SHIFT OF RIGIDITY PERCOLATION IN RAPIDLY QUENCHED Ge-As-Te CHALCOGENIDE GLASSES

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Chalcogenide glasses based on tellurium are difficult glass formers. They cannot be prepared over a wide composition range like Se based chalcogenide glasses by the normal melt quenching method where a cooling rate of 10^2 K/s is achieved. To achieve higher cooling rates we rapidly quenched the melts with the help of a home built twin roller melt spinning apparatus. Thin flakes of $Ge_{10}As_xTe_{90-x}$ glasses ($0 \leq x \leq 70$) were prepared over a wide composition range covering average coordination numbers (Z_{av}) from 2.20 to 2.85 in a single composition tie line. The glass transition (T_g) vs. average coordination number (composition) does not show any signatures of rigidity percolation threshold (RPT) at $Z_{av} = 2.40$, instead a maximum in T_g is observed at $Z_{av} = 2.70$. Among the constituents in Ge-As-Te system, tellurium is the biggest and the most electronegative. The electronic polarization of the Te atoms decreases the degree of covalency of the Ge-As-Te network. According to the modified constraint counting theory,two additional internal degrees of freedom can be assigned to Te, which alters the balance between the constraints and the number of degrees of freedom available to the atoms. Correspondingly, a shift in RPT to higher coordination number <r> = 2.70 is observed.

(Received March 15, 2014; Accepted May 16, 2014)

1. Introduction

Chalcogenide glasses are based on the Group VI elements S, Se and Te. These glasses are well known for their infrared detection, phase change and memory applications and photo-induced transitions [1-4]. Glasses based on tellurium are difficult glass formers. For example, in the Ge-As-Te system there are two glass forming regions (GFR) separated by a few compositions gap [5]. The cooling rate achieved in the normal melt quenching method 10^2 K/s is not sufficient for the compositions which separate the glass forming regions. Due to this there is no continuity in the property vs. composition graphs which leads to difficulty in understanding the composition dependence properties and interpret the data wrongly(Fig.1). For example, based on the composition dependence of glass transition data for Ge-As-Te glasses (which has discontinuity in data due todifficulty in glass formation) the rigidity percolation threshold was assumed to occur at the average coordination number 2.40 [6]. In our earlier work, we showed that glasses can be prepared in $Ge_{7.5}As_xTe_{92.5}$ glasses ($0 \leq x \leq 70$) without any discontinuity over a wide composition range [7]. The composition dependence glass transition (T_g) and glass forming ability (K_{gl}) showed a maximum around x = 55.

The constraint counting theory (CCT) or mechanical threshold (MT) or Rigidity percolation threshold (RPT) model proposed by Phillips and Thorpe explains the composition dependence of glass transition and many other properties of covalent network glasses [8 - 10]. The CCT model attempts to relate the glass forming tendency with the constraints acting on the network (n_c) and the number of degrees of freedom (n_d) available for the atoms in the network. The total number of constraints acting on the network is the sum of the bond stretching and bond

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*Corresponding authour: kramesh@physics.iisc.ernet.in bending constraints. Phillips considered n_d is 3 for the cross linked network structures. The glass network

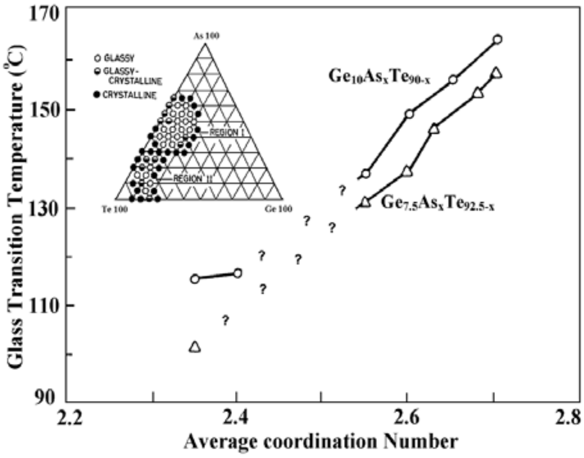

Fig. 1.T_g of Ge-As-Te glasses as a function of average coordination number shows the discontinuity in data for few compositions range where the formation of glasses by normal melt quenching is difficult. The inset shows the glass forming region of Ge-As-Te determined by normal melt quenching technique

