Study of Glass Transition Temperature in Se-Te-Pb Glassy System Using Modified Gibbs-Di Marzio Law

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Abstract

In this study, the modified Gibbs-Di Marzio law is used to ascertain glass transition temperature (T_g) in Se-Te-Pb glassy system. Herein, the amorphous $Se_{80-x}Te_{20}Pb_x$ (x = 0, 1 and 2) glasses are synthesized with melt-quenching process. The structural characterizations; surface morphology and amorphous nature of these samples were deduced using X-ray diffraction and scanning electron microscopy (SEM). Phase separation in SEM micrographs clearly reveal inhomogeneity and amorphous nature of primed chalcogenide alloys. Experimentally observed T_g via differential scanning calorimetry has been compared with theoretically calculated T_g using Gibbs–Di Marzio relation. Thus determined T_g are also compared with the other empirical approaches to analyse the utility of these approaches.

Keywords: Chalcogenide Glass, DSC, Gibbs–Di Marzio Law, Glass Transition Temperature.
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Introduction

Among the fascinating parameters in the field of materials engineering and science is the origin of glass-forming inclination along with the estimation of the temperature at which glass transition (T_g) occurs. This is necessary in some circumstances to maximise the glass formation process, not only for purely scientific reasons but also for technological ones. Thus, many attempts have been made to relate the value of T_g to certain readily measured parameters as well as to comprehend the nature of glass transition. Chalcogenide glass undergoes structural changes and crystallises when reheated at a steady rate during the DSC experiment [1]. In DSC, an initial endothermic peak (before exothermic peak of crystallization) represents the glass transition. The rapid shift in enthalpy that occurs when glassy alloy relaxes rapidly owing to decline in viscosity at T_g can result in the reflection as an endothermic variation in chalcogenide glasses. To study the thermal relaxation of glasses, the DSC approach is helpful [1–2].

Glassy materials have a long history that predates nearly all human civilizations. It is long believed that chalcogenide glasses are non-semiconductors due to absence of long-range order [3]. During 1950 -1960, this field again attracted the interest of material's scientists and start broad research due to potential and current applications in infrared (IR) lasers, photonic crystals, transistors, optical memories and IR transmitting optical fibres because of their switching, photoconductive, memory retention and semiconducting qualities [4-6]. This field has become the central field of research as it is technologically sensitive. Moreover, Se-based glasses remain quite popular because of their special ability to undergo reversible transformation, which has numerous device applications [7]. But Se has drawbacks including a short lifespan and low sensitivity [1]. Alloying this with impurity like Te, Ga, Ge etc may resolve these issues [8]. From a technological perspective, however, Se-Te based alloys are shown to have lower glass transition temperature, reduced crystallisation and lower reversibility [7]. The physical, structural, optical, thermal and electrical characteristics of Se-Te system are significantly impacted by addition of metallic additives like Pb, which alters system's fundamental bonding network and structure of

bands [9]. Mott discovered that in some chalcogenide systems, charged additions like Pb could alter the ratio of valence-alternation pairs to the point where the Fermi energy becomes unpinned, resulting in carrier type reversal [4-6, 10]. Scientists are now investigating the basic characteristics of Pb additive semiconductors because of their many exciting, appealing and distinctive characteristics. To illustrate the potential applications of chalcogenide systems, it is useful to recognise their distinct properties.

Recent observations of intermediate phases in chalcogenide system indicate that glassy alloy has optimal stress-free network as well as an optimised glass-forming inclination [11]. Understanding nucleation along with crystalline development of glassy materials is crucial for cost-effectiveness and straightforward material synthesis in device fabrication [12]. Glassy solid state has a large viscosity, the relaxation kinetics are very slow leaving a few opportunities for local arrangements of bonds and atomic displacements. This type of thermal relaxation depends upon the annealing temperature and may be quite fast near the glass transition temperature.

In order to analyse transport processes, thermal-stability, ease of glass formation and ultimately to identify the appropriate operating temperature range for particular technological appliance prior to crystallisation, the kinetics of crystallisation are crucial [13]. Neither a generalised formula for all materials nor even one for a particular material within a broad range of heating rates exists for the T_g with respect to the heating rate. To explain that glass might be in that state at operating temperature, it is crucial to use the glass transition.

