American Mineralogist, Volume 91, pages 894–906, 2006

Heat capacities and entropies of mixing of pyrope-grossular ($Mg_3Al_2Si_3O_{12}$-$Ca_3Al_2Si_3O_{12}$) garnet solid solutions: A low-temperature calorimetric and a thermodynamic investigation

EDGAR DACHS[1,*] AND CHARLES A. GEIGER[2]

[1]Fachbereich Materialwissenschaften, Universität Salzburg, Hellbrunnerstrasse 34, A-5020 Salzburg, Austria
[2]Institut für Geowissenschaften, Abteilung Mineralogie, Christian-Albrechts-Universität Kiel, Olshausenstr. 40,D-24098 Kiel, Germany

ABSTRACT

The low-temperature heat capacities for a series of synthetic garnets along the pyrope-grossular (Py-Gr) join were measured with the heat capacity option of the Physical Properties Measurement System (PPMS) produced by Quantum Design. The measurements were performed between 5 and 300 K on milligram-sized polycrystalline garnets that have been well characterized in previous studies. The C_P measurements indicate positive excess heat capacities (ΔC_P^{xs}) for all solid-solution compositions at temperatures <50 K with a maximum value of 2.31 ± 0.18 J/(mol·K) for the composition $Py_{50}Gr_{50}$ at about 35 K. Pyrope-rich garnets (i.e., $Py_{90}Gr_{10}$ and $Py_{75}Gr_{25}$) have no or slightly positive ΔC_P^{xs} at higher temperatures, whereas grossular-rich garnets (i.e., $Py_{10}Gr_{90}$ and $Py_{25}Gr_{75}$) show negative ΔC_P^{xs} values in the temperature range between 50 and 150 K. At $T > 150$ K, ΔC_P^{xs} values scatter around zero for all compositions and the experimental error is too large to permit a clear determination of whether ΔC_P^{xs} is different from zero within 2σ uncertainty. Excess entropies (ΔS^{xs}) at 298.15 K, calculated from the C_P data of the various solid-solution members, are asymmetric in nature with the largest positive deviations in pyrope-rich compositions. An asymmetric Margules mixing model was found to be inappropriate for modeling the ΔS^{xs}-X data and, thus, a two-parameter Redlich-Kister model was used to describe the excess entropy-composition relationships. Using this macroscopic mixing model for the excess entropy, a T-X diagram for Py-Gr garnets was calculated using different published values for the excess enthalpies of mixing. The effect of short range Ca-Mg order in the solid solution also was considered in the calculations. The calculations give a solvus for the pyrope-grossular join with a higher critical temperature in the range 850–1330 °C at $X_{Gr} = 0.35$ compared to previous thermodynamic models ($T_{crit} < 600$ °C) that use symmetric mixing models to describe the excess entropy. Unmixing of garnets in nature, as documented from occurrences in ultramafic diatremes may, therefore, have occurred at higher temperatures than previously thought. The atomistic and lattice-dynamic properties of Py-Gr garnets are reviewed and compared to the macroscopic C_P data. Published IR and Raman spectra are consistent with the occurrence of positive ΔC_P^{xs} values at low temperatures.

Keywords: Calorimetry, pyrope-grossular garnet solid solutions, thermodynamics, excess heat capacities, excess entropies