J Therm Anal Calorim (2010) 100:347–353
DOI 10.1007/s10973-009-0011-x

Analysis of thermodynamic behaviour of bulk metallic glass forming melts and glass forming ability

P. K. Singh · K. S. Dubey

Received: 2 March 2009 / Accepted: 12 May 2009 / Published online: 10 June 2009

Abstract The thermodynamic behaviour of bulk metallic glass (BMG) forming melts have been studied by analyzing the temperature dependence of the Gibbs free energy difference (ΔG), entropy difference (ΔS) and enthalpy difference (ΔH)between the undercooled melt and the corresponding equilibrium solid phases. The study is made by calculatingΔG, ΔS and ΔH in the entire temperature range T_m (melting temperature) to T_g (glass transition temperature) using the expressions obtained on the basis of Taylor's series expansion. The entire analysis is made for La-based five samples of BMGs; $La_{55}Al_{25}Ni_{20,}$ $La_{55}Al_{25}Ni_{15}Cu_5$, $La_{55}Al_{25}Ni_{10}Cu_{10}$, $La_{55}Al_{25}Ni_5Cu_{15,}$ and $La_{55}Al_{25}Ni_5Cu_{10}Co_5$ and a comparative study is also performed between present results and results obtained in the framework of expressions proposed by earlier workers. An attempt has also been made to study the glass forming ability for BMGs.

Keywords Bulk metallic glasses · Gibbs free energy · Glass forming ability · Thermodynamics of undercooled liquids

Introduction

The advent of a new family of bulk metallic glasses (BMGs) has prompted new interest for the understanding of non-crystalline materials due to their promising technological applications. It provides a wide supercooled liquid region and high thermal stability against crystallization, which offers a large experimentally accessible time and temperature window to investigate nucleation and growth in glass forming metallic melts. The studies of the thermodynamic behaviour of glass forming liquids are essential for understanding the origins of glass forming ability of materials. The Gibbs free energy change ΔG on crystallization of multicomponent undercooled systems is an important parameter in understanding the nucleation and growth processes. In principle, ΔG can be calculated by using the elementary thermodynamic procedures from the knowledge of experimentally measured values of the specific heat difference (ΔC_P) between the undercooled liquid and corresponding equilibrium solid phases. However, the metastability of undercooled liquid precludes the measurement of specific heat of supercooled phase over the temperature range of interest. In absence of these data, several investigators [1–10] prompted to suggest appropriate expressions for ΔG in terms of more easily measured parameters such as enthalpy of fusion ΔH_m, melting temperature T_m etc. Most of these expressions are based on the various kinds of assumptions related to either temperature dependence of ΔC_p or its magnitude. Recently, Lele et al. [11] obtained an expression for ΔG using Taylor's series expansion, which has been successfully employed [12, 13] to calculate ΔG for organic, oxide, polymeric and simple glasses. Following the earlier work of Lele et al. [11], the aim of the present work is to study ΔG for bulk metallic glasses (BMGs) in the temperature range T_m to glass transition temperature (T_g). The enthalpy difference ΔH and entropy difference ΔS between undercooled liquid and corresponding equilibrium solid phases have also been studied. The entire study is made for La-based five samples of BMGs; $La_{55}Al_{25}Ni_{20,}$ $La_{55}Al_{25}Ni_{15}Cu_5$, $La_{55}Al_{25}Ni_{10}Cu_{10}$, $La_{55}Al_{25}Ni_5Cu_{15,}$ and $La_{55}Al_{25}Ni_5Cu_{10}Co_5$. A comparative study is also made

P. K. Singh · K. S. Dubey (✉)
Department of Applied Physics, Institute of Technology,
Banaras Hindu University, Varanasi 221005, India
e-mail: dubeyks@gmail.com

P. K. Singh
e-mail: om.pavansingh@gmail.com

between present results and results obtained using the expressions proposed by earlier authors.

Glass forming ability (GFA) is an important factor for understanding the origin of glass formation and it is a very crucial parameter for designing and developing new BMGs. As a result, a number of attempts [14–20] have been made to predict GFA among the BMGs on the basis of various characteristic temperatures measured [21–23]. The most commonly used are the reduced glass transition temperature $T_{\mathrm{rg}} = T_{\mathrm{g}}/T_{\mathrm{l}}$ and supercooled liquid region $\Delta T_{\mathrm{rg}} = (T_{\mathrm{x}} - T_{\mathrm{g}})/T_{\mathrm{l}}$, where T_{l} is the liquidus temperature and T_{x} is the onset crystallization temperature. Some of the workers [17] have also suggested to use ΔG as an indicator for GFA. Dubey et al. [24, 25] have also attempted to discuss the GFA of simple glasses in terms of reduced Kauzmann [26] temperature ($T_{\mathrm{k}}/T_{\mathrm{m}}$) and $\Delta C_{\mathrm{p}}^{\mathrm{m}} \big/ \Delta S_{\mathrm{m}}$, where T_k is the Kauzmann temperature, $\Delta C_{\mathrm{p}}^{\mathrm{m}}$ is the specific heat difference between liquid and solid phases at T_{m} and ΔS_{m} is the entropy of fusion. Following the earlier work of Dubey and his coworkers [24, 25], an attempt has been made to discuss the GFA for BMGs on the basis of reduced Kauzmann temperature $\delta = T_{\mathrm{k}}/T_{\mathrm{m}}$, $\Delta C_{\mathrm{p}}^{\mathrm{m}} \big/ \Delta S_{\mathrm{m}}$ and $(T_{\mathrm{g}} - T_{\mathrm{k}})/T_{\mathrm{m}}$.

