Chapter 4

GLASS FORMING ABILITY (GFA) OF METALLIC GLASS, ZBLAN GLASS AND POLYMERS

4.1 Introduction

Researchers are doing a constant effort to form amorphous metallic alloys with extremely high glass forming ability. Recently, they have succeed and developed a number of multi component glass forming alloys with cooling rates of less than 100K/s, which exhibit a high glass forming ability. Glass forming ability (GFA) is the ability of a material to cool down the melt slowest to glass transition temperature (Tg) without crystallization [4.1] where [glass transition refers to the slowing down of the kinetics of liquid dynamics due to super-cooling of melt.] During glass formation, there is a competition between super-cooled liquid and the related crystalline phases. Whole event is closely related to structural, thermodynamic and kinetic characteristic.

The super cooling increases the viscosity of metallic melt thereby arresting the constituents of the alloy in a random structure that is away from equilibrium. Thus, it plays an important role in formation of glass. Vogel-Fulcher-Tammann (VFT) equation [4.2-4.4] is the most common expression of the relationship between the viscosity and temperature. Another expression for variation of viscosity with temperature is proposed by Doolittle [4.5]. Further, the free volume of bulk metallic glasses (BMGs) by either direct density measurements [4.6-4.9] or by viscosity [4.10-4.14] is studied by many researchers. One more model was proposed by Van den Beukel and Sietsma [4.15] for computing free volume in terms of enthalpy measured by differential scanning calorimetry (DSC). Following this method, many researchers have calculated free volume in terms of enthalpy at temperatures below Tg [4.16-4.24].

The glass transition process is decided by the cooling rate. Higher cooling rate ensures the glass formability at lower temperature, far from the crystallization temperature (Tx). The super-cooled liquid region, i.e., $\Delta Tx = Tx - Tg$ is the difference between the crystallization temperature and the glass transition temperature . A large value of ΔTx indicates that the glassy phase is thermally stable with respect to the crystalline phase.

BMGs have very high ΔTx values (≈ 102 K) and require very low cooling rates for their synthesis.Bulk glass forming alloys in multicomponent systems based on Mg [4.25, 4.26], La[4.27], Zr [4.28,29], and Pd [4.30, 4.31] have a wide supercooled liquid region upto 120 K before crystallization and large reduced glass transition temperature. For making an alloy having excellent GFA, many empirical approaches have been proposed, but there are no justified theories and scientific rules [4.32-4.34] which can be generalized for the whole class of glass forming systems. Inoue suggested a set of empirical rules for predicting GFA of different metallic glasses [4.35]. Different GFA parameters have been put forward through criteria like reduced glass transition temperature (Trg), order parameter(η), parameters Q, γ, γm and the Gibb's free energy difference (ΔG) between the super-cooled liquid and crystalline phases. Multi component compositions of BMGs is possessed high GFA. According to the empirical multi component rule proposed by Inoue et al [4.36], minor substitution of some elements in amorphous alloys may strongly influence the GFA and crystallization of metallic alloys [4.37].

4.1.1 Thermodynamic Aspect

The main reason behind the formation of a glass is the lack of appropriate number of crystal nucleation sites. A large thermodynamic driving force and a rapid kinetics of crystal nucleation favour the process of crystal nucleation. When we start the cooling process, the molecules of melt have two ways either tends to move towards their equilibrium state or get super-cooled. It is depended on the amount of the available thermodynamic driving force and the briskness of crystallization kinetics. The thermodynamic driving force can be calculated in terms of Gibbs free energy difference (ΔG) between the super-cooled liquid and the corresponding crystalline phase. The nucleation frequency has an exponential dependence on ΔG. Generally, good glass formers exhibit low driving force, i.e., lower ΔG value, which results in low nucleation rates and hence a better GFA. ΔG is a function of the heat capacity difference between metastable liquid and crystalline solid. Lesser the driving force of crystallization more is the glass forming ability Driving force for crystal nucleation can be estimated by the calculation of a thermodynamic parameter i.e ΔG. The value of ΔG increases with lowering of temperature due to decrease in entropy of metallic alloy. It indicates that at lower temperature ample amount of driving force is available for crystallization. Hence nucleation starts at lower temperature is followed by growth of crystal. As temperature increases growth of stable nuclei takes place. At glass transition temperature (Tg), the driving force is maximum which allows the amorphous alloy to move towards crystallization. With further increase in temperature, ΔG approaches towards zero.