The constraint counting theory (CCT) or mechanical threshold (MT) or Rigidity percolation threshold (RPT) model proposed by Phillips and Thorpe explains the composition dependence of glass transition and many other properties of covalent network glasses [8 - 10]. The CCT model attempts to relate the glass forming tendency with the constraints acting on the network (n_c) and the number of degrees of freedom (n_d) available for the atoms in the network. The total number of constraints acting on the network is the sum of the bond stretching and bond bending constraints.Phillips considered n_d is 3 for the cross linked network structures.The glass network is maximally optimized at a critical composition or coordination number where the number of constraints and the number of degrees of freedom are equal. Hence, the condition for maximum glass formation is

$$n_c=n_d \tag{1}$$

This condition is achieved for a covalent network glass at an average coordination number (Z_{av}) of 2.4. The rigidity of the network is sharply increases at this coordination number and is called rigidity percolation threshold (RPT) and continues to increase for higher Z_{av}. These glasses also exhibit another threshold called chemical threshold (CT), which occurs at higher coordination numbers (usually at Z_{av} = 2.67). At CT, the bonding between the atoms is heteropolar and the network achieves a maximum chemical ordering [11-13]. It is also reported that a shift in RPT to higher coordination numbers for glasses with layered structure [14 - 18]. Binary As-Se glasses show pronounced maximum in T_g at Z_{av} = 2.40, whereas in Ge-Se glasses, merely a change in slope is observed. Ge-Se glasses also exhibit a maximum in T_g at Z_{av} = 2.67 which has been explained by Tanaka, in terms of the change in the network dimensionality for glasses with layered structure [14 - 18]. In binary As-Se glasses, T_g exhibits a maximum at Z_{av} = 2.40. However, extrema in various physical properties have been observed at these thresholds [19 – 22]. For example, the photosensitivity of the Ge-As-Se glasses was shown to be strongly dependent on the rigidity of the glass network [24]. The discovery of intermediate phases (IPs) or Boolchand phases in covalent network glasses suggests RPT occurs between two critical compositions where the non-reversible heat flow (ΔH_{nr}) is found to vanish. The compositions forming the IPs are found to be stress free and donot show physical ageing [25 - 27]. When the covalent interactions between atoms are reduced by the presence of electronegativeand electropositive atoms a shift in RPT is expected[21, 22, 28 - 31]. Ionic interactions between atoms, since they are not directional, reduce the angular constraints on them. In other words, the polarizing ability of the atoms acts as additional internal degrees of freedom which modify the embedding dimension. The effect of metallic atoms on glass formation in chalcogenide glasses has been explained by the formal valence shell (FVS) model [29 - 31]. The influence of one fold coordinated halogens atoms are explained by extending the constraint counting theory [32, 33]. To observe RPT and CT, glasses should be prepared over a wide range of compositions. Se based glasses such as As-Se, Ge-Se and Ge-As-Seare easy glass formers. Ge-Se and Ge-As(Sb)-Se and can be considered as model system to understand the topological thresholds (RPT and CT) as they can be prepared over a wide composition range [34, 35].Such kinds of studies are not available in Te based chalcogenide glasses due to the difficulty in glass formation. There are few reports available on binary As-Te glasses [36, 37]. The properties measured as a function of composition exhibit anomaly at 40 atom % of As (Z_{av} = 2.40). At this composition both the RPT and CT coincide and it is difficult to quantify the relative contribution of these thresholds to the observed anomaly in various properties. In the case of Ge-Te, glass formation is limited to 28 atom % of Ge [5]. CT occurs at 33 atom % (Z_{av} = 2.67) of Ge [38]. Hence, observation of CT is not possible in this system. Addition of a third element greatly improves the glass formation. Hence, studying the properties of ternary chalcogenide glasses are very important to understand the RPT and CT.For example, addition of As, greatly increases the glass forming ability of the Ge-Te glasses. Though the addition of As increases the glass forming ability of Ge-Te, there are some compositions still require high cooling rates(see inset of Fig.1). In the Ge-As-Te system, there are two glass forming regions separated by a few composition gap [4]. Glasses can be obtained by varying As between 15 and 20 (GFR I) and between 30 and 60 (GFRII). Hence, T_g data is not available for the compositionswhich falls in between the two glass forming regions [5]. As an example, T_g of $Ge_{7.5}As_xTe_{92.5-x}$ and $Ge_{10}As_xTe_{90-x}$ glasses as a function Z_{av} showing discontinuity without any data points particularly around Z_{av}= 2.40 is shown in figure 1.Though the recent work of Sen et.al.[39] on Ge-As-Te glasses shows a wider composition range, our work is covers compositions which lies outside glass forming regions.

