Thermodynamics of mixing in pyrope-grossular, Mg$_3$Al$_2$Si$_3$O$_{12}$-Ca$_3$Al$_2$Si$_3$O$_{12}$, 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, 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

INTRODUCTION

Due to the importance of the activity-composition relations of garnets in petrologic calculations, the pyrope-grossular solid solution, Mg$_3$Al$_2$Si$_3$O$_{12}$-Ca$_3$Al$_2$Si$_3$O$_{12}$, has been extensively studied in recent decades. The availability of calorimetric, volumetric, spectroscopic, and phase equilibrium constraints makes this solid solution a convenient test system for various models of mixing. The calorimetric studies of Newton et al. (1977), Haselton and Westrum (1980), and Dachs and Geiger (2006) have shown that both the enthalpy of mixing and the excess vibrational entropy deviate significantly from the ideal behavior. The enthalpy of mixing reaches about 3 kJ at $x_{pyr} = 0.75$. The excess vibrational entropy is of the order of 1.5 J/(K·mol) at $x_{pyr} = 0.6$ (Haselton and Westrum 1980). Ganguly et al. (1993) and Bosenick and Geiger (1997) have shown that the mixing volumes are positive and asymmetric with a maximal value of about 0.008 J/(bar·mol) at $x_{pyr} = 0.3$. (All the excess effects are scaled here to one mole of the exchangeable Ca and Mg cations.) There have been many studies that have attempted to derive the mixing properties of garnets directly from phase equilibrium experiments and from compositions of garnets in well-characterized metamorphic rocks (e.g., Berman and Aranovich 1996; Ganguly et al. 1996; Mukhopadhyay et al. 1997). These studies have shown that the phase equilibrium data can be satisfactorily fitted together with the volumetric and calorimetric constraints within the regular solution model. It was clear, however, that these modeling results can be applied only to garnets crystallized at relatively high temperatures or to samples in which Ca-Mg interactions are significantly diluted by the presence of extra components such as Fe$^{2+}$ and Mn$^{2+}$. Only at these conditions the mixing properties can be approximated with the regular solution model. Bosenick et al. (1995, 1999) have performed $^2$Si NMR studies on garnets synthesized at high pressures and temperatures and observed that the frequencies of local Ca-Mg configurations deviate from the probabilities of random events. These studies suggested that at lower temperatures the configurational entropy might be significantly decreased from the ideal mixing values due to the development of short-range ordering. To be able to predict the thermodynamic behavior of pyrope-grossular garnets in a wide range of temperatures, several recent studies have attempted atomistic simulations of mixing properties (Dove 2001; Bosenick et al. 2000, 2001a, 2001b; Warren et al. 2001; Vinograd 2001; Vinograd et al. 2004a; Sluiter et al. 2004; Lavrentiev et al. 2006). Although these studies have shown that modern computational tools permit simulation of any observable function of mixing, none of them has been able to demonstrate quantitative agreement with all available experimental constraints. Specifically, none of the studies was able to reproduce the magnitudes of both the enthalpy of mixing and the excess vibrational entropy. No attempts have been made to explain the origin of the observed asymmetry of the functions of mixing. Here we show that a superior model can be developed along the following steps: (1) Development of a transferable set of empirical interatomic potentials. (2) Static lattice energy calculations (SLEC) and lattice dynamics (LD) calculations on a set of structures with

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