COMPUTATION OF THERMODYNAMICAL PARAMETERS OF BMGS ON BASIS OF TAYLOR'S SERIES EXPANSION

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Abstract- The BMGs are the materials of interest of present and future scientific interest as these materials show good structural and functional applications and hence viewed as important metallic materials due to their exceptional properties of great strength at room temperature and high flexibility at high temperature. As a result, there is a race to study the thermodynamical properties of Bulk Metallic Glasses (BMGs). The Taylor series expansion is a mathematical tool used to represent a function as an infinite sum of terms calculated from the values of its derivatives at a specific point. However, the success of a Taylor series expansion depends on the behavior of the function and the range of temperatures one is interested in. In the context of thermodynamics and material science, Taylor series expansions can be used to approximate thermodynamic properties or expressions. In the present study, Taylor's series expansion is used to compute the thermodynamical parameters of some selected undercooled melts characterized under the class of BMGs.
Keywords: Bulk metallic glass; Taylor's series expansion; Thermodynamic parameters; Under-cooled melts;

1. INTRODUCTION

Bulk Metallic Glasses (BMGs) are a class of materials that exhibit unique thermodynamic and mechanical properties. BMGs are typically alloy systems that undergo a transition from a liquid to a glassy state during rapid cooling, bypassing the crystalline phase. This process is known as amorphization.
Here are some thermodynamic properties associated with Bulk Metallic Glasses:

1.1 Glass Transition Temperature (Tg)

The glass transition temperature is a critical parameter for BMGs. It represents the temperature at which the amorphous solid transitions from a glassy, rigid state to a more flexible, rubbery state. Tg is influenced by the alloy composition and cooling rate during solidification.

1.2 Specific Heat (Cp)

The specific heat of BMGs can vary depending on the alloy composition. Generally, it is lower than that of crystalline metals, and the absence of a distinct phase transition contributes to a more uniform specific heat over a wide temperature range.

1.3 Viscosity

The viscosity of the supercooled liquid during the rapid cooling process is a critical factor in the formation of BMGs. Higher viscosities at lower temperatures promote the avoidance of crystallization, allowing for the glassy state to be achieved.

1.4 Free Volume

The atomic structure of BMGs contains regions with a higher free volume compared to crystalline alloys. This free volume contributes to the unique mechanical properties of BMGs, such as high strength and elasticity.
The three important parameters required to study the important thermodynamical properties of BMGs are:

1.5 Gibbs Free Energy Difference (ΔG)

The Gibbs free energy (G) is a thermodynamic potential that combines the enthalpy (H) and entropy (S) of a system in a way that reflects the spontaneity of a process.
For a process occurring at constant temperature and pressure, the Gibbs free energy difference (ΔG) is related to the enthalpy (ΔH) and entropy (ΔS) changes by the equation: $\Delta G = \Delta H - T\Delta S$ where T is the absolute temperature. If ΔG is negative, the process is spontaneous.

1.6 Enthalpy Difference (ΔH)

Enthalpy is a measure of the total heat content of a system and is often associated with processes at constant pressure for a process is the heat transferred at constant pressure and is related to the heat of reaction or phase transition.

1.7 Entropy Difference (ΔS)

Entropy is a measure of the degree of disorder or randomness in a system. The entropy difference (ΔS) for a process is related to the heat transfer and temperature by the equation: ΔS=ΔH/T, where T is the absolute temperature.

The Gibbs free energy difference, enthalpy, and entropy differences are thermodynamic quantities that describe the energy changes associated with a process, such as a phase transition or a chemical reaction. These concepts can be applied to understand the behavior of bulk metallic glasses (BMGs) during various processes. For bulk metallic glasses (BMGs), these thermodynamic quantities can be used to understand and predict their behavior during processes such as cooling or heating, phase transitions, or alloying. Gibb's free energy difference (ΔG), entropy difference (ΔS) and enthalpy difference (ΔH) between the two states, i.e., the under-cooled liquid and equivalent equilibrium solid phases are proved to be incredibly invaluable in the investigation of thermodynamic conduct of the bulk metallic glass (BMG) forming melts. ΔS plays the key role in the learning of the viscous behaviour of the under-cooled melts. On the other hand, ΔH is an important parameter to formulate the crystallization heat and ΔG has been proved to be a significant factor to realize the conformist theory of nucleation and growth processes.

