

First year 2007 Long Term Project report CH2234

The implementation of a simultaneous Raman-X-ray diffraction/absorption approach for the in situ investigation of solid state transformations and transitions at non ambient conditions.

Abstract of the original proposal:

X-ray diffraction (XRD) and absorption spectroscopy (XAS) are the principal techniques used to investigate long and short-range order of atoms and molecules in the solid state, respectively. The Raman technique, in contrast, has the ability to probe the length scale between these two extremes. The synergy between these methodologies has attracted application to many scientific studies where the Raman and XRD or XAS techniques have been performed *ex-situ*. The purpose of this LTP proposal is to marry these fundamental probes in the development of the first beamline station offering *in-situ* Raman spectroscopy combined with powder XRD or single crystal XRD or XAS. This new approach will open up many new avenues of research and offer vital new detail in the study of materials and solid state sciences. To develop and fully exploit the combined Raman and XRD/XAS techniques on the SNBLs requires the design, testing and application of new instrumentation such as dedicated *in situ* reaction chambers and non-ambient conditions sample environments, along with the commissioning of a suitable commercial Raman spectrometer. To facilitate this new initiative we are requesting beam time on the BM01A and B instruments. All manpower and ancillary equipment costs will be provided for by the consortium's research groups. This project constitutes a major development in synchrotron methodology and will be made available for future user applications and thus offering ESRF excellent value-for-money and world class new science. It is important to note that the aim of this project is to provide long standing support for combined Raman – XRD/XAS at the ESRF. In doing so, it is essential that a broad range of user needs are taken into consideration. The LTP is essential not only to provide the resources required for the project, but also to enable a number of representative users, who will be stationed at the ESRF for an extended period, to directly contribute to its development. These users have been carefully chosen to cover a wide range of experiments from zeolite and metal-organic framework chemistry to electronic properties of oxides and mixed valence polycyanides.

Abstract of the background to the original proposal:

This work has been organized from the start on in very close contact and agreement with the SNBL's management and staff. The proposal was also accepted by the SNBL review committee despite the fact that all consortium members are neither Swiss nor Norwegian. The beamtime requested to both committees was hence relatively modest compared to the vast planned experimental program. Both committees granted the beamtime and the full experimental program can be performed.

Main scientific achievements and dissemination of the results:

An almost full one-year experimental program has been performed in the last 6 month of the year, just after the installation of the novel Raman spectrometer on BM1a and b.

Four out of five User groups have come to carry out experiments. All experimental reports are included in this document. The remaining 5th experiment of the first round is planned in February 2008.

Two publications appeared from Consortium members out of the test case experiments performed prior to the LTP. One of these papers was awarded a front-page on PCCP. The work has also been presented at several international conferences with 2 oral and 1 poster presentations.

Paper 1

In situ simultaneous Raman/high-resolution X-ray powder diffraction study of transformations occurring in materials at non-ambient conditions

Enrico Boccaleri, Fabio Carniato, Gianluca Croce, Davide Viterbo, Wouter van Beek, Hermann Emerich and Marco Milanesio
J. Appl. Cryst. (2007). **40**, 684–693.

Paper 2

X-Ray induced radiation damage in taurine: a combined X-ray diffraction and Raman study

Beukes, F. Mo and W. van Beek
Phys. Chem. Chem. Phys., 2007, 9, 4709. DOI: 10.1039/b703000b



J. A.

Congress presentation

2007 ACA Annual Meeting Salt Lake City, Utah In Situ Simultaneous Raman and High-Resolution X-ray Powder Diffraction X-ray Powder Diffraction Study of Transformations Occurring in Materials at Non-Ambient Conditions. D. Viterbo^a, E. Boccaleri^a, M. Milanesio^a, F. Carniato^a, G. Croce^a, W. van Beek^b, H. Emerich^b, ^aDISTA, Univ. del Piemonte Orientale, Alessandria, Italy, ^bSwiss-Norwegian Beamlines, ESRF, Grenoble Cedex, France.

