Heat capacities and entropies of mixing of pyrope-grossular (Mg$_3$Al$_2$Si$_3$O$_{12}$-Ca$_3$Al$_2$Si$_3$O$_{12}$) garnet solid solutions: A low-temperature calorimetric and a thermodynamic investigation

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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 ($\Delta C_P^e$) for all solid-solution compositions at temperatures $<$50 K with a maximum value of 2.31 $\pm$ 0.18 J/(mol·K) for the composition Py$_0$Gr$_{30}$ at about 35 K. Pyrope-rich garnets (i.e., Py$_{50}$Gr$_{50}$ and Py$_{75}$Gr$_{25}$) have no or slightly positive $\Delta C_P^e$ at higher temperatures, whereas grossular-rich garnets (i.e., Py$_{30}$Gr$_{70}$ and Py$_{30}$Gr$_{70}$) show negative $\Delta C_P^e$ values in the temperature range between 50 and 150 K. At $T >$ 150 K, $\Delta C_P^e$ values scatter around zero for all compositions and the experimental error is too large to permit a clear determination of whether $\Delta C_P^e$ is different from zero within 2$\sigma$ uncertainty. Excess entropies ($\Delta S^e$) 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 $\Delta S^e$-$X$ 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 $\Delta C_P^e$ values at low temperatures.

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

INTRODUCTION

The determination of thermodynamic properties of minerals plays a central role in the fields of mineralogy, petrology, and geochemistry. Indeed, after many years of work there exists, today, good data for the different thermodynamic functions for most end-member oxides and silicates (e.g., Robie and Hemingway 1995; Berman 1988; Holland and Powell 1998). It is a fact, however, that most rock-forming silicates are solid solutions and thus it is imperative to determine their mixing properties to understand their thermodynamic behavior. However, although much effort has been undertaken in this regard, truly quantitative thermodynamic mixing properties for many rock-forming silicate and oxide solid solutions are still not available (Geiger 2001a). This lack of data hinders thermodynamic calculations for many problems in the Earth Sciences and, therefore, much work needs to be done in this area.

Heat capacity ($C_P$) is a fundamental thermodynamic property and it is measured using various calorimetric methods (see for example, Gmelin 1987 or Cezairliyan 1988, for a review). Unfortunately, there is a dearth of heat-capacity measurements on mineral solid solutions and, thus, their entropies of mixing are poorly known (Geiger 2001b). Through $C_P$, the vibrational part of the third-law entropy ($S_r$) of a substance at 298.15 K can be determined via (e.g., Ulbrich and Waldamba 1976):

$$S_r = \int_{T_0}^{298.15} \frac{C_P}{T} dT + \Delta S_{trans} + S^e = S_{r}^{0} + S^e + \Delta S_{trans}$$

(1)

where $\Delta S_{trans}$ is any entropy change resulting from a phase transition between 0 and 298.15 K, and $S_r$ is the residual entropy incorporating all quenchable contributions such as frozen-in structural disorder (often referred to as configurational entropy). The $C_P$ integral in Equation 1 is generally the most important contribution to the entropy and it is accessible by calorimetric

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