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High-pressure IR-spectra and the thermodynamic properties of chloritoid

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ABSTRACT

Using IR radiation from a synchrotron source, high-quality absorbance spectra were obtained from polycrystalline powder of chloritoid (cld) from ambient conditions up to pressures of 10 GPa over 50 to 4000 cm^{-1}. The idealized chemical composition of the chloritoid group is $M_2Al_4O_2(SiO_4)_2(OH)_4$ where M = Fe or Mg in our experiments. All of the 42 expected fundamental IR modes were observed. These data, combined with the response of the IR bands to substitutions of Fe for Mg, and of D for H, constrained the band assignments. Heat capacity (C_P) and entropy (S_o) for the triclinic and monoclinic polymorphs of Fe- and Mg-cld were calculated from the Kieffer-type model, using our detailed band assignments. The calculated heat capacity and entropy for the monoclinic and triclinic polymorphs differ negligibly. The results at temperatures above 298 K are described by the following polynomial expressions in J/(mol·K): $C_P = 7.835 \cdot 10^2 - 5.170 \cdot 10^3 T^{-0.5} - 1.648 \cdot 10^7 T^{-2} + 1.934 \cdot 10^9 T^{-3}$ for Mg-cld and $C_P = 7.848 \cdot 10^2 - 5.185 \cdot 10^3 T^{-0.5} - 1.548 \cdot 10^7 T^{-2} + 1.783 \cdot 10^9 T^{-3}$ for Fe-cld. At room temperature, $S_o = 293$ J/mol·K for Mg-cld and 335 J/mol·K for Fe-cld. These values differ somewhat from entropy estimated from various internally consistent databases (–3 to –9% for Mg-cld and –9 to +5% for Fe-cld). However, using our new S_o and C_P values in conjunction with the enthalpy of formation, $H_f = -7101$ kJ/mol for Mg-cld or $H_f = -6422$ kJ/mol for Fe-cld (estimated in this study), we can closely reproduce the experimental data for the reactions Mg-chloritoid + talc = clinochlore + kyanite (Chopin 1985) and Fe-chloritoid = almandine + diaspore + water (Vidal et al. 1994).