Broken Bond-Bending Constraints and Glass Formation in the Oxides

M. Zhang and P. Boolchand argue that properties of the glassy state in systems like SiO₂ and (Na₂O)₉(TeO₂)₁₋ₓ can be understood in terms of a constrained network picture (1). The key elements of this treatment are the enumeration of the bonding interactions that make up the network and of the constraints to which they are subject. To accomplish the first of these tasks, Zhang and Boolchand apply the “8 − N rule” (2, 3). They thus conclude that, in (Na₂O)₉(TeO₂)₁₋ₓ, the coordination numbers of tellurium, oxygen, and sodium are, respectively, 4, 2, and 1. We find, however, that the coordination number of sodium in oxide materials, including in (Na₂O)₉(TeO₂)₁₋ₓ, is not 1 according to experimental evidence and the fact that the 8 − N rule does not apply to alkali ions.

The 8 − N rule, where N is the group number, predicts that each atom participates in enough directed bonds to fill its valence shell with an octet of electrons (3). This rule works well for compounds formed of covalent bonds with negligible d-orbital contribution (for example As₂⁺,Se₁₋ₓ). For sodium, the rule fails because sodium obtains an octet of electrons by shedding its valence electron to reach oxidation state +1. If Na(I) were to participate in a directed bond, its local electron environment would not be an octet, but rather a pair of σ-bonding electrons. We know of no evidence for this type of bonding for sodium in solids. Rather than participating in directed bonds with covalent character, Na(I) interacts through predominantly electrostatic forces with typically four to six coordinating atoms (4). For example, in NaCl (rock salt structure), sodium has coordination number six, and in Na₂O (antifluorite structure) the coordination number is four. For crystalline Na₉Te₂O₁₅, the composition of primary interest in the present case, we showed that the two sodium ions interact with four and five neighboring oxygen atoms, respectively (5). Some of the oxygen in the coordination sphere are nonbridging, and some are bridging. Contact distances to the nonbridging oxygen are not significantly shorter than those to bridging oxygen.

In oxide glasses the sodium coordination is similar to that in crystalline materials. This has been shown in silicates by extended x-ray absorption fine structure (6) and by nuclear magnetic resonance (NMR) (7), and in (Na₂O)₉(TeO₂)₁₋ₓ by NMR (8). These studies conclude that the coordination number in both cases is in the range of four to six. Including the constraints for sodium coordinated in this experimentally determined way leads to a large increase in the total number of α and β constraints. Consequently, a vastly overconstrained network is predicted for all compositions of the (Na₂O)₉(TeO₂)₁₋ₓ system. We thus conclude that the constrained network theory as applied by Zhang and Boolchand is not an appropriate explanation for the behavior of glasses in this system.

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REFERENCES
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Response: Although in general Zwaninger et al. (1, 2) use a reasonable approach to analyze their NMR results in (Na₂O)₉(TeO₂)₁₋ₓ glasses, there is now evidence (3) to suggest that the Na local order in the stable c-Na₉Te₂O₁₅ compound (4) is different from that in its glass counterpart, and therefore the crystal would be an inappropriate reference point from which to model the glass. This evidence comes from three types of measurements: (i) Time-temperature-transformation studies (3) reveal multi-step nucleation and growth processes to be responsible for crystallization of g-Na₉Te₂O₁₅, which indicates that nuclei of the stable crystalline phase are not present in the glass; (ii) Powder x-ray diffraction scans of air-cooled (Na₂O)₉(TeO₂)₁₋ₓ melts (Fig. 1) reveal a metastable crystalline phase to nucleate as a precursor before the stable c-Na₉Te₂O₁₅ phase is formed (4), which suggests that the local order in the metastable phase may have a bearing to that of the glass and, finally; (iii) NMR studies of the metatellurite glass reveal that the nuclear quadrupole interaction (NQI) (1.9 ± 0.3 MHz) resides outside the range of values (4) of corresponding crystalline site parameters [NQI: 4.4 ± 0.2 MHz (site 1) and 3.6 ± 0.02 MHz (site 2)], which again suggests that the Na local order in the glass and the stable crystal are different. But perhaps the central issue to applying constraint theory (5) to glassy networks is to distinguish between atomic constraints that are intact and therefore relevant, from those that are broken (6) and therefore irrelevant. In the present glass system, the (α,β) constraints associated with the trigonal bipyramidal building blocks are all intact as revealed by neutron RDF (7) and ⁱ²⁷Te Mössbauer quadrupole interactions (3). TeO₂ melts (τ = 2.67) tend to easily crystallize even after a water quench (6) because the network is slightly overconstrained (τ > 2.4). Na₂O alloying to pure TeO₂ breaks a bridging oxygen bond to produce two nonbridging oxygen (O²⁻) to which the two Na⁺ ions become electrostatically coupled. In the more open structure of the glass, our conjecture is that Na⁺ ion will be closest to one of these NBO sites and hence the mechanically effective Na coordination will be 1. For onefold coordinated atoms, only a bond-stretching (α) constraint is effective (8), and for this reason the nature of bonding, whether covalent or ionic becomes irrelevant, as either type of interaction can provide a central force constraint. In the more compacted structures of crystalline solids in relation to glasses, a higher coordination number can emerge if such an arrangement lowers the free energy of the system as it apparently does in the stable form of c-Na₉Te₂O₁₅. The Na coordination of 5 or 6 in this crystalline phase leads to Na-O bonds that are mechanically inequivalent, however. In the glassy state, we believe only one Na-NBO bond length of about 2.5 Å will remain intact while all other Na-O bond lengths will exhibit a significant spread (broken constraints) for glass formation to occur. In NaCl, where the Na coordination is 6 both chemically and mechanically, bulk glass formation is precluded because the network is highly overconstrained.

Constraint theory has worked remarkably well in the chalcogenides (5, 9). It can be extended (6) to SiO₂, and to the present oxide glass system if one includes the appropriate atomic constraints that are intact in these networks. By taking the mechanically effective Na coordination of 1, then one is able to not only understand the glass forming range, but quantitatively also predict optimization of the glass forming tendency near x = 0.20, for which there is convincing experimental evidence (6). X-ray diffraction scans (Fig. 1) show that there is a propensity of glass formation in the composition range 0.15 < x < 0.20 and near x = 0.27. The former compositional