



**Experiment title:**  
Solute Speciation in Green Recycling of GaAs and ITO

**Experiment number:**  
CH-3232

**Beamline:**  
BM26A

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**Shifts:**  
12

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*Received at ESRF:*

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**Report:**

EXAFS spectra were acquired for gallium, arsenic, indium and tin salts in the deep eutectic solvents Ethaline (ethylene glycol and choline chloride) and Oxaline (oxalic acid and choline chloride) as well as solid reference samples. Gallium arsenide samples were also measured with the addition of 30 mM, 300 mM or excess iodine. Spectra of iodine in both Ethaline and Oxaline were also obtained, along with potassium iodide as a solid reference sample.

The majority of the EXAFS data was of a high quality and generally glitch free. Useable EXAFS spectra for a total of 28 samples were obtained and speciation of the metal complexes could be determined from these. Liquid samples were investigated using fluorescence mode and solid samples were diluted in a boron nitride matrix and recorded in transmission mode. The speciation of gallium and indium was found to be dominated by chloride, while the speciation of arsenic was found to be dominated by oxide. The tin oxides did not produce spectra of sufficient quality at the given concentrations.

Metal-ligand distances are 1.8 Å for O and 2.2 to 2.5 Å for Cl, which is consistent with both the solid reference samples and with previous EXAFS data.

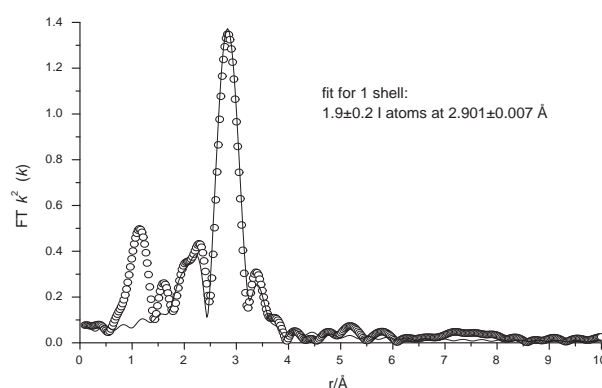
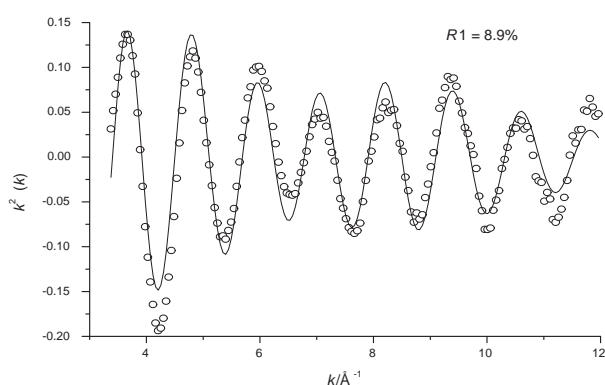
Tin chloride produced good spectra and these could be fitted with either a chloride or a mixed chloride-oxide shell. Both fits were of similar quality but the edge shifts indicated that there may be a pure chloride shell for low concentrations and mixed chloride/oxide shells for higher concentrations. We are currently further investigating trends in the edge shifts and will try to also verify our results with Raman spectra.

We have found that indium exhibits a pure chloride coordination shell in both Ethaline (CN=5) and Oxaline (CN=6). The coordination is higher in Oxaline however the two samples are not comparable as they are different salts.

Gallium is also seen to exhibit a pure chloride coordination shell in both Ethaline and Oxaline (CN=4). The use of iodine to chemically oxidise gallium metal into solution does not appear to significantly affect the speciation. As<sub>2</sub>O<sub>3</sub> shows a pure oxide shell in both Ethaline and Oxaline but in the oxidised GaAs sample a second shell (CN=1) was observed which could be fitted to chloride. Both of the As<sub>2</sub>O<sub>3</sub> in Oxaline samples showed radiation damage after measurement in the form of both burnt streaks and bubbles. Substantial steps in the EXAFS baseline meant that scans of the 20 mM sample could not be fitted.

We found that iodine does not act as a ligand for either gallium or arsenic when used as an oxidising agent. This is consistent with the electrochemical behaviour during recovery of the single elements via electroreduction.

Measuring the iodine K-edge was pushing the beam line limits, as it is outside of the specifications of the BM26A limit of 32 keV (the I K-edge is nominally at 33169 eV). Mirrors had to be re-aligned to allow the beam to pass at the required monochromator angle. However, data of reasonable quality could be obtained for iodine in Ethaline and oxialine. In Ethaline iodine was not coordinated by further ligands whereas Oxaline showed the presence of triiodide ions: In pure Oxaline we see a single coordination shell of two iodides (triiodide I<sub>3</sub><sup>-</sup> complex) which suggests that the iodine is oxidising the liquid. This is consistent with the much higher redox potential of iodine in Ethaline compared to Oxaline.



### EXAFS of the iodine K-edge of I<sub>2</sub> in Oxaline.

These results enable us to understand the parameters that influence the redox behaviour of the given compounds during recycling with respect to electrolytic and chemical oxidation as well as subsequent electroreduction of pure components. In particular the speciation of iodine and the knowledge of oxide or chloride based coordination shells provides key information for applications in the recycling of semiconductors.