



Theoretical analysis of relative changes of the Hruby, Weinberg, and Lu–Liu glass stability parameters with application on some oxide and chalcogenide glasses

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ARTICLE INFO

Article history:

Received 14 August 2009

Received in revised form 16 October 2009

Accepted 31 October 2009

Available online 10 November 2009

PACS:

64.70.dg

64.70.kj

64.70.Q-

Keywords:

Glass stability

Characteristic temperatures

Relative change

Glass-forming ability

ABSTRACT

This paper establishes relations between the magnitudes of relative changes of the Hruby (K_H), Weinberg (K_W) and Lu–Liu (K_{LL}) parameters and differences when moving from one glassy system to another. The parameters K_H , K_W and K_{LL} are expressed using the reciprocal value of the reduced glass transition temperature (T_m/T_g) as well as the ratio of the crystallization temperature and glass transition temperature (T_c/T_g). The obtained expressions show that all three parameters are in correlation with the mentioned ratios of temperatures. Hence, the number of independent variables by which K_H , K_W and K_{LL} are expressed is reduced from three to two. That way we can present their functional dependence in the form of three-dimensional graphs. The goal of this paper is to ascertain which of the three parameters has the most relative change when moving from one glassy system to another i.e. which one is the most sensitive. The expressions were derived for the relative changes of these parameters, i.e. for dK_H/K_H , dK_W/K_W and dK_{LL}/K_{LL} . We found that the mutual relations between the magnitude of the change of the ratios of T_c/T_g and T_m/T_g determine the order of the values of dK_H/K_H , dK_W/K_W and dK_{LL}/K_{LL} . If the relative change of the ratio of the crystallization temperature and glass transition temperature is greater than the change of the reciprocal value of the reduced glass transition temperature, the greatest relative change will be of the parameters K_H and K_W , in this order. In the opposite case, greater relative change will be in K_W than in K_H . In both cases, the relative change of the parameter K_{LL} is smallest. This affects the value of the free term in all relations of linear dependencies between the critical cooling rate i.e. in q and GS parameters. Our tests on two series of oxide glasses and one series of chalcogenide glasses show full agreement with all the results of this theoretical study.

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1. Introduction

Glass stability (GS) represents the resistance of the glass to devitrification at heating. There are several parameters by which this stability is estimated, and they are based on the characteristic temperatures in the process of glass heating: T_g – glass transition temperature, T_x – onset temperature, i.e. T_c – maximum of the crystallization peak temperature, and T_m – melting temperature. These temperatures are usually determined by DTA and DSC analyses. Some of the GS parameters take into account only two of these temperatures. One way to evaluate GS is based on the difference between T_g and T_m , or on the ratio of these two temperatures [1]. Also, the ratio of T_x and T_m [2], as well as the difference between T_x and T_g [3] can be taken as a GS parameter. The most popular parameters are those that involve three characteristic temperatures [4]. Of these parameters the most widely used are the Hruby parameter [3] $K_H = (T_x - T_g)/(T_m - T_x)$, parameter used by Weinberg [5]

$K_W = (T_c - T_g)/T_m$, and more recently, the parameter proposed by Lu and Liu [6,7] $K_{LL} = T_x/(T_g + T_m)$. When switching from one glassy system to another one, the glass resistance in relation to devitrification changes, and the GS parameters change, too. Larger values of the K_H , K_W and K_{LL} parameters imply higher stability of the glass in respect to devitrification [3,4]. Also, when comparing one glass to another, it is essential to know how large is the relative change of the given parameter and how it can be compared with the relative change of some other GS parameter. In other words, it is necessary to know which of the GS parameters shows the fastest change.

Let us take as an example the values of the K_H , K_W and K_{LL} parameters for oxide glasses from [8]. The results of these parameters, according to the characteristic temperatures in [8] are shown in form of histograms in Fig. 1. It is obvious that the three parameters do not change in the same way for different oxide glasses. The modification of the K_{LL} parameter is the smallest. The question is, can this be generalized for all glassy systems?

The GS parameters are not important only as indicators of the glass resistance to devitrification. Recently, several important studies have appeared, which demonstrate correlation between the GS parameter and the critical cooling rate, maximum section thickness

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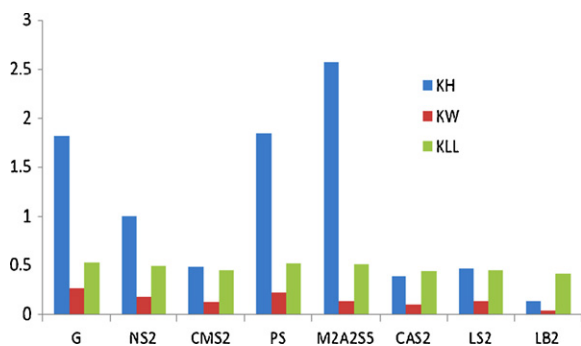


