Thermodynamics of mixing in pyrope-grossular, $Mg_3Al_2Si_3O_{12}$-$Ca_3Al_2Si_3O_{12}$, solid solution from lattice dynamics calculations and Monte Carlo simulations

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ABSTRACT

Static lattice energy calculations (SLEC), based on empirical pair potentials have been performed for a set of 125 different structures with compositions between pyrope and grossular, and with different states of order of the exchangeable Mg and Ca cations. Total energies of a subset of these configurations have been calculated with a density functional electronic structure method (ab initio). The excess energies derived from ab initio and SLEC results agree well with each other. Excess free energies of the 125 structures have been calculated at 300 and 1000 K and at 0 and 3 GPa and cluster expanded in a basis set of 8 pair-interaction parameters. These ordering parameters have been used to constrain Monte Carlo simulations of temperature-dependent properties in the ranges of 300–1500 K and 0–3 GPa. The free energies of mixing have been calculated using the method of thermodynamic integration. The calculations predict the development of a significant short-range and long-range ordering at the intermediate 50/50 composition. The long-range ordered phase with $I4_1 22$ symmetry becomes stable below 600 K. Two miscibility gaps driven by the stability of the intermediate phase develop at both sides of the 50/50 composition. Activity-composition relations in the range of 600–1500 K and 0–3 GPa are described with high-order Redlich-Kister polynomials.

Keywords: Pyrope-grossular solid solutions, ab initio calculations, atomistic simulations, activity-composition relations