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^{29}Si and ^{27}Al MAS-NMR spectroscopy of β-eucryptite ($LiAlSiO_4$): The enthalpy of Si,Al ordering

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ABSTRACT

By combining data from oxide melt solution calorimetry and ^{29}Si MAS-NMR spectroscopy, the enthalpy for short-range Si,Al ordering in β-eucryptite ($LiAlSiO_4$) was determined for a series of samples prepared by glass annealing. Si,Al ordered β-eucryptite gives a single ^{29}Si NMR peak for two unresolved crystallographic sites, but two distinct ^{27}Al resonances that differ in both chemical shift and quadrupolar coupling. Samples of β-eucryptite crystallized from glass contain additional ^{29}Si NMR peaks, indicating significant levels of short-range Si,Al disorder. This disorder decreases exponentially with annealing time at 1173 K, from 0.55(±0.04) Al-O-Al linkages per formula unit after one hour to 0.05(±0.01) after 70.5 hours. The decrease in the concentration of Al-O-Al linkages with annealing time correlates linearly with enthalpies of drop-solution in molten lead borate, giving an enthalpy of $\Delta H_{ord} = -26 \pm 3$ kJ/mol for the reaction: Al-O-Al + Si-O-Si → 2(Si-O-Al).

Additional NMR results are presented for samples synthesized along the SiO_2-$LiAlSiO_4$ join (quartz to β-eucryptite). Solid solution samples with compositions 20 and 69 mol% quartz appear to have very few Al-O-Al linkages (<0.04 per formula unit).