

# Forty years of the Hrubý glass-forming coefficient via DTA when comparing other criteria in relation to the glass stability and vitrification ability

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**Abstract** The revision of the meaning of the famous Hrubý glass-forming coefficient (as well as of other analogous coefficients by, e.g., Weinberg and Lu–Liu) reveals some generalized correlations between glass-forming ability (GFA) and glass stability. The relative change of the Hrubý parameter is supreme in almost all cases. The Hrubý parameter is more sensitive in relation to the change of both the super-cooled region and the reduced glass-transition temperature. The only exception is the restricted sensitivity respecting the reciprocal reduced glass-transition temperature in some cases of the bulk metallic glasses. The correlation of the Hrubý coefficient with GFA is agreeable for oxide glasses and thus can be commonly employed as a reliable and precise glass-forming criterion. Associated problems are the experimental determination of relevant temperatures, most pertinent that for glass transition which is dependent to preparative condition of glass formation.

**Keywords** Glass transition · Reduced quantities · Hrubý criterion · Sensitivity · Glass-forming ability · DTA/DSC determination · Temperatures

## Introduction

In the 1960s, the former Institute of Solid-State Physics of the Academy of Sciences was one of the leading institutions in solid state physics within the so called Eastern socialist block then dominated by the former Soviet Union. They knew how to prepare super-pure single-crystalline as well as glassy Si and Ge, were capable of their various doping and even tackled the secrecy of transistor but did not realized its technical usefulness yet. The research turned then to the field of amorphous (mostly chalcogenide) semiconductors recognizing that the band gap does exist in spite of the absence of atomic long-range order and is not empty containing an appreciable amount of localized states but having its edges no more sharp. Transport band edges coincide with so called mobility edges where the mobility of carriers dramatically changes while the optical band gap is determined by the extrapolated absorption curve. It was discovered by Jan Tauc (1922–2010) [1, 2] who later immigrated to the US (Brown University, Rhode Island). His coworker Arnošt Hrubý (1919–) was technologist who synthesized and analyzed thousands of chalcogenide compounds and glasses and investigated their thermal behaviors [3, 4]. He proposed the evaluation of glass-forming tendency by means of DTA (lately known as the renowned Hrubý glass-forming criterion), which was published in a less known Czech journal of physics [4] even though having received up to now several hundreds of citations becoming the best cited paper in the journal history. Besides giving a tribute to the masterwork of Arnošt Hrubý, the purpose of this article is to revise the meaning and usefulness of Hrubý criterion in comparison with the other analogous coefficients and uncover some generalized correlations between glass-forming ability (GFA) and glass stability (GS).

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## Glass-forming ability and GS

Glass is a specific matter reflecting its original liquid makeup and can be prepared by a suitable freeze-in of various, even non-stoichiometric, combinations of elements/compounds. Such a disordered matter still presents stringent conceptual difficulties [5–9]. The often confused concepts of amorphous and glassy states have recently been re-examined and previous attempts to trace the distinction revised [5, 6]. Currently, Queiroz et al. [7] considered thermodynamic aspects of glasses focusing to their behavior in glass-transition region (GTR). Suñol et al. [8] examined phenomenological and atomic methods by which glass transition can be described. This new generic and phenomenological approach describes the kinetics and thermodynamics of vitrification as a real non-equilibrium process. Volume and enthalpy relaxation in the GTR was analyzed by Svoboda et al. [9]. The finding that the activation energy of viscous flow in the glass-transition range was identical with the effective activation energy for relaxation process. This subject received abundant number of citation responses [10].

