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CRITICAL RATE OF COOLING GLASSY MELTS UNDER CONDITIONS OF CONTINUOUS NUCLEATION. THE APPLICATION TO SOME CHALCOGENIDE GLASSES

A. F. Petrović, S. R. Lukić[*], D. D. Štrbac

Department of Physics, Faculty of Sciences, University of Novi Sad,
Trg D. Obradovića 4, 21000 Novi Sad, Serbia and Montenegro

The aim of this work is to derive a more exact expression for the critical cooling rate and to verify it experimentally on the systems As_2Se_3, AsSeI, $Cu_5[As_2Se3]_{95}$, $Cu_{15}[As_2Se_3]_{85}$, and $Cu_{15}[AsSe_{1.4}I_{0..2}]_{85}$. We assume that in addition to the growth of the nuclei, one should take into account the continuous increase in their number, i.e. the occurrence of new nucleation events. The obtained equation shows the dependence of the ratio of crystalline phase volume on the critical cooling rate. In principle, this relation allows for the calculation of the cooling rate b that should be applied under the condition that the crystallization rate does not exceed a value α_o, given in advance. The calculated cooling rates for the investigated systems can be considered as more exact compared to those previously reported for similar systems and are in agreement with our previous experimental findings.

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1. Introduction

The tendency of a glass to crystallize represents one of its important physico-chemical characteristics. The possibility of glass formation from a melt of a given composition and potential formation of crystals in it can be estimated on the basis of different parameters [1]. These are, among the others, the magnitude and position of the glass formation area, crystallization ability, and the critical cooling rate. Starting from the ratio of characteristic temperatures, it can be predicted whether the nucleation will be homogeneous or heterogeneous [2-4]. Strictly speaking, the critical cooling rate is defined as the minimal rate by which melt should be cooled so as not to produce any crystallization center in it but will continue to grow [5]. In practice, however, depending on the experimental conditions, more realistic criteria are introduced. It is usually taken that the ratio of crystalline phase volume should be 10^{-6} [6,7], the critical cooling rate being related to this value. Some authors [8,9] consider that several percents of crystalline phase in the glass matrix is the level that can be reliably detected and they based their calculations on this data.

Changes in the matrix of some glasses and the occurrence of crystallization in them have been subject of our previous works [10-13]. In them, we used the formula for the degree of crystallinity defined as the volume ratio of the crystalline phase in the glass matrix in dependence of the cooling rate, based on the Kolmogorov-Johnson-Mehl-Avrami (KJMA) theory [14-16]. In a similar form, this theory was also presented in a recent work [17]. On the basis of it, under the given assumptions, one can calculate the rate at which the melt should be cooled so as to obtain the glass with a minimal (given in advance) degree of crystallinity. The aim of this work was to derive a more exact expression for the critical cooling rate under the conditions of continuous nucleation. In other words, we assumed that in parallel with the growth of the existing nuclei new ones are formed all the

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[*] Corresponding author: svetdrag@im.ns.ac.yu

time. The concrete calculation was carried out for the known chalcogenides As_2Se_3, AsSeI and complex copper-involving systems that have been subject of our long-term investigations [18-21].

2. Experimental part

2.1. Experimental methods

Thermogravimetric (TG), differential thermogravimetric (DTG) measurements and differential thermal analysis (DTA) were carried out on a Paulik-Paulik-Erdeey (MOM, Model 1000) derivatograph. An amount of 100 mg of the sample was heated from room temperature to 1000 C at a rate of 10 °C/min.

DSC analysis was carried out on a DuPont, Model 910 calorimeter. The sensitivity was 10 μJ/s, and the heating rate 10 °C/min. Measurements were carried out in the air atmosphere at atmospheric pressure, from room temperature to 500 °C.

X-ray measurements were performed on an automatic powder diffractometer PW 1376-PW 1065/50 (Philips) with high – temperature camera HTK 10 (Paar) and automatic temperature controller HTK 2-HC (Paar). The heating rate was 1 to 50 °C/min in the interval from room temperature to 800 °C.