Hence this study examines the utility of modified Gibbs-Di Marzio law to determine glass transition temperature in Pb doped $Se_{80-x}Te_{20}Pb_x$ (x = 0, 1 and 2) glassy system primed by melt quenching process. The amorphous nature of the composition under examination and its surface appearance was examined via XRD and SEM methodology. Experimentally observed T_g using DSC at a rate of 10°Cmin^{-1} is compared with theoretically calculated T_g using the empirical approaches namely Gibbs–Di Marzio, Tichy-Ticha, Lankhorst and Tanaka approaches to analyse the utility of these relations.

Experimental Details

The process of melt quenching is utilised to prime the bulk samples. After being weighed based on their atomic percentages, 5N extremely pure materials (99.999%) at a vacuum of around ~ 2×10^{-5} mbar is sealed in a quartz ampoule about 12 mm in diameter and 5 cm long. A furnace is used to elevate the temperature of the sealed ampoules to 900°C at a pace of 3–4°C per minute. For 24 hours at maximum temperature, ampoules are rocked repeatedly to ensure a uniform melt. Rapid quenching is carried out in the ice-cooled water to avoid crystallisation. The ingots of bulk samples are procured from the ampoules. A fine powder is made by grinding these ingots. Structural examination is carried out in room temperature using x-ray diffractometer source (PANalytical X′Pert), which utilising Cu K_α–radiation (wavelength = 1.54056 Å) as X-ray equipped with a Ni filtered, to capture XRD patterns of examined glassy alloys in range $10° < 2\theta < 90°$ at rate of scanning 1°/min. The lack of identifiable, sharp peaks in XRD spectra indicates that chalcogenide alloys under investigation are amorphous as reported previously [14]. Surface morphology along with amorphous nature of system under consideration is further analysed with SEM (QUANTA FEG 250) operating at 15 kV accelerating voltage; which suggests that XRD results are consistent with SEM outcomes. The scanned image of $Se_{79}Te_{20}Pb_1$

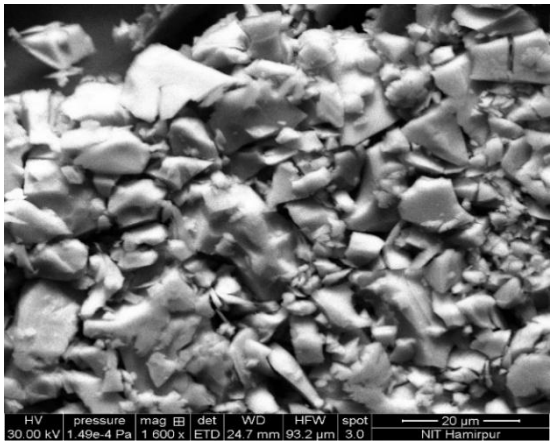

Figure 1: SEM micrograph of $Se_{79}Te_{20}Pb_1$ chalcogenide alloy.

chalcogenide alloy is displayed in Figure 1. Amorphous character of primed chalcogenide alloy is also indicated by SEM micrograph, which clearly illustrates phase separation of the sample due to inhomogeneity. Other samples also yield similar results. A temperature-modulated DSC instrument (TA instrument, DSC 2910) is used to analyse the thermal behaviour of the composition under investigation. The thermal analyzer microprocessor has the temperature accuracy of ±0.1°C and heat flow accuracy of ±0.01 mW. 3–5 mg of the material was placed in a typical alumina pan under a dry nitrogen environment at 40 mlmin^{-1}. The samples undergo reheating at 10°Cmin^{-1}. The thermal analyzer's microprocessor is utilised to note down the T_g.

Results and Discussion

When the sample is reheated, a glass softens and experiences a qualitative shift in molar volume and enthalpy at a specific temperature, called the glass transition

temperature [15]. For analysing the glass transition kinetics, the non-isothermal DSC methodology is being extensively employed in literature [7-10]. Because of its ease of use, low sample preparation requirements, high sensitivity and independence from sample geometry; this approach is especially significant. Hence in this work, we have also used the non-isothermal DSC methodology. DSC thermograms of primed Se-Te-Pb chalcogenide compositions under study are showing characteristic glass transition temperature (endothermic variation) displayed in Figure 2. It is evident from the endothermic variation at T_g that the alloys under investigation are of single-phase. It is found that when the Pb concentration rises at the expense of Se, T_g also acquires a higher value. Table 1 and Figure 3 provides the experimentally observed T_g for the glassy alloys under investigation, determined at 10°Cmin^{-1}. The rising T_g trends illustrate that system becomes stiffer when Pb is added to binary $Se_{80}Te_{20}$ alloy by compromising Se.

