INTERNATIONAL SYMPOSIUM
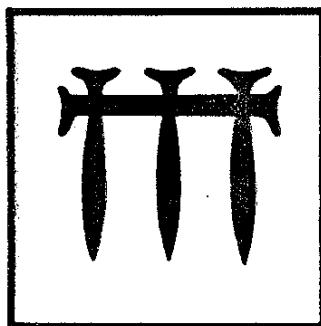# ON GLASS SCIENCE & TECHNOLOGY

October 6-8, 1993
Athens, Greece

Organized by the
HELLENIKOS HYALOURGIKOS SYNDESMOS
(Greek Glass Federation)

Under the auspices of the
INTERNATIONAL COMMISSION ON GLASS

Proceedings of the
INTERNATIONAL SYMPOSIUM
ON GLASS SCIENCE AND TECHNOLOGY

Athens, 6-8 October 1993

Editors: G. D. Chryssikos and E. I. Kamitsos

Fragility and decoupling in glass: A chemical perspective

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Abstract

Glass forming liquids often experience chemical alterations upon cooling. The identification of the nature and extent of these alterations as a function of composition is possible by spectroscopic and devitrification experiments. This paper provides several examples where the chemistry of vitrification can be related to trends in properties such as the strength/fragility and the decoupling of the conductive motions from the structural relaxations.

INTRODUCTION

The formation of glass is associated with the capture of high temperature structures in a metastable solid configuration. Hence, the knowledge of the channels available for the chemical relaxation of a system upon quenching is of special interest. The gamut of liquids that vitrify upon fast cooling (quenching) is enormous and the chemical understanding of vitrification requires a broad structural perspective based on the hierarchy of local, intermediate and long-range structural correlations.

The real time mapping of the chemical relaxations accompanying the quenching of a melt is rarely available. More easily accessible is the temperature dependence of 'physical' properties such as the heat capacity (C_p), and the shear viscocity (η). Angell has employed the variation of these properties in the glass transition range to cast a broad classification of glassforming substances (1). According to this classification, 'strong' liquids approach the glass transition range with Arrhenious viscosity-temperature dependence and exhibit small changes in C_p on going from the liquid to the glassy state. On the other hand, 'fragile' systems exhibit sublinear $\log\eta$ vs $1/T$ dependence and larger ΔC_p values. Another index particularly valuable for the classification of ionically conducting glasses involves the extent of the decoupling between structural and conductivity relaxation modes in the glass transition range (2).

The scope of this paper is the identification of the compositional dependence of strength/fragility and decoupling in selected glass families and the advancement of a chemical reasoning for their understanding. The study focusses on binary and ternary alkali borates because these systems have broad glass forming ranges and significant chemical richness (3).

ON THE GLASS STRUCTURE

Figure 1, adapted from Liu and Angell (4), shows the spectral response of a typical sodium borate glass from d.c. up to the beginning of the infrared, and for temperatures up to Tg. In a logarithmic frequency scale, each spectrum is dominated by a dc plateau and a dielectric dispersion region, both due to relatively long range ionic motions. Over these frequency ranges, the effect of the chemical microstructure on the dispersion of the glass is averaged out, at least to some extent. It is of no surprise then that time-temperature superpositions work out well (5) and lead to the establishment of 'universalities' (6). As the frequency increases, the spectral response is due to