2.2. Theoretical background

To determine the degree of crystallinity α in the glass matrix and the cooling rate b one can start from the assumption that in the course of cooling the melt at a temperature T', from the melting point T_m to the softening point T_g, where $T_g < T' < T_m$ in a time interval $d\tau$, the number of nuclei formed is dN. If the volume ratio of the crystalline phase in the material is $\alpha(T')$, the number of nuclei is given by the relation,

$$dN = j(T')[1-\alpha(T')]d\tau \tag{1}$$

where $j(T')$ is the nucleation rate. If expressed via the cooling rate b, which is $b(T') = \frac{dT'}{d\tau}$, the expression (1) is transformed into

$$dN = \frac{j(T')}{b(T')}[1-\alpha(T')]dT' \tag{2}$$

It is assumed that all the newly formed nuclei at the temperature T' have a finite radius r_c. Also, it is usually assumed that the distance between their centers is larger than r_c. Thus the volume increment of the crystalline phase $d\alpha_c$, which is a consequence only of the formation of these dN nuclei is given by

$$d\alpha_c = V_c dN, \quad V_c = \frac{4}{3}r_c^3\pi \tag{3}$$

In the course of cooling, considering only what happens with the nuclei formed at T', the volume increment of the crystalline phase in the temperature interval from T' to T_g will be

$$d\alpha = V(T')dN \tag{4}$$

where $V(T')$ is the volume of the nuclei formed at T' and grown during the cooling to T_g,

$$V(T') = \frac{4}{3}\pi\left(r_c + \int_{T_g}^{T'} \frac{u(T)dT}{b(T')}\right)^3 \tag{5}$$

where *u(T)* is the rate of linear growth. Thereby, it is assumed that all the nuclei grow according to the same law, i.e. their growth is described by the same functional dependence of the rate of linear growth, similar to that given in [22].

By substituting (2) and (5) into (4) we obtain

$$d\alpha = \frac{j(T')}{b(T')}[1-\alpha(T')]\frac{4}{3}\pi\left(r_c + \int_{T_g}^{T'} \frac{u(T)dT}{b(T')}\right)^3 dT' \tag{6}$$

In this work we assume that, in addition to the growth of the *dN* nuclei, one should take into account the continuous increase in this number, i.e. the occurrence of new nucleation events. In order to obtain the overall ratio of the volume of the crystalline phase in the glass matrix it is necessary to carry out the integration with respect to *T'* in the region of cooling in which is plausible to consider the possibility of the occurrence of crystallization, i.e. from T_m to T_g. Thus we obtained that the overall volume ratio of the crystalline phase in the glass matrix is:

$$\alpha = \int_{T_c}^{T_m} \frac{j(T')}{b(T')}[1-\alpha(T')]\frac{4}{3}\pi\left(r_c + \int_{T_g}^{T'} \frac{u(T)dT}{b(T')}\right)^3 dT' \tag{7}$$

In this relation, the volume of crystalline phase remains a function of temperature, and it is the integrand in the above expression. In principle, from this expression one can calculate the cooling rate *b* that should be applied under the condition that the crystallization rate does not exceed a value of α_0, given in advance.

However, since $\alpha(T') < \alpha_0 \ll 1$, expression (7) can be transformed into a simpler form.

$$\alpha = \int_{T_c}^{T_m} \frac{j(T')}{b(T')}\frac{4}{3}\pi\left(r_c + \int_{T_g}^{T'} \frac{u(T)dT}{b}\right)^3 dT' \tag{8}$$

We will assume that the crystallization rate is constant over the whole interval of cooling, i.e. $b(T') = b$. By this approximation, and after introducing the substitution,

$$\int_{T_g}^{T'} u(T)dT = p(T') \tag{9}$$

equation (1.8) is transformed into a relation containing four integrals

$$\alpha = \frac{4}{3}\pi\{ \frac{r_c^3}{b}\int_{T_g}^{T_m} j(T')dT' + \frac{3r_c^2}{b^2}\int_{T_b}^{T_m} j(T')p(T')dT' + \frac{3r_c}{b^3}\int_{T_g}^{T_m} j(T')p^2(T')dT' + \frac{1}{b^4}\int_{T_g}^{T_m} j(T')p^3(T')dT' \} \tag{10}$$

This expression can be written as,

$$\alpha = \frac{4}{3}\pi\left[kr_c^3 b^{-1} + 3mr_c^2 b^{-2} + 3nr_c b^{-3} + ab^{-4}\right] \tag{11}$$

where the designations for the integrals are

$$k=\int_{T_g}^{T_m} j(T')dT';\quad m=\int_{T_g}^{T_m} j(T')p(T')dT';\quad n=\int_{T_g}^{T_m} j(T')p^2(T')dT';\quad a=\int_{T_g}^{T_m} j(T')p^3(T')dT' \qquad (12)$$

Numerical calculation of these integrals by standard programs can be done without any difficulty, so that the obtained expression (10), i.e. (11), can be successfully used to calculate the cooling rate *b*.