Hence crystallization event ends due to increase in entropy of the alloy resulting in melting of alloy. So estimation of ΔG at Tg becomes important to study the GFA of metallic alloys. The value of ΔG can be calculated by measurement of specific heat difference ΔCp, between super cooled liquid and corresponding crystalline phase. But due to non availability of the experimental ΔCp data, different theoretical approximations of ΔCp results in variety of expressions of ΔG.

4.2 Theoretical Formulations

4.2.1 Different Expressions of ΔG

The thermodynamic driving force, i.e., Gibbs free energy difference (ΔG) between the super cooled liquid and the corresponding crystalline phase, can be determined by the following equation:

$$\Delta G = \Delta H - T\Delta S \qquad (4.1)$$

$$\Delta H = \Delta H_m - \int_T^{T_m} \Delta C_p dT \qquad (4.2)$$

And

$$\Delta S = \Delta S_m - \int_T^{T_m} \Delta C_p \frac{dT}{T} \qquad (4.3)$$

where, ΔS_m, ΔH_m and T_m are the entropy, enthalpy and temperature of fusion, respectively. They are related to each other by the relation:

$$\Delta S_m = \Delta H_m / T_m \qquad (4.4)$$

ΔC_p, defined as $C_p^l - C_p^x$, is the difference in specific heats of the liquid and corresponding crystalline phases of metallic alloy.

So the equation becomes,

$$\Delta G = \Delta S\left(T_m - T\right) - \int_T^{T_m} \Delta C_p dT + T\int_T^{T_m} \Delta C_p d(\ln T) \qquad (4.5)$$

From the above eq.(4.5) the experimental value of ΔG can be obtained provided the value of ΔC_p is available for the undercooled and the crystal phases. But the experimental determination of ΔC_p is difficult because the metallic liquids are generally not stable over an extended temperature range in the supercooled liquid. Thus different theoretical expression of ΔC_p that effectively represents the temperature dependence of ΔC_p is considered. Hence, approximating the values of ΔC_p, the correct evaluation of ΔG is possible.

Firstly, Turnbull [4.38] assumed ΔC_p to be zero and derived the following equation of ΔG:

$$\Delta G = \Delta H_m \left(\frac{\Delta T}{T_m} \right) \tag{4.6}$$

The expression given by Turnbull shows very large deviation as it is evident that ΔC_p will never be zero. Further assuming ΔC_p = constant, one gets

$$\Delta G = \Delta S_m \left(T_m - T \right) + \Delta C_p \left[T \ln \left(\frac{T_m}{T} \right) - (T_m - T) \right]$$

To simplify the above equation, Thomson and Spaepen (TS) [4.39] used the following approximation:

$$\ln \frac{T_m}{T} \cong \frac{2\Delta T}{T_m + T}$$

And they derived an expression given as

$$\Delta G = \frac{\Delta H_m \Delta T}{T_m} \left(\frac{2T}{T_m + T} \right) \tag{4.7}$$

This equation is only valid for small ΔT, and leads to error in calculations of ΔG values at larger undercooling. Generally, multicomponent metallic glasses exhibit larger undercooling range. Hence, eq. (4.7) cannot be used for a wide range of metallic glasses.

Lad et al. [4.40] assumed $\Delta C_p = \Delta H_m/T_m$ and used Taylor series expansion of $\ln(T_m/T) = \ln(1+\Delta T/T) = \Delta T[1-\Delta T/2T] / T$, retaining terms upto second order and derived the following expression of ΔG:

$$\Delta G = \frac{\Delta H_m \Delta T}{T_m} \left(1 - \frac{\Delta T}{2T} \right) \text{ [Lad-1]} \tag{4.8}$$

This expression provides good result to estimate ΔG for various metallic glass forming alloys. But, it was found that the calculated values of ΔG showed deviation a large undercooling for the alloys which possess very high glass forming ability.

Again, considering Taylor series expansion of $\ln(T_m/T) = \ln\,(1 + \Delta T/ (T_m+T)/2)$ and retaining up to second order terms i.e, $\ln(T_m/T) = 4T\Delta T / (T_m+T)^2$.