increasingly localized motions. As a result, the particular chemical characteristics of a glass become incresingly more important. For instance, in the higher frequency end of the spectra in Fig. 1a, the far-infrared response involves the localised vibrations of the alkali cations in their equilibrium sites (7 , 8), and constitutes the limit of d.c. conductivity at infinitely high temperatures (4). At higher frequencies (not included in Fig. 1), the mid-infrared spectrum is governed by the composition-specific local vibrations of the glass network units (8).
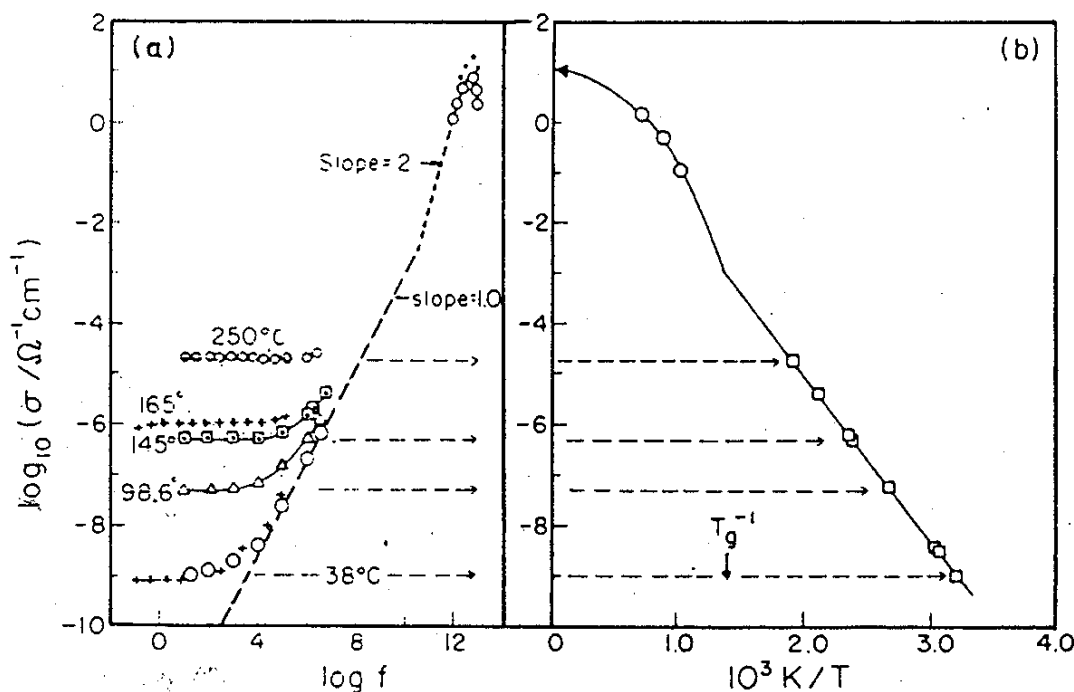

Figure 1. (a) *Conductivity spectra of 0.35Na$_2$O 0.65B$_2$O$_3$ glass and (b) Temperature dependence of d.c. conductivity (from ref. 4).*

The temperature range of interest here is from above the liquidus to below the glass transition and includes the passage through the crystallization zone. This temperature range is often marked by the pronounced non-Arrhenian dependence of the structural (1) and conductivity (9) relaxation times (see also Fig. 1b). A complete spectroscopic investigation of the type of Fig. 1a, emphasizing the temperature dependence of the far- and mid-infrared response of typical glass forming systems, would be critical in evaluating whether the extent of non-linearity is related to identifiable structural changes occuring at Tg. To perform such investigations by varying systematically the composition is a Herculean task. Nevertheless, for widely studied glasses such as the alkali borates, some information on the temperature and composition dependence of the structure is available.

It is now known that the structure of B$_2$O$_3$ changes upon increasing temperature: the six-membered boroxol rings which are abundant in the glassy solid are progressively destroyed above Tg (10). In this particular case the structural changes involve mostly the extent to which the borate polyhedra (triangles) combine below Tg to form ring structures with well-defined intermediate range order. Binary glasses containing moderate fractions of alkali oxide modifiers M$_2$O are known to contain a fraction of borate tetrahedra, N$_4$, which depends on the M$_2$O mole

