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Aluminum ordering and clustering in Al-rich synthetic phlogopite: $\{^1H\} \rightarrow {}^{29}Si$ CPMAS HETCOR spectroscopy and atomistic calculations

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Abstract

The cationic ordering in the octahedral and tetrahedral sheets of Al-rich synthetic phlogopites with composition $K(Mg_{3-x}Al_x)[Al_{1+x}Si_{3-x}O_{10}](OH)_2$ ($0.0 < x < 1.0$) has been investigated using a combined approach of Monte Carlo simulations based on the "*J* formalism" (Bosenick et al. 2001; Warren et al. 2001) and ^1H, ^{29}Si MAS and $\{^1H\} \rightarrow {}^{29}Si$ CPMAS/HETCOR solid-state NMR spectroscopic experiments. Our results are compatible with the well-established Loewenstein's rule of Al-Al avoidance in the tetrahedral sheets, but the $Si/^{IV}Al$ and $Mg/^{VI}Al$ distributions show a tendency to segregation of the excess Al atoms, and we observe a preference for ^{VI}Al and ^{IV}Al to occupy directly neighbored octahedral and tetrahedral sites. As a result the structure is separated into clusters of original phlogopite composition $\{K(Mg_3)[AlSi_3O_{10}](OH)_2\}$ and clusters of "eastonite" composition $\{K(Mg_2Al)[Al_2Si_2O_{10}](OH)_2\}$ that encompass a whole T-O-T layer package, although Al is solved in the phlogopite structure homogeneously on a macroscopic level.

Keywords: HETCOR CPMAS NMR, phlogopite, Monte Carlo simulations, *J* formalism, total-energy calculations, GULP, SIESTA