Indian Journal of Pure & Applied Physics
Vol. 58, June 2020, pp. 465-469

Glass forming ability of ZBLAN glass

Prapti B Pandya & Arun Pratap*

Condensed Matter Physics Laboratory, Applied Physics Department, Faculty of Technology & Engineering,
The M S University of Baroda, Vadodara 390 001, India

Received 25 October 2018; Accepted 30 January 2020

A ZBLAN glass of the following composition: 53 mol.% ZrF4, 20 mol.% BaF2, 4 mol.% LaF3,3 mol.% AIF3, 20 mol.% NaF is studied for predicting its glass forming ability (GFA). The GFA of a ZBLAN glass is evaluated by estimating the Gibbs free energy difference (ΔG) between the undercooled liquid and the corresponding equilibrium solid phases. Other GFA criteria ($T_{rg}=T_g/T_l$, T_x/T_l, $\gamma=T_x/T_g+T_l$, $\Delta T_{xg}=T_x-T_g$, T_g/T_m) are also calculated. Here, the approximation for ΔG considering constant specific heat difference (ΔC_P) over a wide temperature range is calculated for a ZBLAN glass. The so-calculated ΔG is compared with the result of other theoretical approaches and experimental data. We can see from the result that the expression with the consideration of constant ΔC_P works well in the entire undercooling for ZBLAN glass forming system. So we can say that the specific heat difference is being constant in the entire undercooling for ZBLAN glass.

Keywords: ZBLAN glass, Glass forming ability, Gibbs free energy difference (ΔG)

1 Introduction

A ZBLAN glass: 53 mol.% ZrF4, 20 mol.% BaF2, 4 mol.% LaF3,3 mol.% AIF3, 20 mol.% NaF is a heavy metal-based fluoride system. ZBLAN glass is the most stable fluoride glass known and is most commonly used to make optical fibre (wiki). Superior infrared transmittance is the advantage of ZBLAN over other glasses available, such as silica. It has a broad optical transmission window extending from 0.3 micrometers in the UV to 7 micrometers in the infrared[1]. Fragility and sensitivity to acids are their drawbacks. Formally, fragility reflects the degree to which the temperature dependence of the viscosity (or relaxation time) deviates from Arrhenius behaviour[2]. So it is interesting to study the glass forming ability (GFA) of ZBLAN glass with thermodynamic point of view, which may help to understand the physical origin of this glass. Since complete investigations and detailed descriptions of heavy metal fluoride (HMF) glasses of their properties can be found in the literature[3–12]. The thermodynamic properties of this system are studied earlier[13] but there are not many studies about the thermodynamic properties of fluoride based glass.

It is found that the glass transition temperature Tg is well separated from the crystallization temperature T_x, in fact it is opposite in ZBLAN glass. In the past, many criteria have been proposed for predicting the glass forming ability (GFA) for metallic glass formers[14-25].

Here we evaluate the GFA by estimating the Gibbs free energy difference (ΔG) between the undercooled liquid and the corresponding equilibrium solid phases. Other GFA criteria ($T_{rg}=T_g/T_l$, T_x/T_l, $\gamma=T_x/T_g+T_l$, $\Delta T_{xg}=T_x-T_g$, T_g/T_m) are assessed. In present paper, we have calculated the value of ΔG by the expression taking the specific heat difference ΔC_p constant without any approximation. It is compared with other expressions and experimental data.

2 Theory

The GFA is considered in three different ways namely kinetic, structural and thermodynamic point of view. From the kinetic point of view, viscosity is closely related to the reduced glass transition temperature ($T_{rg}=T_g/T_l$) where T_g is glass transition temperature and T_l is liquidus temperature[14]. Higher T_{rg} leads to the higher GFA[26]. The T_x/T_l ratio is also an indicator of the GFA where T_x is onset crystallization temperature and T_l is liquidus temperature. The large T_x/T_l ratio indicates a lower R_c and therefore the higher GFA[27]. R_c is a critical cooling rate, which is the minimum cooling rate necessary for keeping the melt amorphous without crystallization. Actually R_c is a key parameter to evaluate the GFA of a melt but it is difficult to measure precisely. So we have used simple and reliable criteria for the GFA.

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*Corresponding author (E-mail: apratapmsu@yahoo.com)

From the structural point of view, higher T_g/T_m ratio and higher $\Delta T_{xg}=T_x-T_g$ [17] is required for the higher GFA. These are the parameters to gauge the glass stability.

Thermodynamically, ΔG is a key parameter for predicting the GFA. Low value of ΔG means the driving force for crystallization is low and glass formation becomes easy. In the relation $\Delta G= \Delta H_f - T\Delta S_f$ for Gibbs free energy, ΔH_f and ΔS_f are enthalpy of fusion and entropy of fusion. In multi component systems, the number of microscopic states is large leading to the increase in ΔS_f, leads to a decrease in ΔG. Small value of ΔG is favourable for the higher GFA.