Parameters predicting the GFA and consequent GS of its constrained state (of freeze-in glass) are of a substantial meaning to all those interested in various applications to which glassy materials lend themselves. A *time–temperature–transformation* diagram for material annealing can provide all necessary data, but such data are rarely available and moreover are often predicted on the assumption of homogeneous nucleation, which is a rather unlikely event in practice. When a glassy matter turn out to be experimentally accessible upon a suitably fulfilled melt quenching (*critical cooling rate*,  $R_c$ ) from its *melting point* ( $T_m$ ) through the GTR [11, 12] (defined by the mean *glass-transition temperature*,  $T_g$ ), certain data became accessible for such a material identification. A liquid with good GFA exhibits a low value of  $R_c$  for the glass formation which, however, has remained a long-standing question as to why one liquid exhibits better GFA than another and how we can portray it.

According to the standard nucleation theory, a liquid with a high viscosity between  $T_g$  and  $T_m$  typically exhibits a high GFA with a low  $R_c$ . Since the viscosity of oxide glasses at  $T_g$  is nearly constant ( $\cong 10^{12}$  Pa s) [13], it was postulated that a high value of the *reduced glass-transition temperature*,  $T_{rg}$  ( $=T_g/T_m$ ), would result in a high viscosity in the undercooled liquid state, and, consequently, lead to a low  $R_c$ . Zanotto [14, 15] showed that glass tendency to homogeneous and heterogeneous nucleation can be distinguished on bases of  $T_{rg}$ . Cabrall et al. [16] pointed out that the maximum homogeneous nucleation rates,  $I_{max}$ , of silicate glasses strongly diminish with  $T_{rg}$  and that  $R_c$  for metallic glass formation also drops with rising  $T_{rg}$ . Correlation between maximum growth rates and  $T_{rg}$  for silicate glasses was shown by Fokin et al. [17, 18].

Significantly before the development of any generalized nucleation theory for condensed systems, Tammann [19, 20] called attention to a tendency revealing that the higher the melt viscosity at the melting temperature ( $T_m$ ), the lower its crystallizability. Qualitatively, this tendency can be explained by an increased inhibition of motion or molecular rearrangement of the basic units of any melt with increasing viscosity. Mentioned by Kauzman [21] but particularly stated by Turnbull [22], who early indicated that when  $T_{rg}$  is larger than 2/3, the homogenous crystal nucleation will be essentially suppressed due to the sluggishness of the crystallization kinetics. Therefore,  $T_{rg}$  became the earliest criterion to evaluate GFA of a liquid. However, experimental observations indicated that  $T_{rg}$  may fail to truthfully predict GFA in various cases, often documented by conventional relationships between  $R_c$  and  $T_{rg}$  for different sort of glasses, where some good glass formers show a low  $T_{rg}$  and vice versa. Referring to a large set of available experimental data obtained for nucleation of several silicate glasses, Zanotto [14] concluded that glasses having  $T_{rg}$  higher than  $\sim 0.58$ – $0.60$  display only surface (mostly heterogeneous) crystallization, while glasses showing volume (homogeneous) nucleation have  $T_{rg} < 0.58$ – $0.60$ . The reduced glass-transition temperature was examined in more details by Sakka and Mackenzie [23], Uhlmann [24], and for metallic glasses also by Davis [25]. Determination of theoretical values of reduced temperatures were approached by Angell [26] based on extension and extrapolation by means of application of the *Vogel–Fulcher–Tammann* (VFT) viscosity equation. Šesták [27] dealt with a greater augmentation of reduced quantities, such as a difference between liquid and crystalline heat capacities  $\Delta C_{pr}$ , and tried to estimate approximate changes of entropy  $\Delta S_r$ , enthalpy  $\Delta H_r$  and chemical potential  $\Delta \mu_r$  assuming the values  $T_{or}$  and  $T_{rg}$ . ( $T_{or}$  is the reduced Kauzman temperature).

In order to unify notations, which use to vary in the cited papers, the following text will employ  $T_x$  to denote the *onset crystallization temperature* and  $T_c$  to indicate the *peak crystallization temperature*, which is convenient today. Let us also remind that GFA is noticeably related to the ease of the reverse process of devitrification related to the difference between temperatures of re-crystallization and glass transition.