3. Results and discussion of calculation of the critical cooling rate

Critical cooling rate was calculated numerically on the basis of the obtained relation for As_2Se_3, AsSeI and $Cu_5[As_2Se3]_{95}$, $Cu_{15}[As_2Se_3]_{85}$, and $Cu_{15}[AsSe_{1.4}I_{0..2}]_{85}$. At that, the input functions were the nucleation rate *j(T)* and linear growth rate *u(T)*. Nucleation rate can be expressed as [23]:

$$j=j_0\exp\left(-\frac{N_A\Delta G_c+\Delta G_{an}}{RT}\right) \qquad (13)$$

With such systems, the pre-exponential factor j_o is [24]:

$$j_o = N_v\, n_s\, Z \qquad (14)$$

where N_v, i.e. n_s is the number of kinetic units in the volume unit of the glass and nucleus surface respectively; ΔG_c is the thermodynamic barrier, i.e. the free energy of critical nucleus formation; ΔG_{an} is the kinetic barrier, i.e. the free energy of activation of the transition of kinetic units from the glass to the crystal nucleus; and *Z* is the Zeldovich factor, which can be determined from the relation [25]:

$$Z=\left[\frac{\Delta G_c}{3\pi kT\left(n^*\right)^2}\right]^{\frac{1}{2}} \qquad (15)$$

where n^* is the number of atoms in the critical crystalline nucleus.
The thermodynamic barrier can also be expressed as

$$\Delta G_c=\frac{16\pi}{3}\frac{\sigma^3}{\left(\Delta G_v\right)^2} \qquad (16)$$

where ΔG_v is the change of free energy per unit volume and σ is the surface tension at the interface glass melt/crystal. Since ΔG_v can be expressed via the critical radius, i.e. via the melting entropy ΔS_m [24-26], the expression for the nucleation rate can be written in the form

$$j=j_0\exp\left[-\frac{A_0\left(T_m-T\right)^{-2}+\Delta G_{an}}{RT}\right] \qquad (17)$$

where $A_0=\frac{16\pi}{3}\frac{N_A\sigma^3V_{mol}^2}{\Delta S_m^2}$, V_{mol} is the molar volume and T_m is the melting point.

The linear growth rate is defined by the function

$$u=u_0\exp\left[-\frac{\Delta G_{am}}{RT}\right]\left[1-\exp\frac{\Delta S_m\left(T_m-T\right)}{RT}\right] \qquad (18)$$

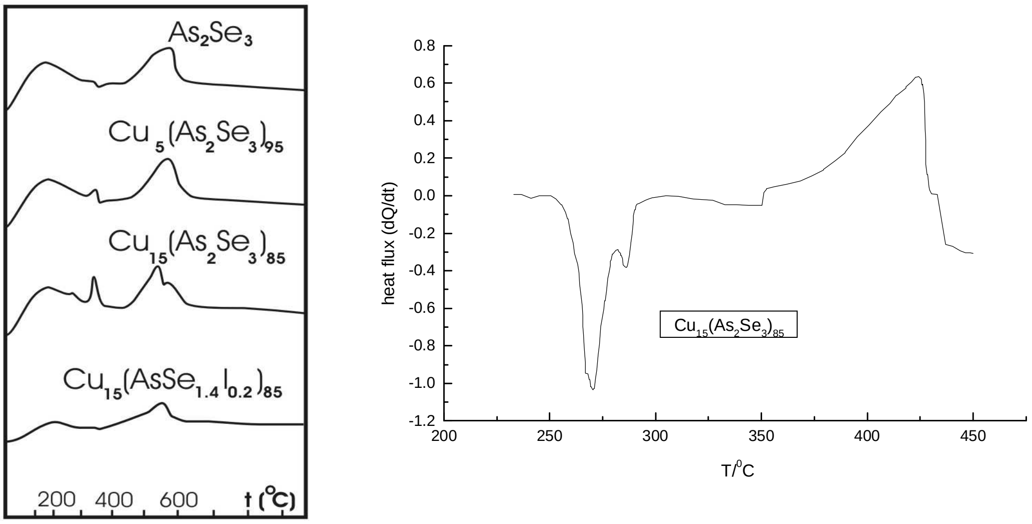
where ΔG_{am} is the free activation energy of crystal growth and u_o represents the preexponential term $u_0 = f \cdot \delta \cdot \nu$, whereby the factor f is the probability factor, which is given by the expression [26]:

$$f = \frac{\delta \, \Delta H_m \, T \, \Delta T}{4\pi \sigma \, T_m^2 \, V_{mol}} \tag{19}$$

where ΔH_m is the molar enthalpy of melting, δ is the jumping distance of kinetic units, and ν is the frequency of thermal atomic oscillations.

Basic difficulties in determining the nucleation rate function j and linear growth rate u are related to the estimation the values of activation energies ΔG_{an} and ΔG_{am}.

The values of input parameters used to define the functions j and u are presented in Table 1. With $Cu_5[As_2Se_3]_{95}$, $Cu_{15}[As_2Se_3]_{85}$ and $Cu_{15}[AsSe_{1.4}I_{0.6}]_{85}$ the values for T_m, T_g and ΔS_m were obtained on the basis of thermogravimetric and DSC measurements. The typical DTA and DSC curves are given in Fig. 1.



a b

Fig. 1. a. The DTA curves of the investigated samples; b. The DSC trace for the sample $Cu_{15}(As_2Se_3)_{85}$.

For the systems involving Cu, the activation energy of crystallization and activation energy of linear growth are determined based on the measurement of the nucleation temperature in the amorphous matrix as a function of heating rate. The graphs of the relations

$$\frac{1}{T_n} = C_n - \frac{R}{\Delta G_{an}} \ln \mathrm{v} \qquad \text{and} \qquad \frac{1}{T_{\max}} = C_m - \frac{R}{\Delta G_{am}} \ln \frac{\mathrm{v}}{T_{\max}^2} \tag{20}$$

served to determine ΔG_{an} and ΔG_{am}. T_n represents the temperature of the beginning of crystallization, whereas T_{max} is the temperature corresponding to its maximum, and v is the heating rate. Namely, it can be assumed that at the temperature of the beginning of crystallization the activation energy of nucleation is predominant, whereas at the temperature of crystallization maximum the decisive influence has the activation energy of linear growth.

In Fig. 2 is shown the experimentally determined dependence between ln v and $1/T_n$ for the samples with 5 and 15 at % Cu.

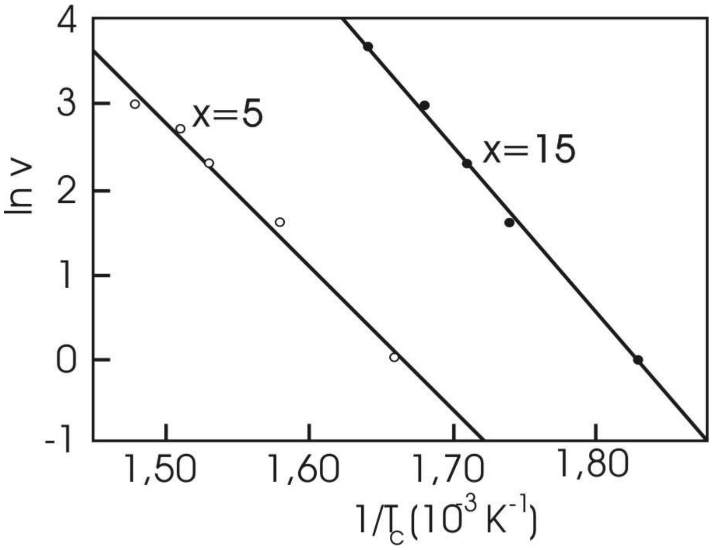


Fig. 2. Correlation of the temperature of nuclei formation and heating rate.

The data presented in Table 1 served as the basis for determining the functional dependence of the nucleation rate and the rate of linear growth on temperature. Graphs of these functions, known as Turnbull's curves, are for our glasses with Cu presented in Figs. 3-5. It is evident from them that in all three cases the maxima of linear growth rate appear at a significantly higher temperature compared to the nucleation maxima *j*. The weak overlapping of these curves indicates that these materials can be effectively obtained in the form of glasses.

