

## The thermal breakdown of Fe<sub>4</sub>O<sub>5</sub> at ambient pressure

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Fe<sub>4</sub>O<sub>5</sub> is a recently discovered Fe-oxide that is stable at pressures of ~10 GPa (Lavina et al. 2011) and magnetite is now known to break down to an assemblage of Fe<sub>4</sub>O<sub>5</sub> + Fe<sub>2</sub>O<sub>3</sub> under such conditions (Woodland et al. 2012). Thus it is important to determine the properties of Fe<sub>4</sub>O<sub>5</sub> as it apparently plays an important role in the simple Fe-O system at high pressures and temperatures. To this end we set out to measure accurate molar volumes of this phase as a function of temperature at ambient pressure conditions to measure its thermal expansion. This goal was compromised by its low thermal stability at 1 bar, which revealed a series of different transformations.

Fe<sub>4</sub>O<sub>5</sub> was synthesised from a mixture of magnetite and Fe at 11 GPa and 1000°C in a multi-anvil press. Ambient P and T lattice parameters are  $a=2.89339(6)$  Å,  $b=9.8067(3)$  Å,  $c=12.5834(3)$  Å and a volume of  $357.05(2)$  Å<sup>3</sup>. Subsequently, a powder was sealed in a glass capillary and run at the high-resolution beamline B2 at HASYLAB/DESY. X-ray powder diffraction measurements were performed as a function of temperature up to 900°C.

Already at 150°C, new diffraction peaks appeared, indicating that Fe<sub>4</sub>O<sub>5</sub> was decomposing to a mixture of Fe<sub>3</sub>O<sub>4</sub> and Fe<sub>x</sub>O. The unit-cell of Fe<sub>x</sub>O reveals a composition of  $x\sim 0.8$ . Diffraction peaks from Fe<sub>4</sub>O<sub>5</sub> virtually disappeared by 200°C. Between 200 and 250°C, metallic Fe and an additional Fe<sub>y</sub>O phase appeared that had a unit-cell more like “typical” wüstite ( $y\sim 0.96$ ), revealing a further reaction where Fe<sup>3+</sup>-rich Fe<sub>x</sub>O breaks down to a mixture of Fe<sub>3</sub>O<sub>4</sub> + Fe<sup>3+</sup>-poor Fe<sub>y</sub>O + metallic Fe. With increasing T, both Fe<sub>x</sub>O and Fe<sub>y</sub>O progressively undergo a disproportionation reaction producing metallic Fe and Fe<sub>3</sub>O<sub>4</sub>. Above 470°C, Fe<sub>y</sub>O disappears and a small amount of metastable Fe<sub>x</sub>O coexists with the stable assemblage of metallic Fe + Fe<sub>3</sub>O<sub>4</sub>. At 600°C, the true wüstite stability field is reached and metallic Fe reacts with magnetite to produce Fe<sub>z</sub>O, where  $z=0.93(1)$ . No further changes are observed up to 900°C. Calculated phase proportions at 900°C are 0.37 Fe<sub>z</sub>O and 0.63 Fe<sub>3</sub>O<sub>4</sub>, which correspond very closely to the initial Fe<sub>4</sub>O<sub>5</sub> composition, indicating that this series of reactions was not driven by oxidation or reduction, but occurred at nearly constant oxygen content. The metastable appearance of Fe<sub>x</sub>O at low T must be related to the fact that the Fe<sub>4</sub>O<sub>5</sub> crystal structure contains wüstite-like octahedral layers that alternate with Ca-ferrite slabs. Initial breakdown favors the formation Fe<sup>3+</sup>-rich Fe<sub>x</sub>O, which may be an indicator of the cation distribution in the original Fe<sub>4</sub>O<sub>5</sub> phase.

Lavina et al. (2011) PNAS, 108, 17281-17285.

Woodland et al. (2012) abstract emc2012-317, this meeting