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Variation of glass transition temperature, T_g, with average coordination number, $\langle m \rangle$, in network glasses: evidence of a threshold behavior in the slope $|dT_g/d\langle m \rangle|$ at the rigidity percolation threshold ($\langle m \rangle = 2.4$)

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Alkali oxide (Ak_2O) addition to telluria lowers glass transition temperature, T_g, of $(Ak_2O)_x(TeO_2)_{1-x}$ glasses systematically, with the slope dT_g/dx displaying a local maximum at $x_c \simeq 0.18$ corresponding to $\langle m \rangle \simeq 2.4$, the rigidity percolation threshold. In covalent network glasses, as in the present alkali tellurate glasses, T_g is found to increase with $\langle m \rangle$ with the slope $|dT_g/d\langle m \rangle|$ displaying a maximum near $\langle m \rangle \simeq 2.4$. It is recognized that this threshold behavior can be traced to a qualitative increase of molecular relaxation time near $\langle m \rangle \simeq 2.4$, where a condition for mechanical equilibrium is locally satisfied. This increase leads to a local $T_g(\langle m \rangle)$ enhancement at $\langle m \rangle = 2.4$ due to a kinetic effect, which is superposed on a quasi-linear $T_g(\langle m \rangle)$ variation with $\langle m \rangle$ due to chemical effects.

1. Introduction

Bulk glass formation is known to occur in alkali tellurate $(Ak_2O)_xTeO_2)_{1-x}$ glasses [1,2], with Ak = Li, Na, K, and x in the range $0.05 \leq x \leq 0.40$, although little is known about the origin of this remarkable behavior and its connection to molecular structure. Basic information on aspects of molecular structure of these glasses and liquids is essential to the understanding of the origin of glass-forming tendency, as well as the thermal, mechanical and optical properties of these technologically important materials.

In the present work, we have used differential scanning calorimetry (DSC) to establish glass transition temperatures, T_g, as a function of alkali content in several alkali tellurate glasses. The dependence of T_g on the DSC scanning rate has been measured. From these measurements we have established (a) the glass-forming range, (b) the variation $T_g(x)$ with alkali content, and (c) the activation energy for enthalpy relaxation, $E_H(x)$, at T_g. Our results show that both the slope, $|dT_g/dx|$, and $E_H(x)$ display an extremum near the composition $x = x_c \simeq 0.18$. We propose that this observation represents realization of the Phillips–Thorpe rigidity percolation threshold in a 1–4–2 coordinated network glass, where the constituent atoms, i.e., alkali, Te and oxygen, are, respectively, onefold, fourfold and twofold coordinated [3,4].

2. Experimental

2.1. Glass sample preparation

Glass samples were produced by reacting 99.99% telluria with either 99.99% alkali carbon-

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ate or Ak_2TeO_3 (Ak = Li, Na or K) precursors in fused quartz ampoules in the temperature range 750–850°C using a vertical electric furnace. The reaction proceeds rapidly (in less than 10 s) at these temperatures. The resulting liquids were equilibrated for several minutes at 750°C before quenching by pouring onto a brass plate. This process yielded transparent glass specimens. We were unsuccessful in obtaining transparent glass samples with the above procedure for $x \lesssim 0.05$. These TeO_2-rich samples were translucent and possessed inclusions of microscopic white precipitates typically a few micrometers in size.

2.2. *Differential scanning calorimetry results*

A DSC instrument, Perkin–Elmer, Model 2C, was used to measure the T_gs of alkali tellurate samples. Two types of DSC scan were undertaken. One was at a fixed scan rate of 10 K/min to obtain T_g as a function of alkali content, x, for Li-, Na- and K-bearing glasses. These results appear in fig. 1(a).

