

Second year 2008 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.

Scientific achievements:

Three out of five User groups have come to carry out experiments. All experimental reports are included in this document. The fourth group had received more time during the first year and the remaining 5th experiment of the second round is planned in February 2009.

Four publications are in preparation or under revision from Consortium members out of the experiments performed during the first and second year of the LTP. The work has also been presented at several international conferences with numerous oral presentations.

Paper 1:

S. Kumar, F. Carniato, A. Arrais, G. Croce, E. Boccaleri, L. Palin, W. van Beek, M. Milaneseo, *Investigating surface vs. bulk kinetics in the formation of a molecular complex via solid-state reaction by simultaneous Raman/X-Ray powder diffraction*, Accepted for publication by *Crystal Growth & Design*

Paper 2:

F. Carniato, M. Milaneseo, E. Boccaleri, L. Marchese, W. van Beek, G. Croce, *The Role of the Conformational Mobility and Disorder of the Aliphatic Chains in the Triclinic-Rombohedral Phase Transition of the Isobutyl Silsesquioxane.*, In preparation for submission.

Paper 3

Manuel Sanchez del Rio, Enrico Boccaleri, Marco Milaneseo, Gianluca Croce, Wouter van Beek, Constantinos Tsiantos, Georgios D. Chyssikos, Vassilis Gionis, George H. Kacandes, Mercedes Suarez, Emilia Garcia-Romero, *A combined synchrotron powder diffraction and vibrational study of the thermal treatment of palygorskite-indigo to produce Maya blue*, In preparation for submission

Paper 4

Chanapa Kongmark, Vladimir Martis, Annick Rubbens, Caroline Pirovano, Axel Löfberg, Wouter Van Beek, Gopinathan Sankar, Elisabeth Bordes-Richard, and Rose-Noëlle Vannier
Elucidating the genesis of a catalyst by combination of synchrotron radiation experiments and Raman spectroscopy: Application to Bi₂MoO₆., Submitted to *Angewandte Chemie*.

Congress presentation

1. M. Milanesio, G. Croce, F. Carniato E. Boccaleri, D. Viterbo, W. van Beek, II International Workshop Layered Material: Structure and Properties, March, 28th-29th 2008 Vercelli (oral presentation).
2. M. Milanesio, Davide Viterbo, Enrico Boccaleri, Wouter van Beek In situ simultaneous Raman/XRPD study of solid-state reactions at non-ambient conditions, XXI Congress of the International Union of Crystallography, Osaka (Japan), August 23rd -31st 2008 (Oral presentation).
3. M. Milanesio, G. Croce, S. Kumar, L. Palin, D. Viterbo, W. van Beek Full implementation of the in situ simultaneous Raman/ X-ray Powder Diffraction setup: methods and applications, 1st SIMP-AIC Joint Meeting, Sestri Levante (Genova) September 7th -12th 2008 (Oral presentation).
4. M. Milanesio, F. Carniato, G. Croce, S. Kumar, L. Palin, W. van Beek, D. Viterbo, E. Boccaleri, In Situ Simultaneous Raman and High-Resolution X-ray Powder Diffraction Study of Transformations Occurring in Materials at Non-Ambient Conditions, XI EPDIC Conference, Warsaw (Poland), September 1th-22th 2008 (oral presentation).
5. M. Milanesio, Invited seminar at PSI (Villigen, Switzerland): In situ Simultaneous Raman/<High-Resolution X-ray Powder Diffraction> Study of Transformations Occurring in Materials at Non-Ambient Conditions, December 5th 2008.

SNBL Workshop on 18th and 19th of June 2008 at the ESRF (Grenoble, France)

A workshop has been organized to highlight the possibilities of the combined and/or simultaneous multi-technique approaches: “Simultaneous Raman-X-ray diffraction/absorption studies for the *in situ* investigation of solid state transformations, and reactions at non ambient conditions”. More than 70 people attended.

*The workshop was focused on 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 attracted application to many scientific studies where the Raman and XRD or XAS techniques have been previously performed *ex-situ*. SNBL has a long record in combining HRPD and XAFS methods. The recent results obtained with the aid of Raman spectrometers available at SNBL have also been described in different presentations by the LTP members.*

1. W van Beek Experimental opportunities, examples and equipment available for combined in-situ studies at SNBL
2. M. Milanesio In situ simultaneous Raman high resolution X-ray powder diffraction study of transformations occurring in materials at non ambient conditions SNBL workshop on simultaneous Raman-X-ray diffraction/absorption studies for the in situ investigation of solid state transformations, and reactions at non ambient conditions
3. Jens Kreisel The effect of high-pressure on functional ABO₃ perovskite-type oxides
4. Dewi Lewis Structure and Dynamics of water in confined pores - dehydration effects in natural zeolites

2008 Experiment reports

Experimental report experiment July 2008

Marco Milanese, Enrico Boccaleri, Sumeet Kumar, Gianluca Croce, Marco Taddei, Daniela Gastaldi, Wouter van Beek

During July 2008 beam time four experiments were carried out:

- 1) In situ study of the decarboxilation of inorganic zirconium aminophosphonates
- 2) In situ Study of the thermal treatment of palygorskite-indigo to produce Maya blue
- 3) In situ study of the thermal stability and degradation of hydrotalcite-based materials
- 4) In situ study of the phase transition of $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Co}][\text{SbF}_6]$.

The first experiment represents the continuation and completion of the experiments in July 2007, while exp.2-4 are fully novel ones.

1) Decarboxilation 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-bismethylphosphonic acids. 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. 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.

In July 2007 the in situ structural characterization, using combined diffraction, spectroscopic of a new layered zirconium aminomethyl diphosphonate, containing caproic acid into interlayer region was carried out to study the preparation process. In July 2008 the study was extended to analogous derivatives containing molecule of different length and shape (proline and glycine) into the layer to exhaustively investigate the organic moiety effect on the synthesis process.

