Geophysical Research Abstracts, Vol. 7, 02993, 2005
SRef-ID: 1607-7962/gra/EGU05-A-02993

Phase relations in pyrope - grossular system: Insights from ab initio and force-field calculations

M.H.F. Sluiter (1) and **V.L. Vinograd** (2)

(1) Tohoku University, Sendai, Japan (marcel@imr.edu), (2) University of Frankfurt, Frankfurt/Main, Germany, (vinogra@uni-muenster.de)

Recent approach to simulation of minerals with order-disorder effects is based on applying 1) ab initio or force-field calculation of static energies of a number of anchor configurations, 2) cluster expansion formalism aimed at constructing a simplified but accurate Hamiltonian and 3) Monte Carlo simulation coupled with the thermodynamic integration analysis. Previous studies of pyrope-grossular mixing using this or similar approaches [1,2,3] have revealed that the most important Ca-Mg ordering interaction occurs at the third near-neighbour distance. Since the third-neighbour pairs form an effectively one-dimensional net, no long-range order was expected in the garnet system. All these studies have missed an important phenomenon: there are two structurally distinct pairs of neighbours at the forth near-neighbour distance. When treated separately, the pairs “4a” and “4b” show contrasting ordering behaviour. The pairs “4b” together with pairs “3” form an unfrustrated 3D framework, which supports the development of alternation-type LRO at the 50/50 composition at temperatures below 800 K. Both ab initio and force-field calculations predict the static energy of the ordered structure to be slightly above the mixture of pyrope and grossular, however, including the effect of the excess vibrational entropy predicts this structure to be stable in a narrow temperature range. The calculated phase diagram of pyrope - grossular shows two miscibility gaps separated by the ordered phase. Below 450 K, where the ordered phase becomes unstable, the two gaps merge in a single gap.

1. Bosenick, A., Dove, M.T., Geiger, C.A. 2000. Simulation studies of pyrope – grossular solid solution. Phys. Chem. Minerals, 27, 398-418.

2. Vinograd, V.L., Sluiter, M.H.F., Winkler, B., Putnis, A., Hålenius, U., Gale, J.D., Becker, U., 2004. Thermodynamics of mixing and ordering in pyrope – grossular solid

solution. Min. Mag., 68, 101-121.

3. Sluiter, M.H.F., Vinograd V. L., Kawazoe, Y., 2004. Intermixing tendencies in garnets: Pyrope and grossular. Phys. Rev. B 70, 184120-1-4.