Alkali tellurite glasses: Bonding, structure and conductivity*

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Abstract. The nature of the Te–O bond and charge transfer between alkali atoms and Te–O polyhedra in alkali–tellurite glasses is discussed in connection with ion transport in these glasses. Experimental results on XPS, neutron and Raman scattering support the empirical picture developed here. The overall kinetics of the interchange transport mechanism for conduction in single and mixed alkali–tellurite glasses is apparently determined by the kinetics of the alkali ion—glass former ion interchange—an aspect to be probed experimentally.

Keywords. Alkali tellurite glasses; bonding; structure; conductivity.

1. Introduction

Alkali tellurite glasses— $A_2O - TeO_2$ ($A = Li, Na, K$) have (i) relatively low melting points (but are non-hygroscopic), (ii) high refractive indices (> 2), (iii) large dielectric constants, (iv) good IR transmission coefficients, (v) high thermal expansion coefficients and (vi) reasonably good ionic conductivity.

These characteristics emerge from unique short-range structural effects, electronic structure and local chemical bonding peculiar to these glasses. As far as electrical conductivity is concerned, non-bridging oxygens, electronic charge transfer and ion hopping play an important role—both in ‘single alkali’ and ‘mixed alkali’ tellurite glasses.

In this paper, we discuss aspects of chemical bonding in, and local structure of, alkali tellurite glasses as they relate to aspects of ionic conductivity. We shall utilize experimental data on neutron and Raman scattering to arrive at an acceptable model for ion conduction in single alkali and mixed-alkali tellurite glasses.

1.1 Bonding

Local chemical bonding holds the key to global structure—whether for crystalline or non-crystalline solids. More precisely, it is the extent of charge transfer among the constituent elements that decides the geometry and stability of the glass-building block. To begin with, one could consider the nature of the Te–O bond from three points of view: (i) electronegativity difference, (ii) radius ratio and (iii) bond energy in relation to boiling point.

The Pauling electronegativities (χ) of Te and O are 2.21 and 3.44 respectively. Thus Te is electropositive ($\chi_{Te} < \chi_O$) and charge should transfer from Te to O. Furthermore, $\Delta\chi = 1.23$ (which corresponds to an ionicity of 39%) is less than 1.90 and makes TeO_2 a glass former according to Stanworth (1971). Furthermore, this number expressed in kcal represents the enthalpy of formation of the Te–O bond (Pauling 1975). When we mix an alkali oxide Li_2O and TeO_2 and melt the mixture to form a glass, the bonds are

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scrambled and frozen. The average electronegativity difference $(\Delta\chi_{\text{Li-O}} + \Delta\chi_{\text{Te-O}})/2 = (2.5 + 4.5)/2 = 1.95$, yet close to the glass forming criterion but more ionic than TeO_2 glass. The radius ratio $r_{\text{Te}^{4+}}/r_{\text{O}^{2-}} = 84 \text{ pm}/140 \text{ pm} = 0.6$ is favourable for the formation of an octahedron of oxygens around Te. Interestingly enough the sum of tetrahedral covalent radii of Te (132 pm) and oxygen (66 pm) is $1.98 \text{ \AA}$ which is found to be close to the average Te–O distance in crystalline and glassy TeO_2 . In fact, neutron scattering experiments on $\text{Li}_2\text{O–TeO}_2$ (Neov *et al* 1979) put the Te–O distance as $1.93 \text{ \AA}$. There is thus, a delicate balance of covalency and ionicity in TeO_2 which makes the bonding unique in this ‘stand-alone’ glass former (Lambson *et al* 1984). Finally consider the ratio of the bond strength to melting point an important criterion for glass formation. This value for TeO_2 is lowest (0.040 kcal/mol K) among canonical glass formers (0.053 for SiO_2 and 0.130 for B_2O_3).

The basic octahedral geometry inferred from the above empirical considerations is found to be correct. Recent work on the electronic structure of tellurite glasses based on the distorted rutile structure of paratellurite has shown that the building block in tellurite glasses is indeed a Te–O_6 octahedron albeit at distorted one, the distortion arising from $5s\text{--}5p$ hybridization of the Te atom and leading to four strong Te–O bonds (Suehara *et al* 1995). Very interesting experimental confirmation of this has come from the valence bond spectra (XPS) of $\alpha\text{-TeO}_2$ (Suehara *et al* 1994) and from the ESR of a hole defect in electron-irradiated paratellurite (Watterich *et al* 1985). Thus the ambiguity over the structural basis of TeO_2 i.e. whether the building block is derived from $\alpha\text{-TeO}_2$ or $\beta\text{-TeO}_2$ has been resolved in favour of the former.

1.2 Structure

The structure of alkali–tellurite glasses is based on (i) the Te–O building block and (ii) the alkali–oxygen bonding, or, more precisely the alkali– TeO_n bonding. The latter assumes great importance in view of the difference in the properties of alkali atoms and thus differences in alkali–oxygen bonding. As the electronic charge transfer depends on these properties (Suehara *et al* 1995), one has to focus on the changes in charge transfer as one alters the concentration of alkali oxide in a single alkali tellurite glass or as one replaces one alkali by another in a mixed alkali–tellurite glass. The subtle differences in alkali–oxygen charge transfer makes the glass structure inhomogeneous by creating a number of Te–O_n ($3 \leq n \leq 6$) and thus the structural changes arise. In turn, these latter influence the ion transport paths and decide the conductivity behaviour.