The results of fig. 1(a), when extrapolated to $x \to 0$, show that T_g of telluria is slightly above 570 K. It may be possible to form pure TeO_2 glass by a fast quench of the liquid, particularly in small samples. Addition of alkali oxide decreases T_g, at first slowly in the range $0.05 < x < 0.10$, then rapidly near $x = 0.18$ and then again slowly for $x > 0.18$. These results are in agreement with those of Heo et al. [1], the only other published T_g results on these glasses of which we are aware. In fig. 1(b), we plot the slope $|dT_g/dx|$ as a function of x, deduced from the $T_g(x)$ results of fig. 1(a). To obtain the slope $dT_g(x)/dx$ from the $T_g(x)$ results, we proceed in two steps as follows. First, we fit a polynomial to the observed $T_g(x)$ trends, shown in fig. 1(a), of the form $a + bx + cx^2 + dx^3$ where a, b, c and d are coefficients. The smooth curve passing through the $T_g(x)$ datapoints represents this polynomial fit. Next, we obtain the derivative of the polynomial, which is shown as the smooth curves in fig. 1(b). We note that a maximum in the slope $|dT_g/dx|$ occurs near $x = 0.18$ and this threshold behavior is nearly independent of the alkali-type. A noteworthy feature of fig. 1(a) is the more rapid

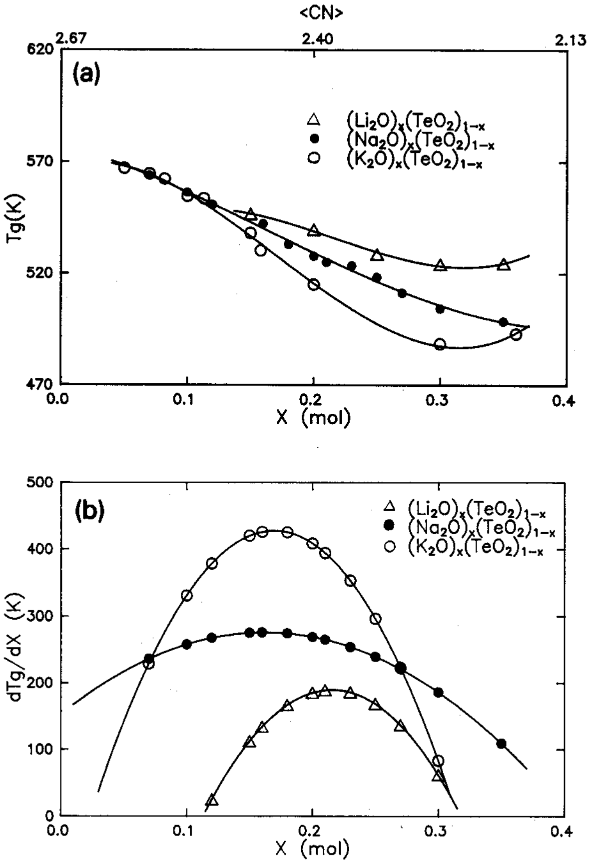

Fig. 1. (a) Glass transitions in indicated alkali tellurate glasses as a function of alkali content x. (b) Slope $|dT_g/dx|$ as a function of x in tellurate glasses displaying a threshold behavior near $x = x_c = 0.18$. See text for details.

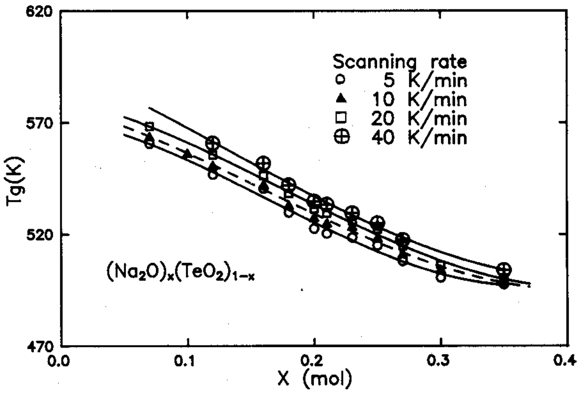

Fig. 2. Scan rate dependence of T_g in sodium tellurate glasses.

decrease in T_g with increasing atomic mass of the alkali atom. The heavier network modifiers are more effective in reducing T_g than lighter ones, and this is a point to which we shall return.

Figure 2 provides a summary of the dependence of T_g on scan rate for Na tellurate glasses. For constant Na content, T_g shifts to higher temperatures with increasing scan rate from 5 to 40 K/min, underscoring the kinetic aspect of the transition. Figure 3 shows a plot of the log of scan rate versus $1/T_g$, from which an activation energy for enthalpy relaxation, E_H, is obtained following the procedure described by Moynihan et al. [5]. In fig. 4 we plot the E_H as a function of Na content and find that a minimum in E_H occurs near $x_c = 0.18$. We discuss these results next.

