



	Experiment titles: Novel Functional Metal-Organic Frameworks with Phosphonate Linkers Novel Lanthanide-Based Photoluminescent, Catalytic and Magnetic Metal-Organic Frameworks	Experiment number: CH-3692 CH-3702
Beamline: ID11	Date of experiment: from: 28 – Nov. – 2012 to: 06 – Dec. – 2012	Date of report: 28 – Mar. – 2013
Shifts: 18	Local contact(s): Dr. Gavin Vaughan (E-mail: vaughan@esrf.fr) Dr. Andy Fitch (E-mail: fitch@esrf.fr) Dr. Yves Watier (E-mail: watier@esrf.fr)	<i>Received at ESRF:</i>
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Initial considerations:

This report concerns two experiments at the ESRF: CH-3692 and CH-3702. These experiments concerned very similar materials that were investigated both at ID11 and ID31. In addition, because the experiments were performed consecutively the shifts allocated (18 in total) were treated and organised as a whole so to maximise the allocated time a collect the best possible data sets. As a consequence, the same report will be submitted online for both experiments.

Introduction:

In the last 15 years or so or research groups at the University of Aveiro have focused their research interest in the development of novel hybrid materials, for which the final properties could be boosted by the symbiotic relation between organic and inorganic components. Never losing touch with the functional zeotype materials which projected our research worldwide, namely the preparation of novel lanthanide silicates,^[1-11] we have more recently started to prepare novel photoluminescent Metal-Organic Frameworks^[12-21] and also expand the dimensionality of Mo(VI)-based catalysts.^[22-24]

The purpose of these two experiments (performed at ID11 and ID31) was to elucidate the crystalline

structures of a series of functional materials prepared in our laboratories, spanning from photoluminescent Metal-Organic Frameworks or lanthanide silicates, to hybrid Mo(VI)-based materials with interesting catalytic activity. Indeed, the detailed knowledge of all structural features of a given material, in particular if it is novel, is of crucial importance to fully understand the observed properties, establish structure-properties correlations and design new, more efficient, materials.

Results and Discussion:

Catalytic Coordination Polymers

Over the last few years we have been investigating the possibility of designing and prepare in the laboratory polymeric Mo(VI) materials in which bipyridine derivative molecules are coordinated to the metallic centers.^[22-24]

Microcrystalline $(DMA)[(MoO_3)(Hbpydc)] \cdot H_2O$ (where DMA^+ stands for dimethylammonium and H_2bpydc for 2,2'-bipyridine-5,5'-dicarboxylic acid) was studied both at ID11 and ID31. The crystals available for this compound, and which could be selected under the microscope, did not possess sufficiently good diffraction images and, therefore, the material has to be investigated using high-resolution powder X-ray diffraction at ID31. Despite the combined use of hard X-rays at ID31 and low temperature data acquisition (*ca.* 100 K), prolonged irradiation of the material to the synchrotron beam led to significant structural damage that could be simultaneously observed by peak shifting of the collected pattern (data not shown) and also to the naked eye as a discoloration of the packed material (Figure 1).

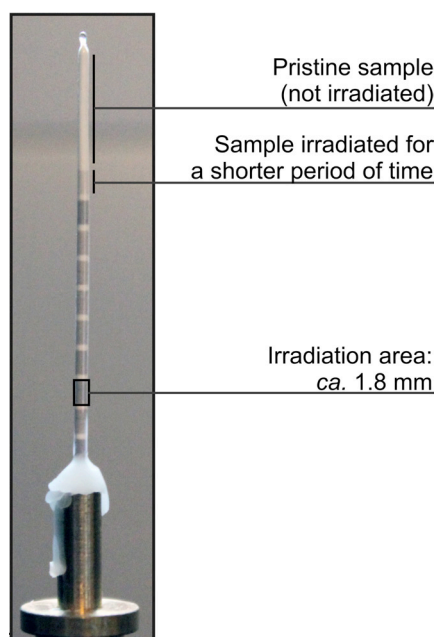


Figure 1. Hilgenberg borosilicate glass capillary (*ca.* 0.9 mm of diameter), packed with $(DMA)[(MoO_3)(Hbpydc)] \cdot H_2O$, which was used for data collection at the ID31 beam line at the ESRF (Grenoble, France).

