Physical origin of chemical trends in glass formation in alkali tellurites: Reconciliation of constraint theory with experiments

R. Aravinda Narayanan*

Department of Chemistry, Indiana University, Bloomington, Indiana 47405
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A chemical trend in glass formation with alkali atom (Li, Na, K) in tellurite glasses is recognized, whose physical origin is revealed by a recently formulated approach to the constraint theory of glasses [Phys. Rev. B **60**, 11 859 (1999)]. In this work, the parameters appearing in the constraint theory are directly related to quantities derived from atomic structure studies, which facilitates the understanding of glass formation in ionic glasses. As a corollary, the issue of coordination number that has to be considered in the theory, and which has been debated in the literature, is clarified.

I. INTRODUCTION

Alkali tellurite glasses $[(M_2O)_x(TeO_2)_{1-x}]$, where M = Li, Na, K, have generated interest, in recent times, for their potential usage as optical switching devices[1] and for their anomalous[2] glass forming tendency (GFT). In this article, we will be concerned with the latter. The poor GFT of telluria (TeO$_2$) when compared to silica (SiO$_2$), the archetypal glass former, has been an intriguing feature in glass science. It is in this context that the GFT of alkali tellurites are termed anomalous since the addition of alkali oxide to tellurites increases their GFT so much that it becomes analogous to that of silica at around $x = 0.20$. Owing to its importance, valuable structural information on these glasses have been obtained over the years by many workers using various techniques, which includes x-ray[3,4] and neutron diffraction,[3,5] nuclear magnetic resonance (NMR),[3,6] Raman,[7] Mössbauer,[8] and X-ray photoelectron spectroscopy,[2] differential scanning calorimetry,[9] and ionic conductivity.[10,11] These are largely crystallographic approaches to understanding glassy materials. Alternatively, topological description of glasses, which deal with connectivity among the structural elements, bear directly on the question of glass formation. The constraint counting theory (CCT) of glasses proposed[12] by Phillips belongs to this class.

Recently, by applying the CCT, with some modifications, Zhang and Boolchand obtained a significant breakthrough[13] in the understanding of glass formation in these oxides: This was a natural step, after the proven success of CCT in explaining the GFT of covalently bonded chalcogenide glasses.[12] The modifications to CCT were necessitated by the suggestions from Raman scattering[7] and ^{125}Te Mössbauer hyperfine structure measurements,[13] that angular constraints (β) around nonbridging oxygen (NBO) sites in (Na$_2$O)$_x$(TeO$_2$)$_{1-x}$ are broken.[13] Physically, the reason for the increased GFT of telluria on the addition of alkali oxide is as follows: The basic coordination polyhedron in TeO$_2$ is the trigonal bipyramid[4,14] (in which one equatorial site is occupied by a lone-pair electron) of TeO$_4$ connected through bridging oxygen. Therefore, given a coordination number (CN) of 4 and 2 for Te and O, respectively, the mean coor-

dination number of atoms ($\langle r \rangle$) in TeO$_2$ can be calculated as 2.67, which according to the CCT lies in the overconstrained regime, where glass formation is poor[12]: In a random covalent network, the *best* glass[15] supposedly occurs at $\langle r \rangle$ = 2.40. The addition of the alkali oxide produces NBO sites, cleaving the network, which consequently reduces $\langle r \rangle$. Assuming a CN of 1 for Na, and by considering the broken β constraints around NBO sites, the network was shown[13] to be indeed optimized at $\langle r \rangle = 2.40$ ($x = 0.20$). However, Zwanziger and co-workers questioned the basis of assuming a CN of 1 for Na and in general, the applicability of CCT to ionic glasses, when NMR experiments reveal a CN between 4 and 6 for Na.[6] Nevertheless, even with such seemingly untenable assumptions, CCT still appears successful[16] in explaining the GFT of oxides.

Constraint theory predicts that at $\langle r \rangle = 2.40$, a rigidity percolation threshold (RPT) occurs, above which the rigidity of the network rapidly increases.[15] It was earlier asserted, on the basis of experimental results, that in alkali tellurites RPT occurs at about $x = 0.18$ ($\langle r \rangle = 2.43$) *independent* of the alkali type.[9,10] The following results, obtained recently, raise questions about this assertion: (1) The CN of the alkali ion deduced from x-ray diffraction experiments,[17] for any x, in general varies as K>Na>Li, (2) NBO concentration is alkali ion specific.[17] For a given x, the largest cation induces the largest NBO fraction. Therefore, the concentration of broken β constraint can be expected to vary accordingly. The main thesis of this article is to reconcile these chemical trends with the CCT of glasses.

