The structure of alkali silicate glasses: a density and Raman spectroscopy study

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Over the past few decades there has been a large interest in alkali silicate glasses, most specifically sodium silicate glasses, because of their importance in both industrial and natural glass-forming processes [1, 2]. This study investigated a series of compositions using Raman spectroscopy across the alkali-silica join in the glassy state. The samples range in composition $x*M_2O - (1-x)*SiO_2$ (M=Li, Na, K, Rb, Cs and x=0, 5, ..., 25, 30) in order to compare the structural differences across the respective joins.

Density measurements were also made in order to directly link changes in the atomic structure (determined by the vibrational spectra) to a macroscopic observable. The molar volume (calculated from the density measurements) is compared to the relative intensities of the D1 and D2 peaks commonly associated to the breathing motion of oxygen in 4-fold and 3-fold membered SiO_4 rings respectively. The intensity of the peak associated to 3-fold rings increases with respect to that of the 4-fold rings with M_2O content [3].

The high frequency envelope (800-1300 cm^{-1}) which is related to the Q^n species was analyzed using a curve fitting technique [3]. We discuss the variation in the Q^n species due to both the alkali content and type of alkali. We interpret our data incorporating recent nuclear magnetic resonance and X-ray photoelectron spectroscopy data [4,5] which have identified different types of bridging oxygen in sodium silicate glasses. In doing so we also will discuss the importance of the local environment of bridging oxygen within the network structure.

[1] Greaves *et al.* (1981) *Nature*, **293**, 611-616. [2] Matson *et al.* (1983) *Journal of Non-Crystalline Solids*, **58**, 323-352. [3] O'Shaughnessy *et al.* (2017) *Chemical Geology,* In press. [4] Nesbitt et al. (2011) *Journal of Non-Crystalline Solids*, **357**, 170-180. [5] Nesbitt *et al.* (2015) *Journal of Non-Crystalline Solids*, **409**, 139-148.