However, other parameters can be included, which can be comfortably monitored by DTA/DSC upon certain precautions (glass heating, etc.). It can provide a choice of data about the non-equilibrium *glass crystallization temperature* laying customary below that for an analogous melt. Then the interval between  $T_m$  and  $T_c$  (and  $T_x$ ) is inversely proportional to GFA and the interval between the onset of crystallization  $T_x$  and  $T_g$  is directly entitled to display GFA. A range of examples revealed that this

difference vary habitually with composition changes and tends to reach its maximum value in a composition range which appears to provide “best/optimum” glasses.

Even a more sensitive interrelation to the glass formation peculiarities can be found on a basis of the widespread Hrubý parameter [4], developed mostly for chalcogenide systems [28], which are typically available only upon physical preparation of a given type of glass. This criterion [3, 29, 30] has an almost matching implication as the difference  $(T_x - T_g)$  alone varying, however, more rapidly when crystallization peak is shifted and taking also into account ease of melting. This factor may not be of a particular significance as the values of  $T_g$  and  $T_m$  are usually correlated [29–31]. A wider applicability of  $K_H$  was discussed by Thornburg [31].

In the recent years, various GS parameters related to the three characteristic temperatures have been investigated. Table 1 contains some popular GS parameters.

Aware that the potential correlation between GS and GFA is of a great importance, this issue became the subject of various theoretical studies as well as of assorted experimentation.

For example, Weinberg [43] made use of the standard theoretical expressions for crystal nucleation and growth rates considering homogeneous nucleation and screw dislocation growth in stoichiometric glasses. In his paper [43], the trends in GFA and GS were compared with systematic changes in the melting entropy,  $\Delta S_m$ , and the viscosity parameters. The resulting conclusion was that GFA and GS, defined by  $(T_c - T_g)/T_m$ , were poorly related [43]. In a subsequent work, Weinberg [33] derived the time necessary for crystallization of a minimum detectable fraction based again on a classical homogeneous nucleation and screw dislocation growth. Worth mentioning are *time criteria* used to assess GFA and test the reliability for two particular GS parameters, given by the expressions:  $(T_x - T_g)/T_m$  and  $(T_x - T_g)/(T_c - T_x)/T_m$ . Weinberg [43]

**Table 1** Some GS parameters based on the characteristic temperatures specified in the text

GS parameter	Envisaged by
$K_H = (T_x - T_g)/(T_m - T_x)$	Hrubý [4]
$K_{SP} = (T_c - T_x) \cdot (T_x - T_g)/T_g$	Saad and Poulain [32]
$K_W = (T_c - T_g)/T_m$	Weinberg [33]
$K_{LL} = T_c/(T_g + T_m)$	Lu and Liu [34, 35]
$\gamma_m = (2T_x - T_g)/T_m$	Du [36]
$\phi = T_{rg}(AT_{xg}/T_g)^a$	Fan [37]
$\omega = T_g/T_c - 2T_g/(T_g + T_m)$	Long [38]
$\beta = T_x T_g / (T_m - T_x)^2$	Yuan [39]

Some unusual criteria you can find in [40–42] involving extra kinetic factors [40, 41] or a contrary interpretation in terms of glass state safeguarding [43]

calculated these data and found that the stability of glasses having parallel viscosity curves  $\eta(T)$  could be qualitatively evaluated according to the two above expressions, but they were not quantitatively reliable and none of them appears to be superior. Moreover, the paper also discloses that for glasses for which  $\eta(T)$  significantly differs from each other in the region of  $T_g$  the stability criteria can become delusive.

### Determinability of glass-transition temperature

Glasses as an important domain of a generalized disordered matter still present experimentally stringent conceptual and thermodynamic difficulties. It was recently reexamined by Wunderlich [44] who revealed that in a continuous random web of a macromolecular system (which can properly model a glass); the network can be a single amorphous phase, mesophase, molecularly coupled multiphases of different degrees of order and metastability or even a modulated crystal-like structure (liquid or plastic crystals) [45].

