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Structural behavior of Al^{3+} in peralkaline, metaluminous, and peraluminous silicate melts and glasses at ambient pressure

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Abstract

Peralkaline and peraluminous glasses close to the metaluminous join in the systems Na_2O-Al_2O_3-SiO_2 (NAS), CaO-Al_2O_3-SiO_2 (CAS), and MgO-Al_2O_3-SiO_2 (MAS) have been examined with Raman spectroscopy. At least three different SiO_2 contents in each of the systems (NAS, CAS, and MAS) have been studied. Each series of glasses spans the metaluminous join at constant silica content. The spectra of glasses in all three systems show changes consistent with a continuous decrease in abundance of depolymerized species and an increase in fully polymerized species as compositions change from peralkaline to peraluminous. There is no evidence for maxima or minima of these abundances across the metaluminous joins for any of the studied series. These observations confirm previous suggestions that non-bridging O atoms are a general feature of "fully polymerized" glasses, and that a population of Al exists in the melt structure that is not associated with a charge-balancing cation, even in peralkaline compositions.

With decreasing peralkalinity, new components appear in the Raman spectra of peraluminous NAS and CAS glasses, but such changes are much less obvious in the MAS system. These additional components are most likely related to the presence of "excess" Al (i.e., Al not associated with a charge-balancing cation). The structural role of this "excess" Al could be in the form of (Al, Si)-triclusters with different Al/Si-ratios depending on composition, but simple distorted AlO_4-tetrahedra and possibly higher-coordinate Al^{3+} cannot be ruled out from the Raman spectra alone. The implications of these results for isothermal variations in viscosity are considered. It is concluded that the diversity and complexity of viscosity variations observed in different aluminosilicate systems may be a consequence of the fact that the difference in bond strength between bridging and non-bridging O atoms in the Ca and Mg-bearing systems is small compared to that in the Na-bearing system.

Keywords: Melt structure, aluminosilicate, spectroscopy, Raman