The present work is an extension of our earlier work [7] where we have shown the extended glass formation along the $Ge_{7.5}As_xTe_{92.5-x}$tie-line by rapid quenching of the melts by melt spinning method.In this work, we have tried to prepare glasses in the $Ge_{10}As_xTe_{90-x}$ tie-line by rapid quenching, without any discontinuity in the composition to understand the RPT and CT. Intrestingly, in both the tie-lines, there was no sharp transitions observed at the critical coordination number Z_{av} = 2.4. This has been understood on the basis of modified constraint counting theory(MCCT) proposed by Dohler et.al. [28]. Later MCCT has been extended to Te based chalcogenide glasses by AravindaNarayanan [22, 23].

2. Experimental

Bulk $Ge_{10}As_xTe_{90-x}$ ($0 \leq x \leq 70$) glasses have been prepared by melt quenching method. In this tie-line, as shown in the inset of the Fig. 1 glasses can be obtained for $10 < x \leq 20$ (GFR I) and for $30 < x \leq 70$ (GFRII). We have attempted at prepare glasses in this system by varying the As content continuously between 0 and 70 at.%. The starting materials Ge, As and Te in the desired proportion were sealed in flattened quartz ampoules evacuated to better than 10^{-5} Torr. These ampoules were heated in a horizontal rotary furnace at 600 ^{o}C for 6 h. Then the temperature was raised to 950 ^{o}C and kept for 42 h. The ampoules containing the melt were continuously rotated to ensure the homogeneity. Before quenching the melt in ice water + NaOH mixture, the temperature was reduced to 850 ^{o}C. All the normally melt quenched samples irrespective of their state (whether amorphous or crystalline) were processed in a twin roller melt spinning apparatus to have a better comparison. The details of the apparatus can be found elsewhere [40]. The amorphous nature of the $Ge_{10}As_xTe_{90-x}$samples prepared by both melt quenching and melt spinning methods was checked with X-ray diffraction (XRD) using Philips X'Pert PRO diffractometer. The wavelength (λ) used was 1.5405 Å (Cu $K\alpha_1$ radiation). Differential scanning calorimetric (DSC) studies were performed on a temperature modulated DSC (MDSC 2920, TA Instruments Inc., USA) in the DSC mode at a heating rate of 10 K/min. Small pieces of the samples weighing about 18 mg were loaded into aluminium pans and then sealed. An empty aluminium pan was taken as reference.

3. Results

Fig. 2 shows XRD spectra of the melt quenched and melt spun $Ge_{10}As_xTe_{90_x}$samples. Fig. 2(a) represents the XRD spectra of few of the normallyquenched samples. The melt quenched samples with 0, 5, 10,20, 25, 30and 65 at.% of As show crystalline in nature as expected since these compositions are not in the glass forming region.These compositions when processed in twin roller melt spinning apparatus are foundto be amorphous in nature as shown in Fig. 2(b). Table 1 gives the details of the glass formation with melt quenching and melt spinning methods.