Different state of a similar network (such as silicate quenched melts and/or solution prepared polysialates) may show a range of glass-transitions processes observable even at a simultaneous manner. Perceptible values needed for a correct recognition of the phase transitions lies in the fact that materials must be pliable for being prepared into its final shape and then experimentally measurable (often by means of DTA/DSC), which involves lot of experimental variability and associated uncertainty. Therefore, the determination of glass-forming criteria requires sustaining certain precautions and data standardizations. There are numerous publications discussing the theme, e.g., [46–49].

However, the best analysis was shown by studies of Illekova [50–54] who separated various influences in alienated areas emphasizing that in metallic glasses the measured  $T_g$  is habitually lower than the true thermodynamic  $T_g$  while for other oxide or chalcogenide glasses, the true  $T_g$  depends also on the inherent fragility of sample glass. Moreover,  $T_g$  of metallic glasses is often affected by aging of glass even at room temperature. There is also an obvious difference for  $T_g$  obtained for either during cooling and heating, moreover for some cases is sketched by mere estimation.

There is a common correlation of both kinetic processes of structural relaxation and crystallization. Nevertheless, the crystallization kinetics is of two major types (JMAYK and NGG) and may contradictory affect the peak position, namely any thermal annealing may shift the exothermic crystallization peak opposite, i.e., to higher temperatures for the classical nucleation-growth (JMAYK) and contrary to, lower temperatures for NGG. Therefore, any thermal

treatment must be avoided during the determination of glass-forming coefficients unless the study is aimed to the resolution of nucleation/growth rates [55–60].

Staying power of individual criteria evidently depends on a correct determination of characteristic temperatures and further more detailed analysis falls beyond the subject of this communication.

### Expressing the Hrubý parameter using temperature relations normalized to $T_g$

After Weinberg's paper [43], Cabral et al. [61] brought into play experimental values and found a correlation between the Hrubý parameter of GS and GFA. However, these results [61] were somehow contradictory in relation to the theoretical calculations of Weinberg [43]. Extending these calculations, Avramov et al. [62] decided to test out these two approaches upon examining different assumptions, which were supported by experimental data. The paper [62] demonstrated that GFA and GS follow the same trend and are directly related to each other.

Several other considerable studies have appeared, which inveterated correlation between the GS parameters and critical cooling rate  $R_c$ , or between the GS parameters and maximum section thickness, i.e., the diameter  $D_{\max}$ , by which the GFA are also estimated [34, 36–39, 63–65]. In the papers [34, 62, 64, 66], a rather good correlation is shown between GFA and GS parameters, which are based on the three characteristic temperatures such as the Hrubý ( $K_H$ ), Weinberg ( $K_W$ ), and Lu–Liu ( $K_{LL}$ ) criteria. Nascimento et al. [64] proved that for the oxide glasses a very good correlation between the Hrubý parameter and GFA exists. Also, very good correlation between  $K_{LL}$  and GFA has been found for the oxide glasses from [64] and for those from [67]. However, the parameters  $R_c$  and  $D_{\max}$  are hard to measure in a sufficiently precise way [35, 38, 39, 66–69] so that of essential importance become the correlations between GFA and GS expressed via characteristic temperatures [61–69]. These temperatures are usually determined by DTA/DSC [3, 30, 37]. A satisfactory degree of correlation between the determined GS parameter and  $R_c$  (or  $D_{\max}$ ) would allow one to use the given GS parameter to assess GFA.

In spite of the criteria discussed above approachable through the three characteristic temperatures, the entire reduced glass-transition temperature shows a weaker correlation with GFA. The work of Nascimento [64] proves that  $T_{rg}$  has a reduced correlation with GFA for oxide glasses than  $K_H$ ,  $K_W$ , and/or  $K_{LL}$ . Furthermore Lu and Liu [34, 35] showed that  $T_{rg}$  had the weaker correlation with GFA than their criterion  $K_{LL}$  for glasses analyzed in [34].

