29Si and 27Al MAS-NMR spectroscopy of β-eucryptite (LiAlSiO₄):
The enthalpy of Si,Al ordering

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ABSTRACT

By combining data from oxide melt solution calorimetry and 29Si MAS-NMR spectroscopy, the enthalpy for short-range Si,Al ordering in β-eucryptite (LiAlSiO₄) was determined for a series of samples prepared by glass annealing. Si,Al ordered β-eucryptite gives a single 29Si NMR peak for two unresolved crystallographic sites, but two distinct 27Al resonances that differ in both chemical shift and quadrupolar coupling. Samples of β-eucryptite crystallized from glass contain additional 29Si 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 \( \Delta H_{\text{ord}} = -26 \pm 3 \text{ kJ/mol} \) for the reaction: \( \text{Al-O-Al + Si-O-Si \rightarrow 2(Si-O-Al)} \).

Additional NMR results are presented for samples synthesized along the SiO₂-LiAlSiO₄ 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).

INTRODUCTION

Order-disorder of Si and Al influence the structural chemistry, energetics, and phase relationships of framework aluminosilicates. A better understanding of Si,Al order has resulted from measurements of the short-range order by NMR spectroscopy (Herrero 1991; Phillips et al. 1992; Phillips and Kirkpatrick 1994) and computational models of extended aluminosilicate structures (Dove and Heine 1996; McConnell et al. 1997). These studies indicate that many phases lacking complete long-range order of Al and Si onto distinct crystallographic positions nonetheless contain large degrees of short-range order. This short-range order is largely a reflection of the so-called Loewenstein rule, or aluminum avoidance principle (Loewenstein 1954), that describes the strong tendency of aluminosilicates to adopt configurations that minimize the concentration of Al-O-Al linkages in tetrahedral frameworks. Calorimetric data and ab initio structure calculations indicate that 2(Si-O-Al) linkages are favored energetically over (Al-O-Al + Si-O-Si) linkages (Sauer and Engelhardt 1982; Navrotsky et al. 1982; Tossell 1993; Angel 1985; Phillips et al. 1992). The net effect of short-range Si,Al ordering can be described thermochemically as an exothermic reaction of the form:

\[ \text{Al-O-Al + Si-O-Si \rightarrow 2(Si-O-Al)} \]  

for which recent theoretical (McConnell et al. 1997; Tossell 1993) and experimental (Navrotsky et al. 1985; Putnis and Angel 1985; Phillips et al. 1992) studies give enthalpy changes (\( \Delta H_{\text{ord}} \)) that range from –19 to –41 kJ/mol for various materials. These values imply that framework aluminosilicates synthesized at high temperature might contain significant concentrations of Al-O-Al linkages at equilibrium.

In contrast, the absence of complete long-range Si,Al order observed for many framework aluminosilicates results from the dominance of the energy between adjacent pairs of framework cations over longer-range interactions and the ability to minimize the number of Al-O-Al linkages without long-range order when Si/Al > 1 (Dove et al. 1996). In addition, the contribution to the free energy from configurational entropy is greatly reduced simply through the exclusion of Al-O-Al linkages (Phillips and Kirkpatrick 1994).

Framework structures having a 1:1 Si:Al ratio are particularly useful for studying Si,Al order-disorder, because any disorder requires the presence of Al-O-Al linkages. NMR spectroscopic data for anorthite (CaAl₂Si₂O₈) demonstrated the presence of Al-O-Al linkages upon initial crystallization from glass and a reduction in their concentration with subsequent annealing (Phillips et al. 1992). A comparison of the number of Al-O-Al linkages with calorimetric data provided an estimate for the enthalpy of the ordering reaction (Eq. 1) of –39±12 kJ/mol. It is unclear, however, whether the energetics of Si,Al order is adequately represented by Equation 1 or if the apparent ordering enthalpy varies with chemical composition or framework topology. Experimental data suggest that additional complications might arise from inhomogeneity in the state of order, particularly the concentration of disorder along the