In a first stage, data collection was performed throughout the entire angular range while shifting periodically the irradiation position on the sample. The data set collected (over more than 16 hours) had a very good signal-to-noise ratio but peak shape was significantly compromised because at higher angle data the effects of radiation damage were already noticeable. This was confirmed with our local contact, Dr. Andrew Fitch, which treated mathematically the data sets showing unequivocally the differences between collected powder patterns (data not shown). To prevent that this inherent structural modification could have a

significant influence of the collected data sets, a new data set had to be recollected. In this second stage of the experiment (which lasted for more than 18 hours) data was collected in continuous mode over three distinct angular ranges ($1 \leq 2\theta \leq 10^\circ$, $10 \leq 2\theta \leq 20^\circ$ and $20 \leq 2\theta \leq 30^\circ$) with increasing times for the higher angle data. Using this new data set a detailed crystallographic description could then be derived using *ab initio* methods (Figure 2): the material, crystallizing in the non-centrosymmetric monoclinic *Pc* space group, is composed by a anionic one-dimensional organic-inorganic hybrid polymer, $\infty^1[(\text{MoO}_3)(\text{Hbpydc})]^{n-}$, which co-crystallizes with charge-balancing DMA^+ cations and one water molecule per metallic center (inset in Figure 2). This truly unique hybrid material has already been published online (as an advance article in the web) in *Inorganic Chemistry*.^[25] The publication has been performed in close collaboration with Dr. Andrew Fitch from ID31.