3 Formulation of Theoretical Expression for Gibbs Free Energy Difference (ΔG)

The difference in Gibbs free energy between the liquid and crystalline phases is given by:

$$\Delta G=\Delta H-T\Delta S \qquad \dots (1)$$

where

$$\Delta H = \Delta H_m - \int_T^{T_m} \Delta C_p dT \qquad \dots (2)$$

and

$$\Delta S = \Delta S_m - \int_T^{T_m} \Delta C_p \frac{dT}{T} \qquad \dots (3)$$

where, T_m is the melting temperature, ΔS_m is the entropy of fusion and ΔH_m is the enthalpy of fusion. $\Delta C_p = C_p^l - C_p^x$, is the difference in specific heats of the liquid and corresponding crystalline phases. ΔS_m and ΔH_m are related to each other by the following relation:

$$\Delta S_m=\Delta H_m/T_m \qquad \dots (4)$$

Thus, if we have experimental specific heat data for the undercooled liquid and the corresponding equilibrium solids, experimental ΔG can be calculated using Eqs (1)-(3). It is difficult to obtain accurately the heat capacity data experimentally because the nature of the undercooled liquid is metastable. So ΔG has to be estimated theoretically. The most common expression of the temperature dependence of a linear relationship of ΔC_p is given by:

$$\Delta C_p=AT+B \qquad \dots (5)$$

where A and B = coefficient for linear variation, T= temperature. Substituting Eq. (5) into Eq. (2) and (3), Eq. (1) can be simplified to:

$$\Delta G=\frac{\Delta H_m \Delta T}{T_m} - \frac{1}{2} A(\Delta T)^2 + B\left(T \ln\frac{T_m}{T} - \Delta T\right) \qquad \dots (6)$$

where $\Delta T=T_m-T$ To simplify Eq. (6), Thompson & Spaepen[28] used the following approximation:

$$\ln\left(\frac{T_m}{T}\right) = \ln\left(1 + \frac{\Delta T}{\left(T_m + T\right)/2}\right) \cong \frac{2\Delta T}{T_m + T} \qquad \dots (7)$$

and derived the expression:

$$\Delta G = \frac{\Delta H_m \Delta T}{T_m}\left(\frac{2T}{T_m + T}\right) \qquad \dots (8)$$

The constant ΔC_p accounted for the enthalpies of crystallization ΔH_x of the metallic glass.

$$\Delta H_x = \Delta H_m - \Delta C_p(T_m - T_x) \qquad \dots (9)$$

$$\Delta C_p = \gamma \frac{\Delta H_m}{T_m} \qquad \dots (10)$$

$$\gamma = \frac{1-\frac{\Delta H_x}{\Delta H_m}}{1-\frac{T_x}{T_m}} \qquad \dots (11)$$

Considering this ΔC_p value of Eqn. (10) Battezzati *et al.*[29] gives the following expression:

$$\Delta G=\frac{\Delta H_m \Delta T}{T_m} - \gamma\frac{\Delta H_m}{T_m}\left[\Delta T - T\ln\frac{T_m}{T}\right] \qquad \dots (12)$$

where the value of γ can be calculated by Eq. (11).

The approximation given in Eq. (7) is strictly valid only for small undercooled region, Δ*T*. But, the multi component glass forming systems exhibit a large undercooled regime. Therefore, to account for the wide undercooled region of the multi component metallic alloys, Lad *et al.*[30] obtained the following expression.

$$\Delta G = \frac{\Delta H_m \Delta T}{T_m}\left(1 - \frac{\Delta T}{2T}\right) \qquad \dots (13)$$

Different approximations for the logarithmic term $\ln\left(\frac{T_m}{T}\right)$ given in Eq. (6) are used by Eq. (8) and Eq. (13) and it has been found that neither Eq. (8) nor Eq. (13) works for many multi component amorphous alloys.

Considering the Taylor series expansion of Eq. (7) up to second order gives the following approximation:

$$\ln\left(\frac{T_m}{T}\right) \cong \frac{4T\Delta T}{(T_m + T)^2} \qquad \ldots (14)$$

Substituting Eq. (14) in Eq. (6) Lad *et al.*[31] obtained the following equation for the Gibbs free energy difference:

$$\Delta G = \frac{\Delta H_m \Delta T}{T_m}\left(\frac{4T^2}{(T + T_m)^2}\right) \qquad \ldots (15)$$

