

Estimation of Glass-Forming Ability and Glass Stability of Lithium-Borosilicate Glasses

D.B.Thombre

Associate professor, Dept of Physics, Jagdamba Mahavidyalaya, Achalpur city, India

ABSTRACT: The structural theory of Glass Forming Ability was proposed with three new conditions; Electronegativity, Hardness, Softness and Orbital potential energy difference. Glass forming ability (GFA) and glass stability (GS) parameters are analyzed from Lithium-borosilicate ternary glass system. Amorphousness was investigated by Differential Scanning Calorimetry (DSC) and X-ray diffractometry (XRD). Differential Scanning Calorimetry was used to study the parameters K_H , K_w , K_{LL} , K_T , K_2 , K_3 and parameters like β , δ , γ and γ_m , are one of the most reliable and applicable GFA parameter has been established. The glass stability parameter γ_m shows an excellent correlation with Glass Forming Ability. Parameters are formulated by different combinations of temperatures. The dependence of characteristic temperatures (T_g), onset crystallization temperatures (T_x) and mid point temperatures (T_m). Good correlations between parameters are found implying a low frequency of homogeneous nucleation in the thermally stable glasses. Statistical correlation factor $R^2 = 0.999$. The results presented herein demonstrate that GS and GFA are indeed related concepts.

KEYWORDS: Glass-forming ability parameter, bulk metallic glasses, Criterion; Thermal analysis, Glass stability; Sensitivity; Super cooled region; Reduced glass transition temperature.

I. INTRODUCTION

The ability of substances to vitrify on cooling from the melt is known as glass-forming ability (GFA) and is the object of theoretical and experimental investigations. Structural and kinetic methods have been proposed to understand GFA. The first structural methods were proposed in the 1920s. Latter on the proposed theories:

- (1) Tamman^[1] according to kinetic concepts, glasses are formed when the nucleation rate versus temperature.
- (2) Goldschmidt^[2], Zachariasen^[3], explains the ratio of ionic radii for glass forming oxides.
- (3) Zachariasen-Warren^[4] claimed, glasses are easily forms polyhedral groups.
- (4) Dietzel, Stanworth^[5-8], included the influence of the interaction of forces between cations and anions by introducing the term field strength F.
- (5) Smekal Stanworth^[9], explains the bonding in E_xO_y oxide.
- (6) Sun's^[10], according to him in the glass forming oxides having single bond strength greater than 90 Kcalmol⁻¹ and modifiers have bond-strength less than 60Kcal mole⁻¹.
- (7) Viscosity, the viscosity of the glass melt can be as high as 10²³ Poise. Generally, viscosity of the glass forming element must lie in the range 10⁵ to 10⁷ poise.
- (8) Dietzel and Wiekert^[11], considered stability against crystallization and how this depends on the crystal growth rate.
- (9) Turnbull and Cohen^[12], they proposed their approach implies an infinitely fast growth rate.
- (10) Gutzow^[13], studied the related glass stability (GS) to the non-steady-state time lag, τ .
- (11) Uhlmann^[14], A kinetic criterion for vitrification; and then extended the kinetic theory of glass formation to include non-steady state effects and heterogeneous nucleation.
- (12) Weinberg^[15,16,17], He found that both GFA and GS increased with an increase of DSm and T_0 ; however, GFA and GS moved in opposite directions (decrease of GFA and increase of GS) with an increase of E From results, Weinberg concluded that GFA and GS are ill-related concepts and Recently
- [13] D.B.Thombre^[18], Introducing three atomistic conditions on the basic of the current study which correlate to, nature of electronegativity, absolute hardness, absolute softness and Orbital potential energy difference. These

International Journal of Innovative Research in Science, Engineering and Technology

(A High Impact Factor, Monthly Peer Reviewed Journal)

Vol. 5, Issue 1, Januray 2016

three conditions can help in having better insight of the process of glass formation. These atomistic conditions are explained as below:

(I) The electronegativity:

(i) The electronegativity of glass forming elements lie in the range 1.916 to 2.253. All other elements in periodic table have either smaller or larger values than these and so they do not fall in the category of glass formers; electronegativity difference with respect to oxygen lie in the range 1.357 to 1.694 in Pauling units respectively. (ii) The electronegativity of glass modifier elements lies in the range 0.706 to 0.912. All other elements in periodic table have electronegativity above 1. Hence, they are not glass modifiers; and electronegativity difference with respect to oxygen lies in the range 2.698 to 2.904 in Pauling units respectively.