Expressions for the thermodynamic parameters ΔG, ΔS and ΔH

The Gibbs free energy difference ΔG between the undercooled liquid and corresponding equilibrium solid phases can be evaluated using thermodynamic relations

$$\Delta G = \Delta H - T\Delta S \tag{1}$$

where,

$$\Delta S = \Delta S_{\mathrm{m}} - \int_{T}^{T_{\mathrm{m}}} \frac{\Delta C_{\mathrm{P}}}{T} \mathrm{d}T, \tag{2}$$

$$\Delta H = \Delta H_{\mathrm{m}} - \int_{T}^{T_{\mathrm{m}}} \Delta C_{\mathrm{P}} \mathrm{d}T \tag{3}$$

$\Delta H_{\mathrm{m}} = T_{\mathrm{m}}\Delta S_{\mathrm{m}}$ and $\Delta C_{\mathrm{P}} = C_{\mathrm{P}}$ (liquid) $- C_{\mathrm{P}}$ (solid), C_{P} (liquid) and C_{P} (solid) are the heat capacities of the undercooled liquid and solid phases, respectively. The experimental data of ΔC_{P} enable one to use Eqs. (1–3) to evaluate ΔG as well as other thermodynamic parameters ΔS and ΔH. However, as stated earlier the metastability of liquid precludes the experimental determination of ΔC_{p}. Because of these experimental difficulties, an analytical expression is needed for the evaluation of ΔG.

Following Lele et al. [11], an expression for ΔG can be achieved by expanding the free energies of the phases viz., undercooled liquid and solid around their values at T_{m} in the form of Taylor's series expansion

$$G^{\mathrm{i}} = G^{\mathrm{i}}_{\mathrm{m}} - \left|\frac{\partial G^{\mathrm{i}}}{\partial T}\right|_{T_{\mathrm{m}}} \Delta T + \frac{1}{2!}\left|\frac{\partial^2 G^{\mathrm{i}}}{\partial T^2}\right|_{T_{\mathrm{m}}} \Delta T^2 - \frac{1}{3!}\left|\frac{\partial^3 G^{\mathrm{i}}}{\partial T^3}\right|_{T_{\mathrm{m}}} \Delta T^3 + \frac{1}{4!}\left|\frac{\partial^4 G^{i}}{\partial T^4}\right|_{T_{\mathrm{m}}} \Delta T^4 - \ \ldots \tag{4}$$

where i stands to L and S to represent undercooled liquid and equilibrium solid phases, respectively, and derivatives are taken at $T = T_{\mathrm{m}}$ and $\Delta T = T_{\mathrm{m}} - T$ is the degree of undercooling. The expansion of series extends the free energy versus temperature (G vs. T) curves to each phase into their metastable regions. The proper substitution of the various thermodynamic derivatives of G^{L} and G^{S}, Eq. 4 yields

$$\Delta G = \Delta S_{\mathrm{m}}\Delta T - \frac{\Delta C_{\mathrm{p}}^{\mathrm{m}}}{(T_{\mathrm{m}} + T)}\Delta T^2 + \left|\frac{\partial \Delta C_{\mathrm{p}}}{\partial T}\right|_{T_{\mathrm{m}}} \frac{\Delta T^3}{(T_{\mathrm{m}} + T)} - \ \ldots \tag{5}$$

During the analysis it is also found that the contributions due to third and other higher order terms are very small in comparison to the contributions due to the first and second terms and these can be neglected without much loss of accuracy. Consequently, a very simple expression for ΔG can be obtained as

$$\Delta G = \Delta S_{\mathrm{m}}\Delta T - \frac{\Delta C_{\mathrm{p}}^{\mathrm{m}}\Delta T^2}{(T_{\mathrm{m}} + T)}, \tag{6}$$

which requires a knowledge of $\Delta C_{\mathrm{p}}^{\mathrm{m}}$, ΔS_{m} and T_{m} and these parameters can be measured experimentally without much complications.