2007 24 th ECM Marrakech Surface vs. bulk kinetics in a solid-state reaction by Raman/XRPD experiment
D. Viterbo

2007 1st Meeting of the Italian and Spanish Crystallographic Associations (MISCA) Copanello di Stalettì (Italy) “Surface vs. bulk kinetics in a solid-state reaction by Raman/XRPD experiment” D. Viterbo

2008 XXXVII Meeting of the Italian Chemical Society, Chemical Physics Camogli (Genova, Italy) “Investigating surface vs. bulk kinetics in a solid-state reaction by Raman/XRPD experiment” M. Milanesio

Combining Raman and X-ray based techniques workshop (ESRF, Grenoble, France): a workshop is planned for June 2008, We will communicate to the USER communittee the results obtained and new experimental opportunities. Participants from other European synchrotrons will also present thier results.

2007 Experiment reports

Experimental report 1 from July 4th to 10th, 2007

Marco Milanese, Enrico Boccaleri, Sumeet Kumar, Fabio Carniato, Sarah Ferretti, Gianluca Croce, Diego Cerri, Ferdinando Constantino, Daniela Gastaldi

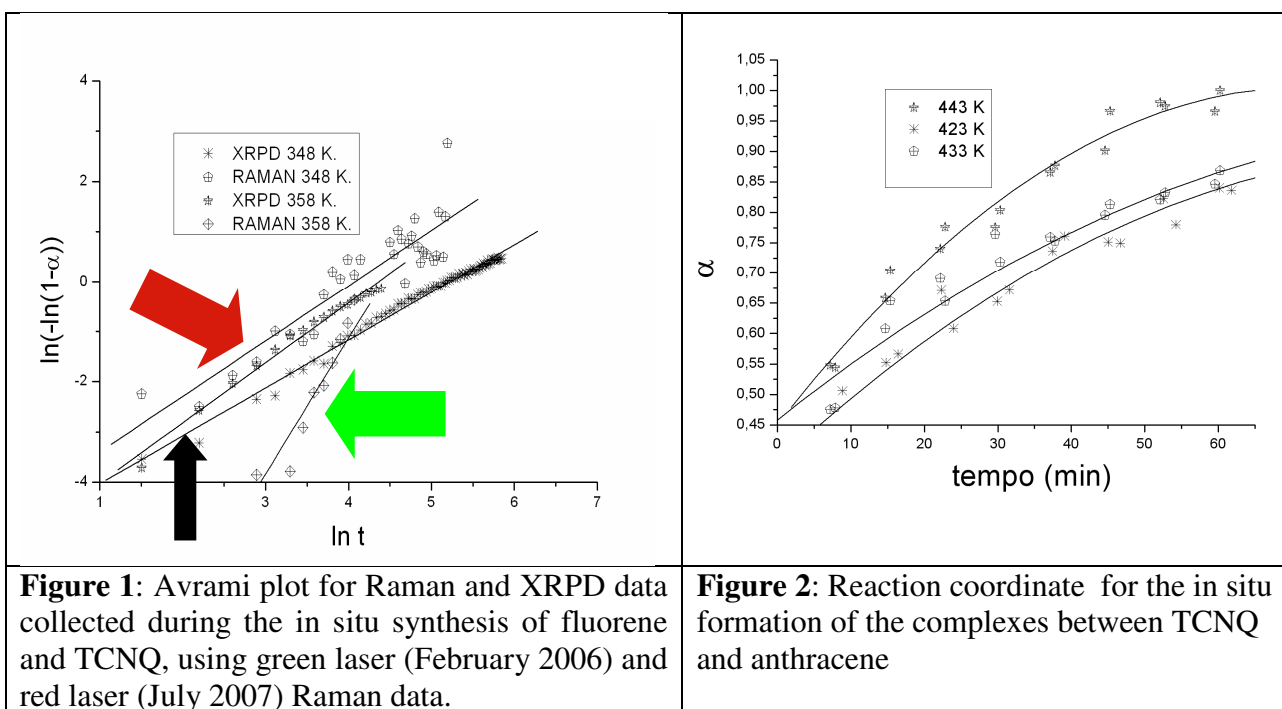
During July 2007 beam time three experiments were carried out:

- 1) In situ synthesis of molecular complexes of naphthalene, fluorene and anthracene
- 2) In situ UV-induced photodimerization of N-acethyl indolone
- 3) In situ study of the decarboxilation of inorganic zirconium aminophosphonates

The first two represent the continuation and full implementation of the test experiments in february 2006 (prior to LTP), while exp. 3 is fully novel one.