(II) The absolute hardness & absolute softness:

(i) The absolute hardness and absolute softness of the glass former element lie between 3.107 to 4.869 eV & 0.205 to 0.321 eV respectively. (ii) The absolute hardness and absolute softness of the glass modifier element lie between 1.845 to 2.387 eV & 0.419 to 0.542 eV respectively. When glass formers having smaller softness value combine with modifiers having larger hardness value then only bond between them break and amorphous material is formed, which possess electrical conductivity. Lithium modifier has least softness value, than sodium and potassium are therefore, no larger breaking of bonds is possible. This way the conductivity of its alloys increases as compared to alloys that are made up of either sodium or potassium and;

(III) Orbital potential energy difference:

Orbital potential energy difference in glass forming element with oxides are lie between, 5.75 to 9.19 eV. Where as in conditional glass former lie between 5.34 to 10.55 eV. The aim of this article is, therefore, to investigate a possible correlation between GFA and GS. GFA and GS are investigated in systems that undergo homogeneous and heterogeneous nucleation. From this discussion it evident those in addition to the till date existing conditions of glass former as the outcome of the present work.

II. GLASS STABILITY PARAMETERS

There are several parameters regarding glass stability on heating. Turnbull^[19] proposed a classical parameter based on the nucleation theory and used K_T as a criterion for glass formation as the avoidance of a single nucleation event which is the ratio of reduced glass transition temperature T_g to the melting point temperature or mid temperature T_m .

$$K_T = \frac{T_{rg}}{T_g} = \frac{T_g}{T_m} \quad (1)$$

it is also called as reduced glass transition temperature (T_{rg}). A high value of reduced glass transition temperature would result in a high viscosity in the under-cooled liquid state and consequently lead to a low critical cooling rate (R_c). According to Zanotto^[20] glass having reduced glass transition temperature (T_{rg}) higher than or in the range 0.58-0.60 display only heterogeneous crystallization, where as lying below the range 0.58-0.60 display homogeneous nucleation. Earlier, Kauzmann^[21] had also mentioned the significance of this same ratio. On the basis of thermal stability associated with the glass transition temperature (T_g), and onset (T_x) crystallization temperature Inoue et.al.^[22,23] gave a another glass-forming ability indicator.

$$K_2 = \frac{\Delta T_x}{T_x - T_g} = \frac{T_x - T_g}{T_m} \quad (2)$$

The temperature difference $T_x - T_g$ is a good indication of thermal stability because the higher the value of this difference, more the delay in the nucleation process^[24]. It is also denoted by ΔT_x . Latter on Weinberg^[25] was introducing another parameter, know as Weinberg parameter K_W or also denoted by ϕ .

$$K_W = \phi = \frac{(T_x - T_g)}{T_m} \quad (3)$$

where, T_x is onset temperature and T_m is melting point temperature or mid temperature. Hruby^[26] suggested a Glass-forming ability parameter as ($K_H = K_{gl}$) is also used as a measure of glass-forming tendency given by,

$$K_H = K_{gl} = \frac{(T_x - T_g)}{(T_m - T_x)} \quad (4)$$

International Journal of Innovative Research in Science, Engineering and Technology

(A High Impact Factor, Monthly Peer Reviewed Journal)

Vol. 5, Issue 1, Januray 2016

$$K_{LL} = \gamma = T_x / (T_g + T_m) \quad (5)$$

which was analyzed for 49 metallic glasses, 23 oxide glasses and 25 cry protective aqueous solutions, showing reasonable, but not excellent, correlations with the respective critical cooling rates obtained by different methods and several authors, it is also called as γ parameter. Larger values of K_H , K_w and K_{LL} parameters imply higher stability of glass in respect to devitrification. Glass Stability Parameters proposed by Nascimento et al. [31] are

$$K_1 = \frac{T_m - T_g}{T_m} \quad (6)$$

$$K_3 = T_x / T_m = \alpha \quad (7)$$

Angell [32] was the first to suggest that $K_2 (\Delta T_x)$ is a good indicator of GS. Drexhage et al. [33], Almeida and Mackenzie [34], Cooper and Angell [35] also reached similar conclusions. With the GFA of various glass formers among the parameters suggested so far are,

α - Parameter: α - parameter can be expressed as:

$$\alpha = T_x / T_m \quad \text{OR}$$

$$\alpha = \Delta T_x / T_m + T_g / T_m = (T_x - T_g) / T_m + T_g / T_m = K_w + K_T = GS + GFA \quad (8)$$

i.e. α includes glass stability and glass forming ability.

