Thermodynamic and crystallographic properties of kornelite [Fe₂(SO₄)₃·~7.75H₂O] and paracoquimbite [Fe₂(SO₄)₃·9H₂O]

SONIA ACKERMANN,[1] BILJANA LAZIC,[2] THOMAS ARMBRUSTER,[2] STEPHEN DOYLE,[3] KLAUS-DIETER GREVEL,[1,5] AND JURAJ MAJZLAN[1,4,*]

[1]Institute of Mineralogy and Geochemistry, Albert-Ludwigs-University, Albertstrasse 23b, D-79104 Freiburg, Germany
[2]Mineralogische Kristallographie, Institute of Geology, University of Bern, Freiestrasse 3, CH-31012 Bern, Switzerland
[3]Forschungszentrum Karlsruhe, Institute for Synchrotron Radiation, Hermann-von-Helmholtz-Platz 1,
D-76344 Eggenstein-Leopoldshafen, Germany
[4]Institute of Geosciences, Friedrich-Schiller University, Burgweg 11, D-07749 Jena, Germany
[5]Institute for Geology, Mineralogy and Geophysics, Ruhr-University Bochum, D-44780 Bochum, Germany

ABSTRACT

Enthalpies of formation of kornelite [Fe₂(SO₄)₃·~7.75H₂O] and paracoquimbite [Fe₂(SO₄)₃·9H₂O] were measured by acid (5 N HCl) solution calorimetry at T = 298.15 K. The samples were characterized chemically by an electron microprobe, and structurally by the means of single-crystal, in-house powder, and synchrotron powder X-ray diffraction. The refined structures for the two phases are provided, including estimates of the positions and concentration of non-stoichiometric water in structural channels of kornelite, location of the hydrogen atoms and the hydrogen bonding system in this phase. The measured enthalpies of formation from the elements (crystalline Fe, orthorhombic S, ideal gases O₂ and H₂) at T = 298.15 K are –4916.2 ± 4.2 kJ/mol for kornelite and –5295.4 ± 4.2 kJ/mol for paracoquimbite. We have used several algorithms to estimate the standard entropy of the two phases. Afterward, we calculated their Gibbs free energy of formation and constructed a phase diagram for kornelite, paracoquimbite, Fe₂(SO₄)₃·5H₂O, and Fe₂(SO₄)₃ as a function of temperature and relative humidity of air. The topology of the phase diagram is very sensitive to the entropy estimates and the construction of a reliable phase diagram must await better constraints on entropy or Gibbs free energy of formation. Possible remedies of these problems are also discussed.

Keywords: Kornelite, paracoquimbite, thermodynamic properties, enthalpy of formation