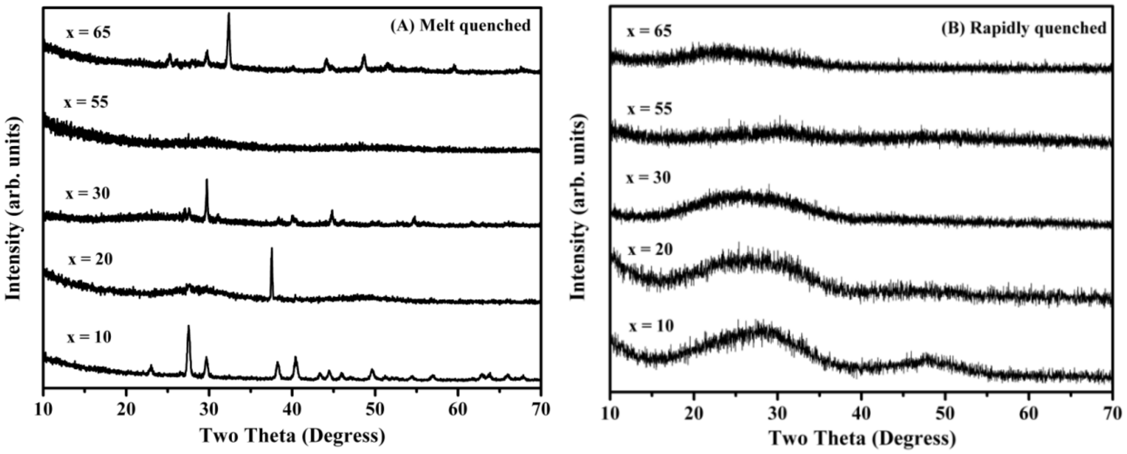

Fig. 2. XRD spectra showing some representative (a) melt quenched and (b) melt spun $Ge_{10}As_xTe_{90-x}$ samples

DSC spectra of the few ofthe melt quenched and twin rolled samples are shown in Fig. 3.It can be seen that for x = 10, only melting endotherm is observed for melt quenched sample whereas for melt spun sample T_g and T_c also observed. Fig. 4 shows the T_g of $Ge_{10}As_xTe_{90\_x}$ glasses as a function of As and average coordination number (Z_{av}). With increase of As an increase in T_g is seen. However, T_g exhibits a minimum at x = 5, a slope change at x = 30 and a maximumat x = 50. The composition dependence of the glass forming ability (K_{gl}) is shown in Fig. 5. Glass forming ability is low for glasses in GFR I (Te -rich glasses) and high for glasses in GFR II (As rich glasses).

Table 1. Atomic% of As, sate nature of the melt quenched samples whether crystalline (Cr) or amorphous (A), glass transition temperature (T_g), crystallization temperatures (T_{c1} and T_{c2}), and melting points (T_{m1} and T_{m2}) of $Ge_{10}As_xTe_{90-x}$ glasses

Atomic % As	**State**	**T_g(°C)**	**T_{c1}(°C)**	**T_{c2}(°C)**	**T_{m1}(°C)**	**T_{m2}(°C)**	**K_{gl}**
0	A/Cr	143	228	-	387		0.53
5	A/Cr	105	171	238	373	408	0.32
10	A/Cr	108	193	237	365	394	0.49
15	A	113	210	237	361	374	0.64
20	A/Cr	117	250	-	351	-	1.31
25	A/Cr	123	208	-	355	-	0.58
30	A/Cr	126	197	-	351	364	0.47
35	A	132	188	-	370	-	0.31
40	A	142	267	-	368	-	1.24
45	A	152	281	-	364	370	1.58
50	A	167	263	282	368	-	0.91
55	A	162	340	-	364	370	6.75
60	A	156	340	-	364	366	6.5
65	A/Cr	150	302	-	363	366	2.46
70	A	139	214	-	349	365	0.57