Lad et al. [4.41] gave another expression of ΔG:

$$\Delta G = \frac{\Delta H_m \Delta T}{T_m}\left(\frac{4T^2}{\left(T+T_m\right)^2}\right) \qquad \text{[Lad-2]} \qquad (4.9)$$

Eq. (4.9), gives good account of *ΔG* in most of the systems. But, since the derivation again involves the approximation of the logarithmic term, the results obtained are not in excellent agreement with the experimental points for all the metallic glasses.

As stated by Hoffmann [4.42]

$$\ln\frac{T_m}{T} = 2\frac{T_m - T}{T_m + T}$$

With this approximation equation becomes

$$\Delta G = \frac{\Delta H_m \Delta T}{T_m}\left(\frac{T}{T_m}\right) \qquad (4.10)$$

According to Battezatti and Garone [4.43] the expression for ΔG is given as follows:

$$\Delta G = \Delta S(T_m - T) - \gamma \Delta S_m\left[\left(T_m - T\right) - T\ln(T_m/T)\right]$$

(4.11)

The γ parameter in above equation is represented as:

$$\gamma = \frac{(1-\Delta H_x/\Delta H_m)}{(1-\Delta T_x/\Delta T_m)} \qquad (4.12)$$

Where, ΔH_x denotes the enthalpy difference at crystallization.

Normally, the value of γ in the above expression (Eq(4.11)) has been taken to be 0.8 for glass forming liquids. Using $\gamma = 0.8$ in Eq.4.11, *ΔG* has been reported for multicomponent amorphous alloys [4.47] and even for bulk metallic glass [4.48].

Following the argument of vanishing ΔS at the Kauzmann Temperature T_k, Substituting Eqn. (4) in Eqn. (3) and ΔS=0 at $T=T_k$, we can get

$$\Delta C_p = \alpha \frac{\Delta H_m}{T_m}$$

On substituting the value of *ΔCp* from eq. (a) in eq. (2) and eq. (3) and using the so obtained values of *ΔH* and *ΔS* in eq. (1), Dhurandhar et al [4.49] derived the following expression of *ΔG*:

$$\Delta G = \frac{\Delta H_m}{T_m}\left[\alpha T \ln\frac{T_m}{T} + \Delta T\left(1 - \alpha\right)\right] \qquad (4.13)$$

The value of *Δ* can be evaluated by taking the constant value of $\Delta C_p = \Delta C_p^{m}$ *m* at melting point in eq. (4.29) as

$$\alpha = \frac{\Delta C_p^{m} T_m}{\Delta H_m} \qquad (4.14)$$

However, in most of the glass forming systems the specific heat difference increases with undercooling, so for such kind of systems □*Cp* at any temperature in the undercooled region can be assumed to be either linearly or hyperbolically dependent on *T*.

Singh and Holz (S & H) [4.50] used the above approximation and gave the following expression:

$$(4.15) \qquad \Delta G = \frac{\Delta H_m \Delta T}{T_m}\left(\frac{7T}{T_m + 6T}\right)$$

Further, Dhurandhar et al [4.49] gave another expression of *ΔG* dependent on hyperbolic variation of *ΔCp* i.e.

$$\Delta C_p = \frac{\Delta C_p^{m} T_m}{T}$$

Substituting *ΔCp* in equations (2) & (3) and using eq. (1), the *ΔG* expression can be represented by the following equation:

$$\Delta G = \frac{\Delta Hm \Delta T}{Tm} - \Delta Cp^{m} Tm\left[\ln\frac{Tm}{T} - \frac{\Delta T}{Tm}\right] \qquad (4.16)$$

Ji & Pan [4.51] considered hyperbolic variation of ΔC_p with T ($\Delta C_p = \Delta H_m / T$) and derived the following expression:

$$\Delta G = \frac{2\Delta H_m \Delta T}{T_m}\left(\frac{T}{T_m + T} - \frac{\Delta T^2 T_m}{3\left(T_m + T\right)^3}\right) \qquad (4.17)$$

The values obtained using Ji & Pan approach under estimate ΔC_p and also at $T = T_m$, $\Delta C_p^m = \Delta H^m / T_m$ provides the reference values of ΔC_p^m which is much below the experimental values. Eventually the expression derived for ΔG does not account well for bulk glass forming alloys.