In this paper, it is shown that the approach to CCT,[18] presented by the author earlier, is suitable for exploring such chemical trends in glass formation, which in the process subtly reveals, the origin of glass formation in alkali tellurite glasses. Also, the important issue of CN to be used in constraint calculations with regard to CN determined from x-ray and NMR experiments is discussed. Through a simple method, a way is shown to extract the covalent coordination from these measurements, which alone provides the mechanical constraints and is needed to be used in CCT. Present estimates correctly reveal that the *covalent* coordination of the alkali ion is approximately 1, which unambiguously explains why CCT works so well in this system.

64 134207-1

II. CONSTRAINT COUNTING THEORY

The optimum condition for glass formation, according to CCT, is achieved when the number of constraints (n_{co}) acting on an atom equals its degrees of freedom/embedding dimension (n_d): The constraints are the bond-stretching (α) and bond-bending (β) constraints, which represent the short-range bonding interactions in the valence force field models.[12] If $n_{co} < n_d$, the structure is floppy and can reorient in a way that is conducive for crystallization. On the other hand, when $n_{co} > n_d$, the structure becomes too compact, and gains long-range order which also leads to crystallization. These simple ideas were quite successful in explaining the GFT of typical glass forming systems such as Ge-Se and As-Se.[12] With the exploration of the properties of more systems, the theory required adjustments: For example, for one-fold coordinated halogen (Cl, Br, I) atoms, only α constraints need to be considered,[19] and in Si_xO_{1-x}, experiments reveal a reduction in β constraint population.[13] Recently, using an alternate approach to CCT, which simply includes both the original CCT and its various extensions, GFT of many glass systems were understood[18]. We shall now briefly describe this approach, which we call the unified approach, and apply it to alkali tellurite glasses.

A. Unified approach

The following formulas are used for counting the constraints in this approach:

$$n_{co}(r,n_d) = (r/2) + (1/2)r(r-1), \quad r \leq n_d - 1, \quad (1a)$$

$$n_{co}(r,n_d) = (r/2) + (1/2)(n_d-1)(2r-n_d), \quad r \geq n_d - 1, \quad (1b)$$

where the first and second terms on the right hand side (RHS) of Eqs. (1a) and (1b) correspond to α and β constraints, respectively. In the above formulas, r is the same as CN. The total number of constraints per atom in a two component system A_xB_{1-x}, is given by

$$n_{co}(A_xB_{1-x}) = x \times n_{co}(r_A) + (1-x) \times n_{co}(r_B). \quad (2)$$

Figure 1, which is central to our discussion, shows the curves of derivatives of the glass transition temperature (T_g) with composition $|dT_g/dx|$, for three alkali tellurite glass systems containing Li, Na, and K, respectively, obtained earlier.[9] Based on this plot it was previously concluded that the composition at which the RPT occurs, seen as the maximum in the curves of Fig. 1, is independent of the particular alkali ion added.[9] But it can be discerned easily in Fig. 1 that as we move from Li to K, the maximum shifts towards greater $\langle r \rangle$ (lower x) values: The maximum approximately occur at $x = 0.22$, 0.18, and 0.17 for Li, Na, and K, respectively. What is the origin for this chemical trend? In our earlier work on aluminum containing Te glasses we found shifts in RPT (Ref. 18) from the mean-field value of $\langle r \rangle = 2.40$ and understood it as due to the dilution of the covalent interactions by the presence of electropositive Al and electronegative Te atoms. In alkali tellurite glasses we have a similar situation with the electronegative oxygen atoms co-
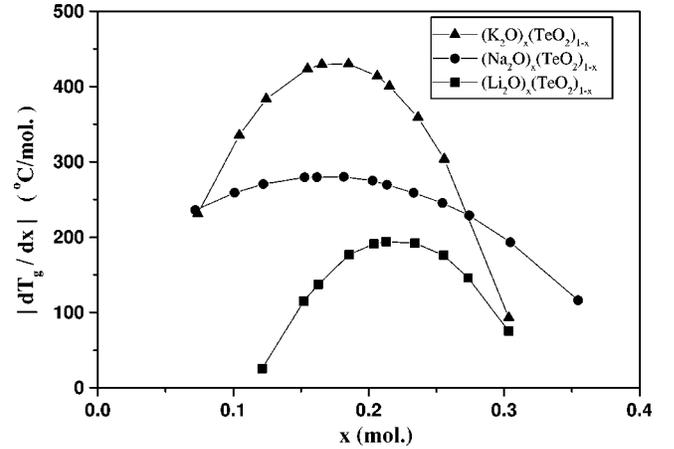