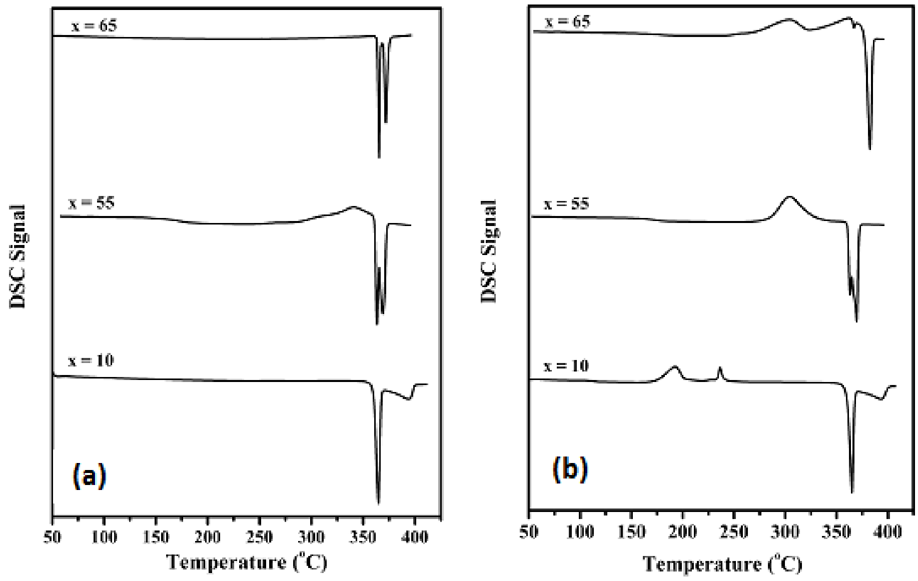

Fig. 3. DSC thermograms of representative (a) melt quenched and (b) melt spun $Ge_{10}As_xTe_{90-x}$ samples

4. Discussions

In the $Ge_{10}As_xTe_{90-x}$ system, the increase of As increases the connectivity by polymerizing the network. This increases the rigidity of the network. With the increase of network rigidity, an increase of glass transition temperature is expected which can be seen from fig.4. However, T_g shows a decreasing trend for the initial addition of As. In the base glass ($Ge_{10}Te_{90}$), the structural network is characterized by Ge-Te and Te-Te bonds. Addition of As, replaces some of the Te-Te bonds by the formation of As-Te bonds [38, 41, 42]. The bond energies of As–As, Te–Teand As–Te are 44.0, 43.4 and 38.6 kcal/mole, respectively [43]. The added As increases the connectivity between the Te- chains by acting as a chain branching point and thus the network rigidity increases. At the same time, the bond energy of As-Te is lower than the Te-Te bonds. This decreases the overall bond energy of the network, which causes the initial decrease of T_g. However, for x > 5, the rigidity of the structural network dominates over the bond energy and thus T_g increases for x > 5. T_g also exhibit a slope change at x = 30.Glasses formed from the GFR I are Te- rich and glasses formed from GFR II are rich in As.

Generally, in covalently bonded chalcogenide glasses the coordination numbers for Ge, As and Te are 4, 3 and 2 respectively. Accordingly, the average coordination number for $Ge_{10}As_xTe_{90-x}$ glasses can be calculated as follows:

$$Z_{av} = \frac{[4*10 + 3x + (90 - x_c)*2]}{100} \tag{2}$$

For example, Z_{av} = 2.40 for glasses with x_c = 20 ($Ge_{10}As_{20}Te_{70}$). Since, glasses have been prepared with continuous variation of As, a transition from the floppy to rigid transition (RPT) is expected at Z_{av} = 2.40 (x = 20). This transition should reflect in the $T_g$vs average coordination number plot. Aravinda Narayanan observed distinct changes in the slope of the composition dependence of electrical switching field at x = 25 (Z_{av} = 2.4) and x = 52.5 (Z_{av}= 2.67) in $Ge_{7.5}As_xTe_{92.5-x}$ glasses [22, 23]. The thresholds observed at Z_{av} = 2.4 and Z_{av} = 2.67 were related to the RPT and CT respectively. In his good work, Aravinda Narayanan prepared a wide range of composition without any discontinuity. Surprisingly, he has not studied the T_g variation with composition though there is scarcity in T_g data for Te- based systems. Moreover, T_g is very sensitive to structural changes and is a direct indication of network rigidity than the electrical switching field. In the present studies on $Ge_{10}As_xTe_{90-x}$ glasses, the composition dependence of T_g, shown in fig. 4 does not show any sharp transitions at Z_{av} = 2.4, instead a maximum at x = 50 (Z_{av} = 2.70) is observed. The observed maximum in T_g at Z_{av} = 2.7, is very close to Z_{av} = 2.67, which is generally understood in terms of CT, at which bonding between unlike atoms (heteropolar bonds) are preferred. In the present case, itcannot be related to CT since this composition is already rich in As with more of As-As bonds. In the Ge-As-Te system, the chemically ordered molecular units in terms of binary Ge-Te and As-Te are represented by $GeTe_2$ and As_2Te_3. In that case, the chemical ordering threshold for both $Ge_{10}As_xTe_{90-x}$and $Ge_{7.5}As_xTe_{92.5-x}$glasses occurs at Z_{av} = 2.46 (x= 28 and 31, respectively). Hence, the maxima observed at x = 50 is not due to the chemical ordering effect.

In $Ge_{10}As_xTe_{90-x}$ glasses, for x ≥ 30, a cross over from Te- rich network to As- rich network occurs and the ratio between the number of As-Te to As-As bonds decreases (increase of As-As bonds). In binary As-Te glasses the shift of the network from Te- rich to As- rich strongly affects the local order by forming the ‘As-As’ locks [41, 42]. In the present $Ge_{10}As_xTe_{90-x}$ glasses, the change in slope at x = 30may be related to the formation of ‘As-As’ locksand the growth of rigidity in the network. The formation of ‘As-As’ locks must influence the local structure of the Ge-As-Te glasses and leading to a change in local structure between GFR I and GFR II. The formation of ‘As-As’ locks, the growth of network rigidity and the change in the local structure are the reasons for the change of slope at x = 35. As see from Fig. 4 there is no sharp transition observed at x_c = 20 (Z_{av} = 2.40). The absence of transition at x_c = 20 and the maxima at x = 50(Z_{av} = 2.70) can be understood with the modified constraint counting theory (MCCT) [21 - 23]. When the covalent interactions are modified by the presence of electronegative and electropositive atoms in the structural network, the balance between the number of degrees of freedom and the embedding dimension are modified. Accordingly, the number of constraints which depends on the coordination number (r) and the degrees of freedom (n_d) is given by [28]

$$n_{co} = \frac{r}{2} + \left(\frac{1}{2}\right) r(r-1) \;\; for\; r < n_d - 1 \tag{3}$$

$$n_{co} = \frac{r}{2} + \left(\frac{1}{2}\right)(n_d - 1)(2r - n_d) \;\; for\; r > n_d - 1 \tag{4}$$

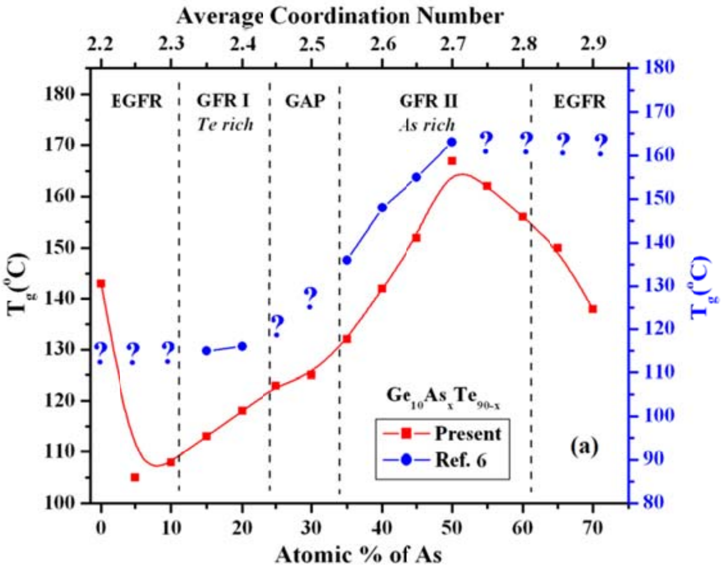

Fig. 4.T_g of $Ge_{10}As_xTe_{90-x}$ glasses as a function of As concentration and average coordination number showing smooth bridging of the two glass forming regions. Data from Ref.[6] is also shown for comparison

