American Mineralogist, Volume 85, pages 1686–1693, 2000

The heat capacity of $MgCr_2O_4$, $FeCr_2O_4$, and Cr_2O_3 at low temperatures and derived thermodynamic properties

STEPHAN KLEMME,[1,2,*] HUGH ST.C. O'NEILL,[1] WALTER SCHNELLE,[3,4] AND EBERHARD GMELIN[4]

[1]Research School of Earth Sciences, The Australian National University, Canberra, ACT 0200, Australia
[2]Department of Earth Sciences, University of Bristol, Wills Memorial Building, Queen's Road, Bristol BS8 1RJ, U.K.
[3]Max-Planck-Institut für Chemische Physik fester Stoffe, Pirnaer Landstrasse 176, 01257 Dresden, Germany
[4]Max-Planck-Institut für Festkörperforschung, Heisenbergstrasse 1, 70569 Stuttgart, Germany

ABSTRACT

The heat capacity of synthetic eskolaite, Cr_2O_3, and of the synthetic spinels magnesiochromite, $MgCr_2O_4$, and chromite, $FeCr_2O_4$ were measured from 1.5 K to 340 K. For $MgCr_2O_4$, a substantial magnetic contribution to the entropy is revealed by a sharp peak in the heat capacity curve at 12.55 ± 0.05 K, which indicates the transition to antiferromagnetic long-range order. Integration of the heat capacity curve yields a value of 118.3 ± 1.2 J/(mol·K) for the standard entropy at 298.15 K, which is in excellent agreement with that calculated from phase equilibria studies on the reaction $MgCr_2O_4 + SiO_2 = Cr_2O_3 + MgSiO_3$. The new calorimetric results for Cr_2O_3 indicate a standard entropy at 298.15 K of 82.8 ± 0.8 J/(mol·K). The measurements for $FeCr_2O_4$ show three distinct heat capacity anomalies, one of which (peaking at 36.5 ± 0.2 K) was missed by previous low temperature heat capacity measurements, which only extend down to 53 K. Integration of the heat capacity curve yields a value for the standard entropy at 298.15 K of 152.2 ± 3.0 J/(mol·K) for $FeCr_2O_4$, some 6 J/(mol·K) greater than the previous calorimetric value.

These low-temperature heat capacity data were combined with high-temperature heat content measurements from the literature to derive heat capacity equations for all three phases to 1800 K. The resulting heat capacity equations were then used to extract revised recommended values of the standard enthalpies of formation and entropies of $MgCr_2O_4$ and Cr_2O_3 from phase equilibrium data. For $FeCr_2O_4$, the phase equilibrium data are of dubious accuracy, the enthalpy of formation is only approximate.