

Molar volumes of mixing of almandine-pyrope and almandine-spessartine garnets and the crystal chemistry and thermodynamic-mixing properties of the aluminosilicate garnets

CHARLES A. GEIGER¹ AND ANNE FEENSTRA^{2*}

¹Mineralogisch-Petrographisches Institut, Christian-Albrechts-Universität zu Kiel, Olshausenstr. 40, D-24098 Kiel, Germany

²Mineralogisch-Petrographisches Institut, Universität Bern, Baltzer-Strasse 1, CH-3012 Bern, Switzerland

ABSTRACT

The aluminosilicate garnet binaries almandine-pyrope and almandine-spessartine were studied by powder X-ray and ⁵⁷Fe Mössbauer methods. Refinements of the unit-cell constants along the almandine-pyrope join show that the volumes of mixing are ideal. Those of the almandine-spessartine join show very small positive deviations from ideality, which can be fitted with a symmetric model having an interaction parameter of $W^v = 0.24 (\pm 0.05)$ cm³/mol. Mössbauer spectra recorded at 298 and 77 K show the presence of small amounts of ¹⁶Fe³⁺, which in the case of almandine-pyrope garnets is also measurable from microprobe analyses. The amount of Fe³⁺ is generally less than 3.5% of the total Fe for the almandine-pyrope garnets and 1–2% for almandine-spessartine garnets. The molar volumes of mixing of the aluminosilicate garnet binaries are interpreted using a crystal-chemical model involving rigid tetrahedral rotation. The degree of tetrahedral rotation is not linear with increasing size of the divalent X-site cation for the four common aluminosilicate garnet end-members or along the solid solution binary pyrope-grossular. The vibrational entropies of mixing should be positively correlated with the volumes of mixing in the case of garnet, but the masses of the X-site cations must also be considered. The phonon density of states at low energies should show the vibrations of the weakly bonded divalent cations and rigid-unit modes related to tetrahedral rotation. Positive excess vibrational entropies of mixing along a binary could result from increased amplitudes and lower frequencies of vibration of the smaller of the two X-site cations substituting within larger and more distorted dodecahedral sites, as compared to the X site in the smaller volume end-member.