SUPPORTING INFORMATION

Quantitative design of glassy materials using temperature-dependent constraint theory

Morten M. Smedskjaer, John C. Mauro, Sabyasachi Sen, and Yuanzheng Yue

Calculation of the fractions of network-forming species

Based on the random pair model of Gupta, the fraction of each network-forming species can be calculated as follows:

\[
N(B^4) = \begin{cases} 
  \frac{2(x + y)}{5 - 4(x + y)}, & x + y \leq \frac{1}{3} \\
  \frac{6 - 8(x + y)}{25 - 2x - 11y - \frac{6x + 3y}{x + y}}, & \frac{1}{3} < x + y \leq \frac{1}{2} 
\end{cases} \tag{S1}
\]

\[
N(B^3) = \begin{cases} 
  \frac{2 - 4(x + y)}{5 - 4(x + y)}, & x + y \leq \frac{1}{3} \\
  \frac{4 - 2(x + y)}{25 - 2x - 11y - \frac{6x + 3y}{x + y}}, & \frac{1}{3} < x + y \leq \frac{1}{2} 
\end{cases} \tag{S2}
\]

\[
N(O) = \begin{cases} 
  \frac{3 - 2(x + y)}{5 - 4(x + y)}, & x + y \leq \frac{1}{3} \\
  \frac{15 - 10(x + y)}{25 - 2x - 11y - \frac{6x + 3y}{x + y}}, & \frac{1}{3} < x + y \leq \frac{1}{2} 
\end{cases} \tag{S3}
\]

\[
N(M^{NB}) = \begin{cases} 
  0, & x + y \leq \frac{1}{3} \\
  \frac{18x + 9y - \frac{6x + 3y}{x + y}}{25 - 2x - 11y - \frac{6x + 3y}{x + y}}, & \frac{1}{3} < x + y \leq \frac{1}{2} 
\end{cases} \tag{S4}
\]
Calculation of $\beta$ constraint onset temperature

In our topological model, we have assumed that the $\beta$ constraint onset temperature is dependent on the ratio of [Na$_2$O] to [CaO] (see Eq. (7)). This is supported by a thorough investigation of various binary alkali borate and alkaline earth borate glasses by Lower et al.$^3$ They show that each type of alkali and alkaline earth cation leads to different values of $T_\beta$, depending on the particular size and valence state of the cation used for charge compensation. In general, alkaline earths always lead to a higher $T_\beta$ compared to alkalis, and $T_\beta$ decreases with increasing cation size. Therefore, Equation (7) indicates that the O-B-O angular constraints are strengthened in the presence of Ca as a charge compensator compared to Na alone.

Glass transition temperature prediction for Donohoe and Shelby’s data$^4$

In Fig. S1 we compare our model results (assuming two rigid $\mu$ constraints per NBO-forming Na) with measured $T_g(x,y)$ values for Na$_2$O-CaO-B$_2$O$_3$ glasses with [CaO]/[Na$_2$O] ratios of 0, 0.25, 1, 4, and $\infty$.$^4$ The agreement between predicted and experimental values is excellent for these glasses, confirming the validity of our topological modeling approach incorporating temperature dependent constraints.
Figure S1. Composition dependence of glass transition temperature for $xNa_2O\cdot yCaO\cdot (1-x-y)B_2O_3$ systems of Donohoe and Shelby\textsuperscript{4} with different $y/x$ values. While some of the glasses studied by Donohoe and Shelby were phase separated, here we consider the non-phase separated glasses only. The lines show the computed $T_g(x,y)$ values using Eq. (10) assuming two rigid $\mu$ constraints per NBO-forming sodium. The experimental data points were determined by using DSC at a heating rate of 20 K/min.\textsuperscript{4}

The compositions of Donohoe and Shelby\textsuperscript{4} are designed in a way that gives a constant $T_\beta(x,y)$ value, and hence, an iso-$T_g$ regime is observed (Fig. S2). From Eq. (2) we know that the product $f[T_g(x,y),x,y]\cdot T_g(x,y)$ must be a constant for all $x$ and $y$. If $T_g(x,y)$ were to increase above $T_\beta(x,y)$, the network would suddenly become more floppy due to an increase in the atomic degrees of freedom. However, to achieve a constant $f[T_g(x,y),x,y]\cdot T_g(x,y)$, $T_g(x,y)$ must decrease in order to compensate for the increased floppiness. On the other hand, if $T_g(x,y)$ were to decrease below $T_\beta(x,y)$, the network would suddenly become more rigid due to a decrease in the atomic degrees of freedom, i.e., $T_g(x,y)$ must increase in order to compensate for the increased rigidity. Consequently, $T_g(x,y)$ is equal to $T_\beta(x,y)$ until enough NBOs have formed to allow $T_g(x,y)$ to decrease below $T_\beta(x,y)$. Thus, our model is able to account for this iso-$T_g$ regime and provide physical insight into the topological origin of this phenomenon that has not been clarified in literature.
Figure S2. Dependence of the constraint onset temperatures and $T_g(x,y)$ on composition for the $xNa_2O\cdot yCaO\cdot (1-x-y)B_2O_3$ glass system with $y/x = 4$.

Preference for sodium or calcium to cause the boron coordination change?

In the model described in the main text, we did not include a preference for sodium or calcium to cause the boron coordination change. To test the validity of this assumption, we build in such preferences in the model and then calculate $T_g(x,y)$ using Eq. (10). The results are shown in Fig. S3. The red curve labeled “with Na preference” shows the computed $T_g(x,y)$ when there is preference for sodium to convert BO$_3$ to BO$_4$, i.e., in this case calcium has preference for NBO formation. The opposite applies for the blue curve labeled “with Ca preference”. The curves only differ in the regime where NBO formation occurs ($x + y > 1/3$) since all sodium and calcium ions serve as charge-compensators for BO$_4$ units for $x + y \leq 1/3$. In the NBO regime, a preference for sodium or calcium to convert BO$_3$ to BO$_4$ results in a lower or higher glass transition temperature, respectively. This is because NBO-forming sodium sets up a rigid environment ($\mu$ constraint), whereas NBO-forming calcium does not. Hence, when there is preference for sodium to convert BO$_3$ to BO$_4$, calcium will be preferred for NBO formation and since it does not set up a rigid environment, $T_g(x,y)$ will be
lower. The opposite argument applied for the other case. Our results in Fig. S3 clearly demonstrate that there is no significant preference for either sodium or calcium to cause the boron coordination change.

**Figure S3.** Modeling of the composition dependence of the glass transition temperature of the studied soda lime borate glasses. The lines show the computed $T_g(x,y)$ values using Eq. (10) with three different assumptions concerning the preference for sodium or calcium to convert boron from three- to four-coordination: (i) no preference (black curve), (ii) preference for Na (red curve), and (iii) preference for Ca (blue curve).

**References**


