Experimental Report

Experiment number: *CH-6627*

Experimental title: *Synthesis, single-crystal X-ray diffraction and Mössbauer characterization of novel iron halides under high pressure*

Metal halides, especially layered halides, possess a wide variety of interesting properties that can result in technologically important applications. Utilizing high pressure is an effective method for fine-tuning physical properties in a desirable manner. Iron halides are strongly *d-d* electronic-correlated compounds and possess interesting physical properties. Iron dihalides are known to be Mott-insulators with a pressure-induced Mott-transition. Recently, it was shown that FeI_2 and $FeCl_2$ exhibit the unusual high-spin to low-spin transition and spin-flop phenomenon (metamagnetism) under high pressure. On the other hand, iron halides are interesting for geophysics, since it is believed they can be formed at the Earth's mantle and can be responsible for its basic properties, including magnetism. Therefore, analyzing their relative stabilities is important in determining the chemical composition of the Earth's core and understanding its dynamics.

Experiment

XRD measurements were performed at the ID15b beamline of the ESRF with the X-ray beam (λ = 0.4103 Å) focused down to $1\times 1\ \mu m^2$, XRD patterns were collected on an Eiger2X CdTe 9 M hybrid photon-counting pixel detector. For single-crystal XRD measurements, samples were rotated in a range ±36°. The XRD images were collected with an angular step $\Delta\omega = 0.5°$ and an exposure time of 1s per frame. Four wide-opening (± 36°) BX90 diamond anvil cells (DAC) with a small piece of ^{57}Fe in $C_{10}F_{12}$ (for Fe-F system), in CCl_4 (for Fe-Cl system), in CBr_4 (for Fe-Br system) and in I_2 (for Fe-I system) were compressed to 50, 52, 40, and 35 GPa at home laboratory, respectively. Laser-heating was performed using in house laser heating setup equipped with two YAG lasers (1064 nm central wavelength). Pressure was determined using the equation of states (EOS) of Re, and additionally monitored by the Raman signal from the diamond anvils.

Results

The chemical reaction of iron and $C_{12}F_{10}$ at pressures of ~50 GPa and temperatures of ~3000°C led to the synthesis of a previously unknown polymorph of iron fluoride, orthorhombic (*Pnma*) FeF_3, with the unexpected coordination number (CN) 8 for iron.

The chemical reaction of iron and CCl_4 at pressures of ~52 GPa and temperatures of ~3000°C led to the synthesis of three previously unknown mix-valence iron chlorides: orthorhombic (*Cmcm*) Fe_4Cl_9 (CN(Fe^{3+}) = CN(Fe^{2+}) = 6), monoclinic (*C*2/*m*) Fe_3Cl_8 (CN(Fe^{3+}) = 6, CN(Fe^{2+}) = 7), and trigonal ($P\overline{3}1c$) Fe_3Cl_8 (CN(Fe^{3+}) = CN(Fe^{2+}) = 6).

The chemical reaction of iron and CBr_4 at pressures of ~ 40 GPa and temperatures of ~3000°C led to the synthesis of a previously unknown trigonal (*P*31*m*) polymorph $FeBr_2$ (CN(Fe^{2+}) = 6).

We weren't able to find any compounds, except for the initial precursors, in the cell containing Fe and I_2. The possible reason for this could be insufficient heating.

Reaction products were characterized by synchrotron SCXRD. Density functional theory-based calculations demonstrate the dynamic stability of all phases at the synthesis pressures. Charge distribution analysis revealed non-integer charges of iron in Fe_3Cl_8, indicating the fast charge transfer $Fe^{2+}\leftrightarrow Fe^{3+}$. A half-metal nature with strong dependency on spin orientation was shown for $FeBr_2$: it is a normal metal for one spin direction and semiconductor for the other and thus electrons near the Fermi level are of a unique spin character.

Thus, iron halides have already showed unexpected cristal chemistry under high pressure and their predicted physical properties seem to be very promising for various industrial application.

Conclusions

The aim of the experiment has been partially achieved, the Fe-*Hal* (*Hal* = F, Cl, Br, and I) system must be further studied at higher pressures in order to expand the field of new exotic iron halides. The publication is under preparation and the ID15 stuff will be included as a co-author.