Fig. 1. Histograms of the K_H , K_W and K_{LL} parameters for oxide glasses from [8].

or diameter by which the glass-forming ability (GFA) is estimated [4,6,8–13]. In our previous work [14], we presented a numerical approach to determine the critical cooling rate. This quantity, as a measure of GFA, is difficult to measure. Hence, it is very important to establish the correlation between the GFA and GS since the GS parameters, based on the characteristic temperatures, can be easily determined. In papers [4,6,8,15], a very good correlation is shown between GFA and GS parameters, which are based on the three characteristic temperatures such as the Hruby, Weinberg, and Lu–Liu parameters. This was an additional reason for us to investigate the magnitude of the relative changes of these three parameters, which are very often used in the GS estimation.

We want also to mention that the paper [12] stresses that GS parameters, which are used to estimate GFA, should be enough sensitive. Paper [12] introduces the new GS parameter, which is very sensitive. This is explicitly proved with our results [16].

The goal of this work is to establish a relation between the relative changes of the Hruby, Weinberg, and Lu–Liu parameters and differences when moving from one glassy system to another. In other words, we want to find out which changes are faster, and which conditions for the established relations hold.

According to [12], some of GS parameters belong inside a narrow range and hence there are just minor differences between them. In the case that they are applied for estimation of GFA, the correlation factor between them and critical cooling rate or maximum section thickness is significant. On the other hand, a low sensitivity can be a hindrance for a practical application, especially because the maximum section thickness is usually represented as an integer.

As has been shown in [8,17], it is possible to use either T_x or T_c , because no significant changes arise in the results. For this reason we will use these two temperatures as alternatives in our calculations. When we derive expressions, we use the temperature T_c in general, which will replace the temperature T_x in the case that T_x existed originally.

2. Theoretical derivation

Our starting point was the fact that all three parameters, K_H , K_W and K_{LL} , include all three characteristic temperatures. For this reason, we can express them in a somewhat different way – using the ratios of the temperatures. In doing so, we assume that in defining both K_H and K_{LL} it is possible to replace T_x with T_c . Let us introduce the substitutions

$$m = \frac{T_m}{T_g}; \quad r = \frac{T_c}{T_g} \quad (1)$$

where m is the reciprocal value of the so-called reduced glass transition temperature $T_{rg} = T_g/T_m$, which is understood as a measure of the easiness of glass formation [18,19]. A relation between the reduced glass transition temperature and crystallization pattern was established by Zanotto [20]. A correlation has also been found

between the maximum of nucleation rate I_{max} and T_{rg} for silicate glasses [21]. Further, it is known that T_{rg} correlates with the maximum of crystal growth rate [22]. Lu and Liu [6] found that in the case of bulk metallic glasses their parameter K_{LL} correlates much better with GFA than T_{rg} . Zhang et al. [23] proved for bulk metallic glass that T_{rg} and K_H , as GFA indicators have a similar trend. Avramov et al. [4] presented graphically the correlation between K_H and reduced glass transition temperature. Hence, it was obvious to suppose that all the three GS parameters can be expressed using T_{rg} that is, using its reciprocal value m , since this is mathematically more convenient.

On the other hand, it is well known that the difference between T_x (or T_c) and T_g is an indicator of GS [3,6,24]. In order to enable a comparison between different glasses that have different T_g , Lu and Liu [6] weighted this temperature interval by $1/T_g$. That way they obtained the factor $(T_x/T_g - 1)$, where the ratio (T_x/T_g) is proportional to the glass stability with respect to the process of reheating. Hence, the second substitution that we introduced here, $r = T_c/T_g$, is justified. Here, T_x was replaced with T_c .

After simple mathematical transformations, it follows that

$$K_H = \frac{r - 1}{m - r} \quad (2)$$

$$K_W = \frac{r - 1}{m} \quad (3)$$

$$K_{LL} = \frac{r}{m + 1} \quad (4)$$

It is necessary to point out that the following relations always hold:

$$m > 1, \quad r > 1, \quad m > r \quad (5)$$

Thus, we obtain the relations linking the K_H , K_W and K_{LL} parameters with the temperature ratios r and m , both of them being a measure of GS. It is evident from these relations that K_W and K_{LL} are directly proportional to r , i.e. to T_c/T_g . Also, it is clear that all the GS parameters are inversely proportional to m . In other words, all of them are directly proportional to the reduced glass transition temperature.

By these transformations we reduce the number of independent variables used to express the GS parameters from three to two. Also, it can be easily shown that the GS parameters are interrelated, so that

$$K_H = \frac{mK_W}{m - r} \quad (6)$$

$$K_W = \frac{(m + 1)K_{LL} - 1}{m} \quad (7)$$

Since $m > r$ (from Eq. (5)), it is evident from the expression (6) that for a given glass, $K_H > K_W$ will always hold.