β - Parameter: β - Parameter is expressed as:

$$\beta = \left[(T_x / T_g) / (T_g / T_m) \right] \quad (9)$$

γ_m - Parameter: γ_m - Parameter is expressed as:

$$\gamma_m = (2T_x - T_g) / T_m \quad (10)$$

γ_m and K_H has the same trends as that of GFA i.e. as ΔT_x and that of T_{rg}

δ - Parameter: δ - Parameter is defined as,

$$\delta = T_x / (T_m - T_g) \quad (11)$$

III.1 EXPERIMENTAL

A series of glass samples of $[42.5 \text{ LiO}_2 + (57.5-x) \text{ B}_2\text{O}_3 + x \text{ SiO}_2]$, where $x = 0, 5, 10, 20$ & 30 mol % and were prepared (Table III.1) by using raw materials all of these are chemically pure and were finally pulverized. The homogeneous mixture was melted in porcelain crucible in an electrically programmable heated furnace, type UAF 15/10 Lenton thermal Designs, equipped with automatic temperature controller. The samples were melted at about $(1100 \pm 20)^\circ\text{C}$ for two hours with heating rate $30^\circ\text{C}/\text{min}$. The molted material were quenched in air and poured at room temperature between two steel plates. The quenched samples were annealed at 300°C for 20 min. The as-made glasses were immediately stored in vacuum desiccators until used for measurements. The samples were examined by X-ray diffraction confirms the amorphous nature of the investigated glass samples. The measurements were carried out using different techniques: (1) Glass density measurements were made at room temperature using the standard "Archimedes principle" with toluene as the immersion fluid of stable density ($0.866 \text{ g}/\text{cm}^3$). The experimental error was about $\pm 0.003 \text{ g}/\text{cm}^3$. (2) The molar volume $[V_m]$ was calculated from molecular weight $[M]$ and (3) the amorphous nature (XRD) and crystallization mechanisms by measurement of Differential Scanning Calorimetry (DSC) were investigated from IUCA, Indore.

International Journal of Innovative Research in Science, Engineering and Technology

(A High Impact Factor, Monthly Peer Reviewed Journal)

Vol. 5, Issue 1, Januray 2016

Table III.1 showing compoion in mol %

System LBS	Li ₂ O	B ₂ O ₃	SiO ₂
LBS L1	42.5	57.5	0
LBS L2	42.5	52.5	5
LBS L3	42.5	47.5	10
LBS L4	42.5	37.5	20
LBS L5	42.5	27.5	30

IV.1 EXPERIMENTAL RESULT AND DISCUSSIONS

IV.1.1 XRD INVESTTIGATIONS

The glass samples of system examined by XRD are shown in Figure IV.1.1

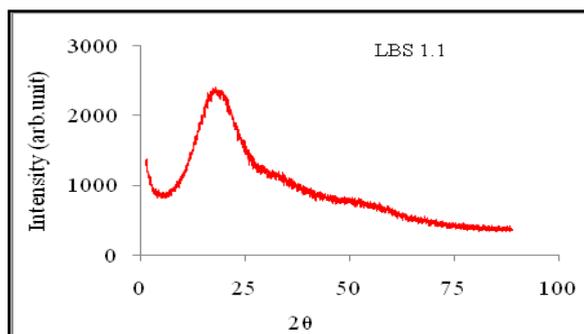


Figure IV.1.1 A typical plots of XRD of sample LBS 1.1.

Figure IV.1.1 shows a broad halo which characteristic of the amorphous structure at around diffraction angle (2θ) $\approx 20^\circ$ to be fully amorphous indicating that these glass samples are composed of glassy phase. This indicates the absence of long range of atomic arrangement and also the periodicity of the three-dimensional network in the quenched materials.