Table 1. The crystal nucleation parameters of investigated glasses: T_g - softening temperature, T_m - melting temperature, ΔS_m – melting entropy, ΔG_{an} – free energy of activation of transfer of kinetic units across the interface glass/crystal nucleus, ΔG_{am}-free activation energy of crystal growth, σ- surface tension, r_c– critical radius.

Glass	As_2Se_3	AsSeI	$Cu_5[As_2Se_3]_{95}$	$Cu_{15}[As_2Se_3]_{85}$	$Cu_{15}[AsSe_{1.4}I_{0.6}]_{85}$
T_g(K).	443	351	438	458	458
T_m(K)	643	503	655	655	655
$d\cdot10^3$(kg/m^3)	4.55	4.57	4.77	5.07	4.99
ΔS_m(kJ/mol)	63.5	47.5	20	10.8	11.8
ΔG_{an}(kJ/mol)	152	125	145	161	161
ΔG_{am}(kJ/mol)	152	100	140	140	148
σ(N/m)	0.05	0.035	0.017	0.028	0.030
$r_c\cdot10^{10}$(m)	8.20	7.35	3.60	3.90	4.99
reference	[24].	[10]	this work	this work	this work

On the basis of the functional dependence of *j* and *u* it was possible to calculate the output parameters, i.e. the values of the integrals *k*, *m*, *n*, *a*, defined by equation (12). In Table 2 are presented the values obtained for these integrals, along with the values of critical cooling rate calculated by introducing them into (11). At that, it is assumed that the given ratio of the crystalline phase volume is 10^{-6} of the given volume of glass matrix.

Table 2. Values of the integrals *k*, *m*, *n*, *a*, defined by equation (12) and calculated critical cooling rate (b) for the investigated glasses.

Glass	k ($m^{-3}Ks^{-1}$)	m ($m^{-2}K^2s^2$)	n ($m^{-1}K^3s^3$)	a (K^4s^{-4})	b (Ks^{-1})
As_2Se_3	$6.89 \cdot 10^{16}$	$1.78 \cdot 10^{3}$	$2.31 \cdot 10^{-10}$	$9.06 \cdot 10^{-23}$	$4.2 \cdot 10^{-4}$
AsSeI	$3.51 \cdot 10^{17}$	$1.70 \cdot 10^{6}$	$2.90 \cdot 10^{-5}$	$1.12 \cdot 10^{-15}$	$9.7 \cdot 10^{-3}$
$Cu_5[As_2Se_3]_{95}$	$2.19 \cdot 10^{23}$	$4.92 \cdot 10^{11}$	·4.16	$7.15 \cdot 10^{-11}$	42.7
$Cu_{15}[As_2Se_3]_{85}$	$1.84 \cdot 10^{23}$	$1.18 \cdot 10^{12}$	19.65	$5.49 \cdot 10^{-10}$	45.8
$Cu_{15}[AsSe_{1.4}I_{0.6}]_{85}$	$2.69 \cdot 10^{21}$	$6.89 \cdot 10^{6}$	$6.27 \cdot 10^{-4}$	$1.16 \cdot 10^{-15}$	1.4

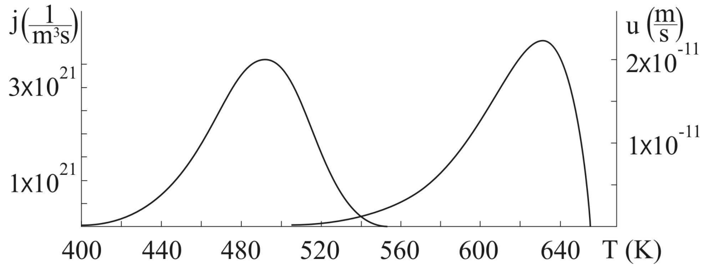


Fig. 3. Temperature dependence of the rates of nucleation and linear growth for $Cu_5[As_2Se_3]_{95}$.

For the glasses As_2Se_3 and AsSeI, the calculated values of critical rates are very small. However, it is known from practice that these systems are readily obtained in the form of glass and that they do not require high cooling rates. It should be pointed out that there are literature data [8] for the critical cooling rate of the As_2Se_3 glass that are higher by about one order of magnitude of which critical cooling rate was calculated.