A similar Taylor's series expansion can also be carried out to get expressions for ΔS and ΔH and resulting expressions take the form of

$$\Delta S = \Delta S_{\mathrm{m}} - 2\Delta C_{\mathrm{p}}^{\mathrm{m}} \frac{\Delta T}{(T_{\mathrm{m}} + T)} \tag{7}$$

and

$$\Delta H = \Delta H_{\mathrm{m}} - \Delta C_{\mathrm{p}}^{\mathrm{m}}\Delta T \tag{8}$$

ΔG, ΔS and ΔH of La-based bulk metallic glasses

The experimental values of ΔG have been calculated with the aid of experimentally measured values of ΔC_{p} reported by earlier workers [17, 27] as

$$\Delta C_{\mathrm{p}} = AT + BT^{-2} + CT^2 \tag{9}$$

with the help of Eq. 1, where A, B and C are constants. The material parameters used in the present analysis are reported

Table 1 The material parameters used for the evaluation of ΔG, ΔS and ΔH of five samples of La-based BMGs

Parameters	Materials				
	$La_{55}Al_{25}Ni_{20}$	$La_{55}Al_{25}Ni_{15}Cu_5$	$La_{55}Al_{25}Ni_{10}Cu_{10}$	$La_{55}Al_{25}Ni_5Cu_{15}$	$La_{55}Al_{25}Ni_5Cu_{10}Co_5$
A/J mol^{-1} K^{-2}	2.194×10^{-2}	2.57×10^{-2}	3.445×10^{-2}	2.823×10^{-2}	2.522×10^{-2}
B/J mol^{-1} K^{-3}	1.235×10^{6}	1.078×10^{6}	1.463×10^{6}	1.666×10^{6}	1.687×10^{6}
C/J mol^{-1} K^{-2}	-1.009×10^{-5}	-9.208×10^{-6}	-3.663×10^{-5}	-2.202×10^{-5}	-1.813×10^{-5}
ΔH_m/J mol^{-1}	7.48×10^{3}	7.51×10^{3}	6.838×10^{3}	7.21×10^{3}	6.095×10^{3}
ΔS_m/J mol^{-1} K^{-1}	10.512	11.384	10.328	10.868	9.222
ΔC_p^m/J mol^{-1} K^{-1}	12.942	15.464	10.089	12.822	12.611
T_m/K	711.6	659.7	662.1	663.4	660.9
T_g/K	490.5	471.9	467.4	459.1	465.7

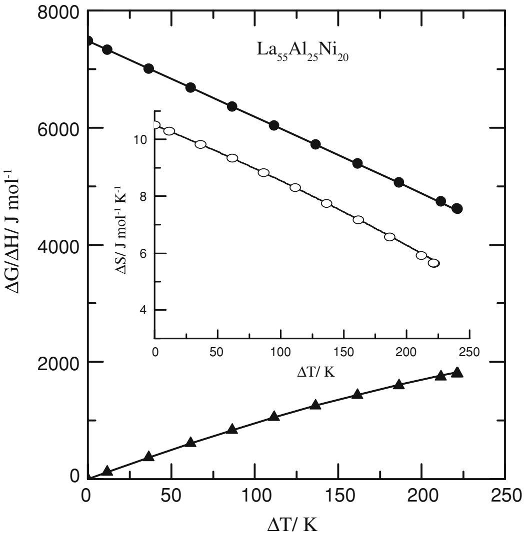

Fig. 1 The variations of ΔG, ΔH and ΔS with ΔT for $La_{55}Al_{25}Ni_{20}$ in the temperature range T_m to T_g. *Solid lines* are calculated values while *triangles*, *closed circles* and *open circles* stand for experimental values of ΔG, ΔH and ΔS, respectively

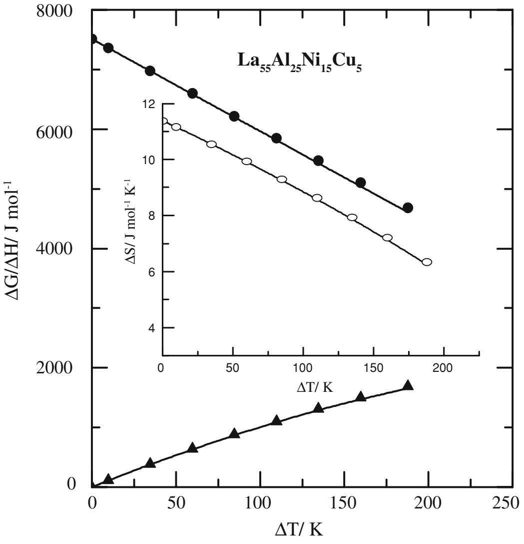

Fig. 2 The variations of ΔG, ΔH and ΔS with ΔT for $La_{55}Al_{25}Ni_{15}Cu_5$ in the temperature range T_m to T_g. The *solid lines* represent calculated values and *triangles*, *closed circles* and *open circles* are experimental values of ΔG, ΔH and ΔS, respectively

in Table 1. To see the applicability of expression for ΔG stated in Eq. 6, ΔG has been calculated for five samples of La-based BMGs; $La_{55}Al_{25}Ni_{20}$, $La_{55}Al_{25}Ni_{15}Cu_5$, $La_{55}Al_{25}Ni_{10}Cu_{10}$, $La_{55}Al_{25}Ni_5Cu_{15}$ and $La_{55}Al_{25}Ni_5Cu_{10}Co_5$ in the entire temperature range T_m to T_g and results obtained are illustrated in Figs. 1, 2, 3, 4, 5. The temperature dependence of thermodynamic parameters ΔS and ΔH has also been studied by estimating ΔS and ΔH for all samples using Eqs. 7 and 8, respectively, in the temperature range T_m to T_g and results obtained are also illustrated in Figs. 1, 2, 3, 4, 5 of the respective samples. The experimental values of ΔS and ΔH are evaluated using Eqs. 2 and 3, respectively.

