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Topological constraint model of alkali tellurite glasses

Collin J. Wilkinson[a], Evgeny Pakhomenko[b], Martha R. Jesuit[b], Anthony DeCeanne[a], Brittney Hauke[c], Michael Packard[b], Steve A. Feller[b], John C. Mauro[a,*]

[a] Department of Materials Science and Engineering, The Pennsylvania State University, University Park, PA, USA
[b] Department of Physics, Coe College, Cedar Rapids, IA, USA
[c] School for the Engineering of Matter, Transport, and Energy, Arizona State University, Tempe, AZ, USA

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ABSTRACT

A topological constraint model is developed to elucidate the coordination environment of alkali tellurite glasses. The model is derived from temperature-dependent constraint theory and provides a quantitative connection between the connectivity of the glass network and the compositional dependence of the glass transition temperature (T_g). Our model gives support to the model proposed by Barney et al. [*J. Phys. Chem. Lett.* **4,** 2312–2316 (2013)], confirming their model of the coordination environment in alkali tellurites. The model simultaneously serves as a framework that can be used in binary alkali glass-formers to predict an expected coordination the network forming cation in an oxide glass.

1. Introduction

Glass formers with the chemical form MO_2 have a strong tendency to form tetrahedrally coordinated units (e.g., SiO_2 and GeO_2), as can be seen both in their crystalline and glassy structures [1,2]. In TeO_2-based glasses, the tellurium cation has been assumed to be fourfold coordinated since the crystalline polymorphs of tellurite are all fourfold coordinated, e.g., as recently measured by NMR [3]. However, Raman [2], neutron scattering [4], and molecular dynamics simulations [5] have suggested that the average coordination of tellurium in tellurite glasses is actually closer to 3.65. Barney et al. [2] published a model predicting the coordination from Raman as a function of alkali molar fraction. This model was digitized by the current authors to give an explicit functional form:

$$r(x) = \begin{cases} 3.65, & x < 0.15 \\ 3.89\text{—}1.6x, & 0.15 \leq x \leq 0.2 \end{cases} \tag{1}$$

This lower average coordination number had previously been interpreted in the context of Gupta-Cooper constraint theory [6] to suggest that TeO_2 should be a relatively good glass-former [3]. Since experimentally it is known that pure TeO_2 is a relatively difficult glass former, this lower coordination may be unlikely [3].

Recently, topological constraint theory has been shown to provide accurate predictions of T_g based on the temperature dependence of the bond constraints in the glass forming network [7–10]. The relationship between T_g and the topology of the glass network is provided through the composition and temperature dependence of the configurational entropy of the system, as shown below [7,8]:

$$\frac{T_g(x)}{T_g(x_r)} = \frac{S_c[T_g(x_r), x_r]}{S_c[T_g(x), x]} \tag{2}$$

where T_g is the glass transition temperature, x is composition, S_c is the configurational entropy, and x_r is a reference composition. According to the analysis of Naumis [11,12], the configurational entropy is largely proportional to the topological degrees of freedom, f, present in the system. With this proportionality, Eq. (2) can be rewritten as [7]:

$$\frac{T_g(x)}{T_g(x_r)} = \frac{f[T_g(x_r), x_r]}{f[T_g(x), x]} = \frac{d - n[T_g(x_r), x_r]}{d - n[T_g(x), x]} \tag{3}$$

where d is the dimensionality of the network (=3 for a three-dimensional system) and n is the average number of rigid constraints per atom. This framework allows for straightforward calculation of the change in T_g based on the changes in the connectivity of a glass-forming network [7–9,13,14].

2. Model

Using Eq. (3), the composition dependence of the average number of constraints per atom can be expressed as

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* Corresponding author.
E-mail address: jcm426@psu.edu (J.C. Mauro).

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$$n[T_g(x),x] = d - \frac{f[T_g(x_r),x_r]T_g(x_r)}{T_g(x)} \tag{4}$$

given an experimental T_g (x) curve.

