ESRF	**Experiment title:** Crystal Structures of Oxides at High Pressures and Temperatures	**Experiment number:** HS-743
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Report:

We carried out three experiments at the high-pressure beamline (ID30) of ESRF in August, 1998, using an externally heated high-temperature diamond-anvil cell. All the experiments require high intense synchrotron source, high resolution, and accurate diffraction intensity information. The high-pressure beamline at ESRF is well developed and suited for those types of experiments.

Experiment 1: *Structure determination of the high-pressure phase of $MgFe_2O_4$.*

Using in situ diffraction data on Fe_3O_4 collected at ESRF, we were able to solve and refine the structure of a high-pressure phase of Fe_3O_4 that has been an unsolved problem since 1975 [Fei et al., 1999]. The high-pressure phase of Fe_3O_4 is of the space group *Pbcm* ($CaMn_2O_4$-type structure). $MgFe_2O_4$ is isostructural with Fe_3O_4 at ambient pressure. The experiment was designed to answer the question that if the high-pressure phase of $MgFe_2O_4$ is isostructural with that of Fe_3O_4 at high pressures and what is the effect of Mg substitution on the crystal chemistry. We compressed a $MgFe_2O_4$ sample to a pressure of 25 GPa and observed the same spinel - $CaMn_2O_4$ type phase transition as in Fe_3O_4.

Experiment 2: *Equation of state of the high-pressure phase of Fe_3O_4 and breakdown reaction at high pressures*

It is expected that the high-pressure phase of Fe_3O_4 may breakdown into Fe_2O_3 and FeO at about 70 GPa because both Fe_2O_3 and FeO transform into denser high-pressure phases at this pressure. We compressed a Fe_3O_4 powder sample to 75 GPa and heated to 750 °C in a high-temperature diamond-anvil cell. No breakdown reaction was observed. It may require higher temperatures to facilitate the reaction. Further experiments will be planed to address this possibility.

Experiment 3: *Phase transitions in Ni_3S_2*

We previously reported a new Fe_3S_2 compound, synthesized at pressures between 14 and 18 GPa in the system Fe-FeS. The formation of Fe_3S_2 changes the melting relations, from a simple binary eutectic system to a binary system with Fe_3S_2 as an intermediate compound which melts incongruently [*Fei et al., Science* **275**, 1621-1623, 1997]. However, the structure of this new compound is still unknown. As an analog to Fe_3S_2, Ni_3S_2 is stable at ambient pressure. We designed an experiment to investigate possible phase transitions in Ni_3S_2 at high pressures and hope to obtain some insight to the structure of the Fe_3S_2 compound. Unexpectedly, we found two phase transitions in Ni_3S_2 up to a pressure of 25 GPa and 400 °C. We are in the process to solve the crystal structures of these two high-pressure polymorphs.

Publications

Fei, Y. D. J. Frost, H. K. Mao, C. T. Prewitt, and D. Häusermann, In situ structure determination of the high-pressure phase of Fe_3O_4, *Am. Mineral., 84,* 203-206, 1999.