From Figs. 1, 2, 3, 4, 5, it can be seen that the agreement between calculated and experimental values of ΔG is very good for all five samples in the entire temperature range T_m to T_g and it can be said that expression reported in Eq. 6 is capable of explaining temperature dependence of ΔG very successfully for BMG samples. From these Figures, it can also be seen that the agreement between calculated and experimental values of ΔS and ΔH is very good for low degree of undercooling while there are some discrepancies for three samples $La_{55}Al_{25}Ni_{10}Cu_{10}$, $La_{55}Al_{25}Ni_5Cu_{15}$ and $La_{55}Al_{25}Ni_5Cu_{10}Co_5$ for large degree of undercooling. Thus one can say that the expressions for ΔS and ΔH reported in Eqs. 7 and 8, respectively, are also quite capable to explain the temperature dependence of ΔS and ΔH.

A comparative study has also been made between the present result and the results obtained in the frame of expressions proposed by earlier workers by calculating ΔG for one sample $La_{55}Al_{25}Ni_5Cu_{10}Co_5$ and results obtained are reported in Table 2. From Table 2, it can be seen that

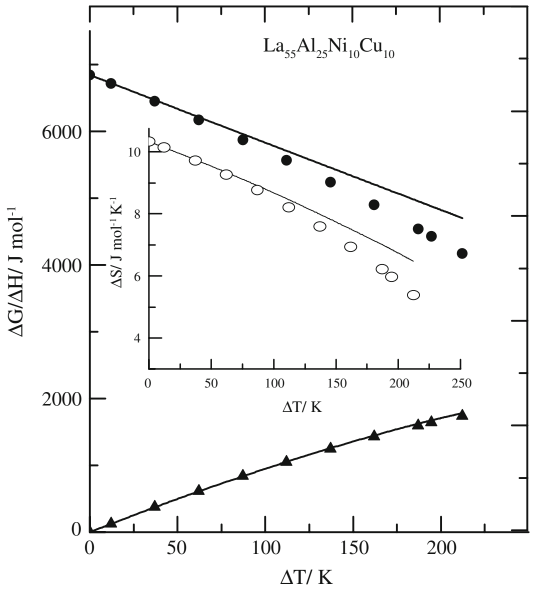

Fig. 3 The variations of **Δ***G, ΔH* and *ΔS* with *ΔT* for $La_{55}Al_{25}$-$Ni_{10}Cu_{10}$ in the temperature range T_m to T_g. Solid lines represent calculated values while *triangles*, *closed circles* and *open circles* show experimental values of **Δ***G, ΔH* and *ΔS*, respectively

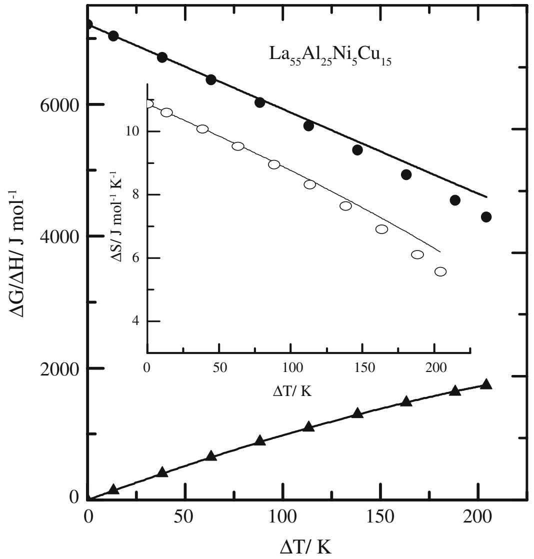

Fig. 4 The variations of **Δ***G, ΔH* and *ΔS* with *ΔT* for $La_{55}Al_{25}$-$Ni_{5}Cu_{15}$ in the temperature range T_m to T_g. *Solid lines* correspond to calculated values while *triangles*, *closed circles* and *open circles* represent experimental values of **Δ***G, ΔH* and *ΔS*, respectively

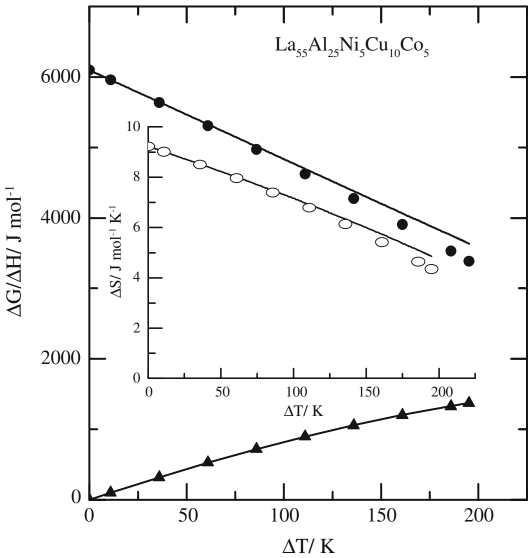

Fig. 5 The variations of **Δ***G, ΔH* and *ΔS* with *ΔT* for $La_{55}Al_{25}Ni_{5}$-$Cu_{10}Co_{5}$ in the temperature range T_m to T_g. *Solid lines* show the calculated results while *triangles*, *closed circles* and *open circles* are experimental values of **Δ***G, ΔH* and *ΔS*, respectively