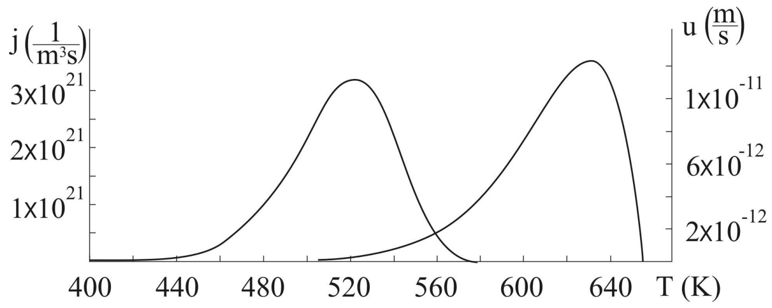


Fig. 4. Temperature dependence of the rates of nucleation and linear growth for $Cu_{15}[As_2Se_3]_{85}$

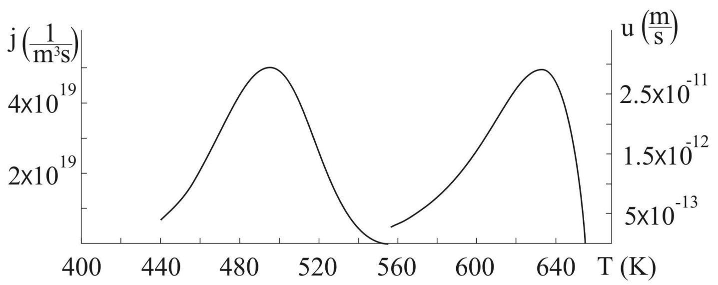


Fig. 5. Dependence of the rates of nucleation and linear growth on temperature for $Cu_{15}[AsSe_{1.4}I_{0.6}]_{85}$.

These values were calculated on the basis of the KJMA theory, whereby of the members containing *b* in the expression for the ratio of crystalline phase volume only the one with power 4 was retained, as its contribution was the highest. It appeared that our calculations are more exact. Besides, it should be noticed that the difference between the values might be also due to the small differences in the input quantities. It is known that the functions *j* and *u* are very sensitive to their changes, which also implies the corresponding changes in the integrals k, *m*, *n* and *a*, on the basis.

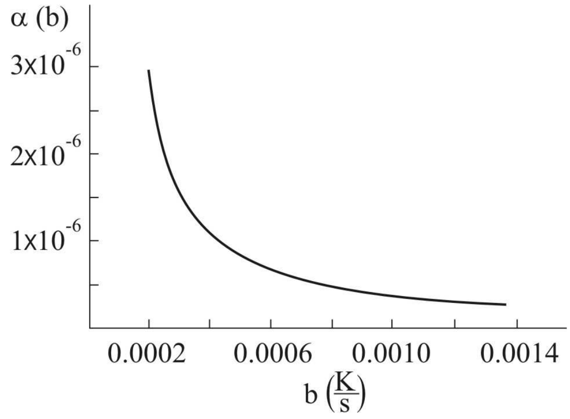


Fig. 6. Dependence of ratio of crystalline phase volume in the glass matrix as a function of critical cooling rate for As_2Se_3.

In Figs. 6 and 7 is shown the calculated dependence of the ratio of crystalline phase volume in the glass matrix *α(b)* as a function of the potential change of the applied critical cooling rate for the glasses As_2Se_3 and AsSeI respectively. It can be seen that the change of cooling rate by one order of magnitude in the given interval produces a change of the same magnitude in the volume of crystalline phase in the glass matrix.

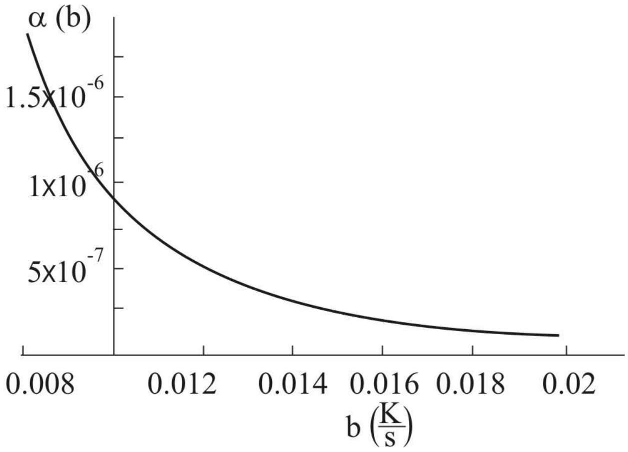


Fig. 7. Dependence of ratio of crystalline phase volume in the glass matrix as a function of critical cooling rate for AsSeI.

