

	Experiment title: Indium fluoride complexation and complex stability under hydrothermal conditions	Experiment number: ES 452
Beamline:	Date of experiment: from: 21.09.2016 to: 26.09.2016 and from: 29.11.2016 to: 02.12.2016	Date of report: 10.09.2017
Shifts: 15+9	Local contact(s): Denis Testemale	Received at ESRF:

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Report:

The high-T autoclave at beam-line BM30B-FAME was used to investigate the fluoride and chloride complexation of indium under hydrothermal conditions. The goal of the study was to identify the dominant complex geometries between room temperature and 500°C in the liquid phase using EXAFS on the In K α -edge at 27.940 keV. Pressure in the autoclave was set to 500 bar for all experiments to ensure vapor saturation. Energy scans were performed from 27.775 to 28.685 keV for all experimental runs. Transmission signal was used for the pellet reference materials whereas all solutions were analyzed in fluorescence mode. Precipitation of solids from the solutions, which leads to concentration reduction of In in solution was monitored with the transmission detector.

Several shifts on the originally planned beam-time (21.09.2016 - 27.09.2016) were lost due to a problem in the optics hutch that caused beam loss. The second beam-time session (29.11.2016 - 02.12.2016) was generously granted to finish the experiment.

Press pellets of In_2O_3 , $\text{In}(\text{OH})_3$, $\text{InF}_3 \cdot 3\text{H}_2\text{O}$ and InCl_3 in boron nitride matrix were used as reference materials. InI_3 pellets could not be prepared due to the extremely hygroscopic behavior of the material. A summary of the experimental conditions for the solutions is given in Table 1. Load numbers 1, 3, 4, and 7 were test loads to test and configure the setup and were not used to produce data. All experimental runs with the same composition were performed starting from the lowest temperature and increase in T stepwise after 4-6 spectra (depending on signal quality).

Table 1: Summary of experimental conditions for solution samples. Pressure was 500 bar and concentration of In was 0.03M for all experiments. Load 1-9 belong to the first, 10-13 to the second beam-time. Load 11 is the continuation of load 9.

Load number	Temperatures [°C]	F_{total} [M]	Cl_{total} [M]	I_{total} [M]
2	30, 100, 200, 300, 400	0.09	-	0.01
5	30, 100, 200, 300, 400	-	-	1.09
6	30, 100, 200, 300	1.09	-	-
8	30, 100, 200, 250	1.09	-	0.01
9	30, 100, 200, 250	0.10	0.10	-
10	30, 100, 200, 300, 400	-	1.09	-
11	300, 350, 400	0.10	0.10	-
12	30, 100, 200, 250, 300, 350, 400	0.50	0.10	-
13	30, 200, 400	0.10	0.50	-

Iodide was not expected to form complexes with indium and was therefore used as a non-complexing acidifying agent in some experimental runs. To test if this assumption was valid, 0.03M InI_3 + 1.0M hydrogen iodide (HI) solution was analyzed. Above 200°C strong iodide complexation was observed, at lower temperature solvation of the In^{3+} ion dominates. Despite the fact that iodide does complex with indium, it was decided to use 0.01M HI for acidification of the chlorine free experimental runs because iodide complexes are very easy to distinguish from fluoride complexes even at low concentrations due to the high mass of iodine. The EXAFS data suggest that no significant iodide complexation takes place at any temperature in runs with 0.01M HI and either 0.09M or 1.09M total fluoride. In the fluoride-rich system, complete precipitation of In from the solution, leading to complete loss of signal occurred at >200°C. All experimental runs were terminated after signal deterioration due to precipitation (250-400°C).

The EXAFS analysis showed that complexation of In^{3+} with fluoride and chloride is strongly temperature dependent (manuscript in preparation). Below 200°C fluoride is the dominant ligand in solutions with 0.1M F_{total} and 0.1M Cl_{total} , above 200°C it is chloride. Both ligands show smooth temperature dependence of ligand number and distance. This means that indium changes from being a hard Lewis acid at low temperature to a softer one at higher temperatures. This has drastic implications for interpretation of natural In-ore forming systems because cooling of a hydrothermal fluid. Complementary data on fluoride and chloride complexation as a function of temperature for cations that typically occur as minor metals in the same deposits as In, most importantly Ga and Ge is needed to develop a full quantitative ore formation model for these critical metals.