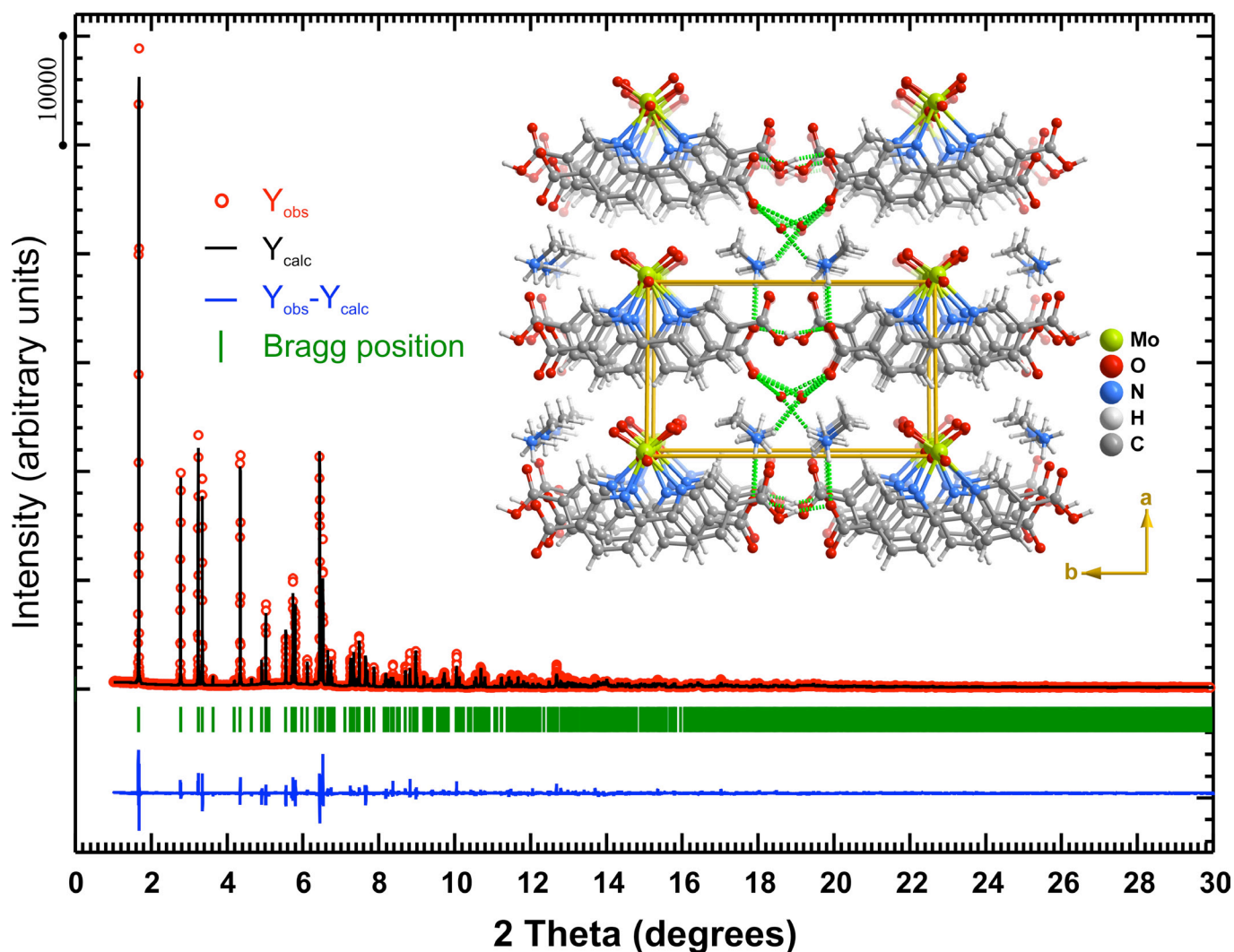


Figure 2. Final Rietveld plot (powder synchrotron X-ray diffraction data) of $(\text{DMA})[(\text{MoO}_3)(\text{Hbpydc})]\cdot\text{H}_2\text{O}$. Observed data points are indicated as red circles, the best fit profile (upper trace) and the difference pattern (lower trace) are drawn as solid black and blue lines, respectively. Green vertical bars indicate the angular positions of the allowed Bragg reflections. A ball-and-stick crystal packing representation of **1** viewed down the [001] crystallographic direction is provided as an inset.

Photoluminescent Lanthanide Silicates

We have also pioneered, over the last two decades or so, the worldwide research focused on the engineering of photoluminescent lanthanide (or rare-earth) silicates. Recently we have prepared at the nano-scale a new scandium silicate which could be doped with known quantities of emissive lanthanide cations leading, thus, to luminescent materials. The compound is, however, systematically isolated as small crystals which often fall in the nanometer range. High-resolution data for this material was collected at ID31 (Figure 3). Our analysis of the data set allowed us to derive to date: (i) unit cell parameters; (ii) space group; (iii) an initial structural model. This model for the material is under development since it has to be refined according to other additional structural data such as solid-state NMR and photoluminescent. We anticipate, however, that a full structural model will be refined by the end of the current year and the results published in a good international journal due to the high novelty of the compound.