To calculate the number of rigid constraints, we must consider all network-forming species in the system. In the case of alkali tellurite glasses, the network-forming species are the tellurium cations and the bridging oxygen anions (non-bridging oxygens can be ignored because they provide no constraints to the network). To calculate the average number of constraints in the system, the mole fraction of each species must be multiplied by the number of rigid constraints associated with that species,

$$n[T_g(x),x] = 2w_0 + \sum_{i=0}^{N} w_i[2r_i - 3] \tag{5}$$

in which w_0 is the molar fraction of oxygen, w_i is the molar fraction of a given network-forming cation, and r_i is the coordination of the associated network-forming cation. The three most important types of constraints in oxide glass-forming systems are: [7].

- α constraints, i.e., the radial constraints between network-forming cations and bridging oxygens: There are the two linear constraints per bridging oxygen associated with Te—O bonds.
- β constraints, i.e., the angular constraints associated with O—Te—O, where the number of independent constraints is expressed as 2r-3.
- γ constraints, i.e., the angular constraints associated with Te—O—Te. There is one angular constraint per bridging oxygen; however, due to the low energy needed to break these constraints ($T_{\text{room}} < T_\gamma < T_g$ for many systems) they typically do not contribute to the rigidity of the network in the glass transition range.

The summation of these constraints is expressed as:

$$n[T_g(x),x] = 2q(T_\alpha)[1-w] + wq(T_\beta)[2r-3] + q(T_\gamma)[1-w] \tag{6}$$

where w is the fraction of network-forming cations in the oxide and $q(t)$ is the temperature onset function as defined by temperature-dependent constraint theory [9,10]. The first term is the expression for the number of α constraints, the second term accounts for the β constraints, and the third term represents the γ constraints. However, since the onset temperature for γ constraints is less than T_g, the last term will be omitted for further calculations (i.e., the γ constraints are too weak to provide rigidity in the temperature range near T_g). Likewise, if the temperature of the system were to increase beyond the onset temperature of the β constraints, those constraints would no longer provide rigidity to the network. Such a case can be seen in the modeling of T_g for alkali borate systems [7].

The fraction of each network forming species is given by the expression:

$$w = \frac{1}{1 + \frac{r}{2}} \tag{7}$$

Combining Eqs. (6) and (7) (leaving out the last term of Eq. (6) because the temperature onset function for γ constraints is assumed to be less than T_g), we obtain a single function expressing the degrees of freedom of a given oxide glass former with coordination r:

$$f[T_g(x),x] = \frac{f[T_g(x_r),x_r]T_g(x_r)}{T_g(x)} = \frac{24-6r}{4+2r} \tag{8}$$

This expression allows for the calculation of T_g from the coordination of an oxide glass-forming composition,

$$T_g = \frac{([f[T_g(x_r)x_r]\cdot T_g(x_r)]\cdot[24-6r])}{4+2r} \tag{9}$$

Another goal of this research is to translate the experimentally derived changes in T_g into an approximation of the mean coordination. To do this, one must solve for r in Eq. (8):

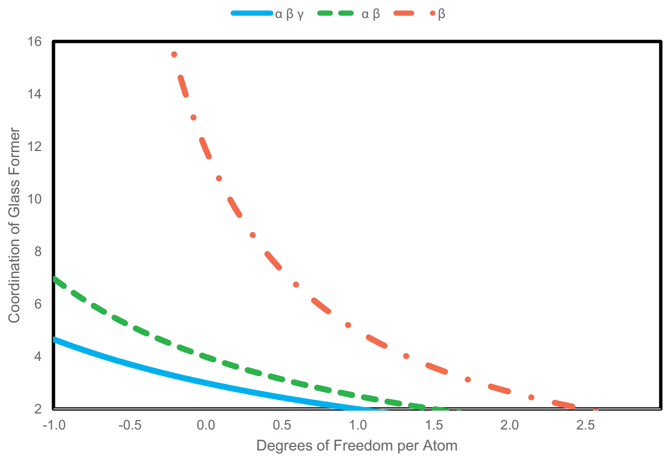

Fig. 1. The plotted expressions for each constraint possibility (All three constraints) [α β γ] (as observed at room temperature), the constraints relevant to T$_g$ [α β] (also seen in SiO_2 and B_2O_3), and just the angular constraint about network forming cation [β] (as seen in Ge—Se systems). The y-axis is terminated at two because anything with coordination less than two does not count as a network former.

