



Experiment Report Form



	Experiment title: Gallium fluoride and chloride complexation and complex stability under hydrothermal conditions	Experiment number: 30-02-1135
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Report:

The high-temperature autoclave at beam-line BM30B-FAME was used to investigate the fluoride (F) and chloride (Cl) complexation of gallium (Ga) under hydrothermal conditions using EXAFS on the Ga $K\alpha$ -edge at 10.367 keV. The goal of the study was to identify the dominant complex geometries as a function of temperature between room temperature and 500°C in the liquid phase using EXAFS. Pressure in the autoclave was set to 500 bar for all experimental runs to ensure vapor saturation. Energy scans were performed from 10.224 to 11.218 keV for all experimental runs.

Gallium oxide (Ga_2O_3) and Gallium metal were used as solid reference materials and analyzed in transmission geometry. The Ga_2O_3 powder was mixed with boron nitride (BN) and pressed to a pellet. The Ga metal was melted and spread in a thin layer over a Kapton foil, which works well due to the low melting point of Ga (29.8°C). The Ga_2O_3 pellet was also used as an energy reference standard in the subsequent measurements of the liquid samples, to monitor the beamline energy stability.

The experimental solutions were all loaded into the same glassy carbon cell for analysis. Chunks of Ga_2O_3 , which had been pressed to pellets and sintered at 1400°C for 30 minutes, were added to the solutions to determine the solubility of Ga_2O_3 in addition to the Ga speciation in solution. After initially slow dissolution kinetics for the first two solutions, the rest of the solutions were pre-saturated with Ga_2O_3 powder for several hours to ensure saturation at the lowest temperature of 30°C .

The following solutions were analysed (in this order):

- Pure water for temperature calibration of the autoclave
- 1.0M HCl (not pre-saturated), $30\text{-}400^\circ\text{C}$
- 3.0M HCl (not pre-saturated), $30\text{-}500^\circ\text{C}$
- 0.1M HCl (pre-saturated), $30\text{-}300^\circ\text{C}$
- 1.0M HF (pre-saturated), $30\text{-}400^\circ\text{C}$
- 1.0M HF + 0.1M HClO_4 (pre-saturated), $30\text{-}400^\circ\text{C}$
- 1.0M HClO_4 (pre-saturated), $30\text{-}400^\circ\text{C}$
- 0.5M HF + 0.5M HCl (pre-saturated), $30\text{-}300^\circ\text{C}$

The experimental runs with pure hydrochloric acid (0.1M, 1.0M, 3.0M) showed increasing solubility of Ga_2O_3 with increasing temperature. The solubility in the pure hydrofluoric acid runs was low and the EXAFS signal weak. According to preliminary data analysis, the solubility seems to decrease with increasing temperature. The lowest detectable concentration for Ga in this set-up is in the low ppm range.

In order to control the speciation of F in aqueous solution (associated HF or free F^-), pH should be set to low values. At $\text{pH} < 2$ it can be assumed that the dissolution reaction of Ga_2O_3 does not involve any F^- but only HF. Due to the strong complexation with chloride, using HCl for acidification of the HF runs was not suitable. Instead, 0.1M hydrochloric acid (HClO_4) was used, which increased the solubility over the pure HF solution. To test if HClO_4 has itself a complexing effect on the Ga^{3+} ion, a pure 1.0M HClO_4 solution was also tested. This solution produced very similar spectra to those of the 1.0M HCl solution.

Preliminary data analysis suggests an identical first shell environment around Ga in both cases. Other shells can not be interpreted with any confidence at this point. It is presently unclear if this similarity is due to Cl^- as the nearest neighbour to Ga^{3+} being identically positioned around the central cation in both cases. It is also possible that HClO_4 was reduced to $\text{HCl} + 2\text{O}_2$ by the glassy carbon of the experimental cell. Therefore usage of HClO_4 for acidification may not be optimal for future experiments despite being the most common method. Hydroiodic acid (HI) may be more suitable for experiments in glassy carbon environment due to its lower oxidation tendency at high temperatures. Moreover it is easy to distinguish iodide ligands from chloride due to their much higher mass.