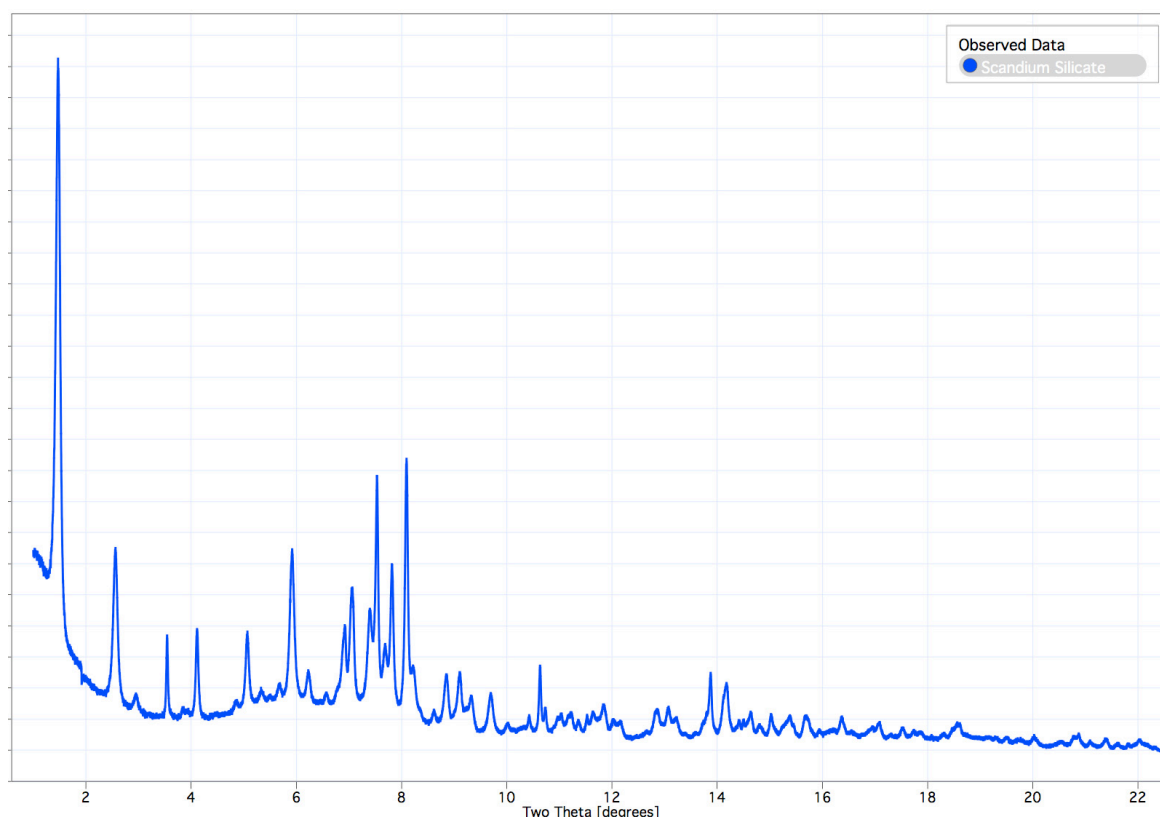


Figure 3. Powder X-ray diffraction pattern collected at ID31 (at 100K) for the novel nano-sized scandium silicate.

Photoluminescent Metal-Organic Frameworks

During the current experiment, high signal-to-noise ratio powder X-ray diffraction data sets have been collected for a series of materials, all initially described in the proposals for the ESRF. Two of these materials are based on the highly flexible nitrilotris(methylenephosphonic acid) which was reacted with a chloride salt of Gd^{3+} (samples FC-GdT100P100t10 in Figure 4 and OXNMP20 in Figure 5). Using the data set for the latter material we were able to index and provisionally solve the crystal structure, being a one-dimensional polymer with two lanthanide centers in the asymmetric unit. Further studies are underway so to gain more insights into the composition of the asymmetric unit and proceed with an overall Rietveld refinement. The former material is, as clearly observed in Figure 4, much less crystalline. We are at the moment combining

partial data from single-crystal X-ray diffraction studies with this collected data set so to refine a structural model for the bulk material.