FIG. 1. Plot [digitized from Fig. 1(b) of Ref. 9] of first derivative with respect to alkali ion concentration (x), as a function of x.

ordinating with electropositive alkali atoms. The difference in electronegativities between these bonding atoms, a measure of the ionicity, increases with the participating alkali atom in the order: Li<Na<K. Let us now see how this influences the location of RPT. In the unified approach, the relative ionicity imparted to the network by the alkali atoms are distinguished in the following way. Ionic interactions are considered by attributing additional degrees of freedom n_i to the metallic atoms causing it. n_i here signifies the depletion of covalent bond charge[20] and in general, represents additional internal fields as in other mean-field models. This modifies the embedding dimension n_d to $n_\delta = n_d + n_i$. Thus the condition for RPT or optimum glass composition will now become

$$n_{co} = n_\delta. \quad (3)$$

Presently, we intend to "simulate" the chemical trend in RPT, assuming n_i as 0,1,2 for Li, Na, K, respectively, which basically portrays the ionicity in the Li-O, Na-O, and K-O bonds.[20] The CN (r) and n_{co} [Eq. (1)] for M, O, and Te when n_d is 3 are correspondingly (1 and 1/2), (2 and 2), and (4 and 7). Using this information and Eq. (2), the total number of constraints acting per atom for the three systems is calculated as

$$n_{co}[(M_2O)_x(TeO_2)_{1-x}] = 1/2 \times (2x_c)/3 + 2 \times (2-x_c)/3 + 7 \times (1-x_c)/3. \quad (4)$$

Now, substituting Eq. (4) into Eq. (3), the optimum glass composition or RPT is derived for the systems as follows.

(A) $(Li_2O)_x(TeO_2)_{1-x}$: Since $n_i(Li) = 0$, $n_\delta = n_d = 3$; the embedding dimension is unaltered. Applying Eqs. (3) and (4), we get $x_c = 0.25$ or $\langle r \rangle = 2.33$.

(B) $(Na_2O)_x(TeO_2)_{1-x}$: As, $n_i(Na) = 1$, $n_\delta = 4(2x_c)/3 + 3(2-x_c)/3 + 3(1-x_c)/3$. Equations (3) and (4) lead to $x_c = 0.20$ or $\langle r \rangle = 2.40$.

(C) $(K_2O)_x(TeO_2)_{1-x}$: $n_i(K) = 2$ and therefore, $n_\delta = 5(2x_c)/3 + 3(2-x_c)/3 + 3(1-x_c)/3$. Employing a similar procedure yields $x_c = 0.167$ or $\langle r \rangle = 2.44$.
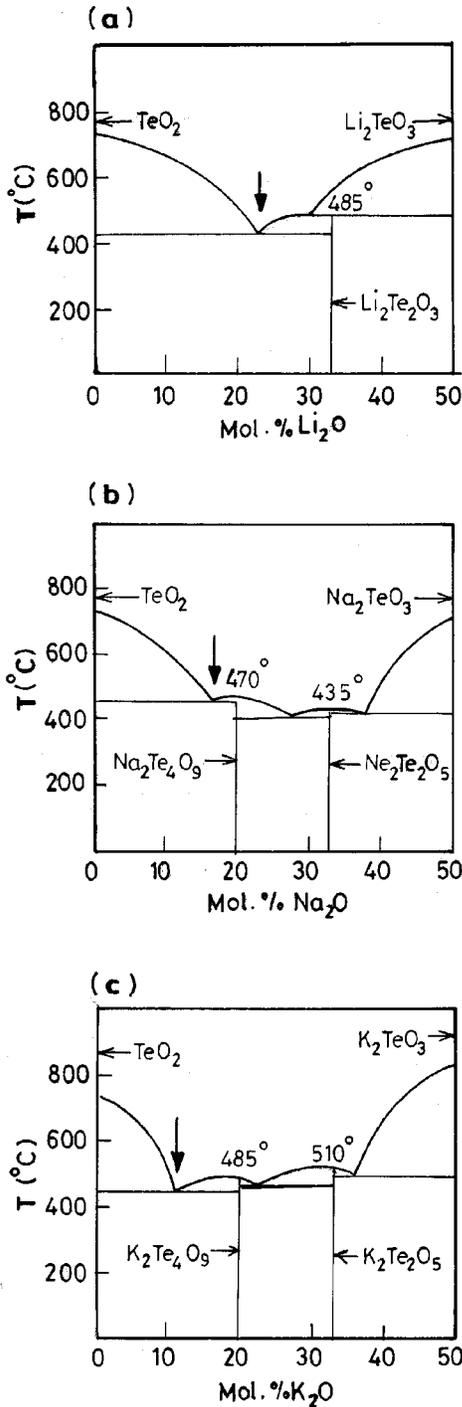
FIG. 2. Liquidus phase diagram of alkali tellurites (adapted from Ref. 22). Please see the text for discussion.