By comparing the obtained results with those of previous investigation [11,18,27] it can be seen that the glasses containing copper are more prone to crystallization compared to the corresponding samples without Cu. Results of the present work support also this observation. Namely, as can be seen from Table 2, the calculated critical rate of cooling of Cu samples is by several orders of magnitude higher compared to the corresponding values for the glasses without this element. In practice, it has been shown that a cooling rate of several tens of K/s is needed to prepare the glasses with Cu.

In Fig. 8 is presented the calculated dependence of the ratio of crystalline phase volume on the applied cooling rate for the Cu glasses. The calculation involved the rates to which corresponds the ratio of crystalline phase of the order magnitude of 10^{-6}. In these cases the cooling rates were of the order of magnitude of tens of K/s, so that the analysis of the contribution of particular members of equation (11) showed that the term with b^{-1} was much larger compared to the other terms. Fig. 8 shows the functional dependence that is obtained from the given equation by retaining only this member. It can be seen that the course of the function for the samples $Cu_5[As_2Se_3]_{95}$ and $Cu_{15}[As_2Se_3]_{85}$ is very similar. If a wider interval for *b* were selected, the graphs could even coincide. With the sample $Cu_{15}[AsSe_{1.4}I_{0.2}]_{85}$, the difference in graph position is evident. It can be assumed that with the first two samples the crystallization process under the same conditions proceeds in a very similar way, whereas with the four-component chalcogenide it is different. This could be a consequence of the presence of iodine in the material, yielding certainly formation of some new structural elements in the glass matrix. It has been shown that such complex systems contain even up to ten structural elements [27].

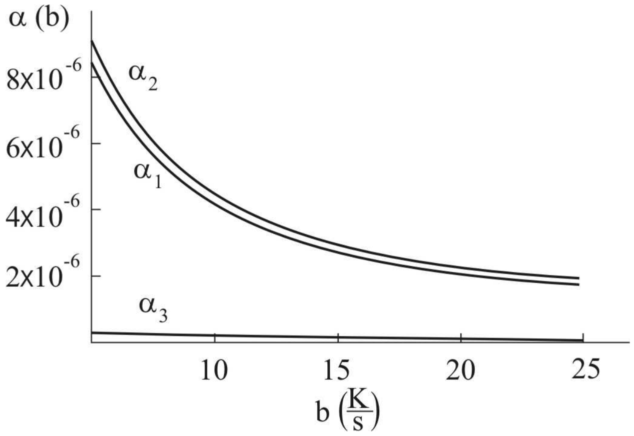


Fig. 8. Dependence of the ratio of crystalline phase volume on the applied cooling rate: α_1 - $Cu_5[As_2Se_3]_{95}$, α_2 - $Cu_{15}[As_2Se_3]_{85}$, α_3 - $Cu_{15}[AsSe_{1.4}I_{0..2}]_{85}$.

4. Conclusion

Starting from the assumption on the constant involvement of nucleation, i.e. the growth of the existing nuclei is also accompanied by the formation of the new ones, an equation has been derived relating the volume of crystalline phase in the glass matrix to the critical cooling rate. The equation allows numerical calculation of the critical cooling rate for the known input parameters and prescribed ratio of the crystalline phase volume. The calculation performed for the chalcogenide glasses As_2Se_3 and AsSeI gave the results that differ to some extent from those previously reported. This can be explained in terms of the approximations that have been made. The results obtained in this work can be considered as more exact since particular members of the equation have not been rejected. The Cu glasses dealt with in this work have also been subject of our experimental investigations, and the obtained value of critical cooling rate is by several orders of magnitude higher compared to that for the glasses without this element. This is also in agreement with our experimental investigations, showing that these glasses are much more prone to crystallization compared to the basic ones, containing no this element.

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