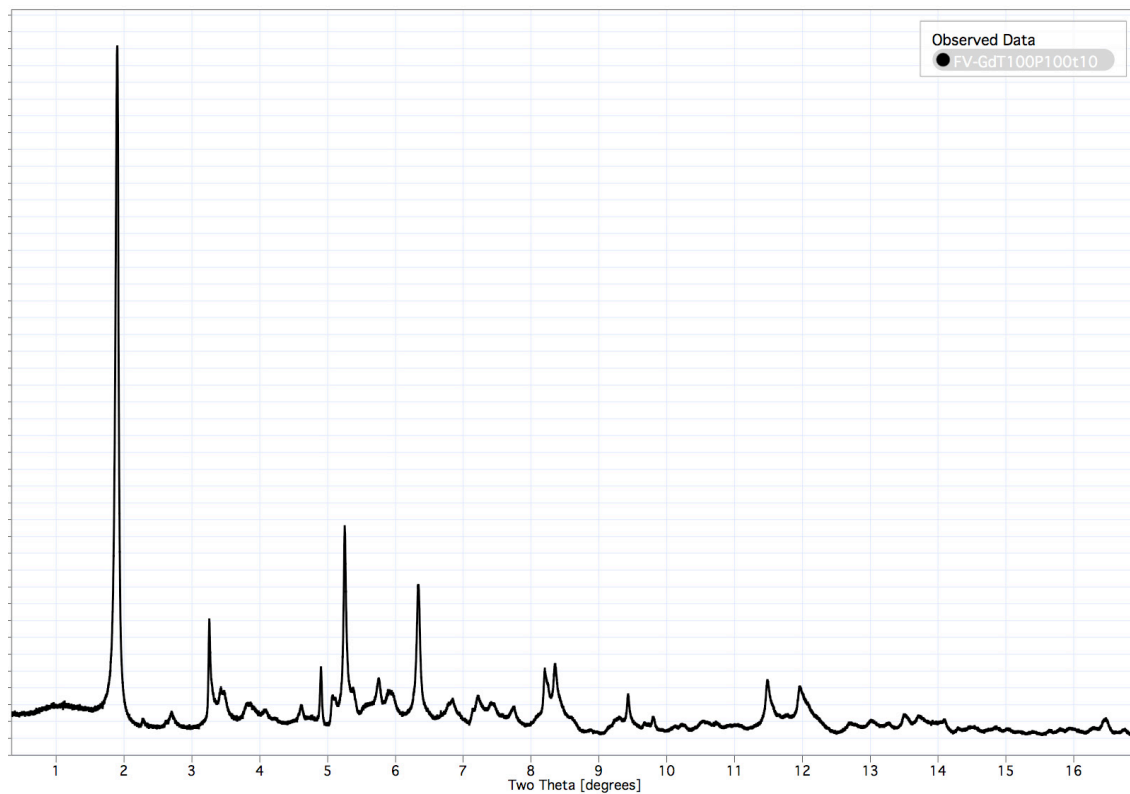


Figure 4. Powder X-ray diffraction pattern collected at ID31 (at 100K) for the novel poorly crystalline material obtained when reacting nitrilotris(methylenephosphonic acid) with Gd^{3+} under static hydrothermal conditions.