1) In situ synthesis of molecular complexes of naphthalene, fluorene and anthracene

From the methodological point of view, the more interesting results resulted from test case 1, where the analysis of the Raman and XRPD is almost complete. In particular the obtained data allowed to demonstrate that the Raman probe is more sensitive to surface phenomena and from the quantitative analysis of the Raman peak positions and intensities the kinetics of the initial stages of the reaction at the crystal surface was obtained. From this point of view it is interesting that the bulk-surface complementarities between XRPD and Raman are fully exploited only if the green (532 nm) laser Raman is employed.



In fact, the comparison of XRPD and Raman data for the reactions at 348 K and 358 K indicated that XRPD data and red laser Raman data have the same slope in the kinetic analysis by the Avrami equation, while the green laser Raman data have a different slope, indicating a larger reaction order and therefore faster reaction at the surface (a paper is ready for submission).

Concerning the chemical results of the experiment it was demonstrated that the ideal reaction temperature with TCNQ is related to the melting points of the two reactants, thus resulting in the order naphthalene < fluorene < anthracene (Figure 2).

2) *In situ* UV-induced photodimerization of *N*-acethyl indolone

In a similar fashion to the previous experiment, it has been seen that the green laser Raman data are more sensible to surface reactivity also in the case of the *in situ* UV-induced photodimerization of *N*-acethyl indolone. The analysis of the data is currently under development, but it is demonstrated that the collected data allowed to establish the structure of the elusive transition state envisaged by some of us (M. Milanesio et al., *J. Org. Chem.*, 65, 2000, 3416-3425) but resistant to all *ex situ* attempts of investigation. A first green laser Raman/XRPD *in situ* study, employing fast reaction conditions (E. Boccaleri et al., *J. Appl. Cryst.*, 2007, 40, 684-693, data collected during test phase in February 2006 before LTP) allowed the characterization of the reaction at the surface and the identification of two intermediate states. Then the experiment was repeated (July 2007 during LTP) but with slow reaction condition and employing the red laser, to obtain the characterization of the reaction at the molecular and interaction level in the bulk of the crystallites. It was possible to i) obtain one intermediate phase alone (indeed mixed with the reactant because of the slow reaction conditions), ii) identify its cell and attempting solving the structure (analysis under development).

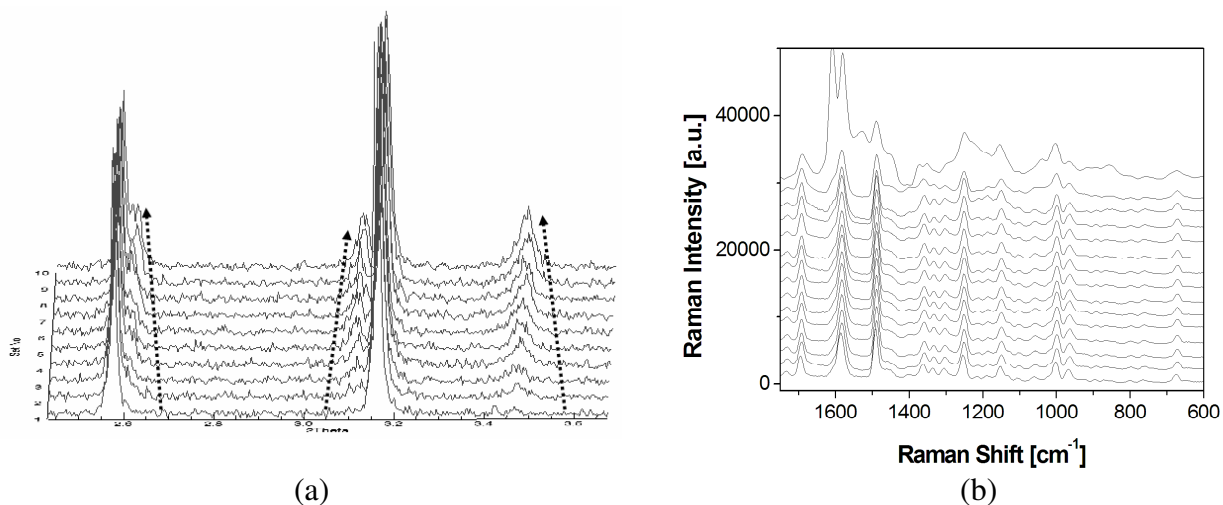


Figure 3: XRPD (a) and Raman (b) data during *in situ* growth of the intermediate phase of the photodimerization product.