the values of ΔG obtained on the basis of expression stated in Eq. 6 based on Taylor's series expansion are closest to the experimental values even for large degree of undercoolings. At $T = T_g$, the difference between the experimental and calculated values of ΔG is only about 0.44% for the undercooling $\Delta T = 195.2$ K while it is 31.58%, 7.3%, 8.77%, 28.0%, 10.09% and 1.75% on the basis of expressions reported by Turnbull [1], Hoffmann [2], Thompson and Spaepen [4], Singh and Holtz [5], Lad et al. [6] and Dhurandhar et al. [9], respectively.

Thus, the expression for ΔG stated in Eq. 6 can be used to study the nucleation and growth processes of bulk metallic glass forming melts. At the same time, it is needed to state that expression for ΔG used is quite simple and needs ΔC_p^m, ΔS_m and T_m as input data which can be measured easily.

Glass forming ability of BMGs

Kauzmann [26] first of all, who studied the importance of rate of entropy loss with temperature in liquids and pointed out that a liquid loses its entropy at a faster rate than the solid resulting in the equal entropy of both phases solid and liquid at some temperature T_k well above the absolute temperature. The iso-entropic temperature T_k is referred as the ideal glass transition temperature. It is also called the Kauzmann temperature and it plays an important role in the estimation of residual entropy ΔS_R and GFA of materials. Realizing that $\Delta S = 0$ at $T = T_k$, and using Eq. 2, the Kauzmann temperature T_k has been estimated for all five samples and results obtained are reported in Table 3.

Kauzmann predicted that the rate of change of reduced entropy $\Delta S/\Delta S_m$ with respect to reduced temperature T/T_m measures the likelihood that T_k exists above the absolute zero. He further argued that the derivative attains a value $\Delta C_p^m \big/ \Delta S_m$ at T_m. Consequently, high value of $\delta(= T_k/T_m)$ can be anticipated for materials with larger values of

Table 2 The Gibbs Free energy difference ΔG between undercooled liquid and corresponding equilibrium solid phases of $La_{55}Al_{25}Ni_5Cu_{10}Co_5$ calculated using various expressions of ΔG given by earlier workers. Experimental value of ΔG is evaluated using experimental data of ΔC_p

T/K	ΔT/K	ΔG (J/mol)							
		Turnbull [1]	Hoffman [2]	Thompson and Spaepen [4]	Singh and Holtz [5]	Lad et al. [6]	Dhurandhar et al. [9]	Present	Experimental
465.7 (T_g)	195.2	1800	1268	1488	5209	1230	1344	1374	1368
475	185.9	1714	1232	1434	5018	1199	1306	1331	1326
500	160.9	1484	1123	1278	4474	1101	1188	1203	1200
525	135.9	1253	996	1110	3884	983	1048	1057	1056
550	110.9	1023	851	929	3252	844	890	895	894
575	85.9	792	689	737	2580	686	715	717	717
600	60.9	562	510	535	1871	509	524	524	524
625	35.9	331	313	322	1126	313	318	318	318
650	10.9	101	99	100	349	99	99	99	99

Table 3 The parameters used in analysis of GFA of BMGs

S·N.	Materials	Materials parameters					
		T_k/K	$T_g - T_k$/K	$\frac{\Delta C_p^m}{\Delta S_m}$	$\delta = \frac{T_k}{T_m}$	$\left(\frac{T_g - T_k}{T_m}\right)$	R_c/K s^{-1}
1	$La_{55}Al_{25}Ni_{20}$	335.869	154.631	1.231	0.472	0.217	67.5
2	$La_{55}Al_{25}Ni_{15}Cu_5$	317.497	154.403	1.358	0.481	0.234	34.5
3	$La_{55}Al_{25}Ni_{10}Cu_{10}$	332.019	135.381	0.977	0.501	0.218	22.5
4	$La_{55}Al_{25}Ni_5Cu_{15}$	340.031	119.069	1.179	0.513	0.179	35.9
5	$La_{55}Al_{25}Ni_5Cu_{10}Co_5$	362.93	102.77	1.367	0.549	0.516	18.8