fraction x and exhibits a maximun at *ca.* $x=0.3$ (3). Interestingly, for lithium and sodium compositions in the $0<x<0.25$ range, N_4 is found temperature dependent and decreasing above Tg. The charged borate unit favoured at high temperatures is the metaborate triangle with two bridging and one non-bridging oxygen atoms (11). A similar conclusion was reached by the detailed vibrational and devitrification study of lithium metaborate glass, 0.50 Li_2O 0.50 B_2O_3 (12). The structural scenario which resulted from the latter studies is depicted schematically in Figure 2. In terms of local structure it involves the abrupt transformation of metaborate triangles to isomeric tetrahedra upon cooling through the glass transition range. Moreover, it implies that glass formation is associated with the formation of rigid pseudophases preserving the structural sequence of tetrahedra-containing $LiBO_2$ polymorphs.
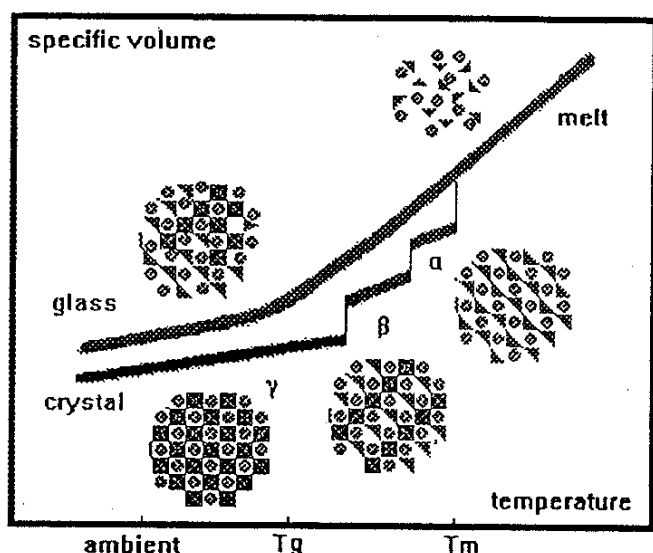

Figure 2. *A typical specific volume vs. temperature plot for the crystallization and vitrification of a metaborate melt, based on data for the lithium system. The structural changes associated with either process are shown schematically. Squares and triangles represent BO_4 and BO_3 units, circles depict lithium cations. The melt to crystal transition involves two polymorphic transformations. Upon fast quenching these occur partially and only with considerable undercooling. Their onset corresponds to the glass transition.*

Structural changes in both local and intermediate ranges of the type described above can have an impact on the viscoelastic and enthalpic aspects of glass transition. In the case of ionic conducting glasses such as the alkali borates, it is expected that the same chemical changes can have an effect on the magnitude and temperature dependence of ionic mobility. These latter aspects will be discussed in the following sections.

LITHIUM BORATE GLASSES

Understanding the strength/fragility trends in melts of variable composition requires the knowledge of the reactions available for the chemical relaxation of the melts upon quenching (13). In the particular case of lithium borates, x Li_2O $(1-x)B_2O_3$, with x increasing from 0 towards the metaborate stoichiometry ($x=0.50$), the increasing capability of the melt to undergo upon cooling chemical transformations of local- (e.g. isomerizations, disroportionations), intermediate- (e.g. ring formation), and long-range (e.g. polymorphic transformations, and formation of pseudophases), would imply that fragility increases with x (14). The trend has been verified recently on the basis of new Differential Scanning Calorimetry measurements (14) and viscosity data (15).