3) *Decarboxylation of layered zirconium aminophosphonates*

Layered zirconium phosphonates are extensively studied, because of their good versatility in building up tailor made compounds in which the structure and the chemical reactivity can be tuned by the right

choice of the pendant organic groups, placed in the interlayer region. Recently, we developed a new class of layered zirconium diphosphonates by reaction of zirconium fluoro complexes with amino-N,N-bis(methyl)phosphonic acids, of general formula $R-N(CH_2PO_3H_2)_2$, with R = *n*-alkyl or aromatic groups.

The *in situ* structural characterization, using combined diffraction, spectroscopic of a new layered zirconium aminomethyl diphosphonate, containing hexanoate groups in the interlayer region was carried out to study the preparation process. The investigated compound has formula $ZrF(O_3PCH_2)_2NHC_5H_{10}COOH$. Due to the presence of carboxylate groups this compound can easily intercalate long-chain polar organic molecules in the interlayer region, and can be even exfoliated with the formation of stable colloidal dispersions of single lamellae of nanometric dimension. This feature opens up interesting prospects for application as fillers for polymer nanocomposites and then the crucial step of decarboxilation was studied by *in situ* Raman/XRPD experiment.

When heated this compound shows a phase transformation with a remarkable reduction of its interlayer distance, due to the loss of 1 mol of HF/mol of compound and to a change in the zirconium environment.

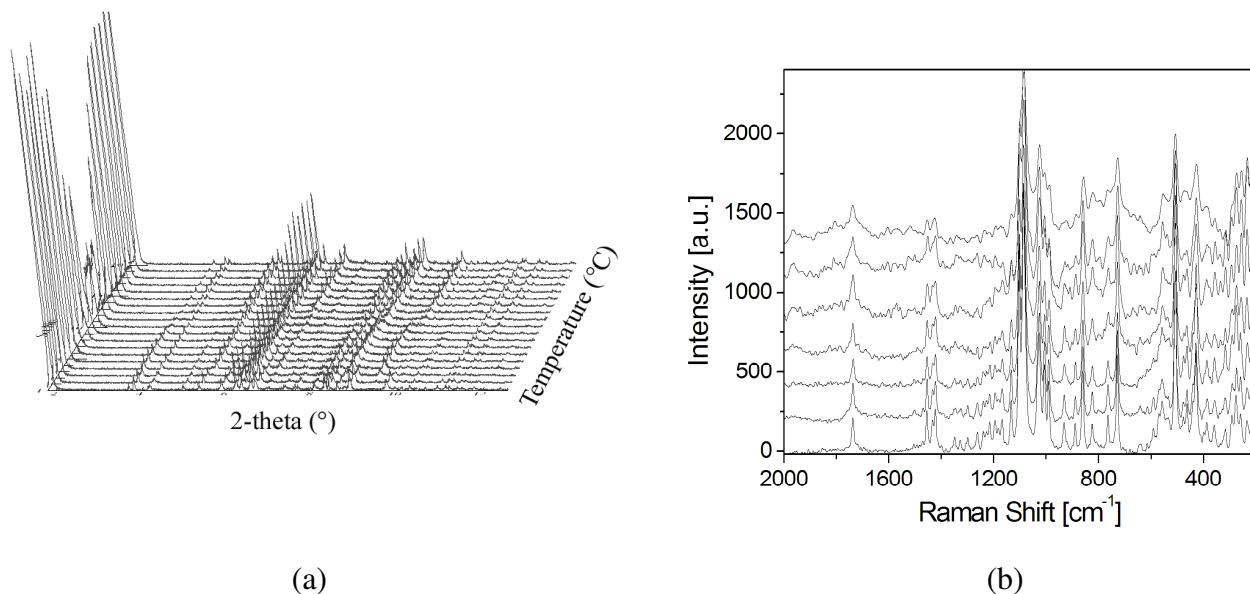


Figure 4: *in situ* high resolution XRPD (a) and Raman (b) data of $ZrF(O_3PCH_2)_2NHC_5H_{10}COOH$

Experimental report 2 from 30 October 2007 to 6 November 2007

Mark Green, Dewi Lewis, Wouter van Beek, Pawel Zajdel, Mohamedally Kurmoo, Louisa Marleny Rodriguez Albelo

By combining Raman spectroscopy and X-Ray diffraction, our project aimed at obtaining the correlation between the local (Raman) and long range (XRD) structural properties in many different classes of materials. During the allocated beamtime we have studied 36 different compounds including 4 molecular magnets, 4 novel lanthanide metal organic frameworks (MOF), 4 natural zeolites, a novel ionic conductor, spinels and other transition metal based MOFs. The Raman spectra

were recorded using two lasers - red (785nm) in case of spinel and low temperature scans of MOF, and green (532nm) in other cases. At the end 3732 powder patterns were recorded, accompanied by similar number of Raman spectra in the wide range of temperatures 80K-850K.