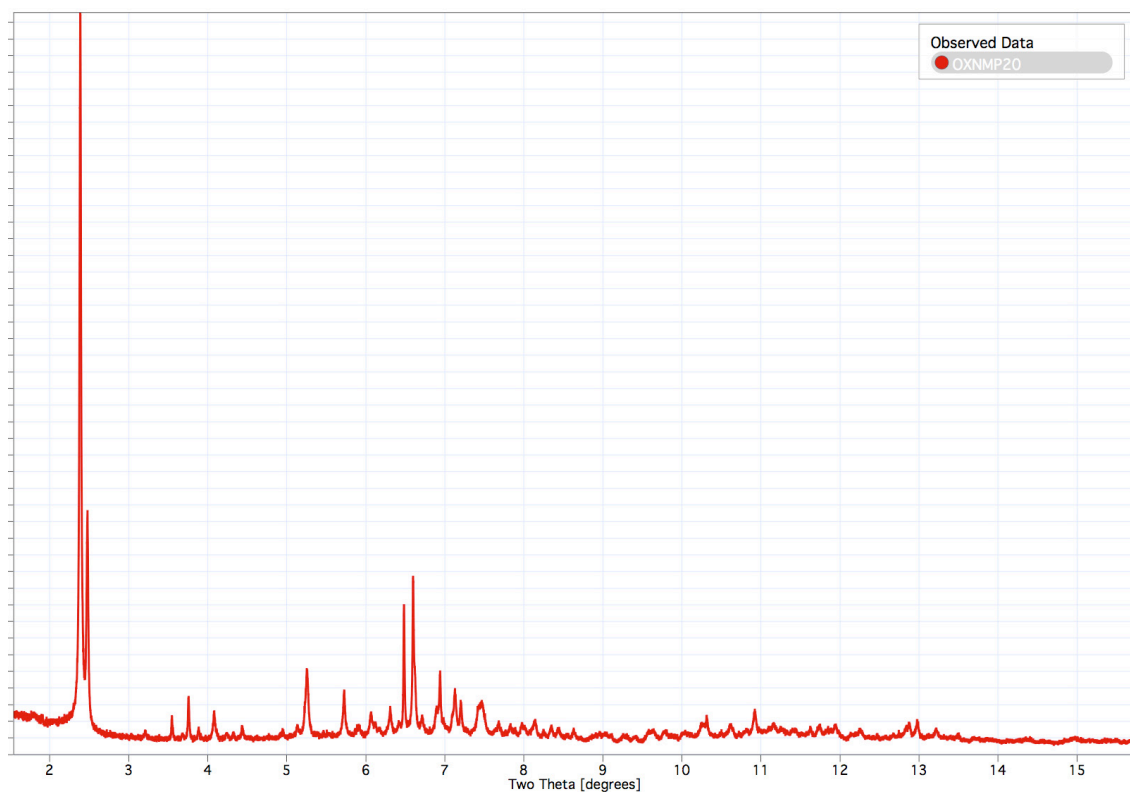


Figure 5. Powder X-ray diffraction pattern collected at ID31 (at 100K) for the novel crystalline material obtained when reacting nitrilotris(methylenephosphonic acid) with Gd^{3+} under one-pot conditions.

