Fig. 1 represents the evolution of $\ln(T_p^2/\beta)$ versus $1/T_p$ for the three alloys. The plots were found to be straight lines in accordance with Eq. (8). The activation energy, E, and frequency factor, K_0, are then evaluated by least-squares fitting method. Table 2 summarizes the values determined by these calculations. After knowing the values of E and K_0, the kinetic parameters $K(T)$ and $K_r(T)$ of studied alloys are calculated and listed in Table 3. Fig. 2 represents the plots of $K_r(T)$ versus T. It is found that $K_r(T)$ of S1 varies slowly with increasing T and the values are on the T-axis indicating a relatively high stability, while $K_r(T)$ of the other two samples varies more rapidly with increasing T, which signifies a minor stability. These considerations verify the thermal stability order of the above-mentioned glassy alloys.

It is known that these existing criteria of glass stability allow to predict the glass-forming ability of a material. It is possible to suggest that the larger their values, the greater should be the glass thermal stability. According to these suggestions, the parameters, ΔT, H_r, H' and S, in Table 1 show that the S1 glass sample is more stable than the other two samples. Also, it is possible to obtain a consistent stable order for these glasses by the reaction rate constant. According to literature [18,19] ($K(T_g)$ and $K(T_p)$ criteria), the smaller the values of these parameters, the better should be the glass forming ability of the material. So the data for both $K(T_g)$ and $K(T_p)$ in Table 3 indicate that the S1 glass sample is the most stable, and the stability orders at different heating rates are S1 > S2 > S3. In addition, by using Eq. (9), the data of $K_r(T_g)$ and $K_r(T_p)$ in Table 3 show that the S1 alloy is also the most stable, and the orders of stability are also S1 > S2 > S3 at various heating rates. This stability result agrees with that of the $K(T_g)$ and $K(T_p)$ criteria.

The above-mentioned stability orders agree satisfactorily with the literature [23], where it is noted that the maximum crystallization ability in the Ge–Sb–Se system is possessed by glasses with large antimony and germanium contents.

Table 2
Straight regression lines (SRL) fitted to values of $\ln(T_p^2/\beta)$ and kinetics parameters of the analyzed alloys

Alloy	SRL	E (kcal mol^{-1})	K_0 (s^{-1})	r
S1	$23.1266 \times 10^3/T_p - 27.7255$	46.3 ± 1.0	2.54×10^{16}	0.9841
S2	$23.8972 \times 10^3/T_p - 25.1218$	47.8 ± 1.1	1.94×10^{15}	0.9947
S3	$28.2718 \times 10^3/T_p - 28.3806$	56.5 ± 1.3	5.98×10^{16}	0.9882

r is the correlation coefficient.