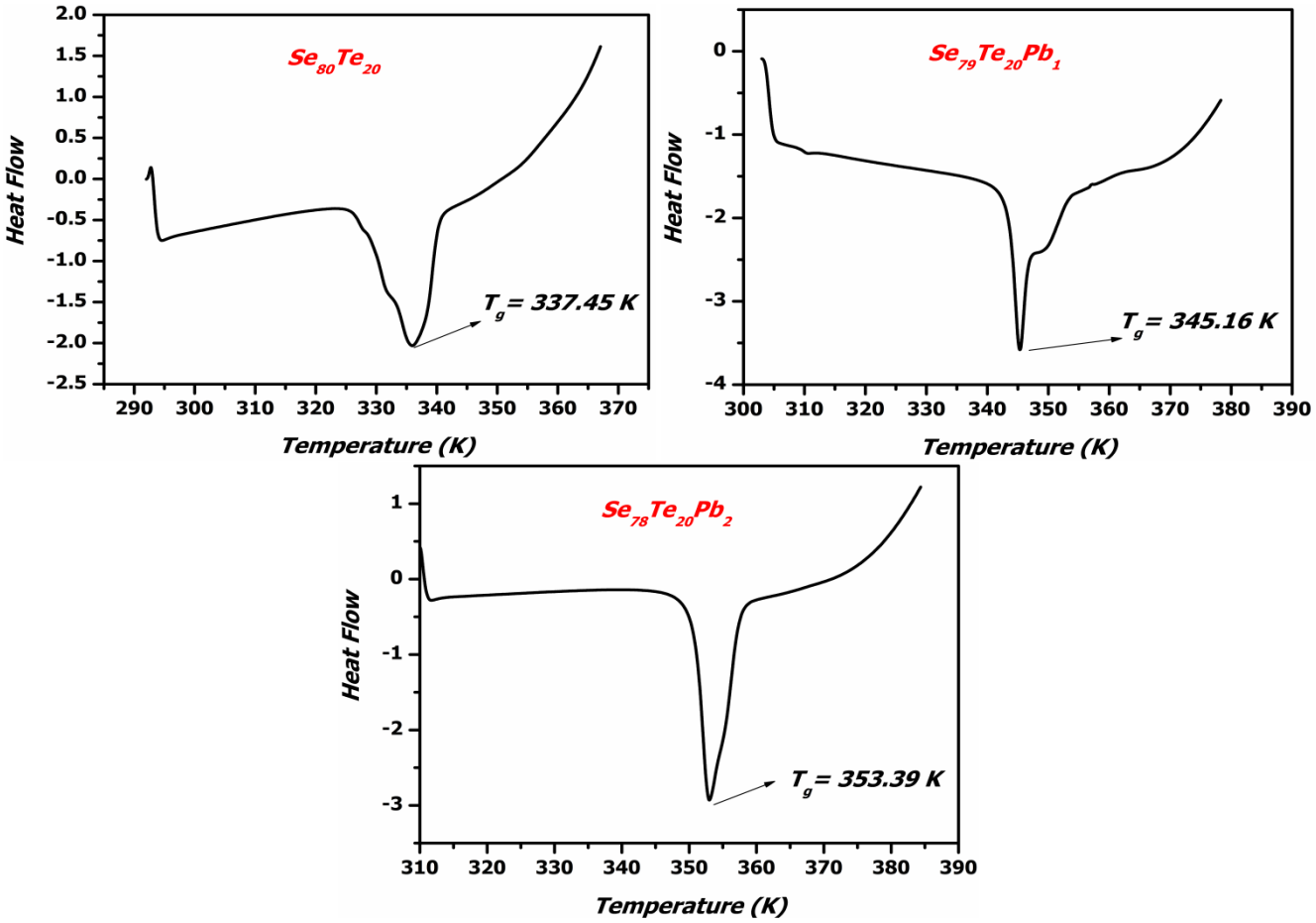

Figure 2: DSC endo-thermic curves obtained along T_g for $Se_{80-x}Te_{20}Pb_x$ (x = 0, 1 and 2) system at the heating rate of 10°Cmin^{-1}.