Several investigators including Dubey et. al. [1,2], Mishra et. al. [3], Gaur et. al recommended the investigative expressions for Gibb's free energy difference in terms of calculated parameters as the entropy of fusion (ΔS_m), melting temperature (T_m), etc. Such articulations rely on the assumptions that depend on the temperature reliance of ΔC_p; however the majority of such articulations are not enough for clarifying the reliance of Gibb's free energy difference on temperature over an extensive range of undercooling. Gaur et. al. [14-17], studied about the formulation of Gibbs free energy difference of the glass forming under-cooled BMGs based on articulations computed through the expansion of Taylor's series.

The Taylor series is a mathematical representation of a function as an infinite sum of terms calculated from the values of the function's derivatives at a single point. The Taylor series for the Gibbs free energy (G) is given by:

$$G(T) = G(T_0) + (T - T_0)\left(\frac{\partial G}{\partial T}\right)_{p,n} + \frac{(T - T_0)}{2!}\left(\frac{\partial^2 G}{\partial T^2}\right)_{p,n} + \frac{(T - T_0)}{3!} + \cdots \quad \cdots (1)$$

Here, T is the temperature, T_0 is a reference temperature, P is the pressure, n represents the composition of the system, and $\partial G/\partial T$, $\partial^2 G/\partial T^2$, etc., are the partial derivatives of G with respect to T at constant P and n. For practical calculations, we might truncate the series to include only a finite number of terms depending on the level of accuracy needed. Typically, the first few terms are sufficient for many applications.

If we know the specific form of G(T) for our system or have access to its derivatives, we can use the Taylor series to approximate the Gibbs free energy at temperatures near T_0. This can be particularly useful when we want to estimate the Gibbs free energy difference (ΔG) between two temperatures close to each other. Keep in mind that accurate calculation of thermodynamic properties often involves detailed knowledge of the system, and experimental data or theoretical models are commonly used to obtain the necessary derivatives for the Taylor series. It's also important to ensure that the temperature range and conditions of the Taylor series are appropriate for the system under consideration.

In the present study, the three important thermodynamical parameters: ΔH, ΔS and ΔG are computed for two selected BMG samples; $Mg_{65}Cu_{25}Y_{10}$ and $La_{62}Al_{14}Cu_{24}$.

2. COMPUTATION OF THERMODYNAMICAL PARAMETERS

The three parameters: ΔG, ΔS and ΔH may be predicted through the support of some important thermodynamical relations that can be deduced through the associated experimental values of specific heat difference (ΔC_p) between the under-cooled melt and the equilibrium solid phases. However, because of the burly propensity of the crystallization that confines the immediate formulation of the thermodynamical parameters, the test assurance of ΔC_p for glass forming melts in their super-cooled states can be completed distinctly only in a limited range of temperature beneath the melting temperature. As a consequence, most of the ΔC_p values of different BMGs are just the harsh approximations dictated via fitting of the restricted experimental data to T_m (melting temperature) in environs of T_g which is termed as glass transition temperature.

The specific values of these quantities will depend on the details of the BMG composition, structure, and the specific thermodynamic conditions under consideration. Understanding the thermodynamics of BMGs is crucial for their processing, fabrication, and potential applications in various industries. Experimental measurements and theoretical calculations can be used to determine these thermodynamic properties for specific BMG systems.