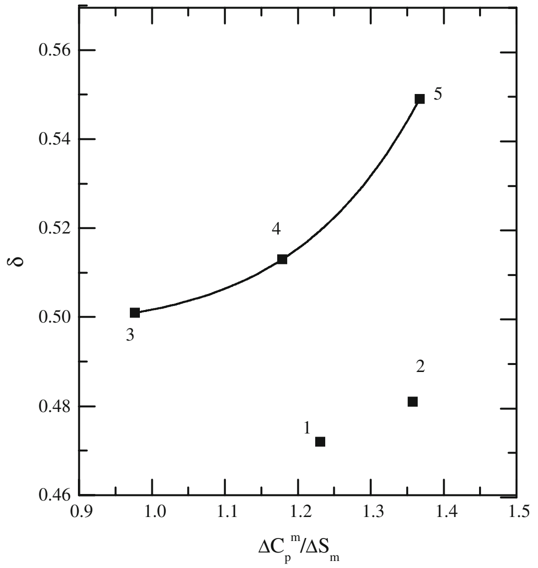

Fig. 6 The variation of δ with $\Delta C_p^m \big/ \Delta S_m$ for BMGs. The numbers in the plot refers to the corresponding material as indicated serial numbers in Table 3

$\Delta C_p^m \big/ \Delta S_m$ and such a correlation can be seen in Fig. 6 which shows the variation of δ with $\Delta C_p^m \big/ \Delta S_m$. The actual relationship between δ and $\Delta C_p^m \big/ \Delta S_m$ requires the knowledge of exact temperature dependence of ΔS which can be arrived at only from the knowledge of $\varDelta C_p$. However, an empirical relation can be obtained as

$$\delta = a_1 + b_1 \left(\frac{\Delta C_p^m}{\Delta S_m} \right)^{m_1} \tag{10}$$

with $a_1 = 0.4977$, $b_1 = 0.0040$ and $m_1 = 8.1822$ and correlation factor 0.9998.

The critical cooling rate R_c can be used for quantifying the glass forming ability of bulk metallic glasses. The smaller R_c, the higher the GFA of a material and such melts are known as better glass former. Dubey and Ramachandrarao [24] studied the GFA of simple glasses and reported the crucial role of δ and $\Delta C_p^m \big/ \Delta S_m$ in the estimation of R_c. Thus, it is interesting to study the role of these parameters in the analysis of GFA of BMGs.

The variation of R_c [28] with δ has been illustrated in Fig. 7 which shows decreasing nature of R_c with increasing δ. It may be argued that materials with a large value of δ are likely to form glasses more easily by requiring a low R_c. It is needed to state that Turnbull [29] as well as Davies [30] have attempted to correlate T_g/T_m with R_c. It is very difficult to have an analytical relation between R_c and δ. However, an attempt has been made to have a simple relation based on experimental data as

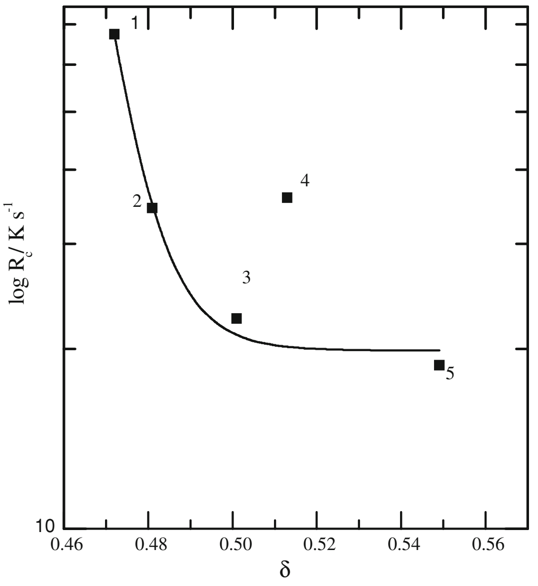

Fig. 7 The variation of critical cooling rate R_c with δ for BMGs. The numbers in the plot indicates the corresponding material as the serial numbers in Table 3

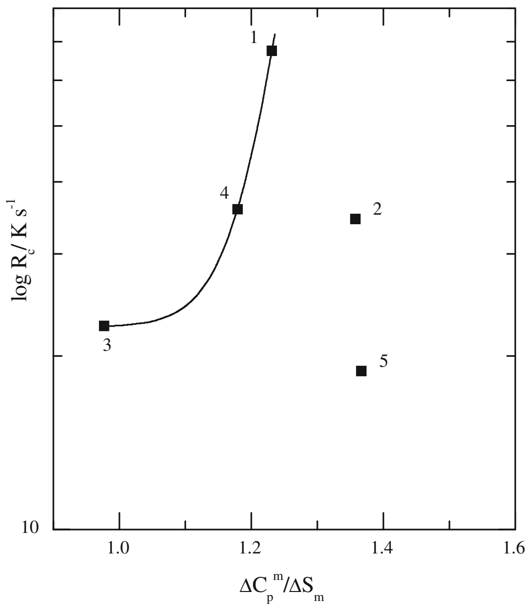

Fig. 8 The variation of critical cooling rate R_c with $\Delta C_p^m / \Delta S_m$ for BMGs. The numbers in the plot is the corresponding material as the serial numbers Table 3

$$\log R_c = a_2 + b_2 \delta^{m_2} \tag{11}$$

with $a_2 = 19.88$, $b_2 = 5.34$ and $m_2 = -61.28$ and correlation factor 0.9978.