3. Discussion

3.1. Molecular structure and rigidity percolation

It has been proposed [6–8] that glassy telluria, TeO_2, in anology to silica (SiO_2), consists of a 4–2 coordinated network of corner-sharing trigonal bipyramids, $Te(O_{1/2})_4$ units and tetrahedral $Si(O_{1/2})_4$ units, respectively. In the TeO_4 units, one of the three equatorial bonds consists of a non-bonding lone-pair primarily of 5sp character, while the other two consist of 5p σ bonds with bridging oxygen nearest neighbors. Addition of

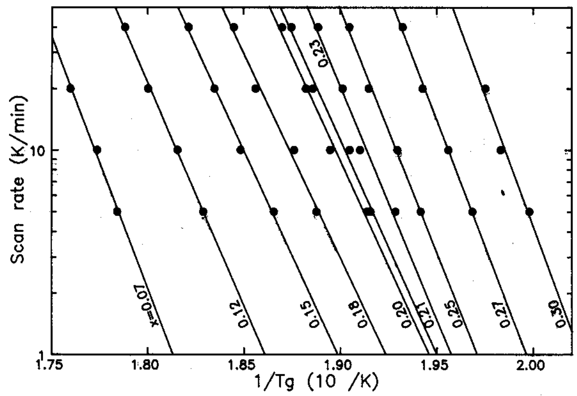

Fig. 3. Semilog plot of scan rate against $1/T_g$ at indicated sodium content, in tellurate glasses. E_H is deduced from the slope of these lines.

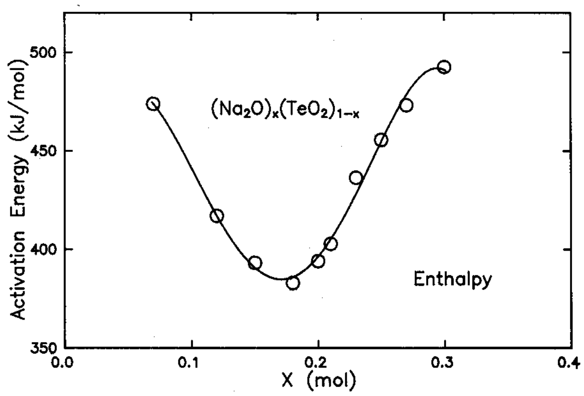

Fig. 4. Activation energy for enthalpy relaxation in Na tellurate glasses displaying threshold behavior at $x = x_c = 0.18$.

monovalent alkali atoms, we suppose, depolymerizes the network as non-bridging oxygen sites emerge in analogy to the situation prevailing in corresponding alkali silicate $(Na_2O)_x(SiO_2)_{1-x}$ glasses. For alkali tellurate glasses, if the coordination numbers of Na, Te and O are respectively 1, 4 and 2, conforming to the $8 - n$ rule, then the average coordination number $\langle m \rangle$ of an alkali tellurate $(Ak_2O)_x(TeO_2)_{1-x}$ glass can be written as

$$\langle m \rangle = (8 - 4x)/3. \tag{1}$$

Phillips [3] and Thorpe [4] independently recognized that a covalent network will in general transform from a floppy to a rigid network with increasing $\langle m \rangle$. They predicted that in a mean-field theory this transition for a three-dimensional covalent network will occur in general at

$$\langle m \rangle = 2.40. \tag{2}$$

These ideas have proved to be extremely useful in understanding the mechanical and vibrational behavior of chalcogenide glasses [9–12]. We recognize from eqs. (1) and (2) that the Phillips–Thorpe rigidity percolation threshold for the present alkali tellurate glasses is then predicted to occur at

$$x = 0.20. \tag{3}$$

The most natural interpretation of the observed extrema in $|dT_g/dx|$ and $E_H(x)$ at $x = 0.18$ in the present glasses, close to the value 0.20 predicted from eq. (3), is that it represents a mechanical critical point. We suggest, from these considerations, that bond-bending and bond-stretching forces are intact [6] for trigonal bipyramid $Te(O_{1/2})_4$ units and that glassy TeO_2 represents the case of an overcoordinated network with $\langle m \rangle = 2.67$. Alkali addition to telluria progressively reduces $\langle m \rangle$, as onefold coordinated Na sites (non-bridging O–Na bonds) emerge until an $\langle m \rangle = 2.4$ is realized at an alkali content of 20 mol%. This simplistic model provides a reasonable description of the molecular structure of alkali tellurate glasses.