3. FORMULATION OF ΔG, ΔH AND ΔS

Recently Gaur et al. [14-17] and Rashmi et. al [17] have obtained an expression for ΔG at $T = T_m$ in the form of Taylor's series expansion. The thermodynamic behavior of non-crystalline BMG has been reported by many researchers on the basis of various kinds of approximations related to ΔC_p. Most of these investigations are confirmed to empirical relations using constant value of ΔC_p at T_g. The study of ΔG has been reported in the form of expression suggested by Dubey and Ramchndrarao [1-2] which was based on $\Delta C_p = 0$.

The aim of present work is to calculate the three thermodynamic parameters of BMGs with the support of Taylor's series expansion. In continuation on Taylor's series expansion, ΔG can be expressed as:

$$\Delta G = \Delta G - \left|\frac{\partial G}{\partial T}\right|_{T_m} \Delta T + \frac{1}{2!}\left|\frac{\partial^2 G}{\partial T^2}\right|_{T_m} \Delta T^2 - \frac{1}{3!}\left|\frac{\partial^3 G}{\partial T^3}\right|_{T_m} \Delta T^3 + \cdots \qquad \text{.... (2)}$$

Here, it is to be noted that expansion series extends the free energy versus temperature. By substitution of approximate form of the various thermodynamic derivatives, one can have

$$\Delta G = \Delta S_m \Delta T - \frac{\Delta C_p^m}{2 T_m}\Delta T^2 \left[1 + \frac{\Delta T}{3 T_m} + \frac{\Delta T^2}{6 T_m^2} + \frac{\Delta T^3}{6 T_m^3} + \cdots .\right] + \left|\frac{\partial C_p^m}{\partial T}\right|_{T_m} \frac{\Delta T^3}{6 T_m} \left[1 + \frac{\Delta T}{4 T_m} + \frac{\Delta T^2}{10 T_m^2} + \cdots\right]$$

.... (3)

It is needed to note that $T = T_m$; while by simplifying above equation (3) the approximation has been employed

$$\ln\left(\frac{T_m}{T}\right) = \frac{2\Delta T}{(T_m + T)} \qquad \text{...(4)}$$

to get the actual equation as

$$\Delta G = \Delta S_m \Delta T - \frac{\Delta C_p^m \Delta T^2}{(T_m + T)} \qquad \text{...(5)}$$

which requires the knowledge of ΔC_p^m, ΔS_m and T_m. These parameters can be measured experimentally without complications.

Similarly by expanding the enthalpies and entropies of both liquid and solid phases in the form of Taylor's series and reducing to the simple form, expressions for ΔH and ΔS can be expressed as

$$\Delta H = \Delta H_m - \Delta C_p^m \Delta T + \left[\frac{\partial \Delta C_p}{\partial T}\right]_{T_m} \frac{\Delta T^2}{2} - \qquad \text{…(6)}$$

$$\Delta S = \Delta S_m - \frac{2\Delta C_p^m \Delta T}{(T_m + T)} + \left[\frac{\partial \Delta C_p}{\partial T}\right]_{T_m} \frac{\Delta T^2}{(T_m + T)} \qquad \text{....(7)}$$

For the derivation of above expressions the approximation stated in equation (3) is considered and the third and higher order terms are neglected due to their trifling contributions.

The material constants used in the present work are taken from the reports of earlier workers are listed in Table 3.1, the experimental values of thermodynamic parameters ΔG, ΔH and ΔS are calculated with the help of experimental data of change in specific heat of the form

$$\Delta C_p = a + b/T^2 + cT^2 \qquad \text{...(8)}$$

and the basic thermodynamic relations:

$$\Delta H = \Delta H_m - \int_T^{T_m} \Delta C_p \, dT \qquad \text{...(9)}$$

$$\Delta S = \Delta S_m - \int_T^{T_m} \frac{\Delta C_p}{T} dT \qquad \text{....(10)}$$

$$\Delta G = \Delta H - T\Delta S \qquad \text{....(11)}$$

Here, a, b and c are constants. Using constants from table 3.1, thermodynamic parameters are calculated on the basis of equations (5), (6) and (7) respectively in the temperature range T_m to T_g. The study is made for two bulk metallic glasses ($Mg_{65}Cu_{25}Y_{10}$ and $La_{62}Al_{14}Cu_{24}$) from a vast range of materials. The results are shown in figures which show that the variation of ΔH, ΔS and ΔG with degree of undercooling ΔT. It can be observed that the agreement between calculated and experimental values of ΔG is very good in the entire temperature range for both the samples.