Dubey and Ramchandrarao [4.52] derived expression for ΔG based on the hole theory of liquids given as:

$$(4.18) \quad \Delta G = \frac{\Delta H_m \Delta T}{T_m} - \frac{\Delta C_p^m \left(\Delta T\right)^2}{2T}\left(1 - \frac{\Delta T}{6T}\right)$$

Finally Lele et al [4.53] derived an expression of ΔG to study its temperature dependence for the entire undercooled region represented as

$$\Delta G = \frac{\Delta H_m \Delta T}{T_m} - \frac{\Delta C_p^m \left(\Delta T\right)^2}{\left(T_m + T\right)} \quad (4.19)$$

4.2.2 **Different GFA Parameters**

In order to evaluate the GFA, many parameters are available. Most of them are based on the various characteristic temperatures like glass transition temperature (*Tg*), crystallization temperature (*Tx*), melting temperature (*Tm*), etc. The most extensively used parameters to predict GFA of metallic glass, are reduced glass transition temperature (*Trg*=*Tg*/*Tl*), thermal stability parameter (*ΔTx*), order parameter (η), critical cooling rate (*Rc*), γ(=*Tx*/(*Tg*+*Tl*)), *β*(=1+(*Tx*/*Tl*)), ω(=Tl(Tl+Tx)/(Tx(Tl-Tx))) etc.[4.54-4.55]. The GFA criterion *Trg* was introduced for purely kinetic reasons to avoid crystallization. Turnbull'[4.56] proposed that the melt having *Trg* ≥ 2/3, is possessed better GFA. The thermal stability of various alloy compositions is studied by their under cooled liquid region, Δ*T*= *Tx* – *Tg* [4.57]. Large Δ*Tx* indicates greater stability against crystallization of the amorphous structure. Mondal et al [4.58] derived the parameter *α* (=*Tx*/*Tl*) which includes both the factors of stability of the liquid (a low *Tl*) and the thermal stability of glass (a high *Tx*). The parameter Q [4.59] is based on theory of liquid phase stability, enthalpy of crystallization and resistance to crystallization.

4.3 Results and Discussions

4.3.1 Glass forming ability of ZBLAN glass

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 heats difference is being constant in the entire undercooling for ZBLAN glass.

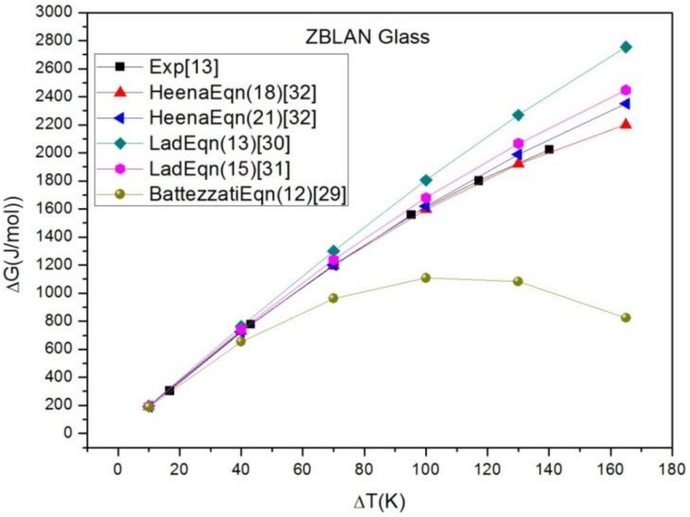

Figure 1.ΔG as a function of ΔT for ZBLAN glass

Figure 1 shows the results of ΔG in the under cooled region for ZBLAN glass obtained using the Eqn. (4.13) and Eqn.(4.16) proposed by Heena et al [4.49], Battezzati Eqn.(4.11)[4.43], Lad-1 Eqn.(4.8)[4.40], Lad-2 Eqn. (4.9) [4.41]. The results for the ZBLAN glass have been compared with the experimental results of

Battezzati et al [4.43]. The parameters used to calculate ΔG for this system are given in table 1.

Table 1 Parameters used for the calculation of Gibbs free energy difference ΔG [4.43]

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

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	-	-

The excellent agreement of the result obtained using Heena et al given by Eqn. (4.13) with experimental data can be observed and the close matching of the two curves up to large degree of undercooling can be appreciated. Eqn. (4.13) does 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 Eqn. (4.13) 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 Eqn. (4.13). 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 in Eqn. (4.16) is used for the evaluation of ΔG. The deviation of hyperbolic expression calculated by Eqn. (4.16) 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, Eqn. (4.8) is obtained using approximation of logarithmic term & 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 by Eqn. (4.9) 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, Eqn. (4.11) 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 Eqn. and used in Eqn. (4.13) for the estimation of ΔG is unique. It requires knowledge of ΔC_p^m, ΔH_m and T_m. Eqn. (4.13) is derived by taking the constant value of $\Delta C_p = \Delta C_p^m$ at the melting point and the result using Eqn.(4.13) gives very good matching 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. However, Optical fibre from this material has excellent transmission characteristics in the IR, but the glass is somewhat susceptible to nucleation and crystallization.