Pb doping may lead to configurational changes and hence rise in T_g. The two molecular forms of amorphous selenium are taken into consideration [16]: (*i*) meandering chains made up of trigonal selenium helical chains, and (*ii*) monoclinic selenium molecules with Se_8 rings. The network of any Se-Te unit formed using melt-quenching procedure is supposed to comprise of Se_6Te_2 and Se_8 rings and Se–Te copolymer chains [16–19]. Because Pb-doping involves compromising Se in each binary Se–Te unit, there are probably more Se–Se long chains than Se_8 rings, which leads to an increase [20] in T_g. As chain length increases, T_g is known to increase and decrease with increasing ring concentration [21].

At T_g, a transition takes place and below T_g, a supercooled liquid transforms in to a glass. It is essential for explaining the vitreous condition. Consequently, atomic movement requires the removal of cohesive forces within the material, and their size is proportional to T_g [15]. Much attention is also dedicated to the estimation of T_g in chalcogen based glasses, which is associated with, a measure of material stiffness and cohesive forces. T_g can be inferred using a number of theoretical methods.

Tichy and Ticha connected T_g with mean bond energy (<*E*>) [22]. They proposed a covalent-bond method for chalcogen additive systems and proposed the following relationship between T_g and <*E*>:

$$T_g = 311[\langle E\rangle - 0.9] \quad (1)$$

Lankhorst [23] proposed the empirical relationship linking T_g and heat of atomization (H_s) as follows:

$$T_g = 3.44H_s - 480 \quad (2)$$

According to Tanaka [24], the average coordination number (<*r*>) and T_g have an exponential connection as:

$$T_g = \exp(1.6 < r > +2.3) \quad (3)$$

T_g derived through above three approaches listed in Table 1. For Tichy-Ticha and Lankhorst approaches T_g decreases when Pb substitutes Se-Se (44 kcal/mol) homo-polar bonds with heteropolar bonds (Pb-Se = 31.47 kcal mol^{-1}) for in system under investigation [14]. Another theoretical method, the Gibbs–Di Marzio law, which takes into account the impact of chemical ordering, can also be used to calculate T_g for Se-Te-Pb glassy alloys. T_g as well as cross-linking density in molecular chain structure are empirically related [2]. Sreeram et al. [25] proposed the following form after modifying the Gibbs–Di Marzio equation:

$$T_g = \frac{T_o}{1-\beta(<r>-2)} \quad (4)$$

Table 1: A comparison of T_g values deduced for $Se_{80-x}Te_{20}Pb_x$ (x = 0, 1, and 2) system.

Composition	T_g *(in kelvin)*				
	Experimental (10°Cmin^{-1})	**Modified Gibbs-Di Marzio Law**	**Tanaka Approach**	**Tichy and Ticha Approach**	**Lankhorst Approach**
$Se_{80}Te_{20}$	337.45	316.00	244.69	314.42	280.24
$Se_{79}Te_{20}Pb_1$	345.16	320.62	252.65	310.38	279.14
$Se_{78}Te_{20}Pb_2$	353.39	325.38	260.86	306.34	278.04

