Viscous Flow and Diffusion in Iron-Bearing Alkaline-Earth Silicate Glasses

Smedskjær, Morten Mattrup; Yue, Yuanzheng; Deubener, Joachim; Gunnlaugsson, Haraldur Páll

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Many technological applications of glasses depend upon the properties of the surface. We have previously shown that reduction of iron or vanadium in silicate glasses by heat-treatment in H\textsubscript{2}/N\textsubscript{2} (1/99 v/v) near the glass transition temperature ($T_g$) requires an inward diffusion (from surface towards interior) of mobile cations, thereby creating a silica-rich surface layer. In this study, our aim is to determine the influence of the nature of the alkaline-earth ion on the above-mentioned diffusion process in SiO\textsubscript{2}-Na\textsubscript{2}O-Fe\textsubscript{2}O\textsubscript{3}-RO (R=Mg,Ca,Sr,Ba) glasses. We also investigate the link between the ionic diffusion and the fragility of the glass melt. The fragility of the glasses increases with increasing ionic radius of the alkaline-earth ion, whereas the $T_g$ decreases. By heat-treating the glasses at their respective $T_g$, it is found that the Mg\textsuperscript{2+} ions are the fastest due to their small size, whereas the Ba\textsuperscript{2+} ions are the slowest. The activation energy of diffusion around $T_g$ ($E_d$) of the alkaline-earth ions increases with increasing ionic radius, and hence, decreasing field strength. Consequently, $E_d$ is found to be proportional to the fragility of the glass melt, i.e., a link between the activation energy of viscous flow at $T_g$ ($E_\eta$) and $E_d$ has been established. Hence, the results suggest that fragility (related to the flow of the glass network) can be used to predict the order of diffusion of fast ions in glasses.

Keywords: inward diffusion, fragility, reduction, surface