When moving from one glassy system to another, the characteristic temperatures change and so do the values for m and r . Therefore, Eqs. (6) and (7) do not offer a possibility of deriving a direct conclusion how the relation between the parameters changes when moving from one glass system to another one. In order to derive expressions for the relative changes of these parameters, and enable their comparison, we started from Eqs. (2)–(4). We take first their logarithms and then differentiate the obtained ln values:

$$\frac{dK_H}{K_H} = \frac{dr}{r - 1} - \frac{dm}{m - r} + \frac{dr}{m - r} \quad (8)$$

$$\frac{dK_W}{K_W} = \frac{dr}{r - 1} - \frac{dm}{m} \quad (9)$$

$$\frac{dK_{LL}}{K_{LL}} = \frac{dr}{r} - \frac{dm}{m + 1} \quad (10)$$

If the relative change of the Hruby parameter has to be greater than the relative change of the Weinberg parameter (according to the Eqs. (8) and (9)), the following condition must be satisfied:

$$\frac{dr}{m-r} > \frac{dm}{m-r} - \frac{dm}{m} \quad (11)$$

After some rearrangements, this expression gives

$$\frac{dr}{r} > \frac{dm}{m} \quad (12)$$

Thus, inequation (12) represents exactly the condition that has to be fulfilled in order to have that

$$\frac{dK_H}{K_H} > \frac{dK_W}{K_W} \quad (13)$$

Knowing that $m > r$ and if the following inequality holds

$$dr > dm \quad (14)$$

the condition given by (12) will always be fulfilled, and the relation of the relative change of GS parameters expressed by (13) will hold, too.

If the relative change of the Weinberg parameter has to be greater than the relative change of the Lu–Liu parameter (according to the Eqs. (9) and (10)), the following condition must be satisfied:

$$\frac{dr}{r-1} - \frac{dm}{m} > \frac{dr}{r} - \frac{dm}{m+1} \quad (15)$$

After rearranging of the inequation above, we obtain the following relation

$$\frac{dr}{r(r-1)} > \frac{dm}{m(m+1)} \quad (16)$$

The expression (16) represents the condition to be satisfied in order to have

$$\frac{dK_W}{K_W} > \frac{dK_{LL}}{K_{LL}} \quad (17)$$

Since $m > r$ and $m+1 > r-1$, it is evident that if the expressions (14) or (12) hold, then the condition given by the inequation (16) will also be satisfied.

This means that if $dr > dm$ (expression (14)) is fulfilled, both conditions given by the inequations (12) and (16) will be satisfied, and the following relation of the changes of the parameters considered will hold

$$\frac{dK_H}{K_H} > \frac{dK_W}{K_W} > \frac{dK_{LL}}{K_{LL}} \quad (18)$$

If expressed using the characteristic temperatures, the inequation (14) can be rewritten as

$$d\left(\frac{T_c}{T_g}\right) > d\left(\frac{T_m}{T_g}\right) \quad (19)$$

Hence we can say that if the change of the ratio of the crystallization temperature and glass transition temperature is greater than the change of the reciprocal value of the reduced glass transition temperature, then the change of the Hruby parameter will be the greatest, followed by the change of the Weinberg parameter, while the change of the Lu–Liu parameter will be the smallest. However, the requirement given by the inequation (14) is unnecessarily stringent. It is the simplest way of expressing that condition. The condition given by the expression (12) is less stringent and it has to be satisfied in order that the relation between the magnitudes of the relative changes of GS parameters would be as shown in the inequation (18). The expression (12) gives the correlation between the relative changes of the temperature ratios T_c/T_g and T_m/T_g . So, the question is: what happens if the conditions given by

the expressions (14) or (12) are not satisfied. In that case, in contrast to the expression (13), the relative change of the Weinberg parameter will be greater than the relative change of the Hruby parameter. However, it remains to be seen what will be the mutual relation between relative changes of K_H and K_{LL} , and which change will be greater. According to Eqs. (8) and (10) and in order to have that $dK_{LL}/K_{LL} > dK_H/K_H$, the following relation holds

$$\frac{dr}{r} - \frac{dm}{m+1} > \frac{dr}{r-1} - \frac{dm}{m-r} + \frac{dr}{m-r} \quad (20)$$

After some rearrangement it follows

$$\frac{r+1}{m+1} dm > \frac{r(r-1) + (m-r)}{r(r-1)} dr \quad (21)$$

i.e.

$$\frac{r+1}{m+1} > \left[1 + \frac{m-r}{r(r-1)}\right] \frac{dr}{dm} \quad (22)$$