Table 3
Kinetic parameters $K(T)$ and $K_r(T)$ for the three alloys

Alloy	β (K min^{-1})	$K(T_g)$ (s^{-1})	$K(T_p)$ (s^{-1})	$K_r(T_g)$ (s^{-1})	$K_r(T_p)$ (s^{-1})
S1	2	1.73×10^{-8}	2.51×10^{-3}	1.35×10^{-23}	3.32×10^{-15}
	4	2.97×10^{-8}	4.97×10^{-3}	2.49×10^{-23}	8.13×10^{-15}
	8	5.06×10^{-8}	1.10×10^{-2}	3.25×10^{-23}	1.86×10^{-14}
	16	9.31×10^{-8}	2.35×10^{-2}	3.94×10^{-23}	3.47×10^{-14}
	32	1.17×10^{-7}	2.96×10^{-2}	5.42×10^{-23}	4.87×10^{-14}
	64	1.70×10^{-7}	7.12×10^{-2}	5.58×10^{-23}	1.34×10^{-13}
S2	2	1.79×10^{-5}	2.67×10^{-3}	1.37×10^{-4}	1.63×10^{-2}
	4	3.02×10^{-5}	4.32×10^{-3}	1.79×10^{-4}	2.11×10^{-2}
	8	4.88×10^{-5}	8.30×10^{-3}	2.37×10^{-4}	3.36×10^{-2}
	16	8.30×10^{-5}	1.61×10^{-2}	3.62×10^{-4}	5.91×10^{-2}
	32	1.37×10^{-4}	3.17×10^{-2}	4.71×10^{-4}	9.34×10^{-2}
	64	2.24×10^{-4}	7.02×10^{-2}	5.85×10^{-4}	1.61×10^{-1}
S3	2	6.37×10^{-5}	2.78×10^{-3}	1.37×10^{2}	1.91×10^{3}
	4	9.91×10^{-5}	4.61×10^{-3}	1.40×10^{2}	2.09×10^{3}
	8	1.52×10^{-4}	9.17×10^{-3}	1.57×10^{2}	2.86×10^{3}
	16	2.32×10^{-4}	1.51×10^{-2}	1.84×10^{2}	3.58×10^{3}
	32	3.53×10^{-4}	3.10×10^{-2}	1.87×10^{2}	4.62×10^{3}
	64	5.37×10^{-4}	7.85×10^{-2}	1.92×10^{2}	7.05×10^{3}

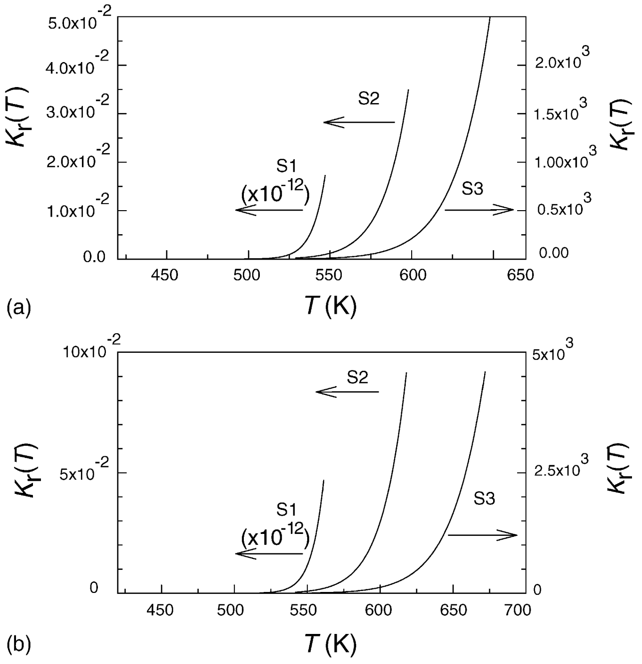

Fig. 2. Plots of $K_r(T)$ versus T for the three glassy alloys to verify the stable order. (a) $\beta = 8$ K min^{-1}, (b) $\beta = 32$ K min^{-1}.

5. Conclusions

The glass forming ability of some alloys in Ge–Sb–Se system has been evaluated by using various thermal stability criteria, based on characteristic temperatures. Moreover, in the present work, the $K_r(T)$ criterion has been considered for the evaluation of the glass forming ability from DSC data. It includes both the kinetic parameters and critical temperatures. Therefore, it is reasonable to think that the obtained data from the quoted criterion agree satisfactorily with the values which result from the existing criteria based on the characteristic temperatures and $K(T)$ criteria. A high value of $K_r(T)$ means poor stability of the glass. In the present work, the non-isothermal devitrification of three glassy alloys in the above-mentioned system has been studied at different heating rates and various temperatures. The above-quoted study has verified that the $K_r(T)$ criterion is slightly affected both by the heating rate and by the temperature, while the other criteria show a bigger variation with the heating rate. Among the three glassy alloys, $K_r(T)$ of the S1 glass sample is smallest, so this glass composition is the most stable. Finally, the stability order of these three glass samples is S1 > S2 > S3.

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