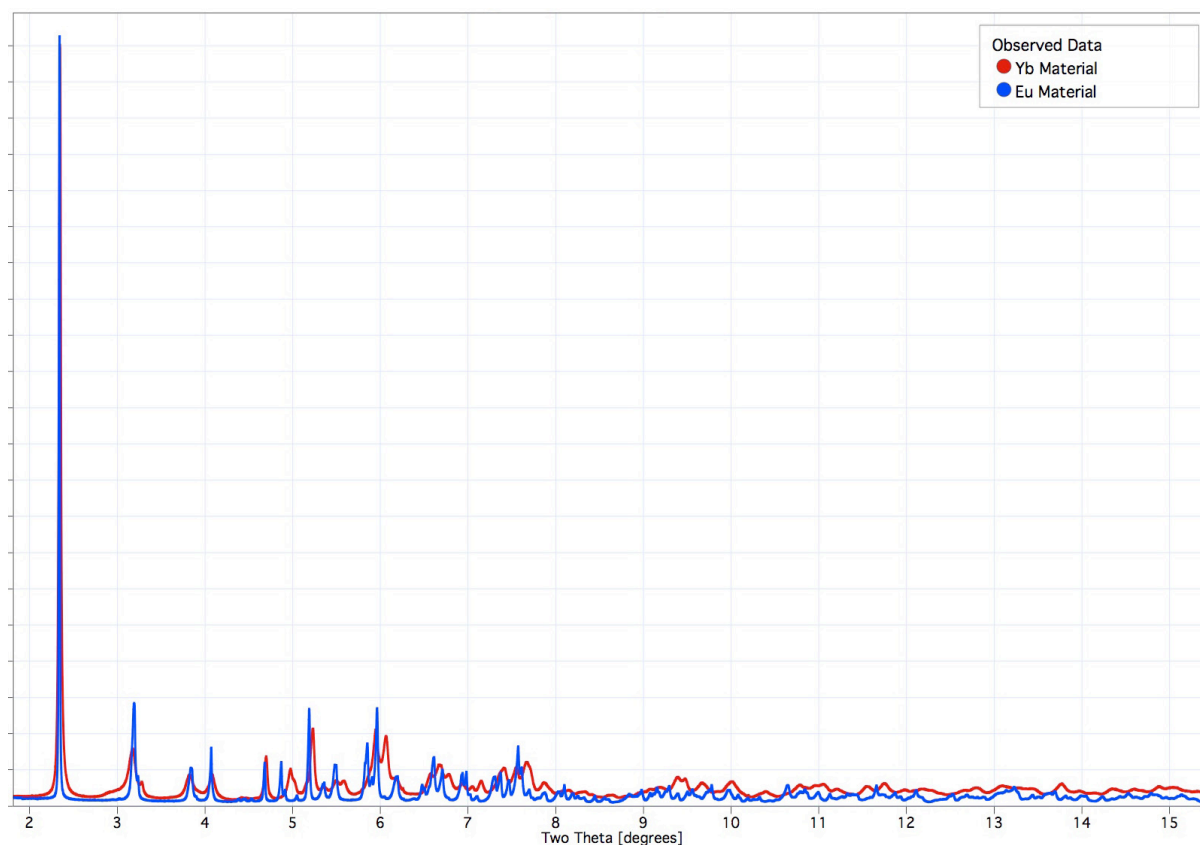


Figure 6. Powder X-ray diffraction pattern collected at ID31 (at 100K) for the novel materials obtained when reacting nitrilotris(methylenephosphonic acid) with Eu^{3+} or Yb^{3+} under hydrothermal conditions.

The reaction between lanthanide cations heavier than Eu^{3+} with the tripodal (benzene-1,3,5-triyltris(methylene))triphosphonic acid lead to the formation of a completely distinct material to those recently published by us.^[14] In addition, from Eu^{3+} to Yb^{3+} there is a considerable reduction of crystal size. Attempts were made during the course of the experiment to collect single-crystal data at ID11 for these materials with no overall success. High-resolution powder X-ray diffraction data sets were then collected for these two materials at ID31 (Figure 6). Investigations to date could be summarized as follows: (i) the powder pattern for the Eu^{3+} material could be indexed and a provisional structural model derived from ab initio studies; (ii) this model agrees well with the experimental features collected for the materials; (iii) there is a clear reduction of crystallite size for the Yb^{3+} material. We were not, however, able to date to refine properly the average crystallite size. In addition, it seems that it is necessary to collect the remaining members of the series so to see a smooth decrease of crystallite size and, in this way, fully describe the system. Further studies are needed and, most certainly, it will be necessary to repeat the experiment for the remaining members of the series.

Conclusions:

A significant portion of the experiments was devoted to the hybrid material $(\text{DMA})[(\text{MoO}_3)(\text{Hbpydc})]\cdot\text{H}_2\text{O}$: besides the need to collect two long data sets, it was also necessary to pack several capillaries because of the extensive structural damage inflicted by the synchrotron radiation.

Nevertheless, the structure was unequivocally solved and at the moment of the writing up of the present report it was already published in a highly reputable international journal (*Inorganic Chemistry* from ACS).^[25] The experimentalists used the remaining time to collect high-resolution data for other materials such as photoluminescent metal-organic frameworks and lanthanide silicates. These results are being treated at the moment, and are expected to be published in the near future in international journals with good impact factor. We emphasize, however, the need in future experiments to collect additional data sets for the materials obtained when using the tripodal (benzene-1,3,5-triyltris(methylene))triphosphonic acid ligand.

In short, the prolonged experiment at the ESRF (due to the combination of two approved experiments) allowed an efficient management of the allocated time and the collection of good data sets, making thus this trip to the ESRF very successful.

Acknowledgements

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