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Grossular: A crystal-chemical, calorimetric, and thermodynamic study

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Abstract

In spite of the amount of research that has been done on grossular, $Ca_3Al_2Si_3O_{12}$, there is still uncertainty regarding its exact thermodynamic properties. Because of insufficient sample characterization in the various published calorimetric studies, it is difficult to analyze conflicting C_P and $S°$ results. To resolve the discrepancies, a detailed and systematic multi-method investigation was undertaken. Three synthetic grossular samples and four natural grossular-rich garnets were characterized by optical microscopy, electron microprobe analysis, IR, and MAS ^{29}Si and ^{27}Al NMR spectroscopy, and X-ray powder diffraction methods. Two of the natural grossulars, crystallized at relatively low temperatures, are optically anisotropic and two from the higher temperature amphibolite faces are isotropic. The natural garnets have between 94 and 97 mol% grossular with minor fractions of other garnet components, as well as small amounts of OH in solid solution. ^{29}Si and ^{27}Al MAS NMR spectra indicate that synthetic grossular crystallized at high-P and high-T conditions is ordered with respect to Al and Si.

Heat-capacity measurements between 5 and 300 K were made using relaxation calorimetry and between 282 and 764 K using DSC methods. For the three synthetic grossulars, the C_P data yield an average $S°$ value of 260.23 ± 2.10 J/(mol·K). The $S°$ values for the four natural grossular-rich garnets, adjusted to end-member grossular composition, range between 253.0 ± 1.2 and 255.2 ± 1.2 J/(mol·K). The results of this work thus confirm earlier low-temperature adiabatic calorimetric studies that show small, but experimentally significant, differences in $S°$ between natural and synthetic grossular samples. The difference in terms of heat-capacity behavior between synthetic and natural samples is that the latter have lower C_P values at temperatures between 20 and 100 K by up to about 20%. Above 298 K, C_P for grossular is given by

$$C_P \text{ J/(mol·K)} = 556.18(\pm12) - 1289.97(\pm394)\cdot T^{-0.5} - 2.44014(\pm0.24)\cdot 10^7\cdot T^{-2} + 3.30386(\pm0.39)\cdot 10^9\cdot T^{-3}.$$

Applying mathematical programming, published high-P-T results on the reaction 3anorthite = grossular + 2kyanite + quartz were analyzed thermodynamically. The calculations yield best-fit values of $\Delta_f H° = -6627.0$ kJ/mol and $S° = 258.8$ J/(mol·K) for grossular. It is concluded that $S° \approx 260$ J/(mol·K) is the best value for end-member grossular. Variations in structural state and composition in natural samples, as well as assumptions used in correcting for solid-solution and OH groups, appear to be the most important factors that could account for the smaller $S°$ values of 253–257 J/(mol·K).

Keywords: Garnet, grossular, crystal chemistry, spectroscopy, calorimetry, entropy, heat capacity, thermodynamics