3.2. *Glass transition temperatures and average coordination number*

The dependence of T_g on x in the present alkali tellurate glasses can be translated into a $T_g(\langle m \rangle)$ dependence using eq. (1) as shown in fig. 1(a). Such a generic plot affords a comparison of T_g with network connectedness [13] in a wide variety of glasses. There are several notable features of the present $T_g(\langle m \rangle)$ trend that appear to be common to T_gs in covalent network glasses. These features may be seen by comparing the $T_g(\langle m \rangle)$ trend in the present glasses with the one in the Ge–As–Se based ternary glasses presented by Tatsumisago et al. [12] recently. For convenience we have reproduced in fig. 5(a) the results of Tatsumisago et al., and have plotted the derivative of T_g with $\langle m \rangle$ in fig. 5(b) for the several families of chalcogenide glasses that encompass the value of $\langle m \rangle = 2.4$. We note that, although the absolute value of T_g for several families of network glasses ($Ge_xAs_ySe_{1-x-y}$, $(Ak_2O)_x(TeO_2)_{1-x}$ glasses) vary widely, in each case T_g is an increasing function of $\langle m \rangle$, with slope $|dT_g/d\langle m \rangle|$, exhibiting a local maximum close to $\langle m \rangle = 2.4$, the rigidity percolation threshold. Such a generic result is suggestive of a common origin, as we comment next.

Important insights to the glass transition have emerged recently from the correlation [12] between fragility [14] of glassy liquids (departure of viscosity from Arrhenius behavior) and percolation of rigidity [7,8] in corresponding glasses. This correlation provides a connection between the T-dependence of viscosity or enthalpy of relaxation of melts with mechanical constraints of the network. Specifically, for a liquid close to a mechanical critical point (where the number of interatomic forces per atom, N_c, equal the degrees of freedom, N_d) as the melt temperature, T_m, is decreased to approach T_g, the times for relaxation processes associated with motion of atomic clusters increase by orders of magnitude [15]. In fact these relaxation processes probably continue to proceed on a timescale longer than minutes, exceeding the timescales usually used in the laboratory to measure T_g. Those increases have the important consequence [12] that the observed glass transition T_g occurs at a temperature much higher than the ideal Kauzmann temperature [16], T_0, associated with the 'entropy crisis', i.e., $T_g/T_0 > 1$. In fragile glassy liquids on the other hand, which are far removed from the mechanical criti-