IV.2 DIFFERENTIAL SCANNING CALORIMETERY

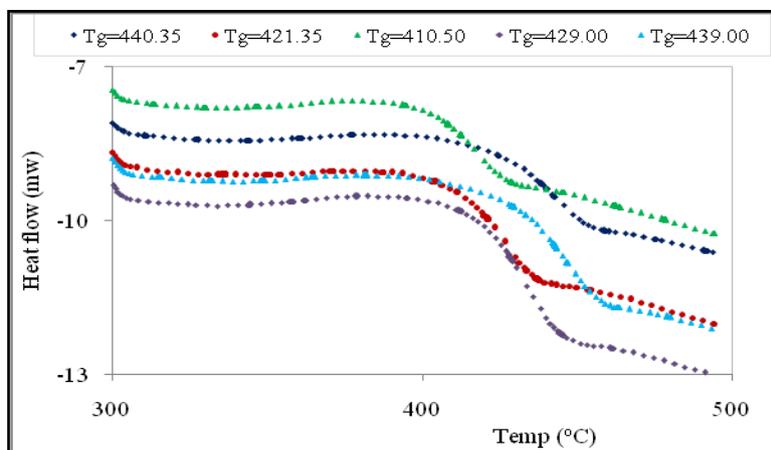


Figure IV.2.1 Thermogram patterns of DSC

International Journal of Innovative Research in Science, Engineering and Technology

(A High Impact Factor, Monthly Peer Reviewed Journal)

Vol. 5, Issue 1, Januray 2016

Figure IV.2.1, shows the thermograms of system and it is observed that there are no maximum or minimum peaks which represent the absence of crystallization and heat of fusion temperatures. A typical thermogram for determine the values of different temperatures is shown in Figure IV.2.2 as below;

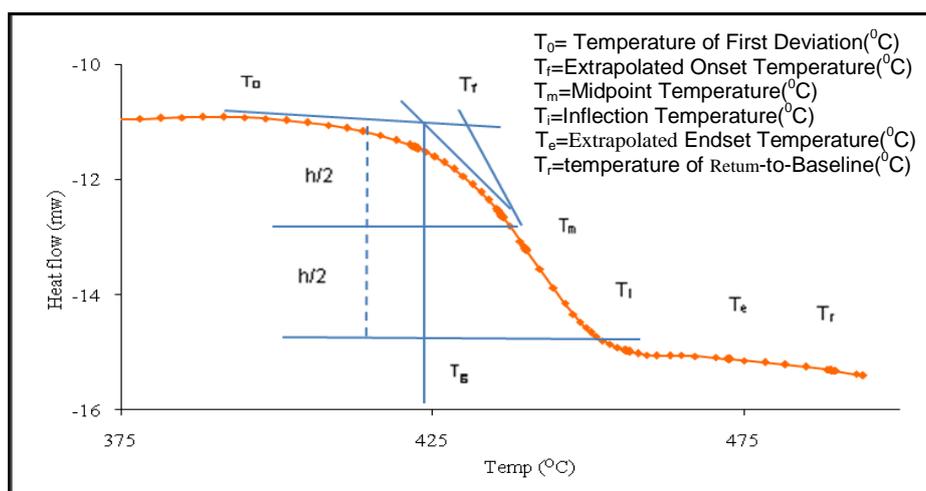


Figure IV.2.2 Determination of T_o , T_r , T_m , T_i , T_e , T_r from DSC thermogram Plot.

The temperature of first derivative (T_o), Extrapolated onset temperature ($T_i = T_x$), Midpoint temperature (T_m), midpoint temperature T_m founds to be higher than glass transition T_g temperature. This indicates that after annealing glass molecules are stable, which proves that these are strong glass forming systems. Inflection temperature (T_i), Extrapolated endset temperature (T_e), Temperature of return- to- Base line (T_r) are noted from the DSC thermogram plot as shown in Figure IV.2.2. The glass transition temperature is a temperature taken to represent the temperature range over which the glass transition took place. Therefore, in the present case for the further work measurements are recorded in the temperature range $T_o - T_m$ in for each system. From the above values glass stability (GS) parameters are determined. The values of T_x , T_m , T_g are determined from DSC thermogram and listed in Table IV.2.2.