In search for the manifestation of the fragility trend in the cationic transport of lithium borates, melt and glass conductivity data are compiled from the literature (16) and plotted in Figure 3 versus inverse temperature normalized by Tg (17), as suggested by Angell (2, 9). For $(Tg/T)<1$, the data have been fitted to the Vogel-Fulcher-Tamman equation, $\sigma=\sigma_0\exp[-DT/(T-T_0)]$ where T_0 and D are constants. The composition dependence D^{-1} which is a fragility indicator, is shown in Figure 4b. The observed monotonic increase of fragility indicated by the conductivity data is in accordance with the trends deduced from viscosity and thermochemical data (14), which are shown in Figures 4c and 4d respectively.
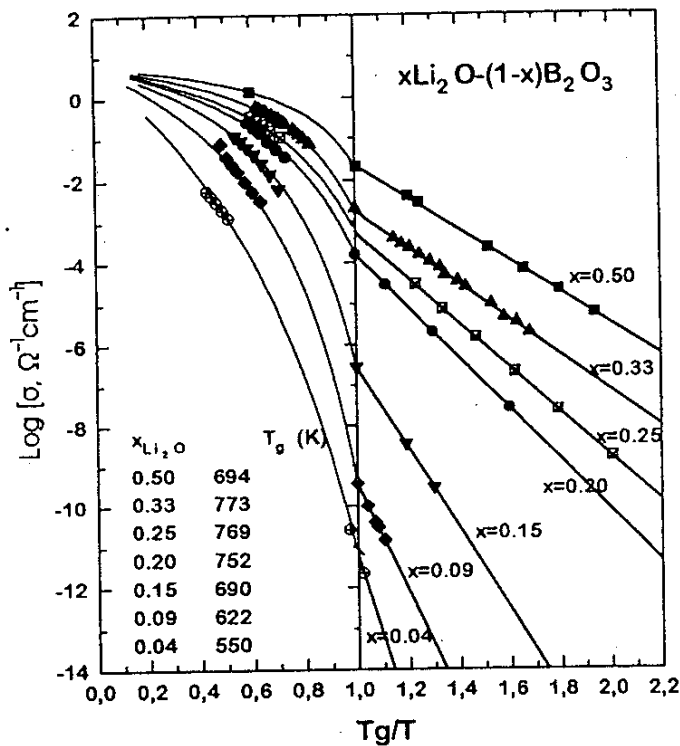
Figure 3. *Conductivity of lithium borate glasses and melts containing 4-50 mol% Li₂O, temperature-normalized at Tg. Conductivity data and Tg values are from refs.16 and 17, respectively. The points at Tg/T=1 are extrapolated from low temperature data. High temperature VTF, and sub-Tg Arrhenious fits are shown. For details see text.*
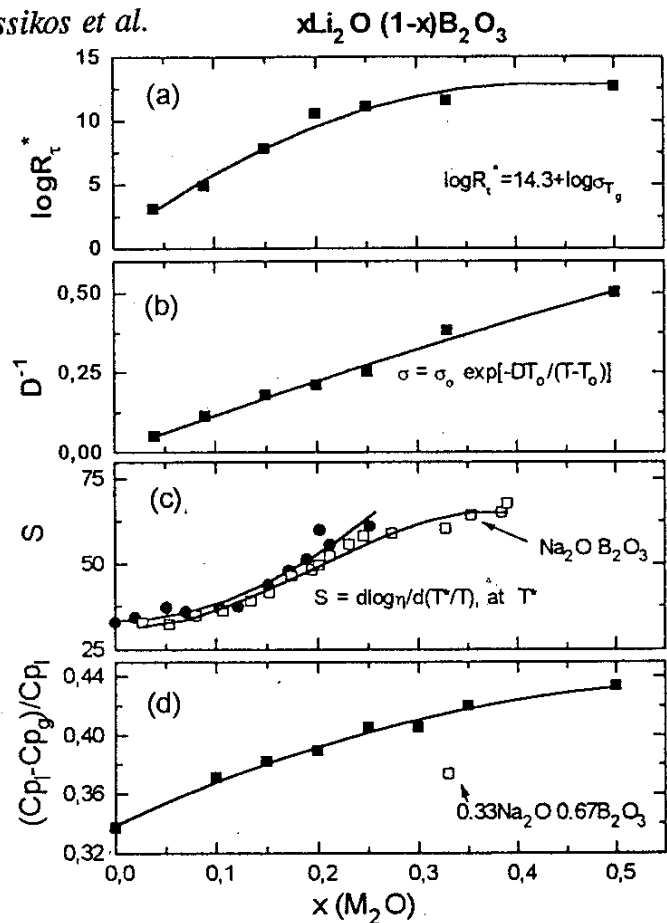
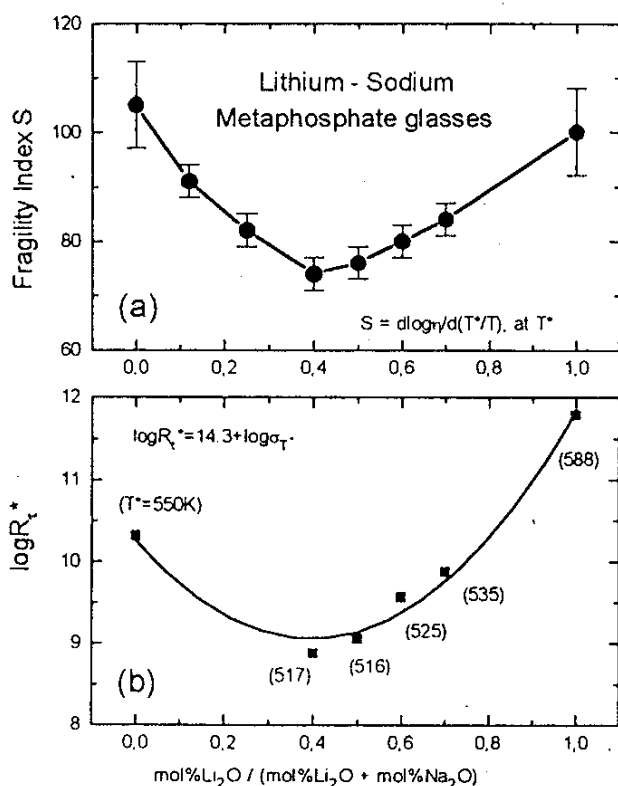**Figure 4.** *Composition dependence of (a) the decoupling index at Tg, (b) the fragility index D⁻¹ obtained by the VTF fitting of the high temperature conductivity data, (c) the viscoelastic fragility index S, taken from ref. 14, and (d), the normalized change of Cₚ at Tg, also from ref. 14. Filled symbols are for lithium borate glasses, open squares for their sodium analogs. Lines are guiding the eye.*