2) In situ Study of the thermal treatment of palygorskite-indigo to produce Maya blue

The Maya blue pigment has attracted the attention of many research groups in the last years. In addition to the continuous interest in the cultural, historic, ethnologic and archaeological aspects of this pigment, a debate has been opened on the structural and chemical aspects of this organo-clay pigment. This compound was synthesized in situ at the SNBL and investigated by Raman and XRPD.

A mixture of indigo and palygorskite has been heated from room temperature to 200° C to allow the interaction between the colorant and the clay to form the Maya blue pigment. The heating process has been performed at *in situ* conditions monitoring the reaction by synchrotron radiation powder diffraction and RAMAN spectroscopy at the same time. The results show that main changes in the indigo molecular structure (revealed by RAMAN) occurred during the partial release of zeolitic water in the 80-120 C interval. The zeolitic water release in palygorskite is accompanied by a reduction of the *a* lattice parameter (XRPD data). This behaviour, similar in the indigo-palygorskite complex and in raw palygorskite, leads to the hypothesis that the indigo molecules are trapped at the entrance of the tunnels,

and allows the understanding of the preparation process of this compound interesting the field of archeometry.

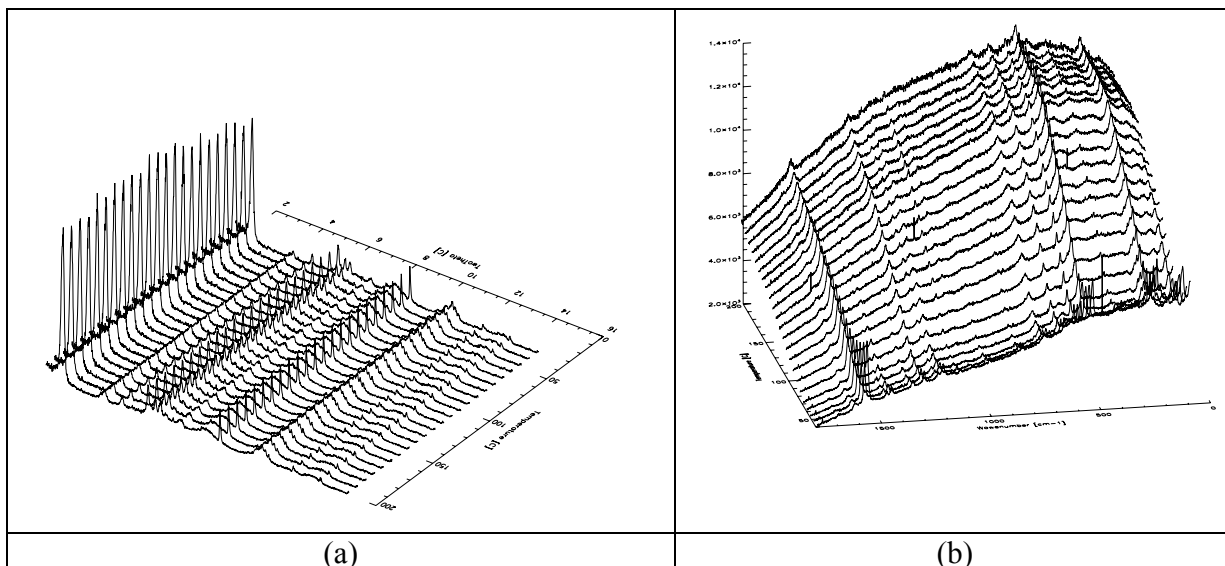


Fig 1. X-ray (a) and Raman (b) data recorded as a function of the temperature for palygorskite and indigo (1% wt).

3) *In situ* study of the thermal stability and degradation of hydrotalcite-based materials

Hydrotalcite (HTLc) based materials resulted interesting because of their inorganic nature and capability to intercalate various organic molecules into the layered structure. Various HTLc's containing lanthanides and/or coumarin were synthesized and measure *in situ* from RT to 700K. XRPD data allowed to follow the contraction/expansion and destruction of the inorganic part, while Raman data gave information of the the transformation degradation and elimination of te horganic moieties.

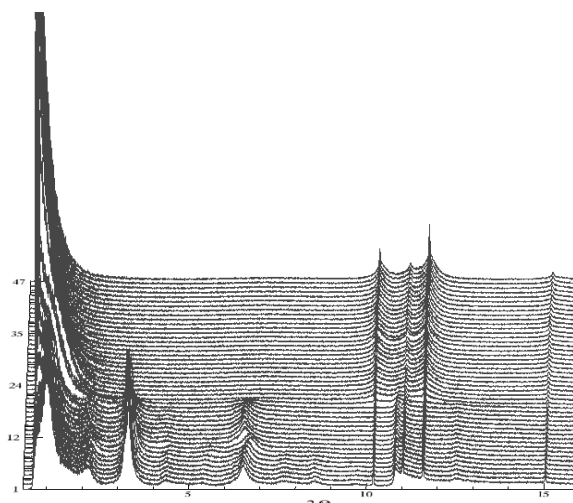


Fig 2. X-ray data recorded as a function of the temperature for coumarin-containing HTLc.

4) *In situ* study of the phase transition of $[(\eta^5-C_5H_5)_2Co][SbF_6]$

Cobaltocinium antimoniate compound are interesting for the investigation of weak CH---F interaction.

A phase transition occurs at 363 K and the breaking of these interactions was observed. XRPD gave information on the long-range structural change while Raman gave information at the interaction level, by monitoring the vibrational model related to the moieties involve dinto these intecations.