Table IV.2.2. Temperatures in $^{\circ}$ C of T_x , T_m and T_g .

System LBS	T_x $^{\circ}$ C	T_g $^{\circ}$ C	T_m $^{\circ}$ C
LBS I.1	437.00	430.50	441.57
LBS I.2	429.45	422.19	434.29
LBS I.3	435.56	430.52	441.57
LBS I.4	410.41	402.78	414.24
LBS I.5	437.87	430.10	442.22

Table IV.2.2. Shows the values of Temperatures in $^{\circ}$ C of T_x , T_m and T_g determined from DSC thermogram.

International Journal of Innovative Research in Science, Engineering and Technology

(A High Impact Factor, Monthly Peer Reviewed Journal)

Vol. 5, Issue 1, Januray 2016

Table IV.2.3: Values of K_H , K_W , K_{LL} , K_2 , and K_3 .

System LBS	$K_W = \phi$	$K_H = K_{gl}$	$K_{LL} = \gamma$	$K_3 = \alpha$	$K_2 = \Delta x$
LBS I.1	0.014720203	1.4223195	0.5011066	0.9896506	6.50
LBS I.2	0.01671694	1.5	0.5014128	0.9888554	7.26
LBS I.3	0.011413819	0.8386023	0.4994439	0.9863895	5.04
LBS I.4	0.018419274	1.9921671	0.5023255	0.9907542	7.77
LBS I.5	0.01757044	1.7862069	0.5019603	0.9901633	7.63

Table IV.2.3.Shows the values of K_H , K_W , K_{LL} , K_2 , and K_3 determine by using above standered equations.

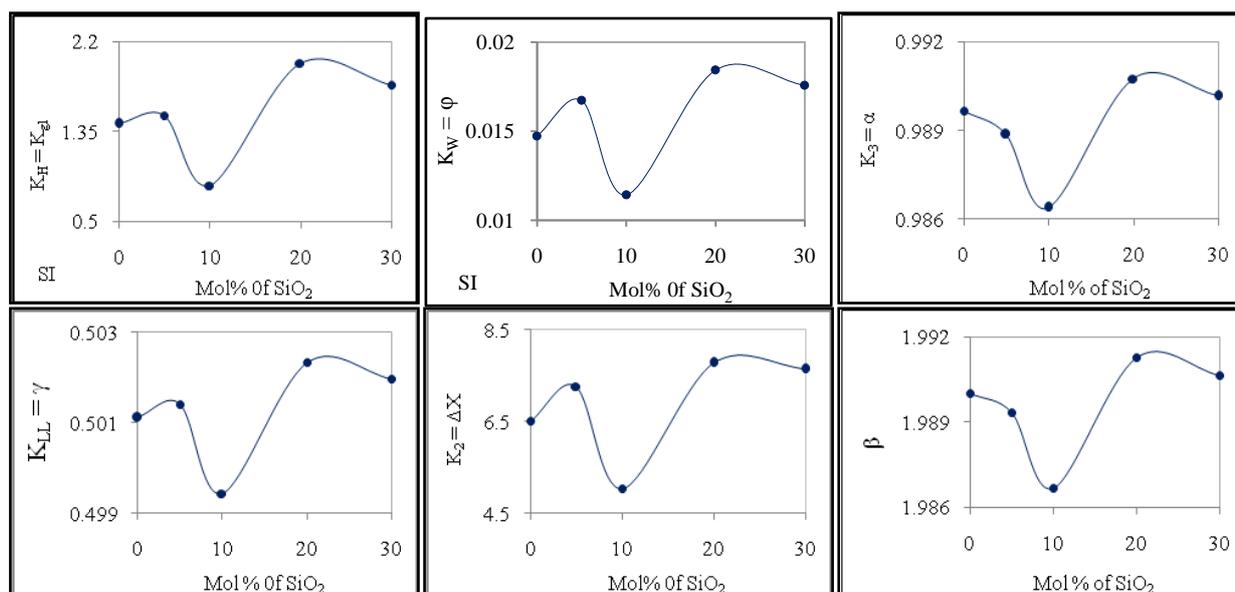


Figure IV.2.3: variation of K_H , K_W , K_{LL} , K_2 , K_3 and β with mol % of SiO_2 .

