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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 SiO_2 and $(\text{Na}_2\text{O})_x(\text{TeO}_2)_{1-x}$ 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 $(\text{Na}_2\text{O})_x(\text{TeO}_2)_{1-x}$, 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 $(\text{Na}_2\text{O})_x(\text{TeO}_2)_{1-x}$, 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 $\text{As}_{2+x}\text{Se}_{3-x}$). 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 Na_2O (antifluorite structure) the coordination number is four. For crystalline $\text{Na}_2\text{Te}_4\text{O}_9$, 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 $(\text{Na}_2\text{O})_x(\text{TeO}_2)_{1-x}$ 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 $(\text{Na}_2\text{O})_x(\text{TeO}_2)_{1-x}$ 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

1. M. Zhang and P. Boolchand, *Science* **266**, 1355 (1994).
2. N. F. Mott, *Philos. Mag.* **19**, 835 (1969).
3. N. F. Mott and E. A. Davis, *Electronic Processes in Non-Crystalline Materials*, (Oxford Univ. Press, Oxford, United Kingdom, 1979).
4. A. F. Wells, *Structural Inorganic Chemistry*, (Oxford Univ. Press, Oxford, United Kingdom, 1984).
5. S. L. Tagg, J. C. Huffman, J. W. Zwanziger, *Chem. Mater.* **6**, 1884 (1994).
6. G. N. Greaves, *J. Non-Crystalline Solids* **71**, 203 (1985).
7. X. Xue and J. F. Stebbins, *Phys. Chem. Minerals* **20**, 297 (1993).
8. S. L. Tagg, R. E. Youngman, J. W. Zwanziger, *J. Phys. Chem.* **99**, 5111 (1995).
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Response: Although in general Zwanziger *et al.* (1, 2) use a reasonable approach to analyze their NMR results in $(\text{Na}_2\text{O})_x(\text{TeO}_2)_{1-x}$ glasses, there is now evidence (3) to suggest that the Na local order in the stable $\text{c-Na}_2\text{Te}_4\text{O}_9$ 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 $\text{g-Na}_2\text{Te}_4\text{O}_9$, which indicates that nuclei of the stable crystalline phase are not present in the glass; (ii) Powder x-ray diffraction scans of air-cooled $(\text{Na}_2\text{O})_x(\text{TeO}_2)_{1-x}$ melts (Fig. 1) reveal a metastable crystalline phase to nucleate as a precursor before the stable $\text{c-Na}_2\text{Te}_4\text{O}_9$ 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 metatellurate 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 ^{125}Te Mössbauer quadrupole interactions (3). TeO_2 melts ($\langle r \rangle = 2.67$) tend to easily crystallize even after a water quench (6) because the network is slightly overconstrained ($\langle r \rangle > 2.4$). Na_2O alloying to pure TeO_2 breaks a bridging oxygen bond to produce two nonbridging oxygen (O^-) to which the two Na^+ ions become electrostatically coupled. In the more open structure of the glass, our conjecture is that a 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 $\text{c-Na}_2\text{Te}_4\text{O}_9$. 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 2.3\AA will remain intact while all other Na-O bond lengths will exhibit a significant spread (broken constraint) 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 SiO_2 , 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