Table-3.1 The material Parameters used for the determination of Thermodynamical Parameters

Parameters	BMG Samples	
	$Mg_{65}Cu_{25}Y_{10}$	$La_{62}Al_{14}Cu_{24}$
A (Jmol^{-1}K^{-2})	0.01750	0.03071

B (Jmol^{-1}K)	1.8×10^5	4.16×10^5
C (Jmol^{-1}K^{-3})	-1.02×10^{-5}	-1.49×10^{-5}
ΔH_m (Jmol^{-1})	8.650×10^3	6.835×10^3
ΔS_m (Jmol^{-1}K^{-1})	11.879	10.156
ΔC_p^m (Jmol^{-1}K^{-1})	10.730	14.840
T_m (K)	730	673
T_g (K)	410	401

Table-3.2 Thermodynamic parameters of Mg$_{65}$Cu$_{25}$Y$_{10}$ calculated using various expressions based on earlier researchers, present study and the experimental values evaluated using experimental values of ΔC_p

T	ΔT	ΔC$_P$	ΔH$_{exp.}$	ΔS$_{exp.}$	ΔG$_{exp.}$	ΔH$_{present}$	ΔS$_{present}$	ΔG$_{present}$	ΔG$_{Turnbull}$	ΔG$_{Hoffmann}$	ΔG$_{Th. \& Sp.}$
710	20	10.85	8434.30	11.55	233.52	8434.33	11.55	234.02	237.00	230.51	233.71
660	70	11.24	7882.28	10.74	791.25	7883.53	10.75	791.72	829.50	749.96	787.73
610	120	11.72	7308.86	9.84	1306.31	7316.11	9.86	1306.83	1422.00	1188.25	1294.66
560	170	12.34	6708.16	8.81	1773.21	6732.07	8.88	1774.41	2014.50	1545.37	1749.02
510	220	13.19	6070.99	7.62	2184.81	6131.42	7.79	2188.69	2607.00	1821.33	2144.47
460	270	14.40	5383.05	6.20	2531.42	5514.16	6.58	2542.97	3199.50	2016.12	2473.56
410	320	16.17	4621.84	4.45	2799.22	4880.28	5.24	2829.35	3792.00	2129.75	2727.58

Table-3.3 Thermodynamic parameters of La$_{62}$Al$_{14}$Cu$_{24}$ calculated using various expressions based on earlier researchers, present study and the experimental values evaluated using experimental values of ΔC_p

