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The degree of aluminum avoidance in aluminosilicate glasses

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ABSTRACT

For two series of aluminosilicate glasses on the SiO_2-$NaAlO_2$ and SiO_2-$CaAl_2O_4$ joins, ^{29}Si magic-angle-spinning (MAS) NMR spectra were measured. Systematic variations in peak positions and widths with composition are closely related to the extent of ordering of Si and Al cations. A statistical thermodynamic model based on the quasi-chemical approximation was formulated to calculate the proportions of SiO_4 groups with varying numbers of Al neighbors and thus to quantify the extent of ordering. Multiple spectra in each compositional series were fitted simultaneously with several peaks representing each of these structural species and with area constraints generated by the model. The extent of aluminum avoidance (Q), which was defined using the relative lattice energy differences among the linkages Si-O-Si, Si-O-Al, and Al-O-Al, was optimized for each series. For the calcium aluminosilicates, the best fit is with $0.8 \leq Q \leq 0.875$, where $Q = 1$ represents perfect Al-avoidance. For the sodium series, Q was found to be larger ($0.93 \leq Q \leq 0.99$), as expected from energetic considerations and from known variations in ordering in minerals. The contributions to the overall configurational entropy and heat capacity from Si-Al disorder can be calculated, and are significant fractions of experimentally estimated values. However, major contributions must also come from other sources of disorder, such as "topological" disorder of bond angles and length.