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An investigation of the phase transitions in bornite (Cu_5FeS_4) using neutron diffraction and differential scanning calorimetry

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Abstract

Bornite (Cu_5FeS_4) exists in three polymorphic forms related by superstructuring, with structural transitions at 200 and 265 °C. The phase transitions and structural behavior in two natural bornite samples were investigated as a function of temperature using differential scanning calorimetry (DSC) to characterize the thermal anomalies associated with each transition and in-situ high-resolution neutron powder diffraction to determine the variation in superlattice intensity and lattice parameters. These two methods, carried out over the temperature range 50–350 °C, provided insight into the short- and long-range interactions, respectively, and a comparison of measurements taken up-*T* and down-*T* enabled thermal hysteresis effects to be quantified. The high to intermediate transition at 265 °C involves long-range cation ordering and vacancy clustering, resulting in a doubling of the high-temperature cubic unit cell (*m*3*m*). The square of both the spontaneous strain and the 2*a* superlattice intensity varied linearly with temperature, indicating that the transition is tricritical in character. Loss of long- and short-range order occurred simultaneously during heating, whereas during cooling, the reappearance of 2*a* superlattice reflections was depressed some 50 °C below the short-range transition recorded by DSC due to the formation of antiphase domains. The presence of antiphase domains also caused the discontinuity in the strain associated with the transition to occur at a different temperature to the appearance of superlattice intensity. The intermediate-low transition associated with the development of a 2*a*4*a*2*a* orthorhombic superlattice (*Pbca*) is strongly first-order and exhibits a large intrinsic hysteresis (38 °C). The down-*T* transition temperature of the intermediate-low transition is shown to be dependent on the degree of order attained in the intermediate phase.