

Modifier cation field strength effects on Al and B coordination in aluminoborosilicate glasses: The role of fictive temperature

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Field strength (valence/square of cation-oxygen distance) of network modifier cations has long been known to have important effects on oxide glass and melt properties, but effects on network structure can be complex. This interplay of network cation coordination changes is relevant not only to glasses used in advanced technologies, but may bear on processes in aluminosilicate melts at high pressures. In one example of recent work on two series of Ba, Ca, La and Y aluminoborosilicates with B/Si ratios of 2 and 4, we report systematic variations in boron and aluminum coordination determined by high-field MAS NMR, and glass transitions and heat capacities from differential scanning calorimetry. Data on glasses with different fictive temperatures allow B and Al speciation to be compared on an isothermal basis, rather than as conventionally done for as-quenched structures. Temperature and compositional effects can thus be isolated. These data and comparison to previous studies on glasses with lower B/Si ratios (0.2 to 0.8) clearly shows that higher modifier cation field strength increases the fraction of five- and six-coordinated Al in all compositions, as has been seen in a number of previous studies of ambient pressure and high pressure aluminosilicates. In contrast, the previously documented trend towards more three-coordinated boron (and thus more non-bridging oxygens, NBO) in low B/Si glasses with higher field strength cations reverses in high B/Si and in high NBO compositions. Remarkably, a similar effect is seen in recent work on binary borate glasses when comparing Na, Ba and Ca. Al and B coordination numbers both decrease with higher fictive temperature in the aluminoborosilicate glasses studied here, suggesting a simple mechanism of coupled structural change.