From Table IV.2.3 and Figure IV.2.3 it is observed that the variation of K_H , K_W , K_{LL} , K_2 , K_3 and β are alike with their good correlations. It is observed that the values of K_H , K_W , K_{LL} , K_2 , K_3 and β are increases with increasing the mol % of SiO_2 , Indicating increase of GS and GFA. At 10 mol % of SiO_2 the values of these parameters is minimum indicating the decrease in GS and GFA. At 20 mol % these parameters have maximum values indicating the increases in GS and GFA; out of these parameters maximum value of the K_H ($=1.992$) K_2 ($=\Delta X=7.77$) and β (1.991), indicates the greater stability of the glass against devitrification on heating, and can be used to estimate the glass-forming ability (GFA) on cooling. So, a strong correlation between GS and GFA parameter is concluded. Hence the K_H , K_W , K_{LL} , K_2 , K_3 and β parameter assess GS and GFA.

International Journal of Innovative Research in Science, Engineering and Technology

(A High Impact Factor, Monthly Peer Reviewed Journal)

Vol. 5, Issue 1, Januray 2016

Table IV.2.4: The values of α , β , δ , γ_m with mol % of SiO_2 .

System LBS	β	δ	γ_m
LBS I.1	1.990029	0.53270953	0.9838
LBS I.2	1.989334	0.558845507	0.9805
LBS I.3	1.986682	0.535655724	0.9757
LBS I.4	1.991278	0.540427407	0.9817
LBS I.5	1.990658	0.539893617	0.9839

Table IV.2.3. Shows the values of β , δ , γ_m determine by using above standered equations.

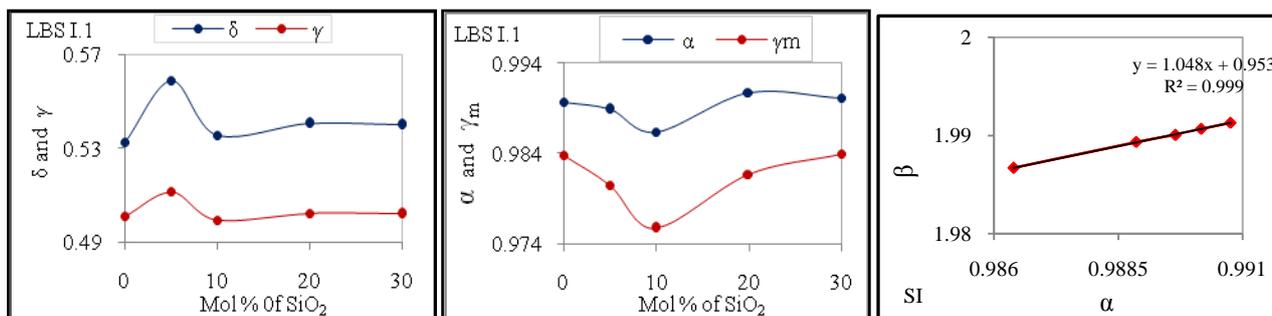


Figure III.2.4: variation of α , β , γ and γ_m with mol % of SiO_2 .

From Table IV.2.4 and Figure IV.2.4 it is observed that the variation of δ and γ are alike with their good correlations then increases, at 5 mol % gives maximum value. The α and γ_m parameters are minimum at 10 mol% of SiO_2 . Increasing, decrease the values of δ & γ and α & γ_m gives rise increasing, decrease the values of GS and GFA; gives a strong correlation between GS and GFA parameter is concluded. Hence the second α , γ , δ , γ_m parameter assesses GS and GFA. α parameter is the summation of glass stability and glass formation where as, β is the summation of glass forming tendency and thermal stability; shows liner relation between them having R^2 value equal to 0.999. Lastly summarise the conclusion of this material by comparing the GS and GFA parameters it gives rise very good nature.