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 Eqn. (4.13) 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.

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 need 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 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.

4.3.2 The Gibbs free energy difference of five glass forming polymeric melts

The thermodynamic behaviour of the undercooled melt is important for understanding the glass forming abilities, viscosity, nucleation and growth kinetics etc. The temperature dependence of the Gibbs free energy difference (ΔG) between the undercooled melt and the corresponding equilibrium solid have been analyzed for glass forming polymeric materials. The Gibbs free energy difference ΔG is calculated for four samples of glass forming polymeric melts; polybutadiene (PB), polyethylene oxide (PEO), polypropylene (PP), polyethyleneterephthalate (PET)and one simple organic liquid; phenyl salicylate (Salol)in the entire temperature range T_m (melting temperature) to T_g (glass transition temperature). The results for these systems are compared with different expressions and the experimental results. A good agreement of the present results with experimental data can be observed.

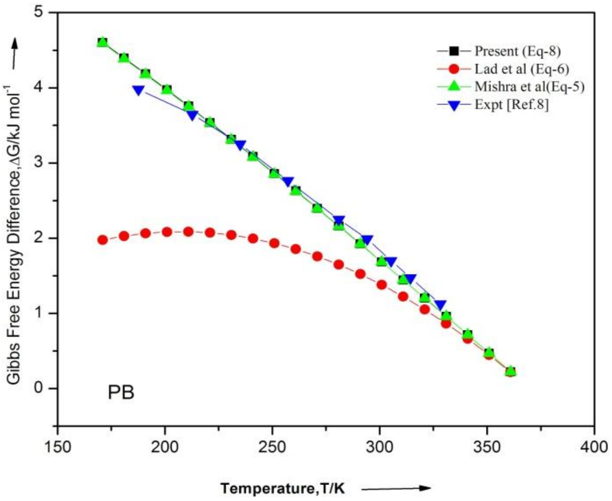

Fig. 2 Gibbs free energy difference, ΔG as a function of temperature, T for polybutadiene (PB)

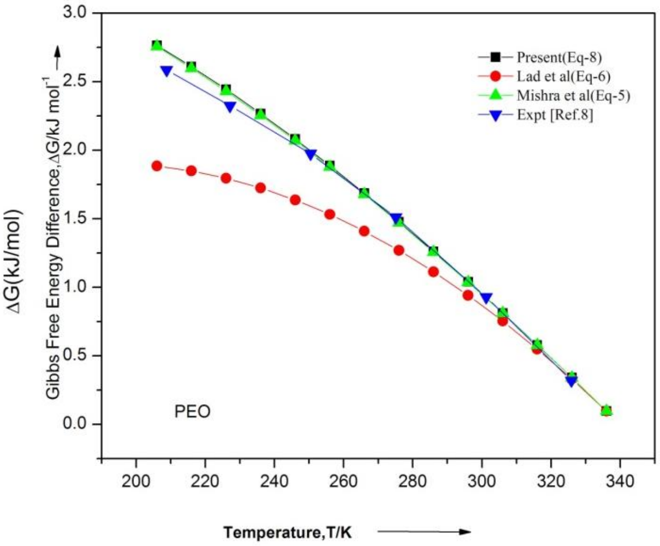

Fig. 3 Gibbs free energy difference, ΔG as a function of temperature, T for polyethylene oxide (PEO),