In addition to the fragility trend, the conductivity data of Figure 3 allow for the estimate of the decoupling index at Tg, $logR_\tau{}^*=14.3+log\sigma_{Tg}$. (2). Increasing x from x=0.04 to 0.50 results in the monotonic increase of the decoupling index by some ten orders of magnitude (Figure 4a). In broad structural terms, this increase of the decoupling index would imply that the average B-O network interactions strengthen with increasing x in comparison to those between lithium and oxygen (c.f. Angell's presentation in these proceedings). One way to confirm this trend involves optical basicity and far-infrared spectroscopic measurements which yield the dependence of oxygen and cationic charges in alkali borate glasses as a function of composition (18).

MIXED ALKALI GLASSES

It is not the purpose of this publication to address fully the phenomenological aspects and suggested explanations of the mixed-alkali effect (19). However, it is now recognized that the non-additive variations of several glass properties upon alkali mixing has a structural counterpart. The synergy of the two alkalis produces network arrangements alient to the single alkali end-member compositions. In mixed alkali borates the structural mixed alkali effect is pronounced and manifested by a minimum in the fraction of four-coordinated boron atoms, N₄ (20 , 21 , see also Kamitsos et. al., these proceedings). Following the reasoning developed above for single alkali borates, decreasing N₄ while keeping the modifier content fixed, would imply that the extent of the

chemical alterations associated with quenching and the glass transition is reduced. Additional evidence for the composition depoendence of what can be called the 'structural smoothness' of the glass transition comes from the devitrification experiments on mixed lithium-sodium metaborate glasses (21). These experiments have been interpreted to indicate that alkali mixing not only reduces N_4, but also results in a less pronounced pathway morphology. All the above suggest that an important manifestation of the mixed alkali effect is the reduced fragility of the intermediate compositions.

Figure 5.

(a) *Dependence of the viscoelastic fragility index S on the alkali mixing ratio of lithium-sodium metaphosphate glasses, based on the viscosity data in ref. 22.*

(b) *Composition dependence of the decoupling index at T* in the same glass family. The index is calculated by extrapolating glass conductivity data from ref. 23 to T*. Values of T*, the temperature at which $\eta = 10^{13}$ Poise, are taken from ref. 22 and shown in parentheses. Lines are guiding the eye.*

To check the generality of this suggestion we present in Figure 5a the dependence of the fragility index S on the alkali mixing ratio in lithium sodium metaphosphate glasses, for which appropriate viscosity and conductivity data are available. The index is calculated on the basis of shear viscosity data (22) as in Figure 4c. A minimum in fragility is clearly observed at roughly maximum mixing. Fortunately, glass ionic conductivity data for the same system are available (23) in the literature and allow the calculation of the decoupling index at T* (Figure 5b). The variation of $\log R_\tau$* with alkali mixing is also shown to be a non-linear function of alkali mixing, exhibiting a minimum at roughly maximum mixing.

CONCLUSIONS

The structural investigation of glass forming oxides as a function of temperature and composition can be correlated with the observed trends in their thermochemical, viscoelastic and ionic transport properties. The understanding of the structural origin of compositional trends in the strenght/fragility or decoupling indexes is of great theoretical and practical value.

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