# Experimental and Computational Study of Glasses with Temperature- and Pressure-Independent Elastic Moduli

by

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# ABSTRACT

The most pronounced elastic anomalies that appear in silica-rich glasses are the positive temperature derivative and negative pressure derivative of elastic moduli, as compared with normal glasses, such as window glass (soda-lime-silica) containing more network modifiers. It would be natural to imagine that there are intermediate glasses with elastic moduli that are independent of temperature and/or pressure. Such glasses will be ideal materials of choice for any device that may experience thermal and mechanical shocks during service, especially in systems made of different materials where strain mismatch can develop across the interfaces after such huge thermo-mechanical impacts. The focus of this research is to search for such intermediate glasses through chemical modifications. Specifically, we utilized both experimental and computational techniques to study $Na_2O$-$SiO_2$ glasses containing a wide range of $Na_2O$ concentration (0-40 mol%) under ambient and high temperature and pressure conditions.

In experiments, in order to investigate the elastic moduli from room temperature to the glass transition temperature for each composition, we employed both nanoindentation and *in-situ* high temperature Brillouin light scattering techniques. Temperature independent shear modulus and Young's modulus were observed in $15Na_2O$-$85SiO_2$ glass up to 400°C, while the temperature independent bulk modulus occurred in glass with 15 to 20 mol% $Na_2O$ in the same temperature range. Raman spectroscopy was used to reveal the possible underlying mechanisms for the evolution of elastic moduli with the change of glass composition and temperature.

In molecular dynamics (MD) simulations, we used a newly parameterized charge-transfer three-body potential to study the structure and properties of sodium silicate glasses under ambient and high temperature and pressure conditions. In MD simulations, $10Na_2O$-$90SiO_2$ and $20Na_2O$-$20SiO_2$ were shown to be intermediate in terms of the temperature and pressure dependence of bulk modulus, respectively. Below or above these compositions, glasses are abnormal and normal respectively. Detailed structural analysis revealed that, in all three types of glasses, the rigidity of $SiO_4$ tetrahedra was well retained in the temperature and pressure ranges we studied, indicated by the small changes in the intra-tetrahedral bond lengths and bond angles as a function temperature

and pressure. At the same time, the degree of the network connectivity in terms of $Q_n$ and ring statistics, once formed based on the compositions, does not change in the temperature and pressure ranges we studied. Therefore, the initial structure at ambient conditions sets the tone for its evolution with temperature and pressure, which in turn determine the response of the elastic and dynamic properties of glass to thermal and mechanical agitations.

By combining the experimental and computational observations in our study, we found a strong correlation between the dynamic properties of glass at ambient conditions and the evolution of its elastic properties with increasing temperature and pressure. If the underlying network structure is well connected in the 3-dimensional space, characterized by the main band in Raman spectra or by modes populated around 400 $cm^{-1}$ in vibrational density of states (VDOS) for glasses containing less than 10 mol% $Na_2O$ at ambient conditions, local conformational changes between $\alpha$- and $\beta$-like rings due to thermal or mechanical agitations bring a larger but opposite change in elastic properties than the anharmonic effect, glasses behave abnormally. In sodium silicates glasses with high $Na_2O$ concentration (>20 mol%), these characteristic bands in Raman or VDOS at ambient conditions gradually diminish due to the loss of the network connectivity. Local conformational changes between $\alpha$- and $\beta$-like are less likely to take place; the anharmonic effect becomes dominant and glasses behave like normal solids. In between these two effects become comparable, intermediate glasses emerge, whose elastic moduli don't change with temperature and pressure.