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Almandine: Lattice and non-lattice heat capacity behavior and standard thermodynamic properties

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Abstract

The heat capacity of three synthetic polycrystalline almandine garnets (ideal formula $Fe_3Al_2Si_3O_{12}$) and one natural almandine-rich single crystal was measured. The samples were characterized by optical microscopy, electron microprobe analysis, X-ray powder diffraction, and 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. For two Fe^{3+}-free or nearly Fe^{3+}-free synthetic almandines, the phase transition is sharp and occurs at 9.2 K. Almandine samples that have ~3% Fe^{3+} show a λ-type peak that is less sharp and that occurs at 8.0 ± 0.2 K. The low-T C_P data were adjusted slightly using the DSC results to improve the experimental accuracy. Integration of the low-T C_P data yields calorimetric standard entropy, $S°$, values between 336.7 ± 0.8 and 337.8 ± 0.8 J/(mol·K). The smaller value is recommended as the best $S°$ for end-member stoichiometric almandine, because it derives from the "best" Fe^{3+}-free synthetic sample.

The lattice (vibrational) 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 modeled. 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 above 298 K is given by the polynomial [in J/(mol·K)]:

$$C_P = 649.06(\pm4) - 3837.57(\pm122)\cdot T^{-0.5} - 1.44682(\pm0.06)\cdot 10^{7}\cdot T^{-2} + 1.94834(\pm0.09)\cdot 10^{9}\cdot T^{-3}$$

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 ± 3.2 kJ/mol.

Using our $S°$ value and the C_P polynomial for almandine, we derived the enthalpy of formation, $\Delta H_f°$, from an analysis of experimental phase equilibrium results on the reactions almandine + 3rutile = 3ilmenite + sillimanite + 2quartz and 2ilmenite = 2Fe + 2rutile + O_2. A $\Delta H_f°$ = –5269.63 kJ/mol was obtained.

Keywords: Almandine, heat capacity, standard entropy, thermodynamics, standard enthalpy of formation, magnetic entropy, Schottky anomaly