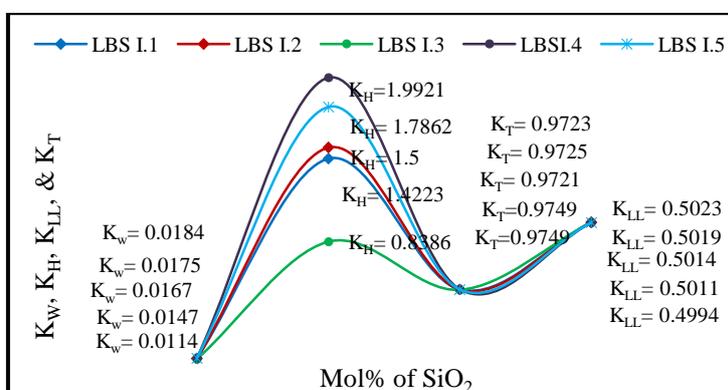


Figure IV.2.5: Comparative study of GS & GFA parameters K_w , K_H , K_T and K_{LL} for system LBSI.1 to LBSI.5.

International Journal of Innovative Research in Science, Engineering and Technology

(A High Impact Factor, Monthly Peer Reviewed Journal)

Vol. 5, Issue 1, Januray 2016

Comparative study of GS & GFA parameters K_W , K_H , K_T and K_{LL} , of glass system LBS.I.1 to LBS I.5 (Figure IV.2.5). On the variation of mol % of SiO_2 the K_W values increases slowly K_H will have significant maximum values, K_T decreases and K_{LL} values slowly increases. The difference is very small therefore, in comparative study they are at a point.

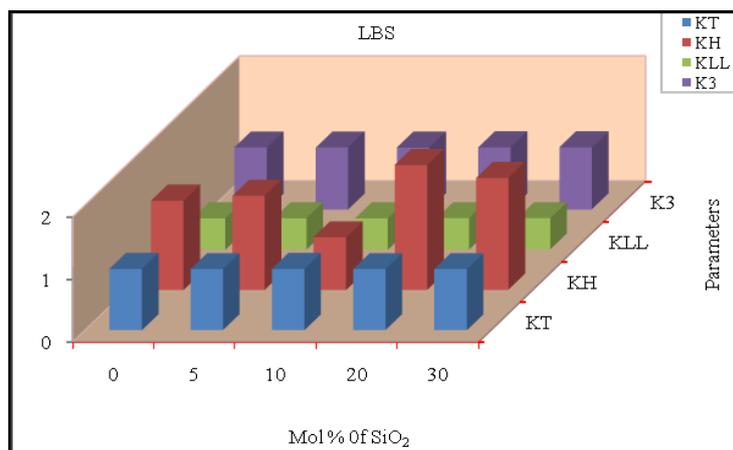


Figure III.2.6: Comparative study of GFA parameters K_H , K_W , K_{LL} , and K_3 for system LBS.I.1 to LBS.I.5.

Similarly the comparative study of K_H , K_T , K_{LL} , and K_3 parameters are shown in 3-D so that we can observe the actual location of parameters simultaneously.

V. CONCLUSION

It is concluded that there are also the new very good three atomistic conditions we proposed here, which helps for GFA and GS. The parameters K_H , K_W , K_{LL} , K_2 , K_3 and α , β , δ , γ , γ_m calculated by using the standard equations satisfies the very excellent results for the glass forming ability and glass stability. 3-D helps to observe the simultaneous positions of GFA and GS parameters. The γ_m parameter also reflects the effects of T_g , T_x , and T_i which are basically measured upon devitrification of glassy samples, the same as the previous γ_m parameter. However, the present result shows that the γ_m parameter exhibits the best correlation with GFA among all parameters suggested so far. This is because the current indicator correctly considers all related factors for the liquid phase stability and the crystallization resistance during glass formation. Since the γ_m parameter can be calculated simply by data on T_g , T_x , and T_i , the current parameter is a simple and user-friendly indicator. The sample LBS I.4 has very excellent GS and GFA parameter values; this sample also has higher conductivity $7.5318 \times 10^{-3} \text{ SCm}^{-1}$ at 400°C .