Since we started from the assumption that the condition given by the expression (14) is not fulfilled, then $dr/dm < 1$, and the inequation (22) will be satisfied if

$$\frac{r+1}{m+1} > 1 + \frac{m-r}{r(r-1)} \quad (23)$$

Since $r < m$, the left-hand side of the expression (23) is always smaller than one. On the other hand, the term $(m-r)/(r(r-1))$ is always greater than zero, so that the right-hand side of the expression (23) is always greater than one. Thus the inequation (23) can never be satisfied. This means that the relative change of the K_{LL} parameter will never be greater than the relative change of the Hruby parameter. Hence, in the case that the conditions given by the inequations (14) or (12) are not satisfied, the relative changes of the parameters will be as follows

$$\frac{dK_W}{K_W} > \frac{dK_H}{K_H} > \frac{dK_{LL}}{K_{LL}} \quad (24)$$

As can be seen from the relations (18) and (24), the relative change of the K_{LL} parameter will always have the smallest value.

During the test phase, where the conditions and relations derived in the theoretical part above apply to the concrete glassy systems, all infinitesimal small quantities were replaced with the finitely small ones. Hence, the symbol for the differential d is replaced with Δ and, as such, is presented in the tables.

3. Testing theoretical results

Results of the above theoretical derivation were tested on two series of oxide glasses and one of chalcogenide glasses. The characteristic temperatures T_g , T_c and T_m were taken from the work of Cabral et al. [9] for the following seven oxide glasses: $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$ (LS₂); $\text{Na}_2\text{O} \cdot 2\text{CaO} \cdot 3\text{SiO}_2$ (NC₂S₃); $2\text{Na}_2\text{O} \cdot \text{CaO} \cdot 3\text{SiO}_2$ (N₂CS₃); $\text{BaO} \cdot 2\text{SiO}_2$ (BS₂); $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$ with 0.2 mol% OH (LS₂OH); $2\text{BaO} \cdot \text{TiO}_2 \cdot 2\text{SiO}_2$ (B₂TS₂) and 0.44 $\text{Na}_2\text{O} \cdot 0.56\text{SiO}_2$ (44NS). From the work of Nascimento et al. [8] we took the characteristic temperatures for the following oxide glasses (coarser powder, with particle sizes 150–177 μm): GeO_2 (G); $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$ (NS₂); $\text{CaO} \cdot \text{MgO} \cdot 2\text{SiO}_2$ (CMS₂); $\text{PbO} \cdot \text{SiO}_2$ (PS); $2\text{MgO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$ (M₂A₂S₅); $\text{CaO} \cdot 2\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ (CAS₂); $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$ (LS₂); $\text{Li}_2\text{O} \cdot 2\text{Ba}_2\text{O}_3$ (LB₂). It is important to note that for all these glasses there is very good correlation between the critical cooling rate and the three GS parameters.

The data for chalcogenide glasses from the system $(\text{Ag}_2\text{Te})_x(\text{As}_2\text{Se}_3)_y(\text{CdTe})_z$ were taken from the work of Vassilev et al. [25]. The glasses presented in [25] have been synthesized for the first time. The temperatures T_g , T_c and T_m for the glasses of this system, with the different molar ratios, denoted as p.3, p.4, p.5, p.6, p.9, p.10, p.11, p.16 and p.17, were taken from this paper.

Table 1The values for r and m , GS parameters (K_H , K_W , and K_{LL}) and ΔK_H , ΔK_W , ΔK_{LL} for the systems used in this paper.

