

The breakdown of magnetite Fe₃O₄ at high temperatures and pressures

Report of Experiment H4223

Magnetite (FeFe₂O₄) is a cubic mixed-valent phase that belongs to the spinel group of minerals. Previous investigations indicate that it undergoes an apparently unquenchable phase transition to a post-spinel phase (h-Fe₃O₄) at high pressures. The structure of the high-pressure phase is still unclear (e.g. Fei et al. 1999; Haavik et al. 2000; Dubrovinsky et al., 2003; Schollenbruch et al. 2011) and must be investigated using in situ methods. Our goals of this experiment were 1) to obtain high quality angle dispersive diffraction data for h-Fe₃O₄ at high P and T near the phase boundary to permit unambiguous determination of its crystal structure, and 2) to study the kinetics of the reaction and the transformation mechanism.

Experimental techniques

Several experiments were carried out using the Paris-Edinburgh cell on beamline ID27, operated with sintered diamond anvils, so that the required pressure-temperature conditions (9-15 GPa at ~1000°C) could be reached. Just before our experiments a new set of soller slits was installed that significantly reduced beam divergence and improved the quality of the diffraction patterns by filtering out contributions from the materials in the pressure cell surrounding the sample.

High-purity stoichiometric magnetite, synthesised at one atm and 1573 K with a log *f*O₂ = -5.5, was loaded into a BN capsule and placed inside a boron epoxy pressure cell. A 10:1 mixture of NaCl and Au was packed into a small hole bored into the side of the BN capsule and served as pressure and temperature sensors during the experiment. Fitting the cell parameters of these two phases simultaneously to their respective equations of state permit pressure and temperature to be monitored without need of a standard thermocouple. Diffraction patterns of the standard mixture and the magnetite sample were measured using a fast, automated imaging-plate detector.

Results

The results are detailed in a publication currently in press (Woodland et al. 2012) and only briefly described here. The breakdown of magnetite was observed at 9.5-11 GPa and around 1000-1200 K. The diffraction peaks that appeared were consistent with those observed by Schollenbruch et al. (2011) in the same P-T range, who referred to it as a “mystery phase” since they could not index their rather poorly resolved diffraction patterns. Repeated attempts at refining the new, much higher quality diffraction patterns could still not be indexed to any known Fe-oxide phase, including those previously proposed for h-Fe₃O₄. However, the recently reported stability of a new Fe-oxide, Fe₄O₅ (Lavina et al. 2011) is consistent with our diffraction patterns.

From our results, we confirm that the breakdown of magnetite at high pressures and temperatures involves its disproportionation into Fe₄O₅ and hematite:



Considering that other workers have identified a h-Fe₃O₄ phase at still higher pressures, this means that the high-pressure phase relations in the “simple” Fe-O system are more complicated than originally thought, at least with respect to relations involving a phase with Fe₃O₄ stoichiometry.

References

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