American Mineralogist, Volume 97, pages 1252–1255, 2012

LETTER

Thermodynamic behavior and properties of katoite (hydrogrossular): A calorimetric study

CHARLES A. GEIGER,* EDGAR DACHS, AND ARTUR BENISEK

Fachbereich Materialforschung und Physik, Abteilung Mineralogie, Universität Salzburg, Hellbrunnerstrasse 34, A-5020 Salzburg, Austria

ABSTRACT

The low-temperature heat capacity behavior of synthetic katoite, $Ca_3Al_2H_{12}O_{12}$, was investigated for the first time using microcalorimetry. The sample was synthesized hydrothermally in Au capsules at 250 °C and 3 kb water pressure. X-ray powder measurements show that about 98–99% katoite was obtained. Heat capacities were measured with a commercially designed relaxation calorimeter between 5 and 300 K on a milligram-sized sample and around ambient temperatures with a differential scanning calorimeter. The heat capacity data are well behaved at $T < 300$ K and show a monotonic decrease in magnitude with decreasing temperature. There is no evidence for any phase transition. A standard third-law entropy value of $S° = 421.7 \pm 1.6$ J/(mol·K) was calculated. Published experimentally based $S°$ values for katoite are slightly lower than this value. Estimations of $S°$ based on empirical corresponding state schemes give $S°$ values that are much too low. This is ultimately attributed to an inability to account for the vibration behavior of the OH groups in katoite that have very weak or no H-bonding. Using this new calorimetric-based $S°$ value and published standard enthalpy of formation data for katoite, a calorimetric-based Gibbs free energy of formation at 298 K can be obtained as $\Delta G_f° = -5021.2 \pm 16.5$ kJ/mol.

Keywords: Katoite, hydrogarnet, heat capacity, standard entropy, Gibbs free energy, relaxation calorimetry, hydrous minerals, cement