

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office using the **Electronic Report Submission Application:**

<http://193.49.43.2:8080/smis/servlet/UserUtils?start>

Reports supporting requests for additional beam time

Reports can now be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.



	Experiment title: In situ studies of steam assisted synthesis on multicomponent mixed oxide molybdates	Experiment number: 26-01-901
Beamline: BM26A	Date of experiment: from: 01/06/11 to: 06/06/11	Date of report: 13/07/011
Shifts: 15	Local contact(s): Sergey Nikitenko	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): Dr Wim Bras, DUBBLE CRG, ESRF, Grenoble, France Vladimir Martis* DUBBLE, CRG, ESRF, Grenoble France /UCL, London, UK Prof G. Sankar, University College London, Dep. of Chemistry, London, UK HUSN-UBAYDA ISLAM* University College London, Dep. of Chemistry, London, UK Thomas DALEY* University College London, Dep. of Chemistry, London, UK		

Report:

Goals of the beamtime at BM26A were to carry a hydrothermal synthesis of Bi_2MoO_6 at various temperatures (below 200 °C) using the in situ cell as well as a capillary reactor for synthesising Bi_2MoO_6 precursor by steam. For a hydrothermal crystallization we used the in-situ hydrothermal cell. Combined XANES/XRD technique enabled us to follow changes in the structure during formation of γ - Bi_2MoO_6 . The XANES data were recorded every 5min, while sequentially recording XRD patterns for 30sec. Information from XANES data were not only used to monitor changes in the molybdenum environment but also to determine kinetic information on the crystallization process. We did a similar experiment last year, but we were able to use XANES data from only 3 out of 5 hydrothermal crystallization temperatures for kinetic analysis. The reason is that the γ - Bi_2MoO_6 at lower temperatures, for instance 120 and 130 °C, did not form.

The initial aim of the experiment was to collect XANES/XRD spectra from freshly prepared Bi_2MoO_6 gel followed by isothermal crystallization at higher temperatures, for instance 170, 120, 130 °C, for several hours. An example of a typical XANES spectra at Mo K-edge recorded during isothermal crystallization is shown in Figure 1. This figure shows a 3D stacked plot of Mo K-edge XANES recorded at 170 °C during the hydrothermal reaction. The first spectrum plotted in red is from freshly prepared Bi_2MoO_6 gel. We expected to see the distinct pre-edge peak which is a typical for tetrahedral coordination of molybdenum in the Bi_2MoO_6 gel at room temperature[1]. It should be noted that we used different source of molybdenum salt compared to previous studies[2, 3]. Nevertheless, the sample was brought to higher temperatures at which hydrothermal crystallizations occur. As you can see from Figure 1, there are no changes both in the pre-edge as well as the edge intensity. Two hours later, after the hydrothermal reaction should have reached completion, there were no features to indicate the formation of the desired phase, γ - Bi_2MoO_6 , either in the final XANES spectrum (blue) or in XRD patterns. According to our previous experiments we were expecting to see molybdenum in

octahedral coordination which is a typical for the γ - Bi_2MoO_6 . Poor quality of diffraction patterns also confirmed that the desired phase was not produced. Therefore, we prepared a new gel and repeated experiment both at the same as well as higher temperatures in order to avoid any uncertainties about the preparation method. In summary, our efforts to prepare new precursors did not succeed: we postulate that our source of molybdenum, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ bought from Sigma-Aldrich, was not suitable for this reaction. In our previous studies we used $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ from Fluka. Not being able to prepare Bi_2MoO_6 precursors we were not able to carry on with synthesising material by steam assisted process, as it was proposed in the proposal.