This is the reason why we shall analyze the individual criteria in more detail respecting the three characteristic temperatures and mentioning assessment in the paper [39], which stresses that GS parameters (estimating GFA) should be enough sensitive. The larger the values of the  $K_H$ ,  $K_W$ , and  $K_{LL}$  the higher is stability of a glass against devitrification [4, 62]. Also, when comparing one glass to another, it is essential to know how large the relative changes of the given parameters are and how they can be compared with the relative change of other GS. In other words, it is necessary to distinguish which of the GS parameters shows the fastest change.

Our starting point is the fact that all the criteria,  $K_H$ ,  $K_W$ , and  $K_{LL}$ , include the same characteristic temperatures. For this reason, we can express them in a somewhat different way based on the intact ratios of the temperatures, namely  $m = T_m/T_g$  and  $r = T_c/T_g$ . In doing so, we assume that in defining both  $K_H$  and  $K_{LL}$  it is possible to replace onset crystallization temperature  $T_x$  with maximum crystallization peak temperature  $T_c$  as was shown in the paper by Nascimento [64]. After simple mathematical transformations [70], one obtains relations  $K_H = (r - 1)/(m - r)$  and  $K_W = (r - 1)/m$  and  $K_{LL} = r/(m + 1)$ .

By using the substitutions of  $r$  and  $m$ , the GS parameters can be expressed indirectly by means of both the reduced glass-transition temperature  $T_{rg}$  and the super-cooled region  $\Delta T_{xg}$ . It is because the parameter  $m$  factually represents the reciprocal value of  $T_{rg}$ , and the parameter  $r$  correlates to  $\Delta T_{xg}$ , as was shown in the work of Lu and Liu [34], Mondal [71], or in a recent work by Zhang et al. [72]. Namely, in order to enable the comparison for different glasses, the value of the super-cooled region is divided by  $T_g$  [34], which gives  $(T_x - T_g)/T_g = r - 1$ . Mondal et al. [71] used the same normalization and proposed that  $T_x/T_g$  (in our cases  $r$ ) can also be considered as a measure of the thermal stability of glass. In [72], Zhang et al. introduced the factor of crystallization resistance  $T_g/(2T_x - T_g)$ , which can be auxiliary expressed as  $1/(2r - 1)$ . From a mathematical point of view, the introduction of the ratios  $r$  and  $m$  allows the reduction of 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  $m$ ) acting as independent variables.

### Relative changes of GS parameters

In order to derive expressions for the relative changes of these parameters, as shown in our previous paper [70], we first employ logarithms of the expressions for  $K_H$ ,  $K_W$ , and  $K_{LL}$  and then make differentiation

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

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

It is necessary to point out that we assume the following relations hold for  $m > 1, r \geq 1, m > r$ .

By comparing the right hand side expressions in Eq. 1 [70], it holds that if the condition  $dr > dm$  is fulfilled, i.e., if  $d(T_c/T_g) > d(T_m/T_g)$  is satisfied, then the following relation keeps continuously valid  $dK_H/K_H > dK_W/K_W > dK_{LL}/K_{LL}$ .

Such a relation of the relative changes of the GS parameters will also hold when a less stringent condition is satisfied, i.e., when  $dr/r > dm/m$ . If the condition  $dr/r > dm/m$  is not fulfilled, then the following relation of the relative changes of the GS parameters will maintain:  $dK_W/K_W > dK_H/K_H > dK_{LL}/K_{LL}$ . As it can be seen, the relative change of the Lu–Liu parameter will always have the smallest value, and will never become greater than the relative change of the Hrubý parameter. The above theoretical derivations were successfully tested on two series of oxide glasses and one series of chalcogenide glasses [70] showing a good agreement with the theoretical results.