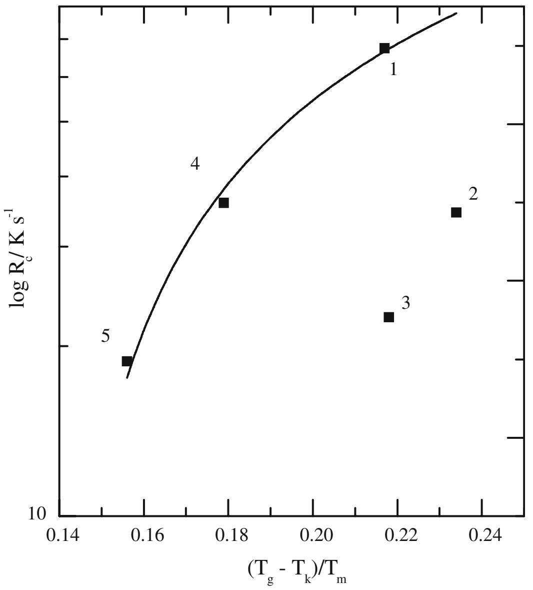

Fig. 9 The variation of critical cooling rate R_c with $(T_g - T_k)/T_m$ for BMGs. The numbers in the plot refers to the corresponding material of the serial numbers as listed in Table 3

As seen above, δ is in self a function of $\Delta C_p^m / \Delta S_m$. Hence, R_c should correlate with $\Delta C_p^m / \Delta S_m$. The variation of R$_c$ with $\Delta C_p^m / \Delta S_m$ is illustrated in Fig. 8 which shows the decreasing nature of R$_c$ with increasing $\Delta C_p^m / \Delta S_m$ except for the sample $La_{55}Al_{25}Ni_{10}Cu_{10}$. It can be understood by looking the correlation between δ and $\Delta C_p^m / \Delta S_m$. Thus, once again it may be seen that the material having large $\Delta C_p^m / \Delta S_m$ requires low R_c and such material can be converted into glassy state more easily. A simple relation can be obtained on the basis of data shown in Fig. 8 as

$$\log R_c = a_3 + b_3 \left(\frac{\Delta C_p^m}{\Delta S_m} \right)^{m_3} \tag{12}$$

with $a_3 = -14522.93586$, $b_3 = 14676.17534$ and $m_3 = -0.02805$ and correlation factor 0.9314.

Both the Kauzmann temperature T_k and the glass transition temperature T_g play a crucial role in viscosity of glass forming melts as well as nucleation and growth processes. As a result, both T_g and T_k play a significant role in assigning the GFA of BMGs and it is interesting to study the combined effect of these parameters in the study of GFA of glass forming melts. The variation of R$_c$ with $(T_g - T_k)/T_m$ is illustrated in Fig. 9 for all five samples which shows decreasing nature of R_c with decreasing $(T_g - T_k)/T_m$. It means, the material having T_k closer to T_g requires low degree of undercooling to convert into glassy state and such material is known as good glass former. It can also be understood in term of residual entropy or frozen-in-entropy ΔS_R. According to Gibbs and Dimarzio [31], the residual entropy or frozen-in-entropy is the amount of entropy of the glass forming melt that has been blocked in at T_g during the glass formation and remains in the glassy state even at $T = 0$ K. The materials having low value of $(T_g - T_k)$ corresponds to low value of residual entropy. Thus the material showing low $(T_g - T_k)/T_m$ can form glasses more readily than those having large $(T_g - T_k)/T_m$.

An attempt has also been made to establish a relation between R_c and $(T_g - T_k)/T_m$ on the basis of data reported in Table 3, and it can be expressed as

$$\log R_c = a_4 + b_4 \left(\frac{T_g - T_k}{T_m} \right)^{m_4} \tag{13}$$

where, $a_4 = -1.03596 \times 10^5$, $b_4 = 1.03890 \times 10^5$ and $m_4 = 1.43 \times 10^{-3}$ and correlation factor $R = 0.9945$.

Conclusion

The thermodynamic behaviour of BMGs have been studied by estimating ΔG, ΔS *and* ΔH for five samples of La-based bulk metallic glasses using expressions obtained on the basis of Taylor's series expansion and results obtained are very close to the experimental values. The value of ΔG obtained in the present work is better than ΔG obtained in the frame of expression reported by earlier workers.

The ideal glass transition temperature T_k has been estimated and GFA of BMGs has been studied on the basis of δ, $\Delta C_p^m \big/ \Delta S_m$ and $(T_g - T_k)/T_m$. It has been found that material having large $\Delta C_p^m \big/ \Delta S_m$ shows a large δ and such material requires a low R_c for glass formation. Thus material having large $\Delta C_p^m \big/ \Delta S_m$ can be said as good glass former. It is further found that material showing T_k closer to T_g requires low R_c for glass formation and such material can be said a better glass former.