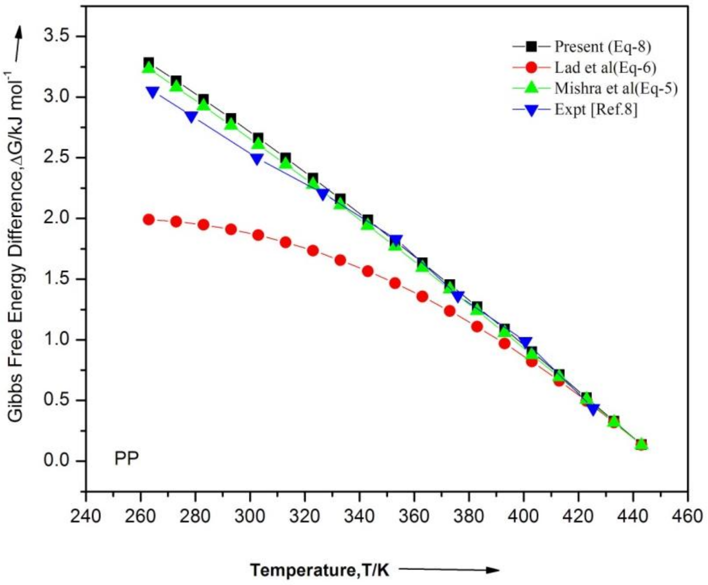

Fig. 4 Gibbs free energy difference, ΔG as a function of temperature, T for polypropylene (PP),

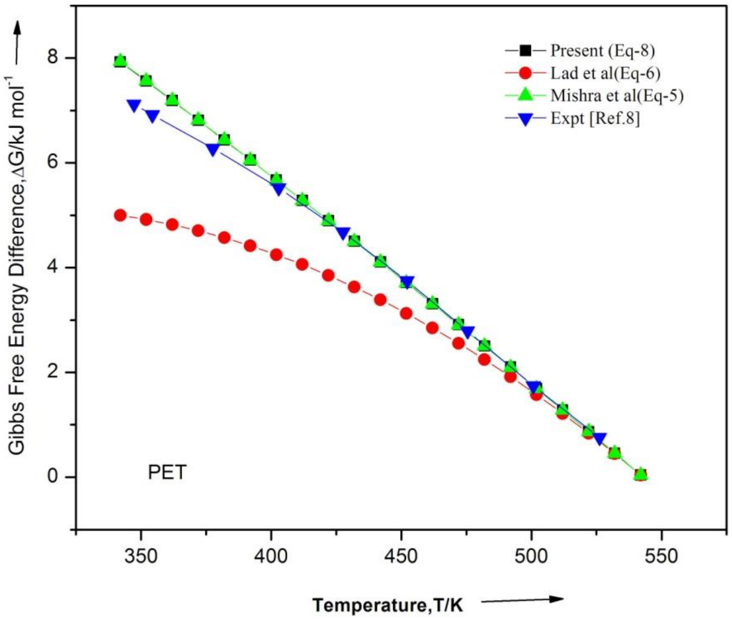

Fig. 5 Gibbs free energy difference, ΔG as a function of temperature, T for poly ethyleneterephthalate (PET)

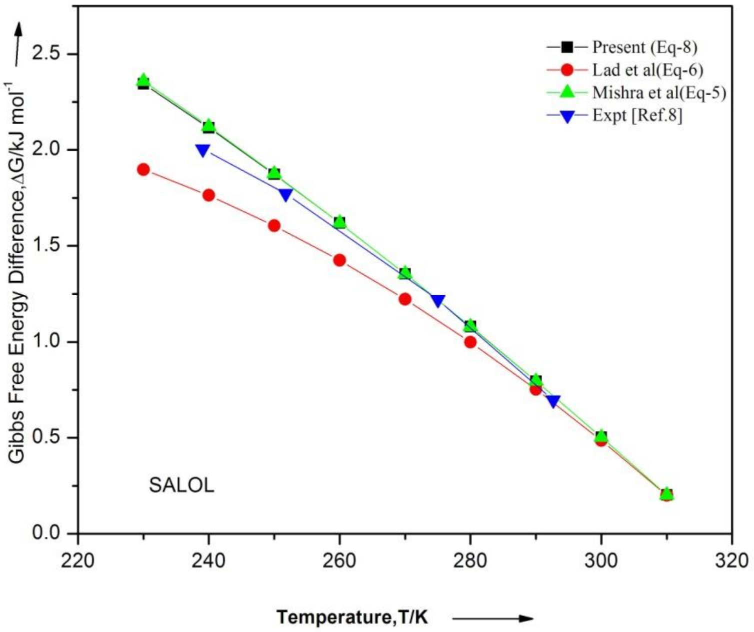

Fig.6 Gibbs free energy difference, ΔG as a function of temperature, T for phenyl salicylate (SALOL)