Most of the bulk glass forming systems shows good result with Eq. (15). But there is some deviation for many systems. It is observed that the specific heat of the undercooled liquid does not vary much with temperature, hence ΔC_p is nearly constant. For constant $\mathit{\Delta} C_p$, assuming A=0, B= ΔC_p =constant then Eq. (6) reduced to:

$$\Delta G = \frac{\Delta H_m \Delta T}{T_m} + \Delta C_p\left(T \ln\frac{T_m}{T} - \Delta T\right) \qquad \ldots (16)$$

Following the argument of vanishing ΔS at the Kauzmann Temperature T_k,

Substituting Eq. (4) in Eq. (3) and ΔS=0 at $T=T_k$, we can get:

$$\Delta C_p = \alpha \frac{\Delta H_m}{T_m} \qquad \ldots (17)$$

where $\alpha = 1/\ln(T_m/T_k)$. Using the Eq. (17) for ΔC_p in Eq. (16) Heena *et al.*[32] obtained following expression:

$$\Delta G = \frac{\Delta H_m}{T_m}\left[\alpha T \ln\frac{T_m}{T} + \Delta T\left(1 - \alpha\right)\right] \qquad \ldots (18)$$

They have not taken any approximation to get Eq. (18) except for the assumption related to constant ΔC_p.

Thus our expression for ΔG (Eq. (18)) considering constant ΔC_p fits very well with experimental data for most of the bulk amorphous alloys. Taking the constant value of $\Delta C_p = \Delta C_p^m$ at the melting point in Eq. (17), have been derived:

$$\alpha = \frac{\Delta C_p^m T_m}{\Delta H_m} \qquad \ldots (19)$$

In this paper, α has been derived using the Eq. (19) obtained from Eq. (17) taking the constant value of $\Delta C_p = \Delta C_p^m$ at melting point.

However, for such systems, in which the specific heat increases considerably with undercooling, ΔC_p at any temperature $T_k < T < T_m$ in the undercooled region can be expressed as:

$$\Delta C_p = \frac{\Delta C_p^m T_m}{T} \qquad \ldots (20)$$

ΔC_p^m *is* being the difference in the specific heats at the melting point. Substituting ΔC_p from Eq. (20) in Eq. (2) & (3) and using Eq. (1), the ΔG values for such systems (Heena *et al.*[32]) is represented by the following equation:

$$\Delta G = \frac{\Delta H_m \Delta T}{T_m} - \Delta C_p^m T_m\left[\ln\frac{T_m}{T} - \frac{\Delta T}{T_m}\right] \qquad \ldots (21)$$

4 Result and Discussion

Figure 1 shows the results of ΔG in the under cooled region for ZBLAN glass obtained using the Eq. (18) and Eq.(21) proposed by Heena *et al.*[32], Battezzati Eq.(12)[29], Lad-1 Eq.(13)[30], Lad-2 Eq. (15)[31]. The results for the ZBLAN glass have been compared with the experimental results of Battezzati *et al.*[13]. The parameters used to calculate ΔG for this system are given in Table 1.

The excellent agreement of the result obtained using Heena *et al.* given by Eq. (18) with experimental data can be observed and the close matching of the two curves up to large degree of undercooling can be appreciated. Equation (18) does

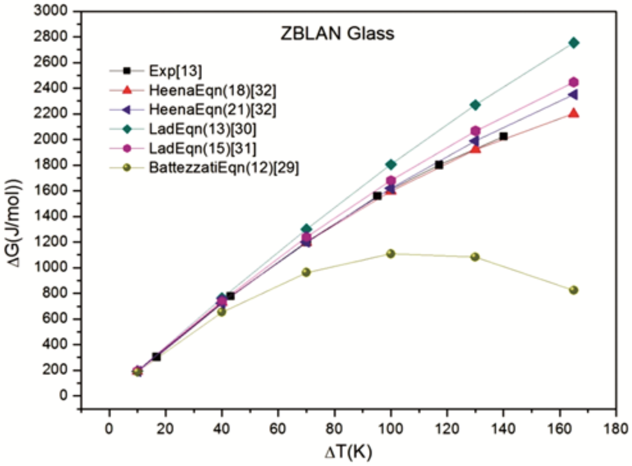

Fig. 1 — ΔG as a function of ΔT for ZBLAN glass.

Table 1 — Parameters used for the calculation of Gibbs free energy difference ΔG^{13}.

