Goldschmidt2017 Abstract

Recent Developments in Low-Temperature Calorimetry and C_p and $S°$ Behavior of Minerals

CHARLES A. GEIGER AND EDGAR DACHS [1]

[1]Universität Salzburg, Salzburg, Austria. ca.geiger@sbg.ac.at

Low-temperature calorimetry is an experimental science that measures the thermodynamic function heat capacity, $C_p(T)$, from which the standard third-law entropy, $S°$, is calculated. The recent technological development of relaxation calorimetry allows new experimental strategies and types of C_p investigations that were not possible using the more established method of adiabatic calorimetry. Relaxation measurements are fast and automated and can be made on mg-sized mineralogical samples between 2 and 400 K. These advantages, when careful measurement procedures are used, permit better determinations and understanding of C_p behavior. The C_p of synthetic single-crystal MgO was measured between 5 and 302 K and $S°$ calculated using relaxation calorimetry to further investigate its precision and accuracy. Synthetic and natural end-member or nearly end-member silicate garnets were investigated in the past via adiabatic calorimetry and more recently and extensively with the relaxation method. First C_p and $S°$ results have been obtained on spessartine ($Mn_3Al_2Si_3O_{12}$) and reinvestigations on pyrope ($Mg_3Al_2Si_3O_{12}$), almandine ($Fe_3Al_2Si_3O_{12}$), grossular ($Ca_3Al_2Si_3O_{12}$) and andradite ($Ca_3Al_2Si_3O_{12}$), often on multiple samples, have resolved uncertainties and certain problems with older adiabatic calorimetric determinations. $S°$ can be affected by low temperature phenomena, such as magnetic phase transitions or Schottky anomalies at $T < 15$ K, which were not fully described in some older studies. Small differences in the thermodynamic behavior between natural and synthetic silicates may exist as demonstrated by extensive work on grossular. The C_p behavior and $S°$ values for the five common garnets are analyzed and the latter are compared to the "best fit or optimized" $S°$ values given in various internally consistent thermodynamic databases. Conclusions will be made on what types and directions of calorimetric study are required in order to obtain better thermodynamic property determinations of minerals.