T	ΔT	ΔC$_P$	ΔH$_{exp.}$	ΔS$_{exp.}$	ΔG$_{exp.}$	ΔH$_{present}$	ΔS$_{present}$	ΔG$_{present}$	ΔG$_{Turnbull}$	ΔG$_{Hoffmann}$	ΔG$_{Th. \& Sp.}$
651	22	14.66	6510.52	9.67	218.07	6510.48	9.67	218.01	223.43	216.13	219.72
601	72	14.23	5788.24	8.51	672.75	5787.21	8.51	670.86	731.23	653.00	689.91
551	122	13.77	5088.31	7.30	1068.21	5083.74	7.29	1058.60	1239.03	1014.42	1115.53
501	172	13.30	4411.56	6.01	1401.16	4400.09	6.01	1372.92	1746.83	1300.39	1490.91
451	222	12.86	3757.56	4.63	1667.64	3736.26	4.64	1604.03	2254.63	1510.90	1809.32
401	272	12.51	3123.78	3.14	1862.66	3092.23	3.19	1740.30	2762.43	1645.97	2062.82
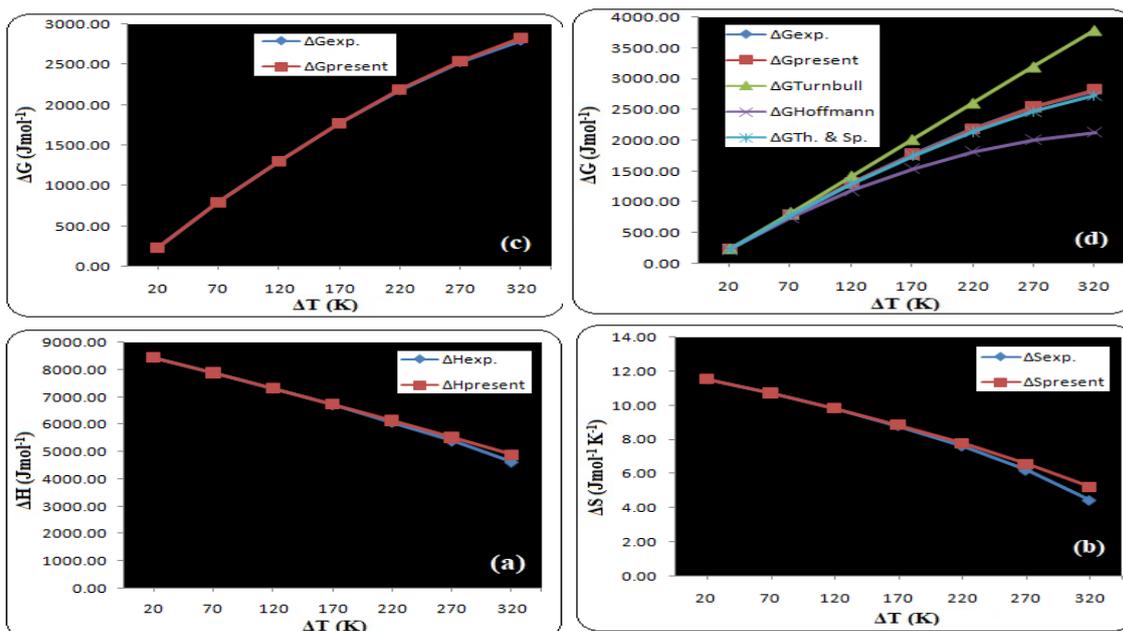
Fig. 3.1 (a) $\Delta H_{exp.}$ and $\Delta H_{present}$ vs ΔT for Mg$_{65}$Cu$_{25}$Y$_{10}$, **(b)** $\Delta S_{exp.}$ and $\Delta S_{present}$ vs ΔT for Mg$_{65}$Cu$_{25}$Y$_{10}$, **(c)** $\Delta G_{exp.}$ and $\Delta G_{present}$ vs ΔT for Mg$_{65}$Cu$_{25}$Y$_{10}$, **(d)** Comparision of various ΔG vs ΔT for Mg$_{65}$Cu$_{25}$Y$_{10}$.
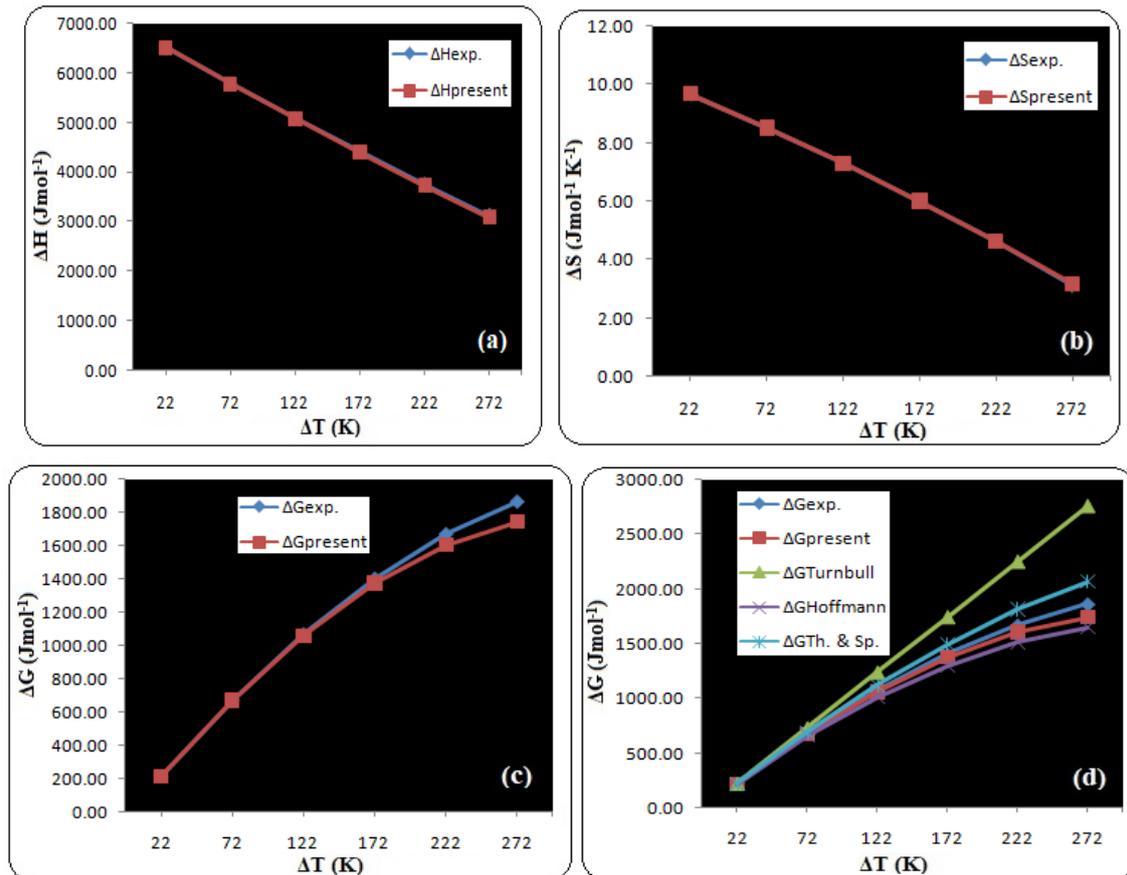
Fig. 3.2 (a) $\Delta H_{exp.}$ and $\Delta H_{present}$ vs ΔT for $La_{62}Al_{14}Cu_{24}$, (b) $\Delta S_{exp.}$ and $\Delta S_{present}$ vs ΔT for $La_{62}Al_{14}Cu_{24}$, (c) $\Delta G_{exp.}$ and $\Delta G_{present}$ vs ΔT for $La_{62}Al_{14}Cu_{24}$., (d) Comparision of various ΔG vs ΔT for $La_{62}Al_{14}Cu_{24}$.

CONCLUSION

The three thermodynamic parameters; ΔH, ΔS and ΔG amid the under-cooled melts and the analogous equilibrium solid phases, are formulated through the expansion of Taylor's series for two different selected samples of BMGs; $Mg_{65}Cu_{25}Y_{10}$ $La_{62}Al_{14}Cu_{24}$ in temperature variation from T_m to T_g. It can be interpreted from table 2 and 3; and also from the plotted curves for both samples that the calculated results on the basis of present study and experimental values of all the three computed thermodynamical parameters are very close to each other as compared to the results obtained in the form of expression produced by earlier researchers. Thus, it may be concluded that the expressions used in the present study are capable to explain the temperature dependence of ΔH, ΔS and ΔG satisfactorily. It is further concluded that the equations (5), (6) and (7) used in the present study for the three computed parameters based on the expansion of Taylor's series are simpler than the study of earlier researchers and are adequately skilled to elucidate the temperature reliance of the three parameters.

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