The number constraints for a binary A_xB_{1-x} system can be calculated by

$$n_{co}(A_xB_{1-x}) = x * n_{co}(r_A) + (1-x) * n_{co}(r_A) \tag{5}$$

For $n_d = 3$, the calculated number of constraints using the equations (3), (4) and (5) for Ge, As and Te are given in table 2. This condition yields $x_c = 0.20$, for $Ge_{10}As_xTe_{90-x}$ glasses. The critical composition $x_c = 20$, corresponds to $Z_{av} = 2.40$. As mentioned earlier, there is no anomaly observed at $x_c = 20$. Generally, the non-observance of anomaly at the critical coordination number 2.40 is considered due to the changes in the constraints (n_{co}) acting on the atoms. Dohler [28] considered the absence of sharp transition at $Z_{av} = 2.40$ is due to the changes in the embedding dimension(n_d). Among constituent elements in the Ge-As-Te system, Te is the biggest and its electronegativity is also high. This leads to electronic polarization and van der Waals interaction between the layers. Hence, two internal degrees freedom, one for electronic polarization and another for van der Waals interactions can be assigned to Te atoms. Based on this Aravinda Narayanan [22] has derived an equation to calculate the critical coordination number for glasses in the $Ge_yAs_xTe_{1-x-y}$ system.

$$14y + 9x = 6 \tag{6}$$

Table 2. Coordination number and the calculated number constraints for Ge, As and Te atoms for the embedding dimension n_d = 3

Ge		As		Te	
R	n_{co}	r	n_{co}	R	n_{co}
4	7	3	9/2	2	2

Eq. (6) yields $x_c = 50$ for $Ge_{10}As_xTe_{90-x}$ glasses. For these compositions the average coordination number is $Z_{av} = 2.70$, at which a maximum in T_g is observed (fig. 4). Hence, the maxima exhibited by T_g at $x = 50$ ($Z_{av} = 2.70$) can be associated with the rigidity percolation threshold in $Ge_{10}As_xTe_{90-x}$ glasses. The present results are a direct evidence for the MCCT and the shift of the RPT when the covalent nature of the structural network is affected by ionic interactions.T_g also shows a decreasing trend after exhibiting the maxima at Z_{av} = 2.70. This decrease is due to the excess As in the network. In binary As_xTe_{100-x} system, glasses can be formed with a maximum of 60 % As (i.e. As to Te ratio is about 1.5:1). For compositions with x > 50, the As to Te ratio exceeds this limit. For example, As to Te ratio for x = 60 in $Ge_{10}As_xTe_{90-x}$ glasses is 2:1. The excess As may lead to nano phase separation which does not contribute to the network connectivity anddepolymerises the network. Hence, the rigidity of the structural network starts weakening which is reflected as a decrease in T_g for x > 50.

K_{gl} is directly proportional to the interval between T_c and T_g and indirectly proportional to the interval between melting temperature (T_m) and T_c [44, 45]. So the glass forming ability is given by

$$K_{gl} = \frac{T_c - T_g}{T_m - T_c} \tag{9}$$

Fig. 5 shows the glass forming ability of $Ge_{10}As_xTe_{90-x}$ glasses.The glass forming ability also exhibits a maximum at Z_{av} = 2.70. This is expected as the composition corresponding to RPT generally exhibits a maximum[8, 46]. The glass forming ability is low for glasses in the GFR I (where Z_{av} = 2.40 lies) and high for glasses in the GFR II.This also supports our idea of associating RPT to Z_{av} = 2.70 in Ge-As-Te glasses.