$$r = \frac{12 - 2f[T_g(x),x]}{3 + f[T_g(x),x]} \tag{10}$$

Eq. (10) allows one to go from the known structure and find the changes in coordination purely based on the change in T_g, as long as the α constraints do not break and the γ constraints stay broken. The expression in Eq. (10) is plotted in Fig. 1, along with cases considering either just β constraints as rigid or all three constraints together rigid (purely for the purpose of comparison).

3. Materials and methods

Roughly 1–1.5 g of tellurium dioxide from Sigma Aldrich Company (reagent grade) was measured in a platinum crucible. The sample of pure TeO_2 was then heated at 1000 °C for ten minutes. After 10 min of heating, the sample was moved in a circular motion, with a 20-cm diameter, until the liquid in the crucible reached a dark orange color. Once the sample reached this color, the crucible was moved in a smaller circular motion of 10 cm until the color reached yellow-orange. Then the bottom of the crucible was quickly dipped into a 1-liter beaker filled with water at approximately 23 °C. The water-quenching procedure was repeated with a five-minute heating at 1000 °C until the sample was glassy.

Vitreous M_2O-TeO_2 samples were made up to 20 mol% M_2O (M = Na, Li, K). These were all made with 6-g samples in platinum crucibles and heated two times at 800 °C for 10 min, measuring the weight loss of the sample between the first and second heating steps. All samples of M_2O-TeO_2 were roller-quenched in a stainless-steel roller-quencher.

Immediately after being formed, Raman spectroscopy was performed as well as differential scanning calorimetry (Perkin Elmer DSC 7). Raman spectra were measured with an objective lens UMPLFL ×20 for two exposures of thirty seconds each. The sample was ground into a fine powder and put into an aluminum pan for measurement with a differential scanning calorimeter at a ramp rate of 40 °C per minute up to 550 °C. The onset method [15] was used to determine T_g (Table 1).

4. Results

The experimentally measured T_g data showed good agreement with literature values [16–18]. A reference point of $x = 0.20$ is chosen for

Table 1
Collected experimental T_g values.

Fraction of akali oxide	Potassium T_g (°C)	Lithium T_g (°C)	Sodium T_g (°C)
0	304.3	304.3	304.3
0.01	302.94	NA	NA
0.02	301.98	NA	NA
0.03	300.46	NA	NA
0.05	297.03	293.23	295.77
0.1	281.76	282.44	281.9
0.15	261.49	270.37	268.01
0.2	239.8	263.37	252.05

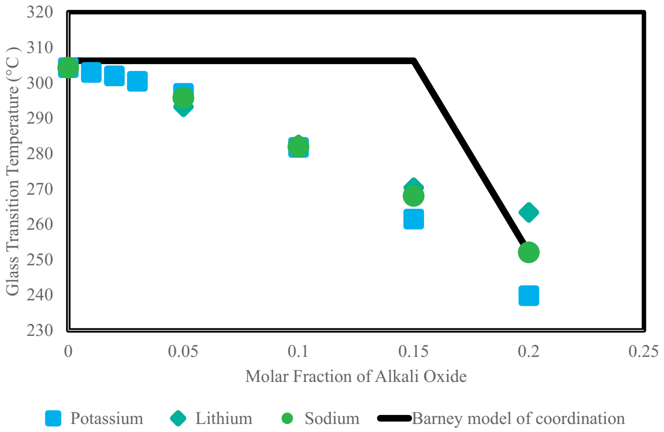

Fig. 2. T_g vs molar fraction of alkali dopant for model as well as measured T_g values. The fit of T_g values are close to that predicted from the Barney model [2] of coordination. We calculated the expected degrees of freedom and then used the average value of T_g at $x = 0.2$ to find the ratio. The final calculated result is in black and appears a bit sharp but at $x = 0$, the T_g values reported and expected are within a few degrees of each other. All other data points are experimentally observed.