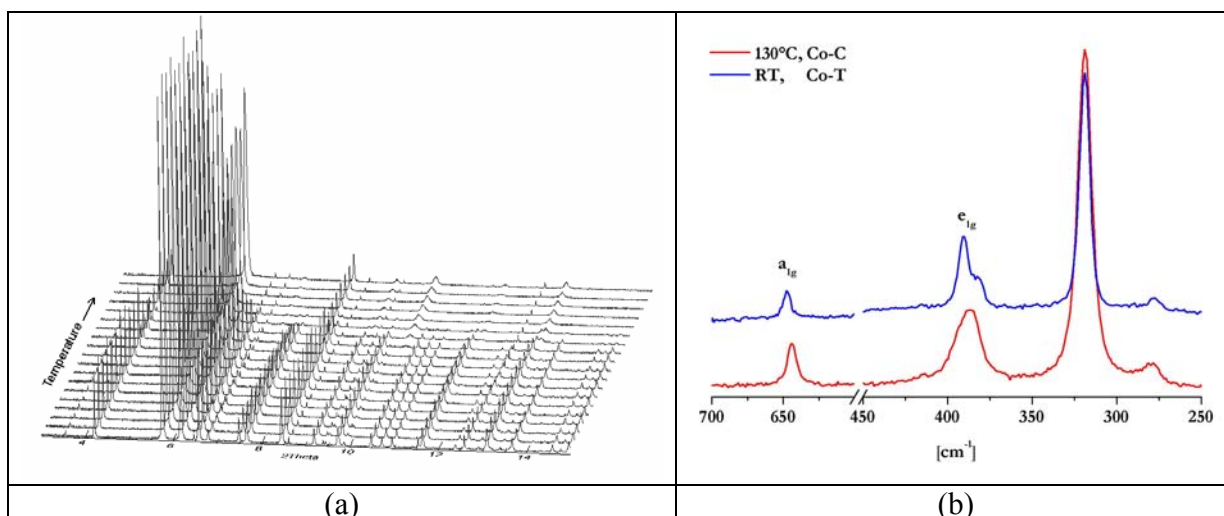


Fig 3. X-ray (a) and Raman (b) data recoded as a function of the temperature for coumarin-containing $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Co}][\text{SbF}_6]$.

Experimental report 2 September 2008

Ping-Yen Hsieh, Wouter van Beek, Pawel Zajdel and Mark Green

This central goal of this project was to study a series of lanthanide metal-organic framework materials by *in-situ* synchrotron X-ray and Raman spectroscopy, with the objective to elucidate the variation in chemical and physical properties as a function of

- (i) various kinds of *f*-orbital metals
- (ii) different molecular structures as a result of variable organic linkages such as benzenedicarboxylic acid (BDC), 1, 3, 5-benzene-tricarboxylic acid (BTC) and 1, 3, 5 -tris(4-carboxyphenyl)benzene (BTB).

We have determined the detailed crystal structures by single crystal X-ray diffractometer prior to the experiment so that we can focus on the thermal stability with and without gas loading. A summary of the experiments performed are given in the table below. Two example of this work are given below to highlight the opportunities offered with combined X-ray/Raman analysis to this field:

(A) Thermal Stability of Holmium Metal-Organic Frameworks as a Function of Organic Linker.

A comprehensive examination of various Ho-MOF systems with different ligands were evaluated (Fig. 1~3.) and clearly demonstrates a higher temperature structure stability for Ho-MOF up to 250°C with BTC ligand (fig. 4) that is absent in the Ho-MOF with BDC and BTB systems. The stability of the structure is strongly influenced by the architecture between central metals and organic linkers. The origin of which is currently under investigation through the analysis of the X-ray and Raman patterns