First part of the experiment concerned the unusual thermal expansion observed in $ZnCr_2Se_4$, which is a geometrically frustrated magnet. While the known magnetic and structural phase transition is observed at 21K, system starts to deviate from linearity at much higher temperatures. Fig 1. The characteristic temperature at which the system goes to zero and then negative thermal expansion is around 100K. Unfortunately the sample has been affected by the both Raman lasers, which was manifested by the appearance of the second phase. We didn't expect such behaviour since the sample was tested off line with higher applied power and this fact is still under investigation.

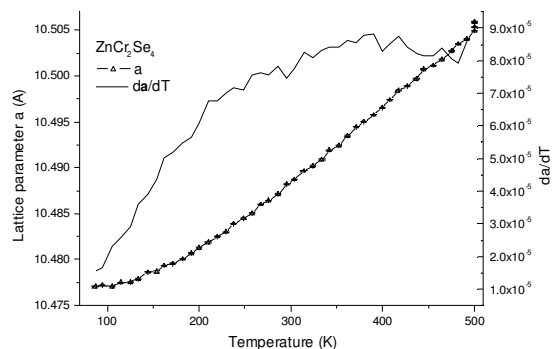
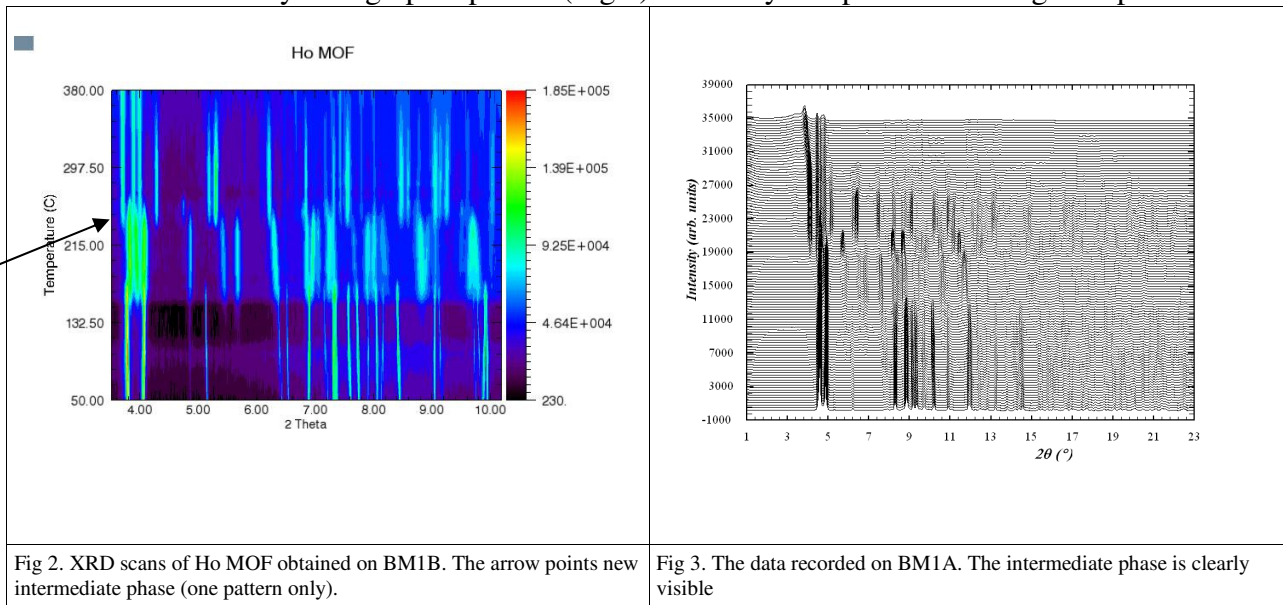


Fig 1

The second part concerned the continuation of the studies from last year of novel lanthanide based MOFs. Previous data for holmium based MOF were recorded with large temperature steps and showed 5 different crystallographic phases (Fig 2) with only one pattern showing new phase.



