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In-situ study of the $R\bar{3}$ to $R\bar{3}c$ phase transition in the ilmenite-hematite solid solution using time-of-flight neutron powder diffraction

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ABSTRACT

The $R\bar{3}$ to $R\bar{3}c$ cation ordering phase transition in the ilmenite ($FeTiO_3$) – hematite (Fe_2O_3) solid solution has been investigated using in-situ time-of-flight neutron powder diffraction. Four synthetic samples of the solid solution containing 70, 80, 90, and 100% $FeTiO_3$ (ilm70, ilm80, ilm90, and ilm100, respectively) were heated under vacuum to a maximum of 1350 °C. Powder diffraction patterns were collected at several temperatures on heating and cooling, with a Rietveld refinement performed in each case. Samples ilm80, ilm90, and ilm100 were fully ordered after quenching from the synthesis temperature to room temperature. Sample ilm70 had a higher degree of quenched in disorder, which is the result of chemical heterogeneities produced during quenching and subsequent heating in the neutron experiments. The degree of order in all samples decreased smoothly at high temperatures, with second-order transitions to the $R\bar{3}c$ phase being observed at 1000, 1175, and 1325 °C in ilm70, ilm80, and ilm90, respectively. The transition temperature in ilm100 was higher than the maximum temperature reached in the neutron experiments, and is estimated as ~1400 °C. The character of the transition is typical of that predicted by three-dimensional Ising models and appears to become more first-order in character with increasing Ti-content. The temperature-dependence of the cell parameters reveals that components of the spontaneous strain tensor, e_{11} and e_{33}, are negative and positive, respectively. Little volume strain is associated with long-range ordering. A small negative volume strain due to short-range ordering within the $R\bar{3}c$ phase is identified. The variations in cell parameters and cation-cation distances can be understood in terms of the competing effects of long- and short-range ordering as a function of temperature and composition.