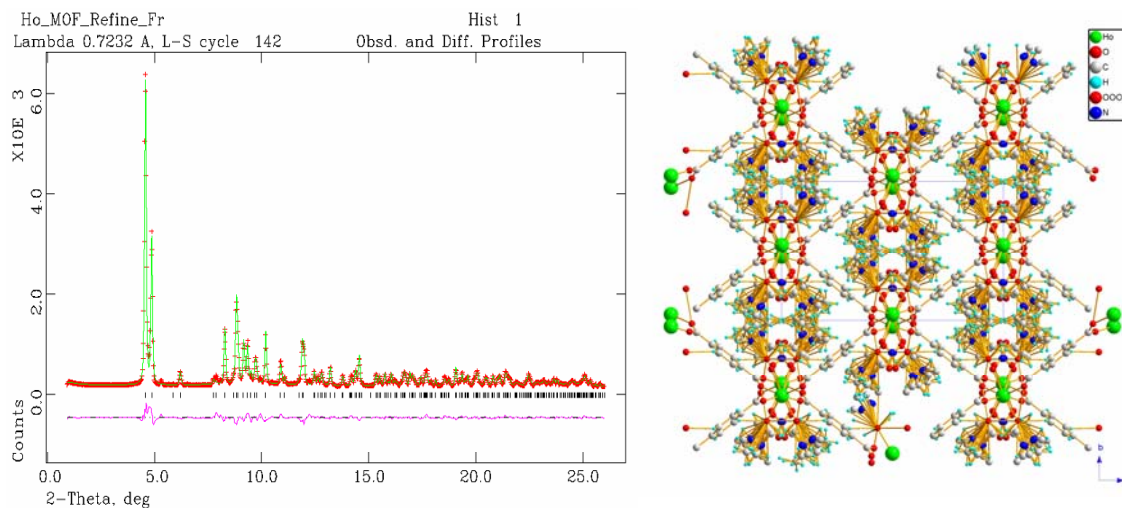


Figure 1. Ho-MOF-BDC molecular structure and XRD

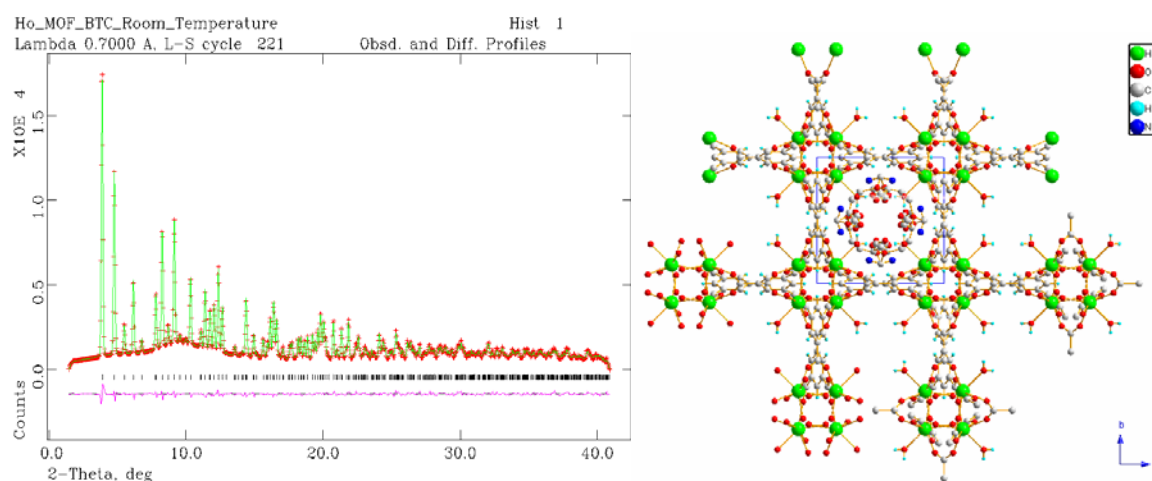


Figure 2. Ho-MOF-BTC molecular structure and XRD

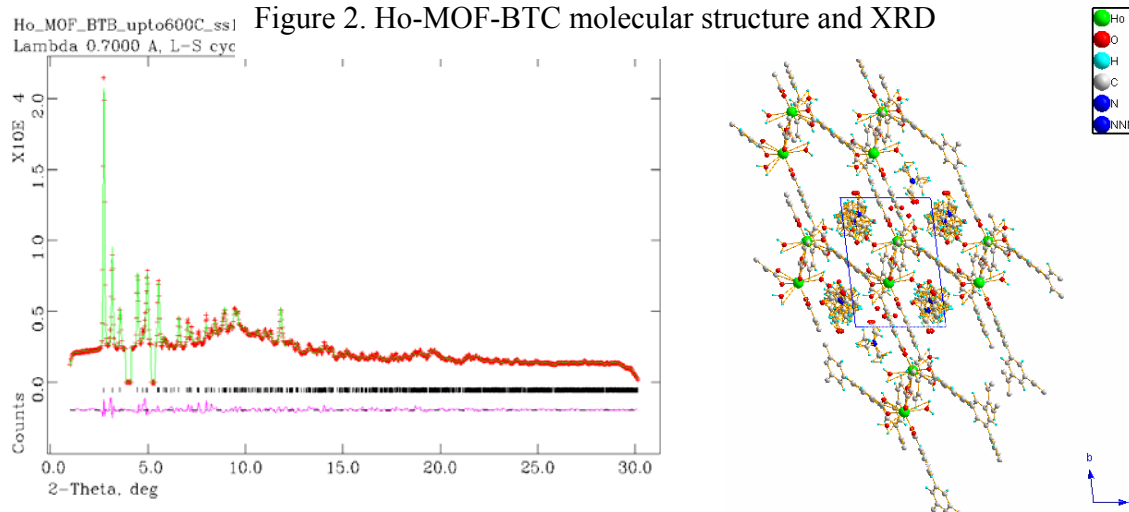


Figure 3. Ho-MOF-BTB molecular structure and XRD

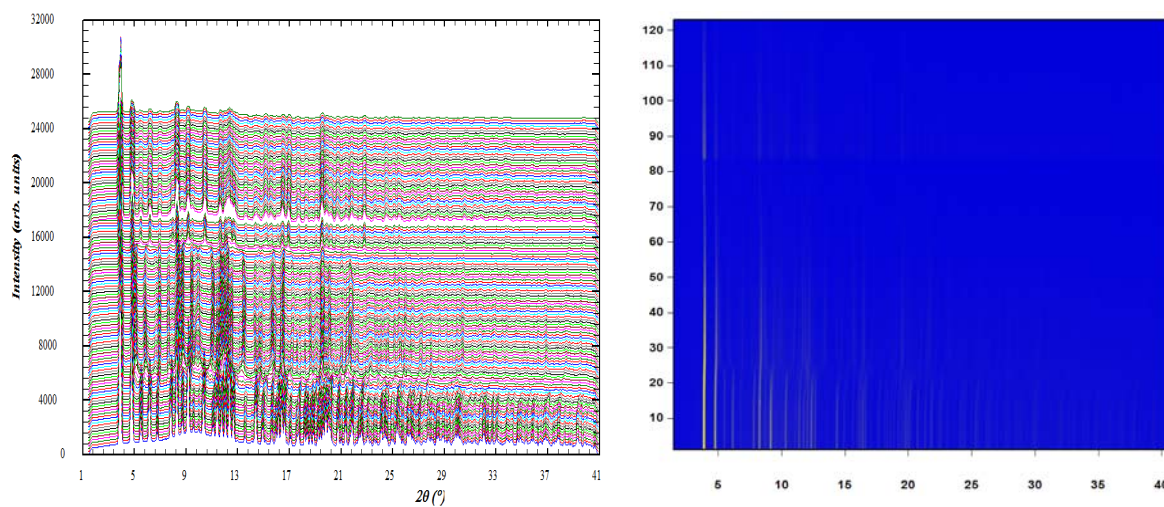
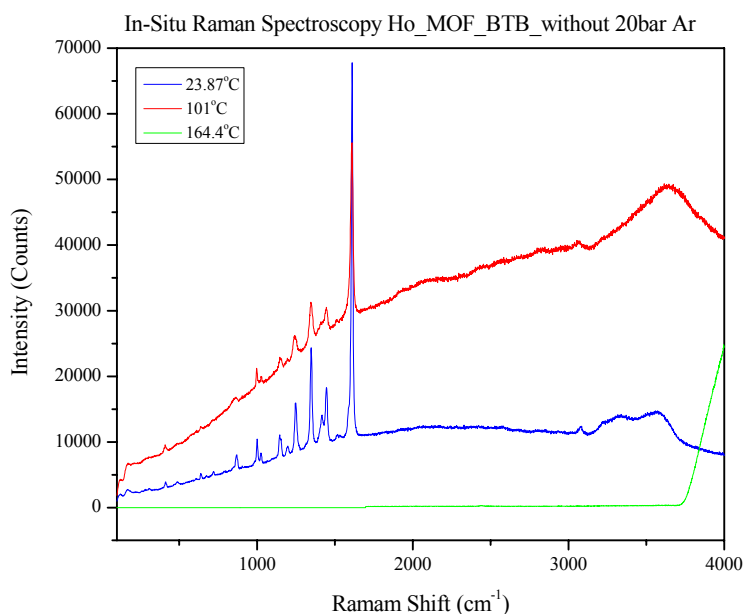
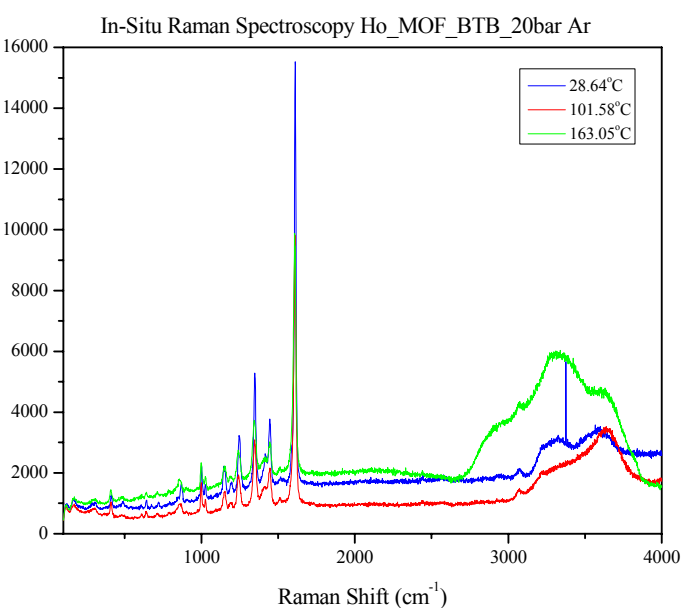
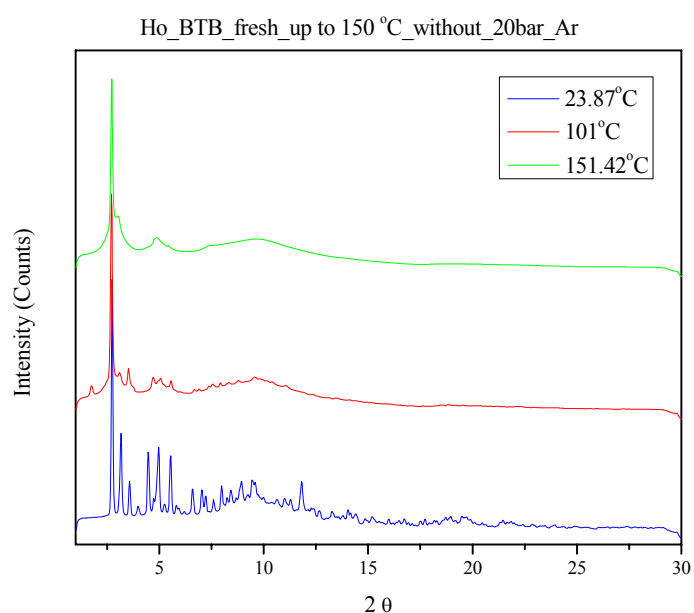
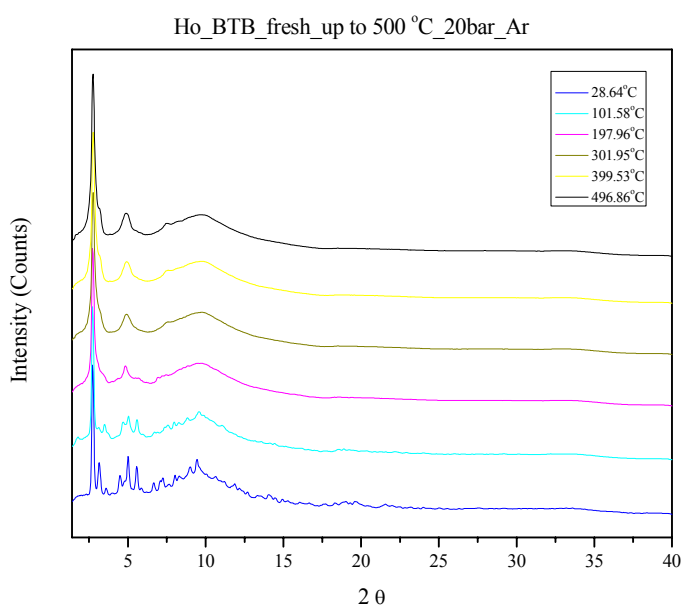


Figure 4. In-Situ XRD data record and 2-D contour profile for Ho-MOF-BTC form room temperature up to 600°C.

(B) Enhanced Thermal Stability on Ho – BTB under Ar Pressure.

The collapse of the Ho-BTB at temperatures little over 100 °C, is in distinct contrast to the thermal stability displayed by related systems. Therefore, the project was extended with the examination of a number of different metal-organic framework systems under gas loading condition. The application of 20 bar of Ar pressure to the Ho – BTB structure dramatically improves the thermal stability. The origin is most likely the result of either (a) the suppression of the dehydration of the solvent molecules with the pores or (b) the exchange of the solvent molecules with Ar gas atoms holding the framework in a rigid fashion. The unique probe of combined X-ray diffraction and Raman spectroscopy has proved to be an ideal method to investigate such systems.