During this year session we continued this investigation obtaining better scans in the region of the intermediate phase confirming its presence (Fig 3). The corresponding Raman spectra will be used to identify the solvent content in the new structure.

Contrary to the Ho MOF case, its yttrium based counterpart doesn't show this extra phase, which is visible on the fig 4. That suggests that the system comes directly from the structure with one solvent molecule per formula unit to the empty one. The solvent content will be compared with the corresponding Raman spectra, which are presented on Fig 5. The large signal around 3600 cm^{-1} comes from solvent molecules which are lost during heating.

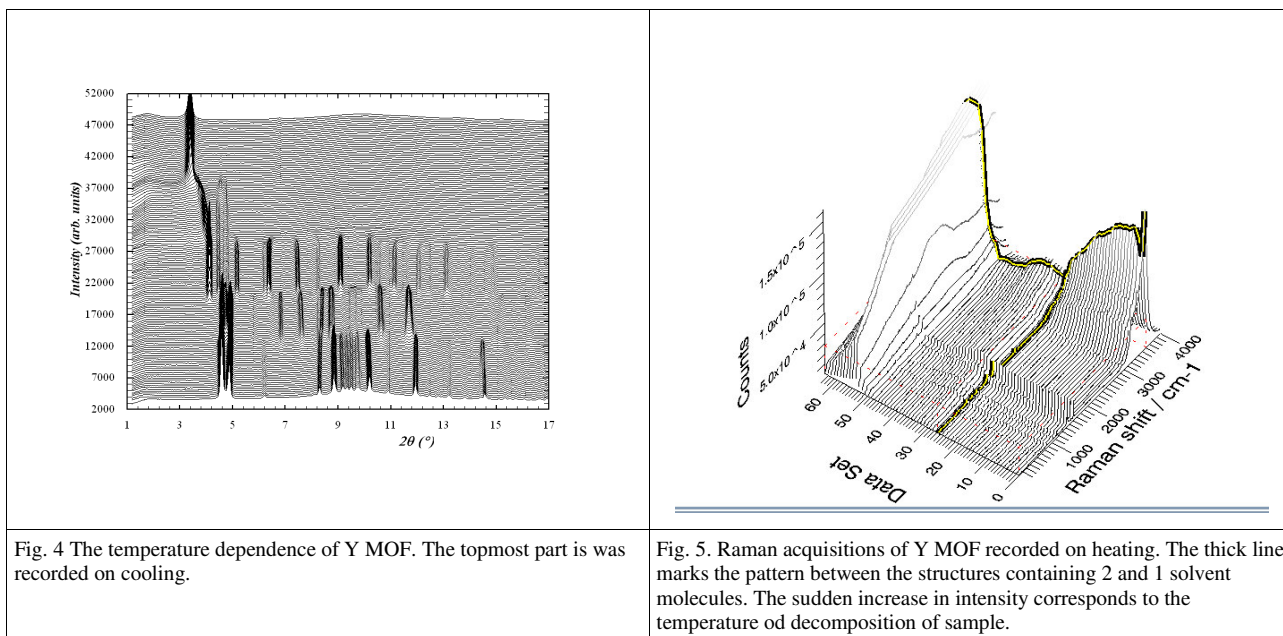


Fig. 4 The temperature dependence of Y MOF. The topmost part is recorded on cooling.

Fig. 5. Raman acquisitions of Y MOF recorded on heating. The thick line marks the pattern between the structures containing 2 and 1 solvent molecules. The sudden increase in intensity corresponds to the temperature of decomposition of sample.

The other case addressed in our study was the temperature stability of the MOFs. As was observed earlier, the single crystals were destroyed while going under 150K. This year powder diffraction study showed that the crystal structure is preserved down to 80K and back to 500K. This is very promising result since this temperature range is optimal to perform gas storage studies on our materials.

Experimental Report 3 on the experiments carried out during the beam time at BM01b from 1/12/2007 to 10/12/2007

Gopinathan Sankar, Wouter van Beek, Vladimir Martis, Martin Martis, Channapa Kongmark, Kerry Simmance, Chris Wright and Cristian Spadoni

We carried out several experiments during this beam time using combined high-resolution powder diffraction (HRPD), X-ray absorption spectroscopy (XAS) and Raman spectroscopy (RS). The aim of the project is to study dense and open frame structures, *in situ* during solid-state transformation and formation under hydrothermal conditions. The following systems were studied.