These calculations, as can be seen, qualitatively reproduce the chemical trend that is experimentally found in tellurite glasses: The RPT shifts to greater $\langle r \rangle$ (smaller x_c) values as the ionicity in the M-NBO bonds increase. A similar result was observed, earlier, in the aluminum based chalcogenide glasses.[18,21] It has been previously noted, that in chalcogenide alloys $T_g(x)$ closely resembles[12] $T_L(x)$, the liquidus curve. Figure 2 shows this to be true in alkali tellurites as well. The arrows indicate the eutectic composition in the

glass forming region that systematically shifts to lower values of x, when we go from Li to K, as predicted by our model. This aspect is being discussed more elaborately in a forthcoming article.

Here, we have used CCT to understand chemical trends in glass formation but there is yet another reason why the present result is significant: This approach correctly identifies the increased GFT in $(M_2O)_x(TeO_2)_{1-x}$ glasses with the added modifier atom M. The alkali atom which polarizes the original overconstrained network of TeO_4 tetrahedra, breaks β constraints around the bridging oxygen atoms. This provides the flexibility necessary in the linkages for the formation of strain free continuous network that aids glass formation.[12]

B. Extended approach

The assignment of internal degrees of freedom to the alkali atoms might seem arbitrary. To dispel such a notion, we now take recourse to the extended constraint theory[13,19] and blend the recent x-ray results[17] with the constraint theory and in the process clearly bring out the correspondence between the two approaches to CCT. In the extended constraint theory the formula that provides the critical coordination number ($\langle r \rangle_c$) pertaining to RPT is the following:

$$\langle r \rangle_c = 2.4 - 0.4(n_1 - m_2)/N. \qquad (5)$$

The term n_1/N accounts for the additional α constraints due to the onefold coordinated atoms, such as the alkali atoms in the present case and m_2/N is the fraction of NBO sites about which the β constraints are broken and hence, should be deducted from the total constraints. Reference 17 contains systematic crystallographic data on various alkali tellurite crystals and among them the information that is vital to us is the number of NBO sites generated for every alkali ion, i.e., the ratio $\gamma = NBO/M^+$. This actually is the *same* as the ratio m_2/n_1. Now, γ, as we mentioned earlier, depends on the alkali ion: The bigger the cation the more the polarization, which leads to more NBO's. For example, at $x = 0.20$, which is in the region of interest, the corresponding crystals $Na_2Te_4O_9$ and $K_2Te_4O_9$ have γ of 1 and 2, respectively. Assuming, this to be the value[23] of γ for any x, we now compute $\langle r \rangle_c$ or x_c in the systems. The left hand side of Eq. (5) which is common for all the systems is

$$\langle r \rangle_c = 2x_c/3 + 2(2-x_c)/3 + 4(1-x_c)/3. \qquad (6)$$

(A) $(Na_2O)_x(TeO_2)_{1-x}$: The RHS of Eq. (5) for this system is simply 2.40 as $n_1 = m_2$ ($\gamma = 1$). Applying Eqs.(5) and (6), we get $x_c = 0.20$, a result that was obtained[13] earlier by Zhang and Boolchand.