The next step was to establish a relation between the maximal value of relative changes of the Hrubý, Weinberg, and Lu–Liu parameters. In order to obtain the maximal value of relative changes notice that the minus signs in expressions (1) should be replaced by the plus ones, because for maximal change we should assume that all changes have the same direction. Thus, we obtain

$$\left(\frac{dK_H}{K_H}\right)_{\max} = \frac{dr}{r-1} + \frac{dm}{m-r} + \frac{dr}{m-r} \left(\frac{dK_W}{K_W}\right)_{\max}$$

$$= \frac{dr}{r-1} + \frac{dm}{m} \left(\frac{dK_{LL}}{K_{LL}}\right)_{\max} = \frac{dr}{r} + \frac{dm}{m+1}$$

After comparing right hand side of expressions in Eq. 2, the following relation between the maximal values of relative changes keeps up [73]

$$\left(\frac{dK_H}{K_H}\right)_{\max} > \left(\frac{dK_W}{K_W}\right)_{\max} > \left(\frac{dK_{LL}}{K_{LL}}\right)_{\max} \quad (3)$$

The relation between maximal relative changes of GS parameters (cf. Eq. 3) has been tested on several series of oxide glasses from [64] and chalcogenide glasses from [74, 75].

The glass having the largest value of  $r$ , that is the largest  $T_c/T_g$  ratio, was selected as reference one, with respect to which we calculated the differences. From these results, it follows that for the considered glasses the relation between the maximal relative changes of GS is in accordance with Eq. 3. It is worth accentuating that the maximal relative change of the Hrubý parameter  $K_H$  subsist the greatest upshot.

### Sensitivity of the glass-stability parameters to the changes of temperature ratios

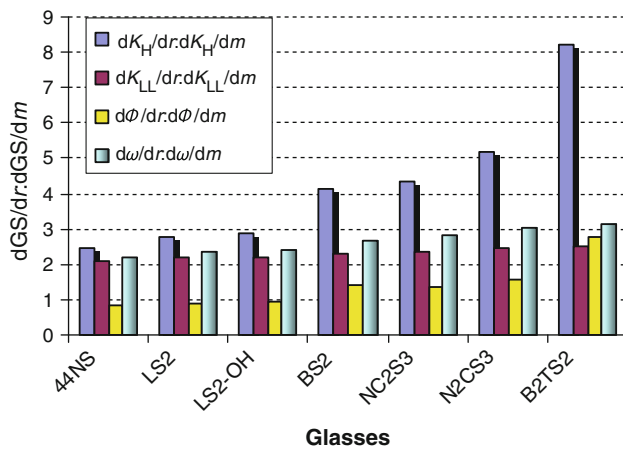
The next objective was to find out how these GS parameters are sensitive to the changes of  $r$  and  $m$ , and whether this is reflected on the correlation of the given parameter with the GFA. Besides the  $K_H$  and  $K_{LL}$ , the newly defined parameters  $\phi$  [37], and  $\omega$  [38], showed also a rather good correlation with GFA for a variety of glasses [37–39]. Thus, it is necessary to include them in our analysis. Simple transformations of the expressions by which they have been introduced allow us to express the parameters  $\phi$  and  $\omega$ , using ratios  $r$  and  $m$ , instead of using the characteristic temperatures [70]. Thus,  $\phi = (r - 1)/m$  and  $\omega = 1/r - 2/(m + 1)$ . In order to determine the change of the investigated GS in relation to  $r$  and  $m$ , we take the derivatives of expressions for  $K_H, K_{LL}, \phi$ , and  $\omega$  with respect to both values of  $r$  and  $m$ . On this way, for  $K_H$  is obtained  $dK_H/dr = (m - 1)/(m - r)^2$  and  $dK_H/dm = -(r - 1)/(m - r)^2$ . The analogous expressions for changing  $K_{LL}, \phi$ , and  $\omega$  in relation to  $r$  and  $m$  can be found in [76].

