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A Structural Connection to the Configurational Heat Capacity of Borate-Silicate Glass Forming Liquids

Hao Liu, a,b Morten M. Smedskjaer a, Haizheng Tao b, Lars R. Jensen c, Xiujian Zhao b, and Yuanzheng Yue a,b

a Department of Chemistry and Bioscience, Aalborg University, DK-9220 Aalborg, Denmark.
b State Key Laboratory of Silicate Materials for Architectures, Wuhan University of Technology, Wuhan 430070, PR China
c Department of Mechanical and Manufacturing Engineering, Aalborg University, DK-9220 Aalborg, Denmark

E-mail of the presenter: hal@bio.aau.dk

When a glass-forming liquid is supercooled to the glass transition temperature ($T_g$), the structural degree of freedom decreases, causing a loss of the configurational heat capacity ($C_{p,\text{conf}}$). In borate-silicate mixed glasses, the $C_{p,\text{conf}}$ exhibits a non-linear increase with substitution of $\text{B}_2\text{O}_3$ for $\text{SiO}_2$. However, its structural origin has not been well understood. In this work, through Raman spectroscopy measurements, we have found an implication for the intermediate range order (IRO) structural connection to the composition dependence of $C_{p,\text{conf}}$ in a series of $(75q)\text{B}_2\text{O}_3-(75(1-q))\text{SiO}_2-15\text{Na}_2\text{O}-10\text{CaO}$ glasses. In the silica-rich composition, the increase of the content of B-O-Si network units ($[\text{B}_2\text{Si}_2\text{O}_8]^2^-$) and 6-membered borate rings causes the rapid increase of the $C_{p,\text{conf}}$ with the addition of $\text{B}_2\text{O}_3$. In the boron-rich composition, the $C_{p,\text{conf}}$ is almost constant, which is likely attributed to the counteraction between the decrease of the fraction of metaborate groups and the increase of the fraction of other borate superstructural units. As shown in Fig. 1, compared to short range order (SRO), the overall results suggest that the IRO structural change has a dominant contribution to the evolution of $C_{p,\text{conf}}$ with composition. Furthermore, IRO is also found to govern the composition dependence of dynamic fragility, as illustrated in Fig. 2, implying that $C_{p,\text{conf}}$ can be seen as the thermodynamic fragility in the studied system.