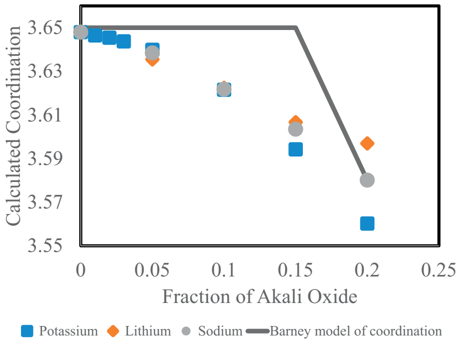

Fig. 3. Expected coordination of tellurium vs the molar fraction of alkali additions. We find that the model prediction gives excellent agreement with the values that are reported [2,4,19] close to 3.65 for pure TeO_2. The calculation at pure TeO_2 matches the model of Barney et al. [2] However in the predicted coordination there is a linear decrease with alkali content rather than an initially flat coordination as predicted by Barney. Despite this difference, there is close agreement between the constraint model and that of Barney et al.

model comparison purposes, since for this composition the two models of Barney et al. [2] and Garanga et al. [3] are in agreement regarding the slope of the Te coordination with respect to changing alkali content. Experimental values were taken with the previously defined algorithm and applied to the Barney et al. model [2] to compare the measured T_g values with those reported. Fig. 2 shows that the error at pure TeO_2 ($x = 0$) is the calculated T_g within experimental error of Barney et al.'s proposed coordination [2].

In order to confirm the model with both T_g and coordination, the expression for degrees of freedom was used to calculate the expected coordination of tellurium based on experimentally observed T_g values. The results are shown in Fig. 3.

5. Discussion

The main conclusion from this analysis is to offer a constraint theory view of tellurium coordination in alkali tellurite glasses. We found that going from experimental T_g values to coordination and vice-versa both show fairly good agreement with the extremes of the model as reported by Barney et al. [2] Even though our endpoint gives very good agreement with the proposed model, there is a difference in the slope of the predicted T_g curve.

The original constraint theory analysis by Garanga et al. [3] states that the TeO_2 glass configuration at a coordination of 3.75 gives 0 degrees of freedom in Cooper-Gupta constraint theory; thus, samples relatively close to that composition should easily form glasses and is often cited as a reason why 3.65 coordination is not a likely solution.

However, this differentiation of the degrees of freedom as related to the glass forming capability only predicts the cooling rate at which a glass sample needs to be quenched, while the nucleation relationship is only qualitatively defined in constraint theory. This lack of a quantitative relationship with nucleation, combined with the experimental findings that if one merely keeps the molten glass swirling in a crucible as it cools it can quite readily form glass even at relatively slow quenching speeds, implies that the degrees of freedom alone is not a good indicator of generalized glass forming capability in TeO_2.

This is further emphasized when one considers atomic constraint counting [20], which is mathematically equivalent to Gupta-Cooper constraint theory [10]. Specifically, for the case of B_2O_3 vs TeO_2 in the temperature region of T_g ($T_\beta > T_g > T_\gamma$), borate glass would have 0.6 degrees of freedom per atom; tellurite has either 0 (for 4-coordinated Te) or 0.18 degrees of freedom (for 3.65-coordinated Te). One would then assume, based on constraint theory, that tellurium dioxide will always be a good glass former. However, experimentally it is easy to form borate glass, but specialized techniques are needed to make pure TeO_2 glass. Unfortunately, there is currently no general theory to accurately predict nucleation and crystallization in glasses.

6. Conclusions

This paper has introduced a model to calculate the coordination of a glass-forming cation in a binary alkali tellurite glass. The proposed model was tested by finding the relative coordination changes of TeO_2 and confirmed by arriving at a coordination that is within 0.02 of that predicted by the Barney et al. [2] model (within their experimental error). Simultaneously, the Barney et al. model lent evidence to the validity of constraint counting method, and using just T_g values, constraint theory lends evidence for the coordination of Te in TeO_2 glass as 3.65.

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