The individual partial sensitivity of the GS parameter to  $r$  and  $m$  is, however, not related to the  $R^2$  coefficient for the correlation of the GS parameter and GFA [76]. The balance of sensitivity of the GS parameter to  $r$  and  $m$ , (i.e., the ratio  $dGS/dr:dGS/dm$ ) implies the magnitude of the  $R^2$  coefficient. At the same time, the degree of correlation of values  $r$  and  $m$  with the GFA is significant.

Results of the above theoretical derivation were tested on series of oxide glasses. The characteristic temperatures  $T_g, T_c$ , and  $T_m$  were taken from the work of Cabral et al. [65] for the following seven oxide glasses:  $Li_2O \cdot 2SiO_2$  (LS<sub>2</sub>);  $Na_2O \cdot 2CaO \cdot 3SiO_2$  (NC<sub>2</sub>S<sub>3</sub>);  $2Na_2O \cdot CaO \cdot 3SiO_2$  (N<sub>2</sub>CS<sub>3</sub>);  $BaO \cdot 2S_2O_2$  (BS<sub>2</sub>);  $LiO_2 \cdot 2SiO_2$  with 0.2% mol OH (LS<sub>2</sub>OH);  $2BaO \cdot TiO_2 \cdot 2SiO_2$  (B<sub>2</sub>TS<sub>2</sub>), and  $0.44Na_2O \cdot 0.56SiO_2$  (44NS).

Figure 1 shows the ratios  $dGS/dr:dGS/dm$  that we calculated for these oxide glasses.

As it can be seen from Fig. 1, the values of the ratios  $dK_H/dr:dK_H/dm, dK_{LL}/dr:dK_{LL}/dm$  and  $d\omega/dr:d\omega/dm$  are always greater than one. This means that  $K_H, K_{LL}$ , and  $\omega$  are more sensitive to the change in relation to  $r$  than to the change in relation to  $m$ . For  $K_H$ , this is easy to predict by comparing the appropriate expressions above. We take the characteristic temperatures and values for critical cooling rate from [65] and calculate the values of GS parameters as well as the values of  $R^2$  factors in correlation with critical cooling rate for mentioned oxide glasses. The higher the  $R^2$  value, the better the correlation between GS parameter with critical cooling rate. With the analyzed oxide glasses,  $r$  correlates well ( $R^2 = 0.900$ ), whereas  $m$  does not correlate with GFA. Since only  $r$  (and not  $m$ ) correlates satisfactorily, it can be supposed that for  $K_H, K_{LL}$ , and  $\omega$  the  $R^2$