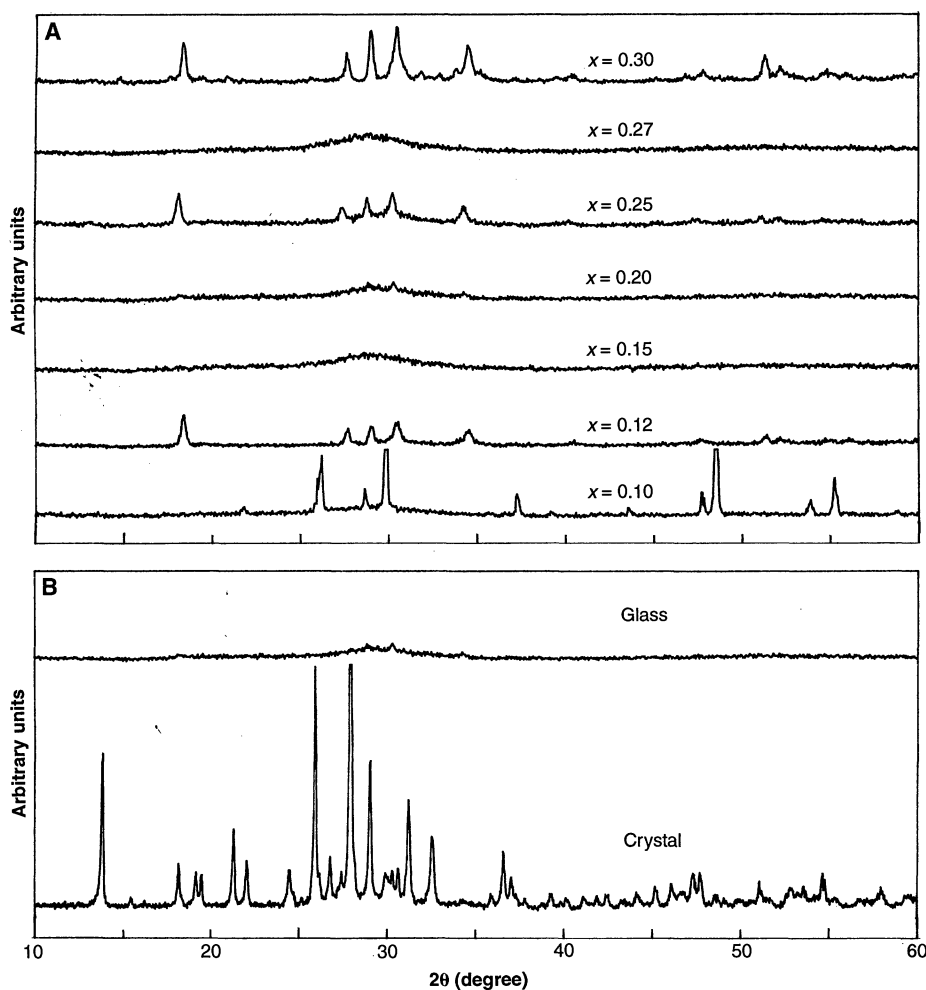


Fig. 1. (A) X-ray powder patterns of air-cooled $(\text{Na}_2\text{O})_x(\text{TeO}_2)_{1-x}$ melts at indicated compositions. These melts received the same undercooling. Note the qualitative absence of crystallization at $x = 0.15$ and 0.20 , and at $x = 0.27$. The former compositions are close to the rigidity percolation threshold $x = 0.18$, while the latter one to the eutectic. Also note that in the glass samples at $x \geq 0.12$, a metastable crystalline phase nucleates (with 2θ reflections at approximately 18° , 26° , 30° , etc.). This phase does not correspond to the stable $c\text{-Na}_2\text{Te}_4\text{O}_9$. Prolonged annealing of the air-cooled $x = 0.20$ glass sample at T_x yields the scan of $c\text{-Na}_2\text{Te}_4\text{O}_9$ shown in bottom panel (B), which corresponds to the stable phase (4). The crystalline phase to nucleate at $x = 0.10$ correspond to $\alpha\text{-TeO}_2$ as expected.

window corresponds to the stiffness threshold near $x = 0.18$ as discussed in our report (6), while the latter coincides with the known eutectic (10) near $x = 0.28$ in the present glass system.

Thus, the physical justification for choosing a onefold coordination for Na

rather than a fivefold or higher as suggested by NMR chemical shifts, rests in identification of the former as the mechanically effective coordination of Na in the $(\text{Na}_2\text{O})_x(\text{TeO}_2)_{1-x}$ glass system. The choice of fivefold coordination or higher for Na in these glasses is qualitatively incompatible

with a wide array of network connectivity-related physical properties such as Lamb-Mössbauer factors (6, 11), glass transition temperature (12, 13), and hardness, each of which decrease with increasing Na_2O molar content in the glasses. Within the context of constraint theory of glasses, a coordination number of 5 or higher for Na cannot even qualitatively explain the glass forming tendency let alone its optimization near $x = 0.20$ for which there is convincing experimental evidence. We thus stand behind our assertions on the microscopic origin of the glass forming tendency in this oxide glass system as discussed in our report (6).

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REFERENCES AND NOTES

1. J. W. Zwanziger, S. L. Tagg, J. C. Huffman, *Science* **268**, 1510 (1995).
2. S. L. Tagg, R. E. Youngman, J. W. Zwanziger, *J. Phys. Chem.*, in press.
3. M. Zhang, P. Boolchand, D. McDaniel, in preparation.
4. S. L. Tagg, L. Huffman, J. W. Zwanziger, *Chem. Mater.* **6**, 1884 (1994).
5. J. C. Phillips, *J. Non-Cryst. Solids* **34**, 153 (1979); *ibid.* **43**, 37 (1981); M. F. Thorpe, *ibid.* **57**, 355 (1983).
6. M. Zhang and P. Boolchand, *Science* **266**, 1355 (1994).
7. S. Neov, I. Gerassimov, K. Khezov, B. Sybzhimov, V. Kozhukharou, *Phys. Stat. Solidi*, **A47**, 743 (1978).
8. P. Boolchand and M. F. Thorpe, *Phys. Rev.* **B50**, 10366 (1994).
9. P. Boolchand *et al.*, *Cryst. Solids* **182**, 143 (1995).
10. B. P. Troitskii, O. K. Yakhind, N. S. Martystchenko, *Inorg. Materials (USSR)* **3**, 661/3, 1967; also see A. K. Yakhind, N. S. Martystchenko, *Inorg. Materials (USSR)* **6**, 12848 (1970).
11. W. Bresser *et al.*, *Phys. Rev.* **B47**, 11663 (1993); An increase in the ^{125}Te Lamb-Mössbauer factor as a function of average coordination number (r) is illustrated for the case Te_3Cl_2 ($r = 2$), ZnTe ($r = 4$), Mg_3TeO_6 ($r = 6$). An increase in bulk elastic constants with (r) is illustrated for the $\text{Ge}_x\text{Se}_{1-x}$ binary glass system in a paper by S. S. Yun, H. Li, R. L. Cappelletti, R. N. Enzweiler, P. Boolchand [*Phys. Rev.* **B39**, 8702 (1989)].
12. M. Zhang, S. Mancini, W. Bresser, P. Boolchand, *J. Non. Cryst. Solids* **151**, 149 (1992).
13. J. Heo, D. Lam, G. H. Siegel, E. A. Mendoza, D. A. Hensley, *J. Am. Cer. Soc.* **75**, 277 (1992).
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