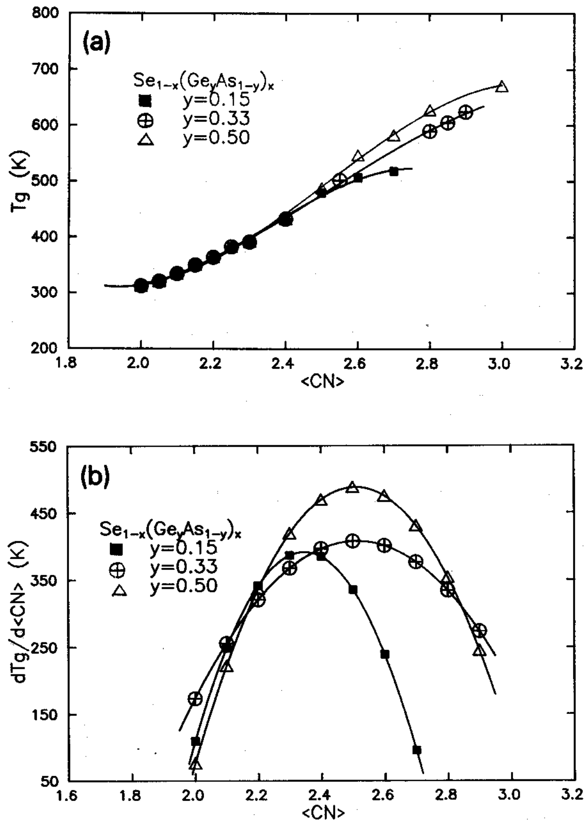

Fig. 5. (a) T_g as a function of average coordination number $\langle m \rangle$ in the As–Ge–Se family of chalcogenide glasses. (b) $|dT_g/dx|$ as a function of $\langle m \rangle$ displaying threshold behavior near $\langle m \rangle = 2.40$.

cal point, we suppose relaxation processes proceed on a timescale comparable to minutes, with the natural consequence that T_g observed in the laboratory now nearly approaches the ideal Kauzmann temperature, T_0, i.e., $T_g/T_0 \rightarrow 1$.

Based on these ideas we propose that, for glassy liquids in the vicinity of the rigidity percolation threshold, there is an additional contribution to T_g, which is largely kinetic in origin. This additional contribution to T_g must clearly depend on the magnitude of the deviation $|\langle m \rangle - 2.4|$ and can be expected to decrease as $\langle m \rangle$ deviates from 2.4. This additional kinetic contribution to T_g is in addition to the much larger contribution which is primarily chemical in origin [13]. Thus in the alkali tellurate glasses, we assume that a progressive removal of onefold coordinated alkali atoms enhances T_g largely because this removal replaces the weaker Na^+–O bonds by the stronger Te–O. However, the non-linear variation of T_g with x, particularly near $x = 0.18$, which leads to a maximum in the slope $|dT_g/dx|$ at $x = 0.18$, we ascribe to an increase in the times for relaxation processes in the network as it approaches the mechanical critical point. This increase results in an increase of T_g over and above its chemically determined value, primarily due to kinetic effects and is responsible for the threshold in $|dT_g/d\langle m \rangle|$ near $\langle m \rangle = 2.40$.

3.3. *Rigidity percolation threshold – theory versus experiment*

There is growing evidence of a small but systematic difference between the observed rigidity percolation threshold ($x_c = 0.18$, which corresponds to $\langle m \rangle = 2.43$) and the mean-field theoretical prediction ($x = 0.20$, which corresponds to $\langle m \rangle = 2.40$) in the present alkali tellurate glasses. Such a systematic difference between theory and experiments has been noted previously in binary Ge_xSe_{1-x} glasses from results of molar volumes [17], Raman scattering [18] and Mössbauer site-intensity ratios [19] where the observed threshold ($\langle m \rangle = 2.46(2)$) deviates from its mean-field prediction ($\langle m \rangle = 2.40$) in the same sense. This is to say that the observed threshold in real glasses apparently occurs in the slightly over-constrained regime as established from mean-field arguments. The same pattern can also be noted in the ternary $Se_{1-x}(Ge_yAs_{1-y})_x$ glasses studied by Tatsumisago et al. [12] (see fig. 5(b)) at $y = 0.33$ and 0.50 but not at $y = 0.15$ (where presumably As_2Se_3 type of clusters must proliferate corresponding to $\langle m \rangle = 2.40$ since the Ge content of the glasses is low). It is possible that the small but systematic deviation between the current mean-field theory [3,4] and experiment may be due to the presence of some medium range structural order present in the glass network and is a point that merits further theoretical investigation.

On the experimental side, we could not rule out the presence of a small fraction of threefold coordinated Te sites co-existing with predominantly fourfold coordinated Te sites in the alkali tellurate glasses. Such sites would, of course, lower the $\langle m \rangle$ of the glass network and could account for the small deviation between $x_c = 0.18(1)$ and the mean-field prediction of $x = 0.20$.

4. Conclusions

Both glass transition temperature $T_g(x)$ and activation energies of enthalpy relaxation $E_H(x)$ in $(Na_2O)_x(TeO_{1-x})$ glasses display extrema at $x = x_c = 0.18(1)$. This critical behavior is identified with onset of rigidity percolation in a glass network where the alkali, Te and oxygen sites are one-, four- and twofold coordinated conforming to the $8 - n$ rule.

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