References

1. Turnbull D. Formation of crystal nuclei in liquid metals. J Appl Phys. 1950;21:1022–8.
2. Hoffmann JD. Thermodynamic driving force in nucleation and growth processes. J Chem Phys. 1958;29:1192–3.
3. Jone DRH, Chadwick GA. An expression for the free energy of fusion in the homogeneous nucleation of solid from pure melts. Phil Mag. 1971;24:995–8.
4. Thompson CV, Spaepen F. On the approximation of the free energy change on crystallization. Acta Metall. 1979;27:1855–9.
5. Singh HB, Holtz A. Stability limit of supercooled liquids. Solid State Comm. 45;1983:985–8.
6. Lad KN, Raval KG, Pratap A. Estimation of Gibbs free energy difference in bulk metallic glass forming alloys. J Non-Cryst Solids. 2004;334–335:259–62.
7. Cai An-H, Chen H, Li X, Wang H, Zhau Y, An W. An expression for the calculation of Gibbs free energy difference of multi-component bulk metallic glasses. J Alloys Comp. 2007;430:232–6.
8. Battezzati L, Ganoue E. On the approximation of the free energy of undercooled glass-forming metallic melts. Z Metallk. 1984;75:305–10.
9. Dhurandhar H, Shanker Rao TL, Lad KN, Pratap A. Gibbs free energy for the crystallization of metallic glass-forming alloys from an undercooled liquid. Phil Mag Lett. 2008;88:239–49.
10. Dubey KS, Ramachandrarao P. On the free energy change accompanying crystallization of undercooled melts. Acta Metall. 1984;32:91–6.
11. Lele S, Dubey KS, Ramachandrarao P. On the temperature dependence of free energy of crystallization. Curr Sci. 1985;54: 994–5.
12. Dubey KS, Ramachandrarao P. Viscous and thermodynamic behaviour of glass-forming organic liquids. Bull Matter Sci. 1992;15:111–20.
13. Dubey KS, Ramachandrarao P, Lele S. On the estimation of the Kauzmann temperature from relaxation data. Polymer 1987;28:1341–4.
14. Du XH, Haung JC, Liu CT, Lu ZP. New criterion of glass forming ability for bulk metallic glasses. J Appl Phys. 2007; 101:086108-1–086108-3.
15. Lu ZP, Liu CT. A new glass-forming ability criterion for bulk metallic glasses. Acta Mater. 50;2002:3501–12.
16. Lu ZP, Fan H, Li Y, Ng SC. The correlation between reduced glass transition temperature and glass forming ability of bulk metallic glasses. Scripta Mater. 2000;42:667–73.
17. Lu ZP, Hu X, Li Y. Thermodynamics of La based La-Al-Cu-Ni-Co alloys studied by temperature modulated DSC. Intermetallics 2000;8:477–80.
18. Sun YJ, Qu DD, Huang YJ, Liss KD, Wei XS, Xing DW, Shen J. Zr-Cu-Ni-Al bulk metallic glasses with superhigh glass-forming ability. Acta Mater. 2009;57:1290-9.
19. Revesz A. Crystallization kinetics and thermal stability of an amorphous $Fe_{77}C_5B_4Al_2GaP_9Si_2$ bulk metallic glass. J Therm Anal Calorim. 2008;91:879–84.
20. Jiang QK, Wang XD, Nie XP, Zhang GQ, Ma H, Fecht HJ et al. Zr-(Cu,Ag)-Al bulk metallic glasses. Acta Mater. 2008;56:1785–96.
21. Mehta N, Kumar A. Comparative analysis of calorimetric studies in $Se_{90}M_{10}$(M=In, Te, Sb) chalcogenide glasses. J Therm Anal Calorim 2007;87:343–8.
22. Gorzkowska I, Jozwiak P, Garbarczyk JE, Wasiucionek M, Julien CM. Studies on glass transition of lithium-iron phosphate glasses. J Therm Anal Calorim. 2008;93:759–62.
23. Pratap A, Lilly Shanker Rao T, Lad KN, Heena KN, Dhurandhar D. Isoconversional vs. model fitting methods: a case study of crystallization kinetics of a Fe-based metallic glass. J Therm Anal Calorim. 2007;89:399–405.
24. Dubey KS, Ramachandrarao P. Rate of entropy loss with temperature in liquids and its relation to glass forming ability of materials. Int J Rapid Solidif. 1984–1985;11:1–14.
25. Mishra RK, Dubey KS. Analysis of thermodynamic parameters of glass forming polymeric melts. J Therm Anal Calorim. 2000;62:687–702.
26. Kauzmann W. The nature of the glassy state and the behavior of liquids at low temperatures. Chem Rev. 1948;43:219–56.
27. Lu ZP, Li Y, Liu CT. Glass-forming tendency of bulk La–Al–Ni–Cu–(Co) metallic glass-forming liquids. J Appl Phys. 2003;93: 286–90.
28. Lu ZP, Goh TT, Li Y, Ng SC. Glass formation in la-based La–Al–Ni–Cu–(Co) alloys by Bridgman solidification and their glass forming ability. Acta Mater. 1999;47:2215–24.
29. Turnbull D. Under what conditions can a glass be formed? Contempt Phys. 1969;10:473–88.
30. Davies HA. The formation of metallic glasses. Phys Chem Glasses. 1976;17:159–73.
31. Gibbs JH, Dimarzio EA. Nature of the glass transition and the glassy state. J Chem Phys. 1958;28:373–83.