Glasses	m	r	K_H	K_W	K_{LL}	ΔK_H	ΔK_W	ΔK_{LL}
Oxide [9]								
44NS	1.7406	1.3012	0.68548	0.173044	0.474787	0	0	0
LS ₂	1.7776	1.2783	0.55738	0.156559	0.460217	0.128099668	0.016484594	0.014569546
LS ₂ -OH	1.7776	1.2715	0.536455	0.152734	0.457769	0.149024754	0.020309977	0.017017703
BS ₂	1.7292	1.1764	0.319103	0.102012	0.431042	0.36637725	0.071031509	0.043744936
NC ₂ S ₃	1.8232	1.1897	0.299448	0.104048	0.421401	0.386032486	0.068996172	0.053385753
N ₂ CS ₃	1.8781	1.1695	0.239204	0.090251	0.406344	0.446275936	0.082793215	0.068442537
B ₂ TS ₂	1.7378	1.0898	0.13858	0.051675	0.398057	0.546899753	0.121369469	0.076730166
Oxide [8]								
G	1.6906	1.4458	1.821078	0.263693	0.537352	0	0	0
NS ₂	1.5908	1.2968	1.009524	0.186573	0.50054	0.81155419	0.077120206	0.036811626
CMS ₂	1.6825	1.2224	0.483373	0.132184	0.455694	1.33770482	0.13150875	0.081657685
PS	1.5341	1.3462	1.842469	0.22567	0.531234	-0.02139140	0.038023226	0.006118031
M ₂ A ₂ S ₅	1.2558	1.1842	2.572626	0.146679	0.524958	-0.75154770	0.117013592	0.012394114
CAS ₂	1.6219	1.1771	0.398156	0.109193	0.448949	1.422921525	0.154500078	0.088402765
LS ₂	1.7601	1.2453	0.476496	0.139367	0.451179	1.344582274	0.124325919	0.086172695
LB ₂	1.5619	1.0706	0.1437	0.045201	0.417893	1.677377613	0.218491643	0.119459030
Chalcogenide [25]								
p.16	1.455	1.1922	0.731355	0.132096	0.485621	0	0	0
p.3	1.4517	1.1401	0.449615	0.096508	0.465024	0.281740109	0.035588457	0.020596731
p.4	1.3949	1.1122	0.396887	0.080436	0.464404	0.33446784	0.051660126	0.021217476
p.5	1.3721	1.1027	0.381218	0.074849	0.464862	0.35013748	0.057247228	0.020758642
p.6	1.3009	1.0498	0.198327	0.038281	0.456256	0.53302764	0.09381481	0.029364752
p.9	1.4426	1.1507	0.516273	0.104464	0.471096	0.215082304	0.027631838	0.014524627
p.10	1.4326	1.1418	0.48762	0.098981	0.469374	0.243734642	0.033115126	0.016246668
p.11	1.3445	1.1029	0.425911	0.076534	0.47042	0.305444404	0.055561972	0.015200868
p.17	1.4161	1.1749	0.725124	0.123508	0.48628	0.006230622	0.008587773	-0.00065854

One glass from each group was taken as a reference, with respect to which we calculated the differences of the corresponding GS parameters ΔK . From each group, the glass having the largest value of r , that is the largest T_c/T_g ratio, was selected as a referenced one. For the group of oxide glasses from [9], the reference was the glass 44NS, whereas for the series from [8], the reference was the glass G. In the group of chalcogenide glasses, the glass denoted as p.16 was a referenced one.

The characteristic temperatures T_g , T_c (T_x) and T_m reported in the papers mentioned above will not be given here, but only the values of our calculations. Table 1 shows the values for r and m together with the values of GS parameters K_H , K_W and K_{LL} calculated from Eqs. (2), (3) and (4), respectively. The Table 1 also contains the calculated differences of these parameters ΔK_H , ΔK_W and ΔK_{LL} for each glass with respect to the reference from the corresponding group.

Table 2The values of the relative changes of $\Delta K_H/K_H$, $\Delta K_W/K_W$, $\Delta K_{LL}/K_{LL}$ as well as the values for Δr , Δm , and $\Delta r/r$ and $\Delta m/m$ for the glasses used in this paper.

Glasses	Δr	Δm	$\Delta r/r$	$\Delta m/m$	$\Delta K_H/K_H$	$\Delta K_W/K_W$	$\Delta K_{LL}/K_{LL}$
Oxide [9]							
44NS	0	0			0	0	0
LS ₂	0.0229	-0.037			0.229825	0.105293	0.031658
LS ₂ -OH	0.0297	-0.037			0.277795	0.132976	0.037175
BS ₂	0.1248	0.0114			1.148148	0.696302	0.101486
NC ₂ S ₃	0.1115	-0.0826			1.289149	0.66312	0.126686
N ₂ CS ₃	0.1317	-0.1375			1.86567	0.917368	0.168435
B ₂ TS ₂	0.2114	0.0028			3.946448	2.348729	0.192762
Oxide [8]							
G	0	0			0	0	0
NS ₂	0.149	0.0998			0.803898	0.413352	0.073544
CMS ₂	0.2234	0.0081			2.767437	0.99489	0.179194
PS	0.0996	0.1565	0.073986	0.102014	-0.01161	0.168491	0.011517
M ₂ A ₂ S ₅	0.2616	0.4348	0.220909	0.346233	-0.29213	0.797751	0.02361
CAS ₂	0.2687	0.0687			3.573775	1.414928	0.19691
LS ₂	0.2005	-0.0695			2.821814	0.892075	0.190994
LB ₂	0.3752	0.1287			11.67274	4.833741	0.28586
Chalcogenide [25]							
p.16	0	0			0	0	0
p.3	0.0521	0.0033			0.626625	0.368763	0.044292
p.4	0.08	0.0601			0.842728	0.642252	0.045688
p.5	0.0895	0.0829			0.918472	0.764839	0.044655
p.6	0.1424	0.1541	0.135645	0.118456	2.687615	2.450676	0.06436
p.9	0.0415	0.0124			0.416606	0.26451	0.030832
p.10	0.0504	0.0224			0.499845	0.334561	0.034613
p.11	0.0893	0.1105	0.080968	0.082187	0.717156	0.725977	0.032313
p.17	0.0173	0.0389	0.014725	0.02747	0.008592	0.069532	-0.00135