Summery of the project:

Sample's name	Process (Temperature and Pressure)	Notes
Goosecreekite	at 1 atm, cooling down and heating up	in-situ structure and Raman variation
Ho_MOF_BTC	at 1 atm, from room temperature to 600°C	in-situ structure and Raman variation
Ho_MOF_BTC (degased)	at 1, 5,10,14 bar of CO ₂ , cooling to 215K then heating up to 400K	CO ₂ absorption (in-situ Raman spectroscopy)
Ho_MOF_BTC (degased)	at 1,5,10,15,20 bar of Ar, cooling to 200K then heating up to 400K	Ar absorption (in-situ Raman spectroscopy)
Ho_MOF_BTC (degased)	at 1,5,10,15,20 bar of CH ₄ , cooling to 200K	CH ₄ absorption (in-situ Raman spectroscopy)
Ho_MOF_BTb	at 1 atm, from room temperature to 600°C	in-situ structure and Raman variation
Ho_MOF_BTb (degased)	at 1, 5,10,15,20 bar of Ar, cooling to 200K then heating up to 500°C	in-situ structure and Raman variation
Ho_MOF_BTb (degased)	at 1, 5,10,14 bar of CO ₂ , cooling to 215K then heating up (interrupt)	in-situ structure and Raman variation
Ho_MOF_BTb	fresh sample at 20bar of Ar, from room temperature to 600°C	in-situ structure and Raman variation
Ho_MOF_BDC	fresh sample at 20bar of Ar, from room temperature to 600°C	in-situ structure and Raman variation
Ho_MOF_BDC (degased)	at 20bar of Ar, from room temperature then heating up (interrupt)	in-situ structure and Raman variation
Ho_MOF_BDC (degased)	at 20bar of Ar, from room temperature then cooling down 200K	in-situ structure and Raman variation
Y_MOF_BTC	at 1 atm, from room temperature to 600°C (stop at 360°C)	in-situ structure and Raman variation
Ce_MOF_BTC	at 1 atm, from room temperature to 600°C	in-situ structure and Raman variation
Pr_MOF_BTC	at 1 atm, from room temperature to 600°C	in-situ structure and Raman variation
Pr_MOF_BDC	at 1 atm, from room temperature to 600°C	in-situ structure and Raman variation
BaFeAs	at 1 atm, cooling to 80K then heating to 300K	in-situ structure and Raman variation
CdCr ₂ Se ₄	at 1 atm, cooling to 80K then heating to 400K	in-situ structure and Raman variation
FeSe ₈₇₅ S ₁₂₅	at 1 atm, from 150K cooling to 80K then heating up to 200K	in-situ structure and Raman variation
Na ₄₄	at 1 atm, from room temperature to 800°C	in-situ structure and Raman variation
Zn ₀₅ Mn ₀₅	at 1 atm, at 80K	structure identification
Zn ₀₉ Mn ₀₁	at 1 atm, at 80K	structure identification
ZnCr ₁₈ Ni ₀₂	at 1 atm, at 80K	structure identification
Tm ₇₇ X ₂₈	at 1 atm, at 80K	structure identification
Fe ₁₂ Se ₇₅ S ₂₅	at 1 atm, at 80K	structure identification
Fe ₁₂ Se ₈₇₅ S ₁₂₅	at 1 atm, at 80K	structure identification
Mg_MOF	at 1, 2, 5 bar of Ar, from room temperature to 420K	in-situ structure and Raman variation
NIST_MOF	at 1 atm, room temperature	structure identification

Experimental report 3 Effect of high-pressure on the model perovskite SrTiO₃: Investigation by combined Raman and X-ray scattering

A. Bartasyte, R. Haumont, P. Bouvier, J. Kreisel, W. van Beek

The understanding of ABO_3 perovskite is an internationally highly-competitive area and among the most challenging topics at the interface between solid state chemistry and solid state physics. The ideal cubic $Pm-3m$ structure of perovskite-type oxides is essentially simple, with corner-linked BO_6 octahedra, the B cations at the centre of the octahedra and the A -cations in the space of co-ordination 12 between the octahedra (Fig. 1.a). Most perovskites deviate slightly from this ideal cubic structure, for instance by a rotation of BO_6 octahedra (Fig. 1.b) or/and by cation displacements (Fig. 1.c).

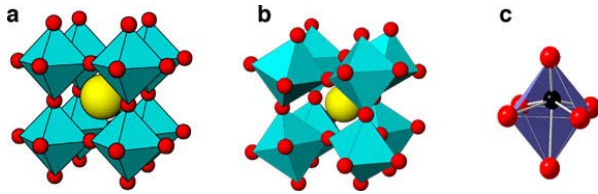


Figure 1

- a) The ideal cubic $Pm-3m$ perovskite structure.
- b) Example of a distortion induced by the rotation (tilt) of BO_6 octahedra.
- c) Illustration of a distortion induced by a $[111]$ cation displacement inside the BO_6 octahedra. It is the 'off-centering' of the A and/or B -cation inside their polyhedra which gives rise to ferroelectric (polar) properties.

The understanding of phase transitions in perovskites induced by external parameters like temperature, pressure, strain, magneto-electric fields etc. remains of great interest. Compared to temperature, the external parameter high pressure is of particular interest since it acts only on interatomic distances and can be much easier simulated by potentially insightful ab-initio calculations.