(B) $(K_2O)_x(TeO_2)_{1-x}$: Here, $n_1 = 2x_c/3$ and since $\gamma = 2$, $m_2 = 4x_c/3$ and thus the RHS of Eq. (5) becomes $2.4 + 0.8x_c/3$. Comparing this with Eq. (6), we arrive at $x_c = 0.167$. In the case of $(Li_2O)_x(TeO_2)_{1-x}$, assuming the formation of negligible amount of NBO sites, it can be easily derived that $x_c = 0.25$. It thus becomes clear that n_i in the unified approach and γ in the extended CCT play a similar role, since the RPT derived using them is the same.

C. Alkali coordination

We shall now briefly comment on the issue of assuming a CN of 1 for the alkali atoms in the constraint counting procedures when NMR and x-ray measurements reveal[6,17] a CN between 3–9 for them. A more appropriate question would be what is the CN that is referred to in CCT? In CCT of concern are the bonds that provide strong mechanical constraints, which means that the covalent bonds are the most qualified. In light of the successful explanation of the GFT assuming an CN of 1, we submit that the CN that is referred to is the covalent coordination. Covalent coordination can be quantitatively estimated in a simple manner from the CN obtained from experiments and the logic used is the following: Here, the assumption is that the total energy of the system is constituted by covalent and ionic energies only, and Pauling's definition[24] is used to determine the fractional ionic character (f_i) in the M-NBO bonds. From this the complement quantity, fractional covalency in the bonds is obtained, which when multiplied with the CN determined, say, from x-ray measurements give the covalent coordination

$$f_i(M,NBO) = 1 - \exp[-(X_M - X_{NBO})^2/4], \qquad (7)$$

where X in the formula denotes the electronegativity of the atom. In this formula, of interest is the second term (exponential) which gives the fractional covalent character. Electronegativities of Li, Na, K, and O are 0.98, 0.93, 0.82, and 3.44, respectively. Let us consider the cases of Na and K which have been found to have coordinations of (4 and 5), and (6 and 7), respectively, around $x_c = 0.20$. Their corresponding covalency factors are 0.208 and 0.18 which leads to a covalent coordination between 0.832–1.04 for Na^+ and 1.08–1.26 for K^+ cation. Thus it can be seen that the covalent coordination is nearly independent of the alkali ion and is about 1. In this context, the recent suggestion[25] to view the constraints provided by alkali atoms bonded to more than one oxygen as resonating constraints is an interesting parallel to the above proposal.

D. Some remarks

Our comparisons of a glass with its corresponding crystal is limited to their short-range interactions. Local coordina-tions that determine the short-range order, in general, closely resemble in the two cases.[26] In the alkali tellurite glass system, macroscopic properties, such as T_g and density, do not reveal RPT as clearly as in chalcogenide glass system.[27,28] Considering this, the recent report[3] of a reduction in sodium pair correlation, derived from NMR measurements, at $x = 0.20$ ($\langle r \rangle = 2.40$) in $(Na_2O)_x(TeO_2)_{1-x}$ glasses, is an intriguing microscopic evidence for RPT in alkali tellurite glasses. For $\langle r \rangle > 2.40$, where the Na concentration is low, Na-Na correlation is found to be small, and when $\langle r \rangle < 2.40$, a region where the structure is relatively floppy, Na-Na correlation is high. So, it will be interesting to see if lithium and potassium pair correlation function confirm the chemical trend in RPT, predicted by this study. Furthermore, the present model can be extended to understand similar chemical trends, seen in alkali and alkaline earth borate glasses observed through NMR (Ref. 29) and other studies.[30]

III. CONCLUSIONS

A chemical trend is discerned in the occurrence of the rigidity percolation threshold, a quantity that is related to the optimum glass composition in a system, in alkali tellurites as a function of the type of alkali ion. This finding is understood using an approach to constraint counting theory of glasses which considers the chemical nature of the atoms. Also, in this study, the number of nonbridging oxygen atoms per alkali ion, a parameter derived from structure measurements is related directly to parameters appearing in the constraint theory. This opens up the possibility of understanding glass formation in many other oxide systems, which are ionic, and are of technological importance.

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*Email address: araghava@indiana.edu

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