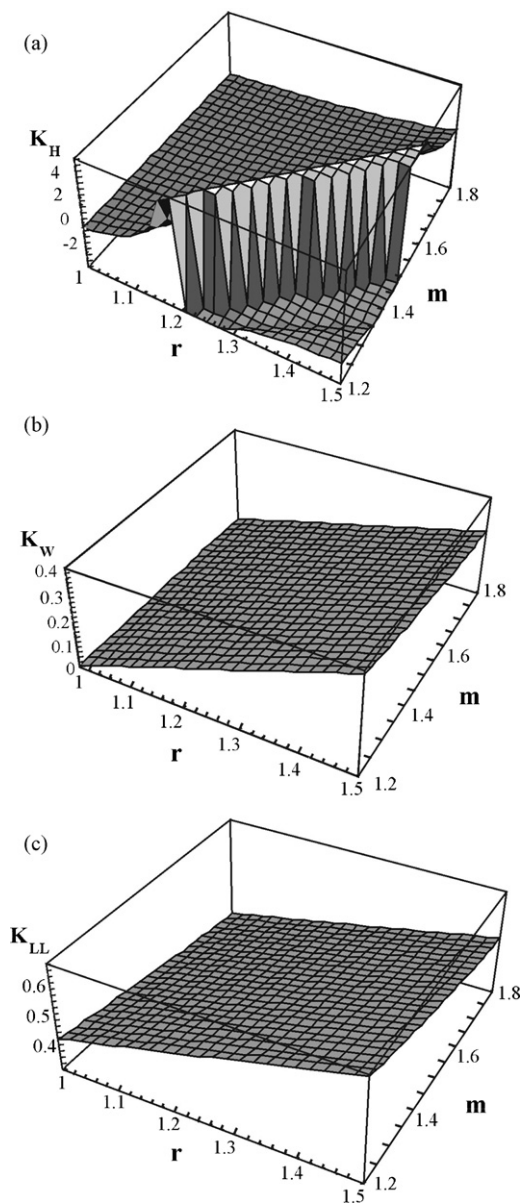


Fig. 2. The dependence of the GS parameters K_H (a), K_W (b) and K_{LL} (c) as a function of r and m .

The three parts of Fig. 2 show the interdependence between r and m and the parameters K_H , K_W and K_{LL} , given by the respective equations (2), (3) and (4). The ranges for r and m used in the figure encompass the values of r and m for the oxide glasses from [9].

Table 2 lists the values of the relative changes $\Delta K_H/K_H$, $\Delta K_W/K_W$ and $\Delta K_{LL}/K_{LL}$, as well as the values for Δr and Δm . The values for the glasses, for which the analysis require further calculations of the values $\Delta r/r$ and $\Delta m/m$, are presented in Table 2, too. Our tables, however, do not give the corresponding errors. The reason for this is that the papers from which we took the characteristic temperatures for our calculations did not always contain errors of their measurements.

As can be seen from Tables 1 and 2, in some cases there exist negative values of Δm and of the changes of some of the GS parameters. This occurs with glasses whose values of the given quantities were greater compared to the analogous values for the corresponding reference glass. In comparing the quantities in the application of our inequations, it is important to note that they are strictly mathe-

matematical relations, and that negative quantities, irrespective of their absolute value, are smaller than the positive ones.

Fig. 3 shows the three histograms of the relative changes of the GS parameters for the glasses from the three groups considered.

4. Discussion

From a mathematical point of view, the introduction of the ratios r and m enabled us to reduce the number of independent variables by which the parameters K_H , K_W and K_{LL} are defined: instead of the three characteristic temperatures we use their two ratios (r and m) as independent variables. For this reason, it is possible to present the dependence of the GS parameters as a function of r and m in the form of 3D graphs. The graph given in Fig. 2(a) shows the area that encompasses those values of the K_H parameter that appear with the oxide glasses from [8]. This is the region of positive values, where the K_H value can be greater than 4. The figure also shows the region of negative areas, that is the negative values of K_H . This has no physical meaning. It is a result of the mathematical combinations of the values for r and m from the given interval in which $r > m$, and this relation of r and m in reality is never fulfilled. As can be seen from Fig. 2(b), there is no negative areas for the quantity K_W . This is a consequence of the type of dependence expressed by Eq. (3) and the condition that $r > 1$, so that the appearance of negative area is not possible. The same also holds for the areas in which the values of K_{LL} (Fig. 2(c)) lie. The values of the function given by Eq. (4) are always positive (in view of the condition from Eq. (5)) and, as with K_W , always smaller than one.