In a seminal paper, Samara *et al.* [1] have proposed general rules for the effect of hydrostatic pressure on displacive phase transitions associated with soft zone-center ferroelectric and zone-boundary antiferrodistortive instabilities. Two striking effects have been proposed and experimentally confirmed: (i) the decrease of the ferroelectric transition temperature with pressure and ultimate vanishing of ferroelectricity. (ii) the phase transition temperatures of antiferrodistortive zone-boundary transitions in perovskites increase with pressure, i.e. the angle of octahedra tilts increases with pressure.

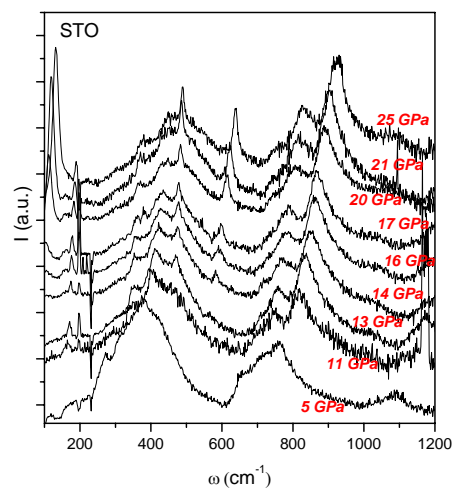
The above general rules have shown to be extremely successful and have guided research in the field for 30 years. The aim of our experiment was to challenge Samara's longstanding rules for the model perovskite SrTiO₃ (STO) which adopts at ambient conditions the ideal cubic $Pm-3m$ perovskite structure. In the present experiment we have been aiming at answering the following questions: (i) does STO remains cubic under high-pressure, or does high-pressure induce phase transitions? and, if yes, (ii) do the potential phase transitions follow Samara rules or not? Finally, (iii) does STO develop ferroelectricity at high-pressure, as was recently suggested for all d^0 transition metal oxides?

Synchrotron X-ray diffraction (XRD) has been in the past a useful probe for the investigation of pressure-induced phase transitions in other perovskites. However, XRD suffers from the fact that 1) oxygen-dominated superstructure reflections, coming from a cell doubling due to oxygen octahedra tilting have only a low intensity (the smaller the tilting the smaller the intensity) and 2) that phase transitions via only small changes in the metric of the unit cell ask for a good resolution to depict a potential splitting of Bragg reflections. In order to address these limitations we have aimed in the present experiment

to combine XRD with Raman scattering which is known to be a complementary and versatile probe for the detection of even subtle phase transitions in perovskites.

In order to answer the above questions, we have loaded a (001) oriented single crystal into a high-pressure diamond anvil cell. In order to fit to the small ($\varnothing = 150 \mu\text{m}$) high-pressure cell in the gasket, the sample has been preliminarily polished down to a thickness of $15 \mu\text{m}$ and only a small piece with a lateral extension of $40 \mu\text{m}$ was used for the experiment to provide best hydrostatic conditions. A single crystal sample has been preferred to a powder in anticipation that superstructure reflections are easier to detect in a single crystal pattern than in a powder diffraction pattern which inherently presents a higher background at a given integrated diffraction angle θ . At the same time a laser beam was directed via a fibre to the diamond anvil cell and focused with a long working distance objective through the diamonds to the small single crystal sitting in the gasket. We would like to point out that the Raman set-up has been working remarkably well and has needed very little alignment for the acquisition of the spectra. Also the change from the Raman to the XRD measurements was quick and reliably.

The beside Figure shows a number of representative Raman spectra obtained for selected pressures. It can be seen that the spectral signature changes significantly with applied pressure as exemplified by the appearance at about 13 GPa of a new band around 600 cm^{-1} or the mode hardening of the intense and sharp band at low wavenumbers. These and other more subtle spectral changes indicate that STO undergoes at two phase transitions in the investigated pressure-range up to 25 GPa.



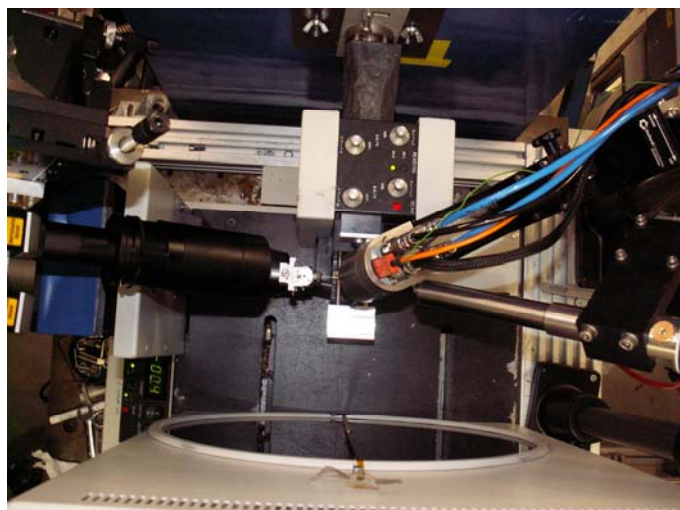
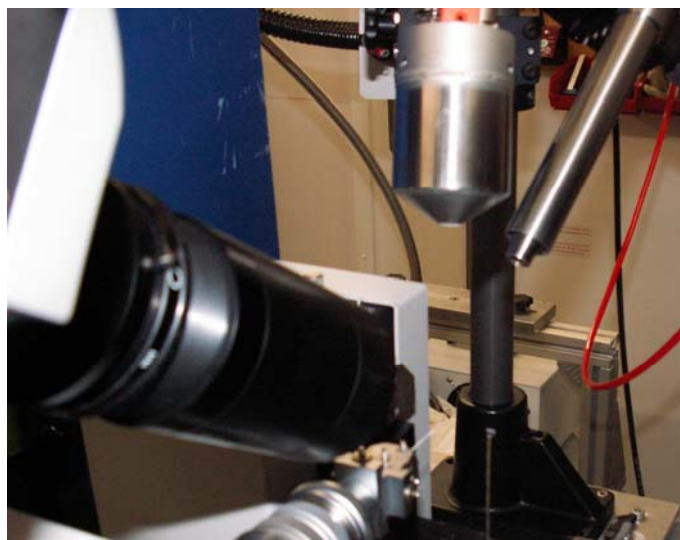
Although these spectra provide clear evidence for phase transitions, the Raman scattering data does not allow proposing the character of the pressure-induced symmetries and even less a specific space group.