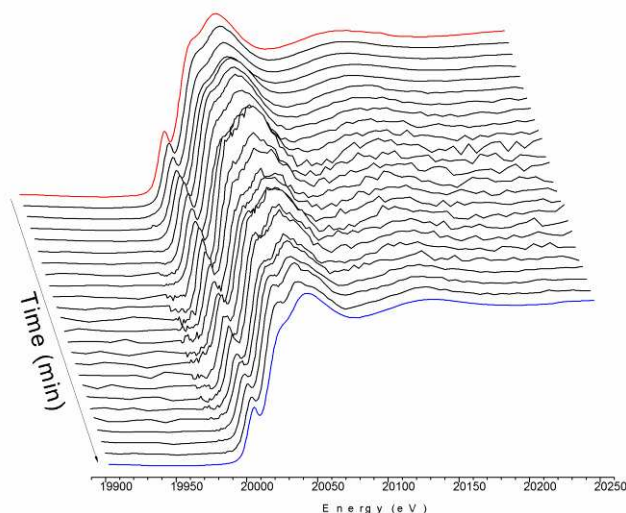


Figure 1 Stacked Mo K-edge XANES data recorded during hydrothermal crystallization of Bi_2MoO_6 gel at $170\text{ }^\circ\text{C}$ as a function of time. A XANES spectrum in red corresponds to freshly prepared gel at room temperature. A XANES spectrum in the blue should be final product of the reaction, γ -phase.

A separate investigation was performed to find evidence for the reactivity of bis(tetra-*n*-butylammonium) tetrakis[benzenethiolato- μ 3 -sulfido-iron] (4), an iron-sulfur containing cubane type structure, to carbon dioxide. The cubane cluster is found in nature on enzymes such as acetyl coenzyme-A and carbon monoxide dehydrogenase (CODH) which specialise in converting carbon monoxide organic molecules. The synthetic counterpart is an ideal candidate for potential catalysis. The cubane was first dissolved in acetonitrile and then bubbled with CO_2 for 30min, *ex situ* EXAFS spectra were taken before and after bubbling (Figure 2). A change in the higher atomic distances of the cubane with CO_2 strongly indicates the presence of an interaction. Modelling must be performed to understand the exact nature of the interaction.

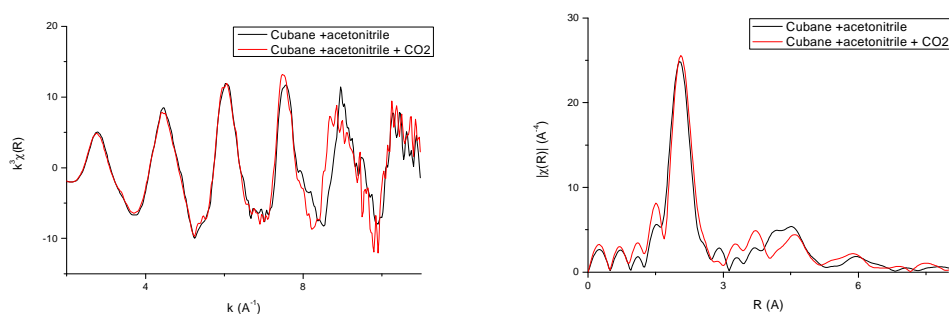


Figure 2 EXAFS data in k-space and R-space for the Fe K-Edge of bis(tetra-*n*-butylammonium) tetrakis[benzenethiolato- μ 3 -sulfido-iron] in acetonitrile (black) and bubbled with CO_2 (red).

References:

- (1) Kongmark, C.; Martis, V.; Rubbens, A.; Pirovano, C.; Lofberg, A.; Sankar, G.; Bordes-Richard, E.; Vannier, R.-N.; Van Beek, W. *Chemical communications* 2009, 4850-4852.
- (2) Beale, A. M., Sankar G. *Chem. Mater.* 2003, 15, 146-153.
- (3) Kongmark, C.; Martis, V.; Pirovano, C.; Löffberg, A.; van Beek, W.; Sankar, G.; Rubbens, A.; Cristol, S.; Vannier, R. N.; Bordes-Richard, E. *Catalysis Today* 2010, 157, 257-262.
- (4) Vanitha P. V.; O'Brien P. J. *Am. Chem. Soc.* 2008, 130 (51), 17256-17257