European Mineralogical Conference
Vol. 1, EMC2012-77-1, 2012
European Mineralogical Conference 2012

Almandine: Heat-capacity behavior and standard thermodynamic properties

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Almandine garnet (ideal formula $Fe_3Al_2Si_3O_{12}$) is a key phase in many metamorphic rocks. Therefore, knowledge of its thermodynamic properties is essential for petrologic investigations. As part of an ongoing calorimetric and thermodynamic study of rock-forming garnets, the heat capacity of three synthetic polycrystalline almandine garnets and one natural almandine-rich single crystal was measured.

The samples were characterized by optical microscopy, electron-microprobe analysis, X-ray powder diffraction and ^{57}Fe Mössbauer spectroscopy. Measurements were performed in the temperature range 3 to 300 K using relaxation calorimetry and between 282 and 764 K using DSC methods. All garnets show a prominent λ-type heat-capacity anomaly at low temperatures resulting from a paramagnetic-antiferromagnetic phase transition. Integration of the low-T C_p data yields calorimetric standard entropy, S^o, values between 336.7 $\pm$ 0.8 and 337.8 $\pm$ 0.8 J/mol·K. The smaller value is recommended as the best S^o for end-member stoichiometric almandine, because it derives from the "best" Fe^{3+}-free synthetic sample. The lattice heat capacity of almandine was calculated using the single-parameter phonon dispersion model of Komada and Westrum (1997), which allows the non-lattice heat capacity (C_{ex}) behavior to be modelled. An analysis shows the presence of an electronic heat-capacity contribution (C_{el} - Schottky anomaly) superimposed on a larger magnetic heat-capacity effect (C_{mag}) around 17 K. The calculated lattice entropy at 298.15 K is S_{vib} = 303.3 J/mol·K and it contributes about 90% to the total standard entropy at 298 K. The non-lattice entropy is S_{ex} = 33.4 J/mol·K and consists of S_{mag} = 32.1 J/mol·K and S_{el} = 1.3 J/mol·K contributions. The C_p behavior for almandine at $T > 298$ K is given by the polynomial (in J/mol·K):

C_p= 649.06($\pm$4) - 3837.57($\pm$122)·$T^{-0.5}$ - 1.44682($\pm$0.06)·$10^7 \cdot T^{-2}$+ 1.94834($\pm$0.09)·$10^9 \cdot T^{-3}$,

which is calculated using the measured DSC data together with one published heat-content datum determined by transposed-drop calorimetry along with a new determination in this work that gives $H_{1181K} - H_{302K}$ = 415.0 $\pm$ 3.2 kJ/mole.

Using our S^o value and the C_p polynomial for almandine, we derived the enthalpy of formation, ΔH_f^o, from an analysis of experimental phase equilibrium results on the reactions almandine + 3rutile = 3ilmenite + sillimanite + 2quartz and 2ilmenite = 2iron + 2rutile + O_2. ΔH_f^o = -5269.63 kJ/mol was obtained.