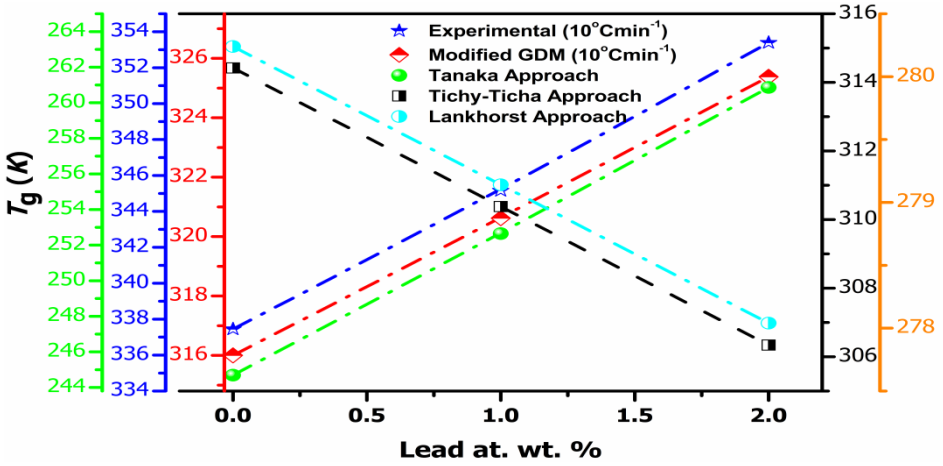

Figure 3: Variation of experimental and theoretical values of T_g for $Se_{80-x}Te_{20}Pb_x$ (x = 0, 1 and 2).

here T_o is the T_g of the base sample (here T_o of Se = 316 K) [1-2]. The parameter β (which depends on the system) is provided by [25]:

$$1/\beta = \sum(m_i - 2)ln[m_i/2] \quad (5)$$

In this case, if the participating atom's coordination number (m_i) is known, the value of β can be calculated. The computed value of β in the Se-Te-Sb system is 0.72. Table 1 and Figure 3 makes it clear that T_g values derived from Tanaka relation, the modified Gibbs-Di Marzio rule and experimental values derived from DSC scans accord well. However, it is peculiar to note that the theoretically deduced T_g using Tichy–Ticha and Lankhorst approaches applied to the Se-Te-Pb system under study does not show accordance with the experimentally obtained values.

The structure of chalcogenide glasses represents the short-range order. Due to lack of translational symmetry, the properties of chalcogenide glasses strongly depend upon the types and concentration of chemical bonds, which hold the atoms together in the glassy network. T_g of multicomponent glasses are known to be dependent on several independent parameters such as bond gap, coordination number, bond energy, effective molecular weight and type as well as fraction of various structural units formed [26]. Mehta et al [27] studied the effect of metallic additives on the kinetics of glass transition in $Se_{80}Te_{20}$ glassy alloy. It has been found that increasing sequence of T_g in ternary glasses is same as that of the atomic weight of third element. Thus, it can be concluded that T_g in these glasses increases with the increase in mean atomic weights. The activation energy of glass transition process is related to glass forming tendency in these glasses and the chalcogenide glasses having higher

activation energy for glass transition process shows less glass forming tendency.

Also, Sushama et al [28] reports the effect of addition of different elements as a dopant to $Se_{80}In_{20}$ at the expense of indium using DSC. When Pb is added to $Se_{80}In_{20}$ at the cost of In, there are two well defined crystallization exotherms. This implies that glassy composition may crystallize into two phases, Se-In & Se-Pb [26] and T_g decreases with Pb. As Pb content dissolved, the number of long chains Se-Se get decreased as compare to Se_8 rings [29]. Also, it forms a two-dimensional growth for ternary Se-In-Pb system. Moreover, $Se_{80}In_{10}Pb_{10}$ is the most stable glass in this system, as value of $T_c - T_g$ is maximum. Activation energy of crystallization is minimum and average coordination number is maximum for $Se_{80}In_{10}Pb_{10}$ which further validate the higher thermal stability of system under investigation.

Conclusions

This study examines the utility of modified Gibbs-Di Marzio law to determine glass transition temperature in Pb doped $Se_{80-x}Te_{20}Pb_x$ (x = 0, 1 and 2) system primed by melt-quench procedure. X-ray diffraction revealed that glassy composition under investigation is amorphous confirmed by SEM. The inhomogeneity in the samples leads to phase separation hence, SEM analysis is consistent with the XRD results. Experimentally observed T_g using DSC at $10°Cmin^{-1}$ is used to make the comparison with theoretically calculated T_g using Gibbs–Di Marzio relation, Tanaka, Tichy-Ticha and Lankhorst approaches. It is observed that the theoretical values obtained by Gibbs–Di Marzio relation and Tanaka approaches are consistent with experimental results. Also, theoretical results obtained by Tichy-Ticha and Lankhorst approaches show inconsistency in comparison to experimentally obtained results.

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