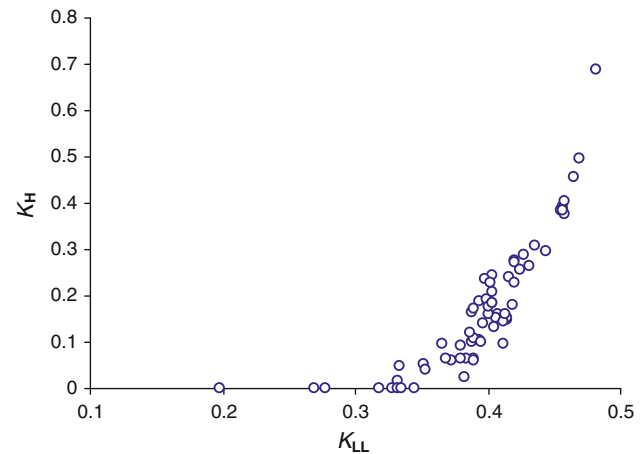


**Fig. 1** Ratios  $dGS/dr:dGS/dm$  ( $GS = K_H, K_{LL}, \phi, \omega$ ) for oxide glasses using abbreviation for  $0.44\text{Na}_2\text{O}\cdot 0.56\text{SiO}_2$  (44NS);  $\text{Li}_2\text{O}\cdot 2\text{SiO}_2$  (LS<sub>2</sub>);  $\text{LiO}_2\cdot 2\text{SiO}_2$  with 0.2% mol OH (LS<sub>2</sub>OH);  $\text{BaO}\cdot 2\text{SiO}_2$  (BS<sub>2</sub>);  $\text{Na}_2\text{O}\cdot 2\text{CaO}\cdot 3\text{SiO}_2$  (NC<sub>2</sub>S<sub>3</sub>);  $2\text{Na}_2\text{O}\cdot \text{CaO}\cdot 3\text{SiO}_2$  (N<sub>2</sub>CS<sub>3</sub>); and  $2\text{BaO}\cdot \text{TiO}_2\cdot 2\text{SiO}_2$  (B<sub>2</sub>TS<sub>2</sub>)

coefficient of correlation with GFA will be larger, because the value of  $r$  has a greater influence than  $m$ . But for  $\phi$ , the influence of  $m$ , which does not correlate with GFA, is significant. Hence, one can expect that  $R^2$  for  $\phi$  is smaller than for  $K_{LL}$ ,  $K_H$ , and  $\omega$ . This was confirmed by our calculation of  $R^2$  obtaining the following values:  $K_H = 0.829$ ,  $K_{LL} = 0.759$ ,  $\omega = 0.784$ , and  $\phi = 0.649$ . These  $R^2$  factors are smaller from the ones obtained for oxide glasses which we investigated in [76], but the tendency of changes of correlation of GS parameters in relation to critical cooling rate is similar. The difference between oxide glasses in [76] and in this analysis is that  $K_H$  has the best correlation with  $R_c$ . Also, in this analysis (as a difference from [76]), values of  $dGS/dr:dGS/dm$  are always the biggest for  $K_H$  if we compare these relations for  $K_H$ ,  $K_{LL}$ , and  $\omega$ .

In this article, we will look (only from the mathematical point of view), what occurs when the  $r < 1$  ( $T_g > T_x$  in the ribbon form of metallic glasses). From above expressions, it easily follows that in this case  $dK_H/dr > dK_H/dm$  too. When comparing the values of  $dGS/dr$  and  $dGS/dm$  for parameters  $K_{LL}$ ,  $\omega$ , and  $\phi$ , for which expressions are given in [76], it follows that  $dK_{LL}/dr > dK_{LL}/dm$ ,  $d\omega/dr > d\omega/dm$  and sometimes  $d\phi/dr < d\phi/dm$  in the case that  $r < 1$  as well as when  $r > 1$ .

By simple transformation the Hrubý parameter  $K_H$  can be expressed through  $K_{LL}$ , thereby obtaining that  $K_H = \frac{(r-1)K_{LL}}{r-(r+1)K_{LL}}$ . As was shown in our paper [77], between  $K_{LL}$  and some others GS parameters, there exists a linear dependence with a very high  $R^2$  factor. It is evident from above expression that  $K_H$  are not linearly related to  $K_{LL}$ . As an example, Fig. 2 shows that  $K_H$  is not linearly related to  $K_{LL}$ , for BMGs from [38]. The value of  $R^2$  factor for the correlation of  $K_H$  with GFA for tested BMGs (0.630) is



**Fig. 2** Correlation between the Hrubý parameter  $K_H$  and parameter  $K_{LL}$  for BMG bulk metallic glasses, adjusted from [38]

significantly different from those of the linear connected  $G$ -criteria for tested glasses. This does not mean that  $K_H$  do not show good correlation with GFA, in cases for example, for oxide glasses.

## Summary

All the results discussed above show that the initially proposed Hrubý criterion [4] is one of the best parameters at all. As can be seen from the theoretical derivations, the relative change of the Hrubý parameter  $K_H$  is the greatest in almost all cases, and the maximal value of the change of the Hrubý parameter occur the greatest too. Also, the correlation of the Hrubý parameter with GFA is very apposite considering oxide glasses.

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