Aiming to understand the underlying structural mechanism in more detail we undertaken a detailed analysis of the obtained single crystal diffraction pattern which have been obtained in a rotating crystal geometry (pattern not shown here). Unfortunately, the analysis of the diffraction pattern at different pressures did not allow detecting neither superstructure reflections (expected for cell doubling) nor the splitting of the fundamental cubic Bragg reflections which we expected to provide evidence for metric changes to discover the structural parameters. From this we conclude the following: 1) Potential superstructure reflections have to be weak thus indicating an only small angle of octahedra tilting and 2) the metric structural distortion has also to be small.

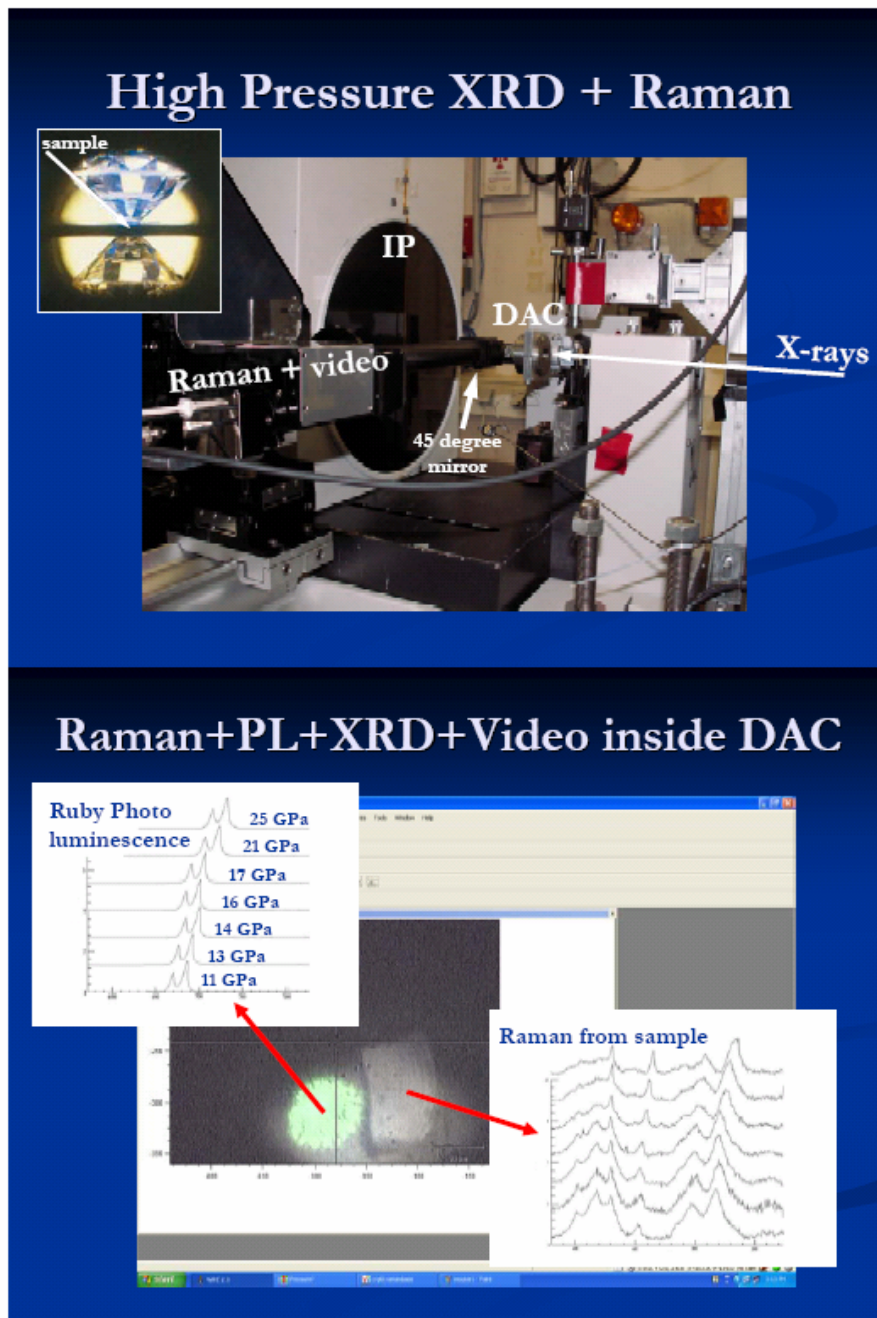
On the experimental side it would be certainly helpful to be able to work with a smaller wavelength of 0.5 \AA . This should allow increasing the resolution of the diffraction pattern significantly which in turn should allow the observation of metric symmetry changes.

Technical achievements

A new compact cyberstar blower (from the ESRF loan pool) has been successfully integrated on the MAR 345. The new setup allows rapid switching between cryostream and blower. This enables the users to access a temperature range from 80 Kelvin up to 1000 Kelvin. All of this can be combined with the gas system and the Raman. The temperature from both instruments can be logged.



A combined Raman High pressure setup has been developed. The Raman instrument was also used to measure the pressure calibrant as detailed in the following picture.



Status of the project, second year results:

During the second year of the LTP the Raman instrument was installed and tested on BM1A with the image plate detector, with particular attention to the high pressure setup. The capillary micro reactor and gas loading systems, developed during year 1, have been implemented and tested.

Two scientists for the LTP consortium have been staying at SNBL for extended periods working at the implementation of the various experiment setup and to the data analysis. Gained experience and know how has been shared and transferred to the permanent beamline staff.