The electronegativity of the alkali atoms in alkali tellurite glasses is smaller than those of Te and O (e.g. $\chi_{\text{Li}} = 1.0$, $\chi_{\text{Na}} = 0.9$ while $\chi_{\text{Te}} = 2.1$ and $\chi_{\text{O}} = 3.5$). Therefore the charge transfer must take place from say Li to TeO_n units. What is the maximum charge transfer? Assuming Li_2TeO_3 (and Na_2TeO_3) as the corresponding crystalline ‘precursors’, the maximum charge transfer would be 2 units. If the net charge on TeO_6 is assumed to be $8\delta^-$ (taking $\text{Te}^{4\delta+}$, and $\text{O}^{2\delta-}$ as charges on individual ions, δ being partial ionic character) then a maximum charge transfer of 2 units would mean $8\delta = \sim 6$ or $\delta = 0.75$. This would make Te triply positive (Te^{3+}) and oxygen $\text{O}^{1.5-}$. Suppose the charge transfer is 1, then $8\delta = \sim 7$, or $\delta = 0.9$ which would yield $\text{Te}^{3.6+}$ and $\text{O}^{1.8-}$. The charge transfer is expected to vary continuously from 0 to 1 as the alkali concentration is increased from 0 to the maximum permissible value. This progressive charge transfer, however would not result in a monotonic change in local structure but

would lead at some specific concentration of the alkali ion to the formation of non-bridging oxygens (NBO) in significant numbers. From the point of view of electrical conductivity this would signal a stage when the activation energy for ion migration would change little with concentration. The recent dynamic angle spinning ^{23}Na NMR study on $\text{Na}_2\text{O}-\text{TeO}_2$ glasses (Tagg *et al* 1995) has shown that there is a change in coordination of Na from about six at low modifier concentration (10 to 18 mol%) to about five at high concentration (> 18 mol%), which has been interpreted as due to the onset of NBO formation. Similar studies on $\text{Li}_2\text{O}-\text{TeO}_2$ glasses using ^7Li NMR probe would be highly desirable.

This net charge transfer is also affected when one alkali atom (Li) is partially replaced by another (Na) atom. The chemical homogeneity of the glass would be naturally affected by this localized charge transfer, by way of the occurrence of different types of TeO_n units randomly distributed over the glass network. These changes would automatically be reflected in the creation of many types of conduction paths leading to different conduction mechanisms in single alkali and mixed alkali tellurite glasses. Thus the addition of alkali (or an alkaline earth oxide) to TeO_2 would lead to a 'depolymerization' of the TeO_2 framework (Yamamoto 1994) and thus create alternative diffusion paths for alkali-ion migration. These changes have been monitored by Raman scattering experiments on rapidly quenched alkali-tellurite glasses (Tatsumisago *et al* 1994).

In an earlier paper (Sunandana 1995) we had raised three questions with regard to the ion interchange transport process as a viable ion-conduction mechanism in single alkali and mixed alkali-tellurite (and other) glasses. These questions relating to the energetics, kinetics and 'local structural collapse' dynamics have been subsequently examined in some detail (Sunandana 1996). There appears to be a hierarchy of energies

$$E_i > E_i > E_{\text{hf}} > E_d > E_{\text{ha}},$$

where E_i is the energy required to remove an alkali (say Li^+) from its interstitial position in the glass network, E_d the energy required to free Li^+ attached to an NBO, E_i the energy required to 'yank out' glass former ion (say Te^{4+}) from its trigonal prismatic site in the network, E_{hf} the energy of hopping of Te to a bound Li^+ and E_{ha} the energy for bound Li^+ to hop back to Te.

The crucial kinetics of this process would be that for the glass former ion-bound alkali ion interchange. The rate of this interchange probably decides the overall kinetics of the problem. The 'local collapse' of the network during the ion interchange also constitutes an interesting (but complicated) process and it would be interesting to probe this experimentally, say using pulsed NMR of the ^7Li nucleus ($I = 3/2$) (Unfortunately, Te, unlike ^{29}Si ($I = 1/2$) and ^{11}B ($I = 3/2$) does not possess a magnetic nucleus so one cannot do Te-NMR). Specifically the general dynamical aspect to be probed is the exchange of Li atoms between sites or the rotation of the relevant species (with respect to the magnetic field) that affects the NMR lineshape appreciably (Stebbins 1988).

2. Conclusion

The nature of the Te-O bond and charge transfer between alkali atoms and Te-O polyhedra in alkali-tellurite glasses has been discussed in connection with the ion transport in these glasses. Experimental results on XPS, neutron and Raman scattering

support the empirical picture developed here. The overall kinetics of the interchange transport mechanism for conduction in single and mixed alkali–tellurite glasses is apparently determined by the kinetics of the alkali ion–glass former ion interchange—an aspect to be probed experimentally.

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