American Mineralogist, Volume 88, pages 846–854, 2003

Thermodynamics of Fe oxides: Part I. Entropy at standard temperature and pressure and heat capacity of goethite (α-FeOOH), lepidocrocite (γ-FeOOH), and maghemite (γ-Fe_2O_3)

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Abstract

The heat capacities (C_P) of goethite (goe, α-FeOOH), lepidocrocite (lep, γ-FeOOH), and maghemite (mag, γ-Fe_2O_3) were measured from below liquid helium temperature up to their decomposition temperatures by a combination of adiabatic, semi-adiabatic, and differential scanning calorimetry. All three phases were synthetic, with <160 ppm of Al. Chlorine content in goe (32 ppm) and lep (202 ppm) is too low to affect the calorimetric results of this study. Phase purity was verified by Rietveld refinement of the powder X-ray diffraction (XRD) patterns; we determined lattice parameters, atomic positions, crystallite size, and microstrain for all three samples. The Brunauer-Emmet-Teller (BET) surface area is 21 (goe), 23 (lep), and 18 (mag) m^2/g. No amorphous impurity was found in the goethite sample by extraction of the oxalate soluble fraction. The excess water, determined from weight loss after firing at 1200 K overnight, is 0.083 ± 0.010 (goe), 0.087 ± 0.005 (lep), 0.042 ± 0.003 (mag) moles of water per mole of FeOOH or Fe_2O_3.

The entropy at standard temperature and pressure (STP) was calculated from subambient C_P data and corrected for the excess water content using a Debye-Einstein representation of the C_P of hexagonal ice. The entropy at STP is 59.7 ± 0.2 (goe), 65.1 ± 0.2 (lep), and 93.0 ± 0.2 (mag) J/(K·mol). The XRD pattern of maghemite lacks superstructure peaks, and complete disorder of the vacancies leads to configurational entropy S_{conf} = 2.0 J/K·mol. Because very weak superstructure peaks can be overlooked, or the vacancies may be short-range ordered, this calculated S_{conf} represents only an upper limit. The heat capacity above 273 K was fitted to a Maier-Kelley polynomial C_P [J/(K·mol), T in K] = a + bT + cT^{-2}. The C_P polynomial coefficients are a = 1.246, b = 0.2332, c = 313900 (goe, valid in temperature range 273–375 K), a = 59.76, b = 0.06052, c = –772900 (lep, 273–390 K), and a = 106.8, b = 0.06509, c = –1886000 (mag, 273–760 K).