4.3.3 Glass forming ability of Metallic glass

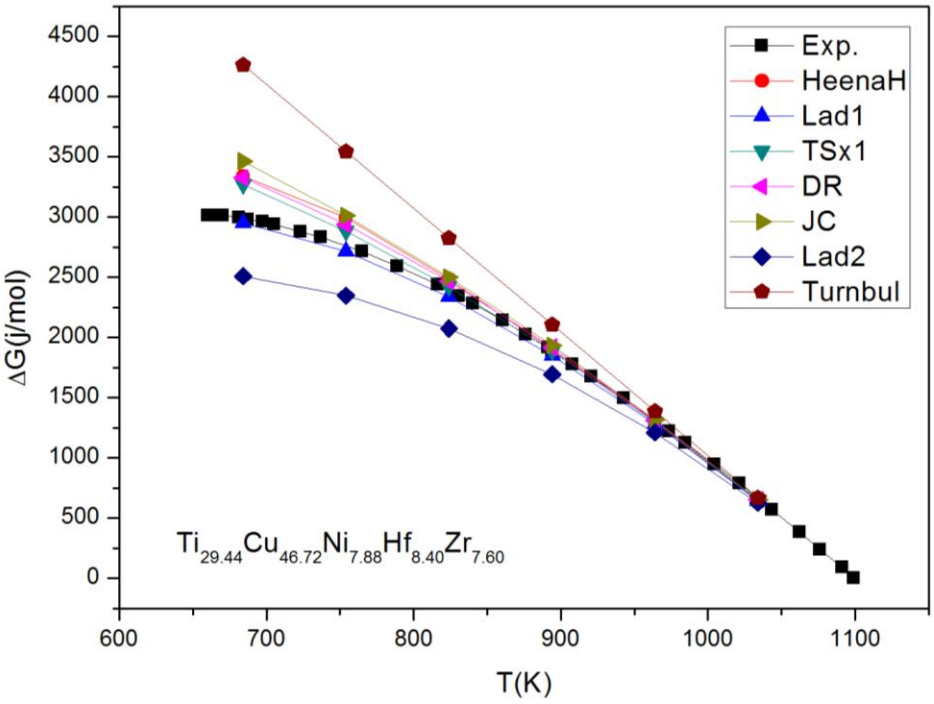

Fig.6 Gibbs free energy difference, ΔG as a function of temperature, T for Ti29.44Cu46.72Ni7.88Hf8.40Zr7.60

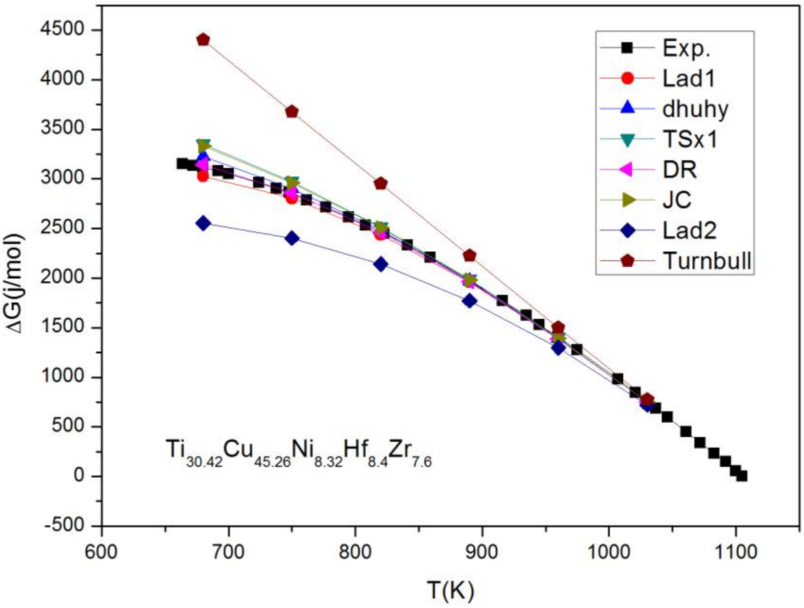

Fig.7 Gibbs free energy difference, ΔG as a function of temperature, T for Ti30.42Cu45.26Ni8.32Hf8.4Zr7.60

