



NMR and XANES at Si and Al K-edges on glasses in the CAS system.

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Investigation of calcium aluminosilicate glasses is important for both earth science and technological applications, due to their highly refractory nature, and their excellent optical and mechanical properties. We have previously observed anomalous behavior of thermodynamic properties in the CaO-Al₂O₃-SiO₂ system (CAS) (Cormier et al., 2000; Neuville et al., 2004a). Consequently, a good understanding of the relationship between structure and properties is highly desirable.

We have synthesized more than 60 different glasses in the CAS system using traditional methods, and 15 glasses using laser heating (fast quench rate). The glasses were studied using ²⁷Al MAS-NMR (17.6 T – 750 MHz) on a Bruker AVANCE instrument equipped with high speed MAS probeheads, X-ray absorption spectroscopy at the Al *K*-edge (SA32 beamline, LURE-France) and at the Si *K*-edge (DCM beamline, CSRF, Madison, USA).

For tectosilicate glasses, aluminium in five-fold coordination (^[5]Al) was found and careful quantification indicates the presence of a significant amount of ^[5]Al (7 % in the anorthite glass) (Neuville et al, 2004b). The proportion of ^[5]Al increases for the

peraluminous glasses with small amounts (<2 %) of six-fold coordination ($[^6]\text{Al}$). The presence of $[^5]\text{Al}$ agrees with previous observations of the existence of non-bridging oxygens (NBO) in tectosilicate compositions. However, the proportion of $[^5]\text{Al}$ in the present study indicates that no major population of triclusters (oxygen coordinated to three $(\text{Si},\text{Al})\text{O}_4$ tetrahedra) is required to explain these NBOs.

XANES spectra at both the Si and Al K -edges are strongly dependent upon the Si/Al substitution along a join at constant $\text{CaO}/\text{Al}_2\text{O}_3$ ratio. The structural differences are mainly due to variation at medium range distances, such as different polymerization units, and different intertetrahedral bond angles and distances.

The changes upon composition both at the local and medium range scale are discussed with relevance to the interpretation of the thermodynamical behaviour of these glasses.

References :

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