Experimental report

27/09/2016

Proposal: **5-24-571**

Council: 4/2015

Title: Low temperature structural characterisation of nickel and copper hexa-ammine ammonia storage materials

Research area: Materials

This proposal is a new proposal

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Samples: [Ni(ND3)6](NO3)2
[Ni(ND3)6]Cl2
[Cu(ND3)6-x]Cl2

Instrument	Requested days	Allocated days	From	To
D20	2	2	19/10/2015	21/10/2015

Abstract:

We are applying for three days of beamtime to investigate the low temperature structures of the three potential ammonia storage materials [Ni(NH3)6]Cl2, [Ni(NH3)6](NO3)2 and Cu(NH3)6-x]Cl2 (resp. their deuterium analogues). The room temperature structures are of high symmetry (Fm-3m for the Ni compounds and I4/mmm for the Cu compound) and show considerable disorder with respect to the ammonia position (and nitrate for [Ni(NH3)6](NO3)2). The low temperature phase transitions are suspected to be due to ordering of the ammonia groups and are therefore best studied with neutron diffraction. Additionally, the multiple low temperature phases of nitrate have only been partially explored in previous studies. We aim to gain a deeper insight into the structure property relationships in metal ammines in order to tune their characteristics when employed as ammonia storage material.

Experimental Report for experiment 5-24-571 "Low temperature structural characterisation of nickel and copper hexa-ammine ammonia storage materials"

Introduction

It was the aim of this experiment to explore the nature of the low temperature phases of the hexa-ammine structures of $[Ni(NH_3)_6]Cl_2$, $[Ni(NH_3)_6](NO_3)_2$ and $[Cu(NH_3)_6]Cl_2$. This class of materials has gained a degree of interest in recent times, due to its potential utilisation as ammonia store.[1] Indeed, reversible gravimetric capacities of *ca*. 50 wt.% NH3 can be achieved with release at temperatures compatible with direct ammonia fuel cells. While the high temperature decomposition of these materials is thoroughly studied,[2] the knowledge of the low temperature behaviour is somewhat ambiguous beyond the fact that low symmetry low temperature phases exist.[3] It was therefore crucial to produce conclusive data on the phase transitions in these materials in order to define the exact nature of the lower temperature phases and to solve the crystal structures of the unknown phases. More specifically, our goal was first to determine the low temperature structures of $[Ni(ND_3)_6]Cl_2$ – the deuterated version of a highly promising ammonia store - in order to fully understand the structural and chemical behaviour at low temperature (especially below 173 K).[4] We secondly intended to characterise the crystallographic structures of the low temperature phases of $[Ni(ND_3)_6](NO_3)_2$ more fully and finally intended to study the sub-ambient behaviour of $[Cu(ND_3)_{6-\delta}]Cl_2$ which we had recently discovered to be tetragonal at room temperature. We wished, in this case, to comprehend the nature of the Jahn-Teller distortion as a function of temperature and (non-)stoichiometry.

Experimental work

The D20 experiment was successful. Single phase deuterated samples were produced *ex-situ* at Glasgow (using ND_3). Data were collected over the complete temperature ranges (17 data points, one every 15 K from 265-10 K with a pattern measurement time of *ca*. 0.5 h and a cooling rate of *ca*. 1 K min^{-1}) for each sample. Hence, all of the three compounds above were ramped down to *ca*. 10 K and reheated to room temperature in order to follow the respective phase transitions. All of the intended individual parts of the experiment were conducted comfortably within the time frame, which was facilitated by superb support from the local instrument team.

Results

A significant amount of data was collected from the experiments and many of these results are still under analysis at the current time. The known phase transitions for all three materials could be verified and the transition temperatures could be determined reliably. One of the main findings to date is that there is no evidence for a fourth low temperature phase in the $[Ni(NH_3)_6](NO_3)_2$ system as previously postulated in the literature.[5] While the previously known phases could be indexed and refined from this data to yield reliable models also including the hydrogen/deuterium sites, the lowest temperature structures of the different compounds are still unknown. This is due to a relatively large peak width and hence a low real-space resolution, which has made the indexing procedure complicated and extremely challenging. It is an ongoing effort in our group to develop a procedure for the indexing of these phases to eventually solve and refine the low temperature phases in the system. The results of this study, however tie in perfectly with our ongoing efforts to thoroughly characterise these potential ammonia stores and makes us confident, that the data collected at ILL will shortly be part of high impact publications of these materials following our initial work.[6]

References

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