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

EDGAR DACHS,1,2 CHARLES A. GEIGER,1,* ARTUR BENISEK,1 AND KLAUS-DIETER GREVEL2,3

1Fachbereich Materialforschung and Physik, Abteilung Mineralogie, Universität Salzburg, Hellbrunnerstrasse 34, A-5020 Salzburg, Austria
2Institut für Geowissenschaften, Friedrich-Schiller Universität, Burgweg 11, D-07749 Jena, Germany
3Institut für Geologie, Mineralogie und Geophysik, Ruhr-Universität, D-44780 Bochum, Germany

ABSTRACT

In spite of the amount of research that has been done on grossular, Ca$_3$Al$_2$Si$_3$O$_{12}$, 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 $S^\circ$ 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 $S^\circ$ value of 260.23 ± 2.10 J/(mol·K). The $S^\circ$ 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 $S^\circ$ 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

$$C_p(J/(mol·K)) = 556.18(±12) - 1289.97(±394) T ^ {0.5} - 2.44014(±0.24) 10 ^ 7 T ^ 2 + 3.30386(±0.39) 10 ^ 6 T ^ 3.$$

Applying mathematical programming, published high-$P$-$T$ results on the reaction $3\text{anorthite} = \text{grossular} + 2\text{kyanite} + \text{quartz}$ were analyzed thermodynamically. The calculations yield best-fit values of $\Delta H^o = -6627.0$ kJ/mol and $S^o = 258.8$ J/(mol·K) for grossular. It is concluded that $S^o = 260$ 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 $S^o$ values of 253–257 J/(mol·K).

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

INTRODUCTION

Grossular garnet, ideal end-member composition Ca$_3$Al$_2$Si$_3$O$_{12}$, and grossular-containing garnet solid solutions are important in various rock types of Earth’s crust and upper mantle. Many investigations have been directed at understanding grossular’s crystal-chemical and thermodynamic properties. For a number of years, considerable effort has been devoted to investigating phase relations in the CaO-Al$_2$O$_3$-SiO$_2$-H$_2$O (CASH) system and, here, grossular plays a central role. This system can be considered as forming a “cornerstone” for various thermodynamic databases. However, in spite of the large and varied amount of research that has been done on grossular, there is still uncertainty regarding its precise thermodynamic properties and phase relations.

* E-mail: ca.geiger@sbg.ac.at

A major issue concerns the value of grossular’s standard third-law entropy, $S^o$. Here, low-temperature heat capacity, $C_p$, measurements are critical, as they offer the most robust means of determining $S^o$. Low-temperature adiabatic calorimetric heat-capacity measurements have been made in the “Westrum laboratory” on a natural garnet containing about 91% of a grossular component (Westrum et al. 1979) as well as on synthetic grossular (Haselton and Westrum 1980). The resulting $S^o$ values given for end-member grossular (i.e., adjusted in the case of the natural sample) are 254.72 ± 0.84 and 260.12 J/(mol·K), respectively. They differ by about 2% and this amount lies outside the error inherent to this precise calorimetric method, which is 0.1 to 0.2% (Robie and Hemingway 1972). There is a third adiabatic calorimetric study that was made on a natural nearly end-member grossular and it gave $S^o = 256.48 ± 1.26$ J/(mol·K)