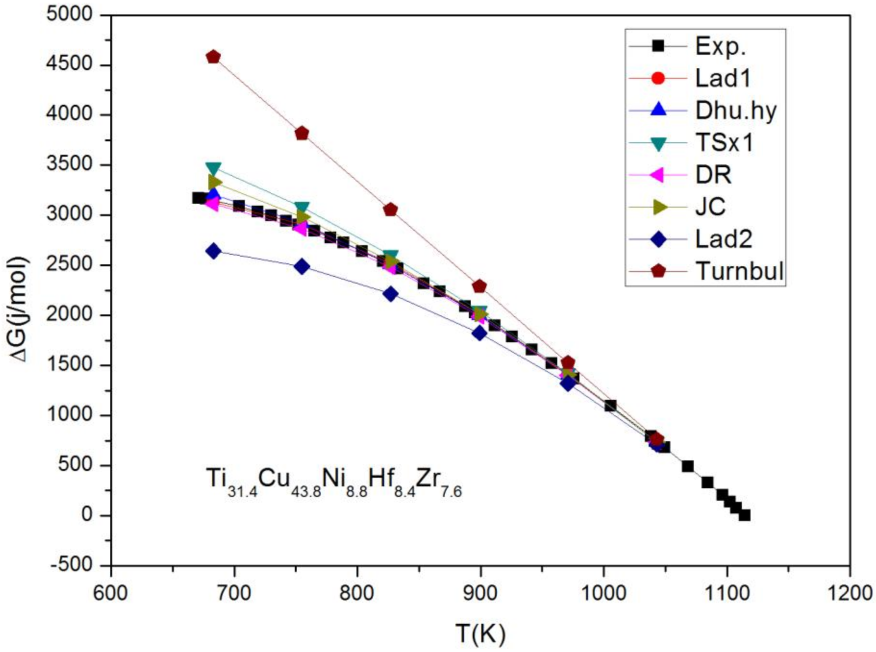

Fig.8 Gibbs free energy difference, ΔG as a function of temperature, T for Ti31.4Cu43.8Ni8.8Hf8.40Zr7.60

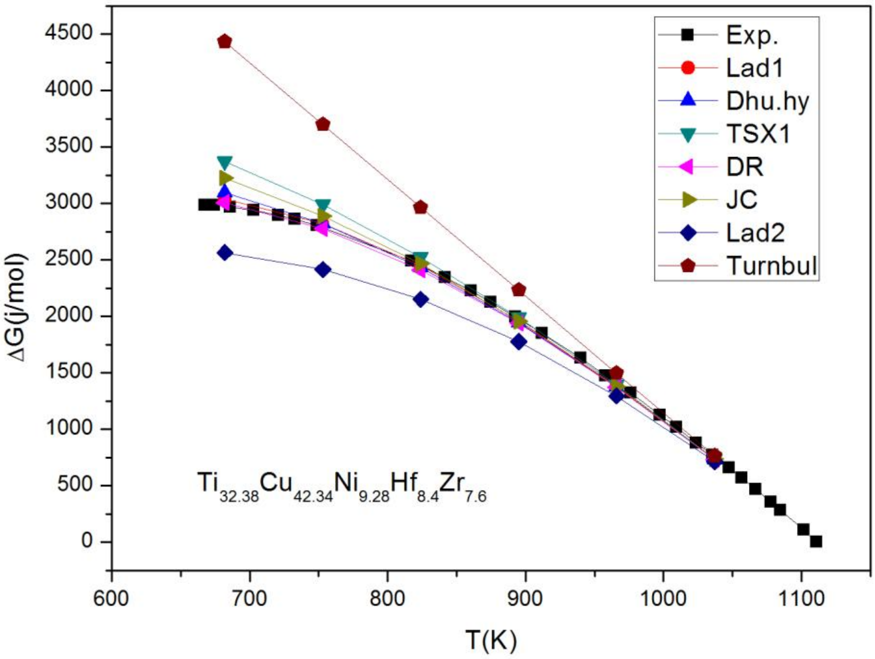

Fig.9 Gibbs free energy difference, ΔG as a function of temperature, T for Ti32.36Cu42.34Ni9.28Hf8.40Zr7.60

4.4 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 $\Delta T_{xg}=T_x- T_g=75K$ is an indication of the devitrification tendency of ZBLAN glass upon heating above T_g. The lower value of ΔG (T_g) =2.2kJ/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 with experimental data.

Ti29.44Cu46.72Ni7.88Hf8.40Zr7.60