System	T_g(K)	T_x(K)	T_m(K)	T_l(K)	ΔH_m J/mol	C_p^m J/mol K
ZBLAN	545	620	710	820	13961.36	50.23

not involve any approximation to evaluate the logarithmic term. Also it is derived considering ΔC_p to be constant, because the specific heat of undercooled liquid of most of the bulk glass forming systems does not vary much with temperature. In ZBLAN glass, the result of Eq. (18) shows exact matching with experimental curve means the specific heat of the undercooled liquid of ZBLAN glass forming system remains nearly constant with temperature. Heena et al include α in Eq. (18). The value of α is 2.55 for ZBLAN system. However, significant deviation is observed at high under cooling with hyperbolic variation of ΔC_p if Eq. (21) is used for the evaluation of ΔG. The deviation of hyperbolic expression calculated by Eq. (21) is due to the consideration of specific heat varying with under cooling which otherwise appears to be constant. The plot using the Lad-1 approach shows a larger deviation from the experimental curve. The expression of Lad *et al.*, Eq. (13) is obtained using approximation of logarithmic term and done Taylor series expansion up to second order. But it does not give good result for ZBLAN glass. Lad *et al.* have also proposed another expression given by Eq. (15) in which they have used Thompson-Spaepen approximation of logarithmic term and have done Taylor series expansion up to second order. The Lad-2 approximation works well only at low under cooling. The result using Battezzati *et al.*, Eq. (12) lies below the experimental curve. At a small undercooling the deviation is small however it is large at large under cooling. Battezzati *et al.* have taken the value of γ to be ~3.5. The value of γ is calculated 5.9 for ZBLAN system in present paper. It is difficult to evaluate γ correctly because a multi component system crystallizes in multiple steps. It is difficult to choose a particular step which should be taken for the derivation of γ. Besides this, T_x is heating rate dependent and even ΔH_x is not constant for all heating rate. So the value of γ is not unique while α given by Eq. (19) and used in Eq. (18) for the estimation of ΔG is unique. It requires knowledge of ΔC_p^m, ΔH_m and T_m. Eq. (18) is derived by taking the constant value of $\Delta C_p = \Delta C_p^m$ at the melting point and the result using Eq.(18) gives very good match with experimental data. Thus, we can say that the value of α is much appropriate than the value of γ for the ZBLAN glass.

The results of the other GFA parameters are given in Table 2. The results obtained using different methods are compared with the corresponding value for typical bulk metallic glasses (BMGs). The value of reduced glass transition temperature $T_{rg}=T_g/T_l=0.66$ shows that ZBLAN glass possesses the higher GFA. The large $T_x/T_l=0.75$ ratio indicates a lower R_c and therefore a higher GFA. The large super cooled region $\Delta T_{xg}=75$ is observed. It indicates that the super cooled liquid has a high resistance to the crystallization. It leads to the higher GFA for ZBLAN glass. Since ZBLAN glass can be cooled more slowly than 1 K/s without noticeable homogeneous nucleation, it has been considered to be as the most stable HMF glass and the most resistant to crystallization under optical fibre pre form-making and drawing condition.[33] However, optical fibre from this material has excellent transmission characteristics in the IR, but the glass is somewhat susceptible to nucleation and crystallization[34].

We obtain $\gamma=T_x/T_g+T_l=0.45$ and $T_g/T_m=0.76$. We obtain the ΔG (T_g) value using Eq. (18) and it is 2.2 kJ/mol while the value of ΔG (T_g) is 1 kJ/mol for the metallic glass former PdCuNiP with the higher GFA.

4.1 Calculation of GFA indicators

Table 1 shows the glass transition temperature T_g, onset crystallization temperature T_x, offset fusion temperature (liquidus temperature) T_l, melting temperature T_m, total heat needed for melting ΔH_m and the specific heat difference ΔC_p^m for ZBLAN glass. All of these characteristic temperatures can be easily determined from single DSC measurements.

Table 2 — Different GFA criteria.

System	$T_{rg}=T_g/T_l$	T_x/T_l	$\gamma=T_x/T_g+T_l$	$\Delta T_{xg}=T_x-T_g$ K	T_g/T_m	$\Delta G(T_g)$ J/mol
ZBLAN	0.66	0.75	0.45	75	0.76	2200.31
Typical BMGs [25]	0.503-0.690	0.53-0.78	0.353-0.464	16.3-117	-	-

Table 2 presents the summary of $T_{rg}=T_g/T_l$, T_x/T_l, $\gamma=T_x/T_g+T_l$, $\Delta T_{xg}=T_x-T_g$, T_g/T_m and ΔG based on the data in Table 1.

5 Conclusions

The higher value of reduced glass transition temperature $T_{rg}=T_g/T_l=0.66$ indicates that the melt of ZBLAN glass becomes more viscous and crystallization becomes difficult. Thus the GFA enhances. This system possesses a large $T_x/T_l=0.75$ could have a lower R_c therefore a higher GFA. Large supercooled liquid region $\Delta T_{xg}=T_x- T_g=75$ K is an indication of the devitrification tendency of ZBLAN glass upon heating above T_g. The lower value of ΔG (T_g) =2.2 kJ/mol for ZBLAN glass leads to the higher GFA. The calculation of Gibbs free energy difference ΔG for ZBLAN glass is done by different expressions. The expression with the consideration of constant ΔC_p without taking any approximation provides fairly accurate result matching with experimental data.

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