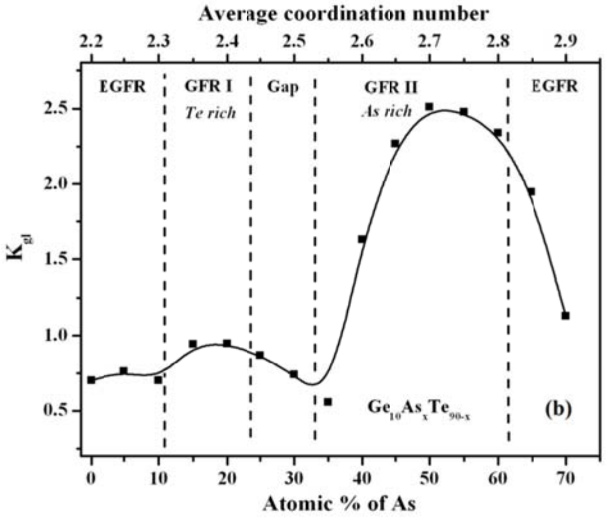

Fig. 5. Glass forming ability of $Ge_{10}As_xTe_{90-x}$ glasses showing the poor glass formation in GFR I and easy glass formation in GFR II

GFR shown in Fig.1is determined by the normal melt quenching method. As mentioned earlier, the formation of 'As-As' locks increases the viscosity and hence the glass forming ability of the glasses in GFR II is high. EGFR is the glasses lie outside of the GFR and prepared by rapid quenching of the melts by twin roller melt spinning method. Glasses are also prepared in the gap region between GFR I and GFR II. Hence, in this work with the twin roller melt spinning, a wide range of glasses have been prepared in a single tie-line without any discontinuity in the composition, which was not easily possible by the normal melt quenching method.

5. Conclusions

$Ge_{10}As_xTe_{90-x}$ glasses with a wide range of compositions covering GFR I, GFR II, Gap between the GFR I and II and EGFR have been prepared by melt spinning method. A smooth bridging of the two glass forming regions with an extended region of glass formation has been achieved. There was no sharp transitions observed in T_g vs composition plots at the expected average coordination number $Z_{av} = 2.4$. The electronic polarization of tellurium influences the structural network and creates an imbalance between the number of degrees of freedom and the number constraints which shifts the RPT from $Z_{av} = 2.40$ to 2.70. Hence, the maxima observed in T_g at $x = 50$ is associated with the RPT and not with CT. However, it would be interesting to see the T_g variation at chemical ordering thresholds of $Ge_{10}As_xTe_{90-x}$ and $Ge_{7.5}As_xTe_{92.5-x}$ glasses (at $x = 28$ and $x = 31$ respectively). K_{gl} is higher for GFR II where the structural network is rich with arsenic. In the GFR I, the network is rich with Te, and Te being more metallic in nature hinders the glass forming ability. For $x > 50$, nano phase separation of excess As occurs and weakens the structural network, due to which, T_g decreases for $x > 50$.

This work covers a wide range of glasses in a Te based chalcogenide system ($Ge_{10}As_xTe_{90-x}$) in a single tie-line prepared by rapid quenching without any discontinuity in the composition to understand the RPT and CT effects, which was not easily possible by the normal melt quenching method. Ge-As-Te system can also be considered as a model system for Te based glasses as the case of Ge-As-Se for Se based glasses. It will be interesting to study the CT effects on composition dependence of T_g by preparing $Ge_{7.5}As_{31}Te_{61.5}$in $Ge_{7.5}As_xTe_{92.5-x}$ series and $Ge_{10}As_{28}Te_{62}$in $Ge_{10}As_xTe_{90-x}$ series respectively. The thermal crystallization by thermally annealing at their respective T_c's of these glasses in both the series will help to indentify the structural units present with As variation. We also planned to measure the non-reversible heat flow (ΔH_{nr}) by modulated differential scanning calorimetry (MDSC) to understand the intermediate phases or Boolchand phases which can also support the present observation of shift in RPT to higher coordination numbers.

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