Fig. 2 shows that there are obvious differences between K_H and other two criteria. In other words, there is a steeper change of K_H for a particular combination of parameters r and m . In this paper expressions for relative changes of K_H , K_W and K_{LL} were found, as well as how the relation of changes of r and m influences them. The particular influence of changes of r and m , in relation to the GS criteria mentioned above, is very complex. The mathematical analysis of this issue and the test using specific glassy systems is the topic of our paper [16].

As can be seen from Table 2, for the group of oxide glasses from [9], the condition given by the inequation (14) ($\Delta r > \Delta m$) holds. Therefore, the inequation (18) holds, too. In other words, the relative change of K_H should be greater than that of K_W and this greater than the change of K_{LL} . This is clear from the data of Table 2, calculated for these relative changes according to experimental data from [9], as well as from the histograms shown in Fig. 3(a).

Data presented in Table 2 for the group of oxide glasses from [8] show that the condition given by the inequation (14) is fulfilled for all the glasses except for PS and $M_2A_2S_5$. With these two glasses neither this condition nor the one given by the inequation (12) are satisfied.

This means that the relation of the relative changes of the GS parameters for these two glasses will hold the relation (24). Hence, with the PS and $M_2A_2S_5$ glasses, the greatest relative change will be for K_W , then for K_H , and for K_{LL} . With the other oxide glasses from this group, the relation of the magnitudes of change of GS parameters given by the inequation (18) will hold, since for them the condition (14) is satisfied.

The obtained values for these changes, presented in Table 2, and the histograms from Fig. 3(b), confirm our conclusion.

All the analyzed chalcogenide glasses do not fulfill the condition given by the inequation (14). For the glasses denoted as p.11 and p.17, the following inequation holds $\Delta m > \Delta r$. In contrast to the other glasses from this group, the values $\Delta r/r$ and $\Delta m/m$ for these two glasses do not satisfy the condition given by the inequation (12). Hence, for the relation of the magnitude of relative changes of GS parameters for glasses p.11 and p.17 the expression in (24) is true. This is also confirmed by the data for $\Delta K_W/K_W$, $\Delta K_H/K_H$ and

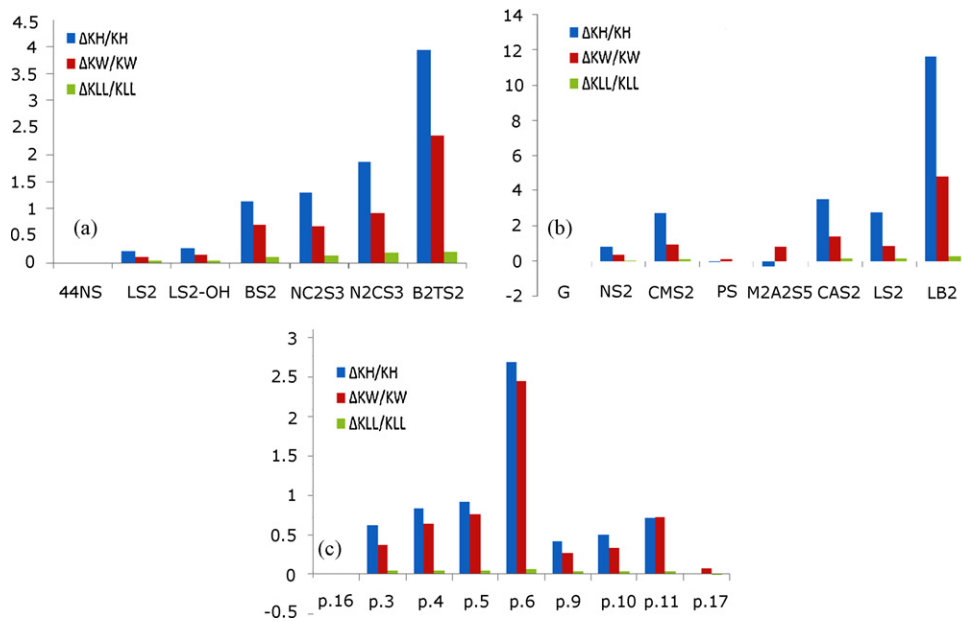


Fig. 3. Histograms of the relative changes of the K_H , K_W and K_{LL} parameters for oxide glasses from [9] (a), oxide glasses from [8] (b) and chalcogenide glasses from [25] (c).

$\Delta K_{LL}/K_{LL}$ given in Table 2, as well as by the histograms shown in Fig. 3(c), from which one can see that for these two chalcogenide glasses the following holds $\Delta K_H/K_H < \Delta K_W/K_W$.

