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The structural behavior of Al^{3+} in peralkaline melts and glasses in the system Na_2O-Al_2O_3-SiO_2

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ABSTRACT

The structural behavior of Al^{3+} in peralkaline glasses and melts along the $Na_2Si_3O_7$-$Na_2(NaAl)_3O_7$ join has been examined to 1200 °C at ambient pressure with ^{29}Si MAS NMR and Raman spectroscopy. The distribution of Al^{3+} among coexisting Q^4, Q^3, and Q^2 structural units in the glasses and melts was determined as a function of bulk Al/(Al + Si) and temperature. The Al^{3+} resides principally in Q^4 structural units, which contain more than 70% of the total amount of Al^{3+}. The Q^2 units contain the smallest amount of Al^{3+} among the Q^4, Q^3, and Q^2 structural units. There is no evidence for temperature-dependent distribution of Al^{3+} among the coexisting structural units at least to 1100–1200 °C.

The equilibrium constant for the speciation reaction, $2Q^3 \leftrightarrow Q^4 + Q^2$, passes through a maximum with increasing bulk melt Al/(Al + Si) at constant temperature. Its temperature-dependence also depends on bulk melt Al/(Al + Si) so that the enthalpy of the speciation reaction, ΔH, passes through a maximum with increasing bulk Al/(Al + Si). This ΔH ranges between 13 and 23 kJ/mol for bulk melt Al/(Al + Si) between 0 and 0.33. These composition-dependent maxima in the equilibrium constant (at constant temperature) and ΔH of the speciation reaction reflect the changes in Al/(Al + Si) of Q^2, Q^3, and Q^4 structural units with Al/(Al + Si) of the melt.