REFERENCES

- [1] G. Tamman, Die Aggregatzustände, Leopold Voss, Leipzig, 1922.
- [2] V. Goldschmidt, Skrifter Norske Videnskaps. Akad. (Oslo) I, Matematisk-Naturwiss. Klasse 1 (1926) 7.
- [2] Goldschmidt V M 1926 Naturwiss 21 477
- [3] W. Zachariasen, J. Am. Chem. Soc. 54 (1932) 3841.
- [4] Zachariasen W H 1932 J. Am. Chem. Soc. 54 3841
- [5] Dietzel A 1941 Naturwiss 29 537
- [6] Stanworth J E 1946 J. Soc. Glass Technol. 30 54
- [7] Stanworth J E 1948 J. Soc. Glass Technol. 32 154,366
- [8] Stanworth J E 1952 J. Soc. Glass Technol. 36 217
- [9] Smekal A 1951 J. Soc. Glass Technol. 35 411
- [10] Sun K H 1947 J. Am. Ceram. Soc. 30 277
- [11] A. Dietzel, H. Wiekert, Glastech. Ber. 29 (1956) 1.
- [12] D. Turnbull, M. Cohen, in: Mackenzie (Ed.), Modern Aspects of Vitreous State, 1960, p. 38.
- [13] I. Gutzow, J. Schmelzer, The Vitreous State, Springer, 1995.
- [14] D.R. Uhlmann, J. Non-Cryst. Solids 7 (1972) 337.

International Journal of Innovative Research in Science, Engineering and Technology

(A High Impact Factor, Monthly Peer Reviewed Journal)

Vol. 5, Issue 1, Januray 2016

- [15] M.C. Weinberg, E.D. Zanotto, Phys. Chem. Glasses 30 (1989) 110.
- [16] M.C. Weinberg, D.R. Uhlmann, E.D. Zanotto, J. Am.Ceram. Soc. 72 (1989) 2054.
- [17] D.R. Uhlmann, B.J.J. Zelinski, E.D. Zanotto, M.C. Weinberg, Sensitivity of critical cooling rate to model and material parameters, Proceedings of the XV International Congress on Glass, Leningrad, USSR, July, 1989, vol. 1A, p. 156.
- [18] D.B.Thombre, Ph.D.Thesis on Study of Lithium-borosilicate glassy solid electrolyte based on Molecular Orbital Theory (MOT).
- [19] [1] D. Turnbull, Contem. Phys. 10 (1969) 473.
- [20] E. D. Zanotto and F. A. B. Coutinho, "How Many Non-crystalline Solids Can Be Made From All the Elements of the Periodic Table?", J.Non-Cryst. Solids 347 [1-3] 285-288 (2004).
- [21] [2] W. Kauzmann, Chem. Rev. 43 (1948) 219.
- [22] A. Inoue, T. Zhang, and T. Masumoto, J. Non-Cryst. Solids 156–158, 473 _1993_.
- [23] A. Inoue, B. Shen, A. Takeuchi, Fabrication, properties and applications of bulk glassy alloys in late transition metal- based systems, Materials Science and Engineering A 441 (2006) 18-25.
- [24] N.Mehta, R.S.Tiwari, A.Kumar, Mater. Res. Bull., 41, 1664 (2006).
- [25] M.C. Weinberg, Phys. Chem. Glasses 35 (1994) 119.
- [26] A. Hruby, Czech J. Phys. B 22 (1972) 1187.
- [27] Z. P. Lu and C. T. Liu, Acta Mater. 50, 3501 _2002_.
- [28] P. Lu and C. T. Liu, Phys. Rev. Lett. 91, 115505 _2003_.
- [29] P. Lu and C. T. Liu, Intermetallics 12, 1035 _2004_.
- [30] P. Lu, H. Bei, and C. T. Liu, Intermetallics _in press_.
- [31] M. L. F. Nascimento, L. A. Souza, and E. D. Zanotto, J. Non-Cryst. Solids 351, 3296 _2005_.
- [32] C.A. Angell, 2nd Int. Symp. Halide Glasses, Troy, New York (1983).
- [33] M.G. Drexhage, O.H. El-Bayoumi, H. Lipson, C.T. Moynihan, A.J. Bruce, J. Lucas, G. Fonteneau, J. Non-Cryst. Solids 56 (1983)51.
- [34] R.M. Almeida, J.D. Mackenzie, Glastechn. Ber. 56K (1983) 850.
- [35] E.I. Cooper, C.A. Angell, J. Non-Cryst. Solids 56 (1983) 75.