It is also evident from Table 2 that the condition $\Delta r > \Delta m$ is not fulfilled for the glass p.6. However, for it as well as for all other analyzed chalcogenide glasses with the exception of p.11 and p.17, the condition in (12) holds. Since this weaker condition is quite sufficient, for all other chalcogenide glasses (with the exception of p.11 and p.17) it follows that $\Delta K_H/K_H > \Delta K_W/K_W > \Delta K_{LL}/K_{LL}$.

One of the results of our theoretical discussion in Section 2 is that the relative change of K_{LL} with respect to the changes of K_H and K_W has always the smallest value. Data in Table 2 and the histogram in Fig. 3 show that the change of the Lu–Liu parameter for the selected series of glasses was the smallest. The values $\Delta K_{LL}/K_{LL}$ are always smaller by almost one order of magnitude than the values of the relative changes of the other two parameters.

The entire testing of the relation of the magnitudes of the relative changes of the GS parameters for the two series of oxide glasses and one series of chalcogenide glasses shows full agreement with our theoretical predictions. In the theoretical derivation we showed that the relation between the magnitude of relative changes of T_c/T_g and T_m/T_g is reflected on the order of the relative changes of the GS parameters. By the testing on concrete glassy systems, this was fully confirmed.

The differences in relation to sensitivity of the GS parameters are significant when they are used to estimate the glass stability upon reheating. On the other hand, these results can be useful for linear fitting during the search of correlation between the critical cooling rate q and the GS parameters. As the results of the papers [8,15] show, there is a logarithmic dependency between q on one side and the GS parameters, on the other. Generally, this dependency can be shown as

$$\ln q = A + BK \quad (25)$$

there A and B are two constants with different values for the different GS parameters and the different glassy systems. When the logarithmic function is applied to the both sides of Eq. (25), it follows that

$$\ln K = \ln(\ln q - A) - \ln B \quad (26)$$

After differentiation, the result is:

$$\frac{dK}{K} = \frac{d(\ln q)}{\ln q - A} \quad (27)$$

As can be seen from the discussion above, the change of the K_{LL} parameter is the smallest. For this reason, it is obvious that the constant A in Eqs. (27) and (25) must have the greatest value for $K = K_{LL}$. For the given glassy system, the constant A in these equations will have smaller values, when K is equal to K_H or K_W . Our conclusion is in accordance with the results of linear correlation between $\ln q$ and K , which are presented in the following papers [8,15]. So, the free term in the logarithmic dependency of q with K_{LL} in [8] has the value 15.6, while with K_H is -3.03 and with K_W is -3.74 for coarse glasses. The corresponding values in the paper [15] are 17.7 for K_{LL} and 4.44 for K_W .

5. Conclusion

The K_H , K_W and K_{LL} parameters can be expressed using the reciprocal value of the reduced glass transition temperature (m) and the ratio of the crystallization temperature and glass transition temperature (r). The obtained expressions show that all three parameters are indirectly proportional to m . The K_W and K_{LL} are directly proportional to r , while the denominator as well as the numerator of K_H are linear dependent on r . Besides that, the number of variables by which these parameters are expressed is reduced from three to two. This enables the presentation of the GS parameters as a function of m and r in the form of 3D graphs.

Depending on the type of the relation between the changes of r and m with the different glassy systems, it is possible to predict the relation of relative changes of the Hruby, Weinberg and Lu–Liu parameters:

- If the condition $dr > dm$ is fulfilled, that is if $d(T_c/T_g) > d(T_m/T_g)$ holds, then it will always hold that $\Delta K_H/K_H > \Delta K_W/K_W > \Delta K_{LL}/K_{LL}$. Such relation of the relative changes of the GS parameters will also hold when a less stringent condition is satisfied, i.e. when $\Delta r/r > \Delta m/m$. It suffices that this condition is fulfilled in order to have such sequence of the magnitude of relative changes of the parameters K_H , K_W and K_{LL} .

- If the condition $\Delta r/r > \Delta m/m$ is not fulfilled, then the following relation of the relative changes of the GS parameters will hold $\Delta K_W/K_W > \Delta K_H/K_H > \Delta K_{LL}/K_{LL}$. In this case, the change of the Weinberg parameter will be greater than of the Hruby one, whereas the change of the Lu–Liu parameter will always be the smallest. This means that the Lu–Liu parameter is always the least sensitive one. This has the following consequence for value of the free term in the relations of the linear dependency between the logarithm of critical cooling rate $-\ln q$ and the GS parameters: If the linear dependency is in relation to the K_{LL} parameter, the corresponding free term will have the greatest value.

The testing carried out on two series of oxide glasses and one series of chalcogenide glasses showed full agreement with the results of our theoretical derivation.

Acknowledgements

This work has been carried out with the financial support of the Serbian Ministry of Science and Technological Development, within the project “*Amorphous and Nanostructural Chalcogenides*”, No. 141026.

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