1. Solid-state transformation of dense framework oxides: Bismuth molybdate, when present in γ - γ' - γ'' phase undergoes transformation from γ - γ' - γ'' phase when heated between 550 and 750°C. We loaded our samples in quartz capillaries and heated using the gas-blower system available at SNBL. Mo K-edge XANES and HRPD were collected sequentially while heating the sample as well as when held at specific temperatures of 550, 600, 625, 650, 675, 700 and 750°C. Raman spectra were collected continuously to follow the changes in Mo environment which complement the XANES results. Similarly, we followed the transformation of CoMoO_4 from α to β phase during the heat-treatment between 300 and 550°C. In this case both Co and Mo K-edge XANES and EXAFS were collected below and above the transition temperatures. Raman spectra were collected when the temperatures were held. Palladium (10%) containing

CaTiO₃ perovskite catalyst was studied during calcination from room temperature to 950°C to follow the segregation of Pd and transformation of PdO to Pd metal.

2. Formation of nanoporous aluminophosphate materials: We followed the formation of large pore aluminophosphate material, AlPO-5 using two different organic templates and in presence of cobalt and zinc to understand the kinetics of formation and at the same time follow the changes in the coordination environment of the metal ions using XANES/EXAFS as well as the changes in the conformation of the organic amine molecule during the formation of microporous structures. We conducted all the experiments at 170°C, under hydrothermal conditions. We also maintained the pH of the starting material at 7 and varied the template and metal ion type to follow the formation of AlPO-5. The results suggest that, irrespective of the metal ion type, when we use methyl dicyclohexylamine, only large pore AlPO-5 structure is formed. When tetraethylammonium hydroxide is used as organic structure directing agent, AlPO-34 structure competes and both phases are formed. Initial analysis suggests that small pore is formed first and the large pore is formed later. However, the full-width at half maximum of the first two reflections suggests that large pore material (AlPO-5) grows into a large crystal with time while the small pore material remained as small particles.
3. Formation of dense framework structures: We also followed the formation of dense framework structures, Bi₂MoO₆ and CoMoO₄ under hydrothermal conditions. We prepared the gel just prior to the experiment and loaded the gel into the cell. The heater block was held at specific temperatures (between 150 and 180°C) and hydrothermal cell containing the gel was inserted and the measurements were started immediately. During the first 20 minutes (depending on the temperature) broad reflections in the XRD are seen between the 2θ range of 8 and 12. These reflections appear to decrease and new peaks appear which correspond to, for example γ-Bi₂MoO₆ phase. At the same time, Mo K-edge XANES showed conversion from tetrahedrally coordinated Mo(VI) to octahedral one. Raman spectroscopy also showed appearance of new bands which support the formation of the specific dense framework structures.

In summary, we successfully performed several in situ combined HRPD/XAS/Raman spectroscopy experiments during the beam time. This experiment was conducted just before the LTP reporting deadline. The data analyses are in progress to extract in-depth structural information on these materials. Concerning our contribution to the LTP we identified through this experiment the necessary modifications for a suitable hydrothermal in-situ cell capable of combining all three techniques. This modified cell will be constructed next year.

Status of the project:

First year results:

The funding for the Raman instrument has been obtained by the SNBL staff in late 2006 and mid 2007.

Instead of testing the portable instrumentation against a research grade spectrometer especially adapted for remote measurements has been ordered and installed. The installation and beamline integration has been done in June 2007. Obviously this is a major step forward in this project and was originally only foreseen for the second year. Four out of five experiments have been performed in the second half of the first LTP year. This enabled us to already start streamlining experiments. Data has been collected combining 4 different X-ray instruments, 1 Raman spectrometer with two excitation sources and a full range of different non-ambient conditions, thus fulfilling all milestones from the original proposal.

During this first year a capillary micro reactor has been developed as well as gas loading systems.

Three scientists for the LTP consortium have been staying at SNBL for extended periods. They have developed software for a fast analysis of the large amount of the X-ray and Raman data collected in the in situ experiments. Gained experience and know how has been shared and transferred to the permanent beamline staff.