ESRF	**Experiment titles:** **Bifunctional Lanthanide-Organic Frameworks with Polyphosphonate Organic Linkers** **Colorimetric Anion Binding Agents with Adequate Structural Features, for Biomedical, Environmental and Sensing Applications**	**Experiment number**: CH-3718 CH-3837
Beamline: ID11	**Date of experiment**: from: 05 – Sept. – 2013 to: 10 – Sept. – 2013	**Date of report**: 03 – Apr. – 2014
Shifts: 15	**Local contact(s)**: Dr. Gavin Vaughan (E-mail: vaughan@esrf.fr)	*Received at ESRF:*

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Initial considerations:

This report concerns two experiments at the ESRF: CH-3718 and CH-3837. These experiments concerned very similar materials that were investigated at ID11. In addition, because the experiments were performed consecutively the shifts allocated (15 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. More recently we have focused our attention on novel photoluminescent Metal-Organic Frameworks (MOFs), particularly those combining lanthanide cations and polyphosphonate organic linkers, many of which have been designed and prepared in our laboratories.[1-16]

The purpose of these experiments performed at ID11 was mainly to investigate the adsorption properties of a novel highly porous $[Y(H_3pptd)]\cdot x(H_2O)$ MOF material, by using for that purpose a constant flow of CO_2. Different temperatures and flow pressures were tested.

The collected results (sumamrized in the following pages) were extremely elucidative of the behaviour of the aforementioned material, allowing us to understand how the material behaves under the tested conditions. Results have been published in Dr. Vilela PhD thesis and are now being compiled for a

publication in an international scientific journal of the area.

Experimental Apparatus

[Y(H_3pptd)]·x(H_2O) was packed in a quartz capillary (Φ = 0.5 mm) and placed in a home-made sample holder (Figure 1). A constant He flow was passed through the material and the capillary was heated from 303 to 375 K (heating ramp of 6 K/h). The latter temperature was kept for 1h30min (while using a constant He flow) to achieve the complete dehydration of [Y(H_3pptd)]·x(H_2O). After dehydration, the temperature was cooled down to 303 K (cooling ramp of 2 K/h) and the gas flow was replaced from He to CO_2. After stabilization of the CO_2 flow (during approximately 45 min), the flow pressure was increased for 1, 2, 3, 4 and 5 bar, remaining constant for 25 min at each pressure level. Then, the CO_2 flow pressure was allowed to decrease to 1 bar and the temperature cooled down to 273 K (cooling ramp of 2 K/h). Achieved the desired temperature, the CO_2 flow pressure was manipulated in a very quite similar way to that used for the measurements performed at 303 K. Finally, the dehydrated form of [Y(H_3pptd)]·x(H_2O) was maintained at 273 K, under a small and constant CO_2 flow for approximately 8 h. In all the experience steps, powder X-ray diffraction patterns were collected from 5 in 5 seconds.

In order to have insights about the structure transformations promoted by the dehydration process and the use of different flow CO_2 pressures in the [Y(H_3pptd)]·x(H_2O) material, pair distribution function (PDF) analysis, an advanced characterization technique, was also performed. As for the investigation described above, the capillary containing the studied material was heated from 295 to 375 K (heating ramp of 1 K/h) using a constant He flow. When the dehydration process was reached, the experimental temperature was reduced to 303 K (cooling ramp of 2 K/h). The He flow was changed for CO_2 and the flow pressure was increased for 1, 3 and 5 bar in order to detect what kind of structural modifications were occurring. Then the temperature was allowed to cool down to 273 K (cooling ramp of 1 K/h) and the structural variations were measured using a CO_2 flow pressure of 5 bar. Finally, the data collection were carried out using the latest experimental conditions (a constant CO_2 flow pressure of 5 bar at 273 K) during 6 h in order to identify some additional structural modifications. After that, the experimental procedure was concluded. As mentioned above, powder X-ray diffraction patterns were collected from 5 in 5 seconds during the measurements.

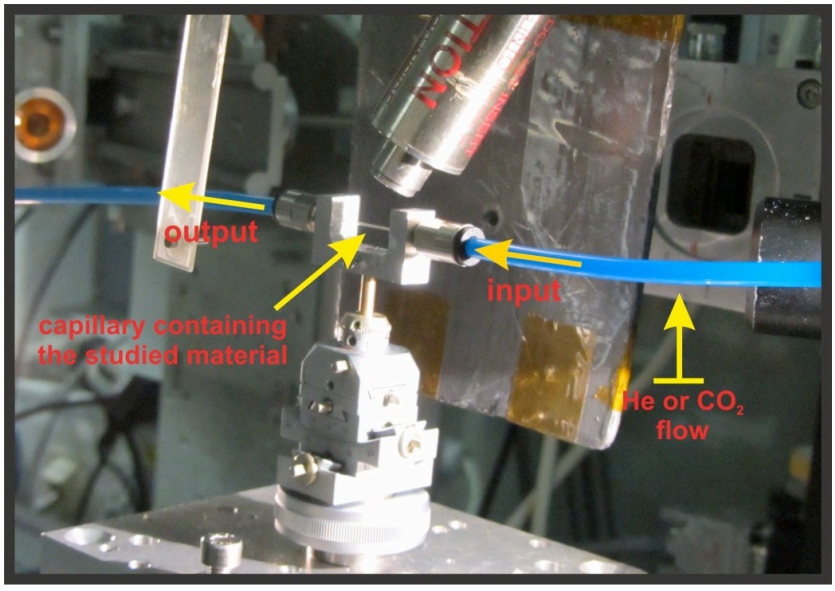

Figure 1. Schematic representation of the sample holder used for the high-resolution powder X-ray diffraction studies.

Results and Discussion

The stability and robustness of the [Y(H_3pptd)]·x(H_2O) material regarding its dehydration process and exposure to a constant CO_2 flow was studied by high-resolution synchrotron powder X-ray diffraction. Studies started with the dehydration of [Y(H_3pptd)]·x(H_2O) using a constant He flow while increasing the temperature from 303 to 375 K. During this process it was observed a structural modification promoted by the release of the solvent molecules. The new phase remained stable for a long period of time and it seems to be more crystalline than the original one (Figure 2). After dehydration step, the experimental temperature was decreased to 303 K. Figure 3 shows a small decrease in the crystallinity of the studied material (mainly observed in the first peak) during the cooling process, however, the crystalline structure remains the same. The flow of He was replaced for CO_2 in order to evaluate if the accommodation of this gas induces some structural modification in the [Y(H_3pptd)] dehydrated form. Therefore, these measurements were initialized allowing the passage of a small CO_2 flow through the capillary containing the material. Pressure was increased for 1, 2, 3, 4, 5 bar and, finally, decreased for 1 bar. Despite some variation in the crystallinity of the material, promoted by the variation of the pressure, its structure remained robust and stable (Figure 4).

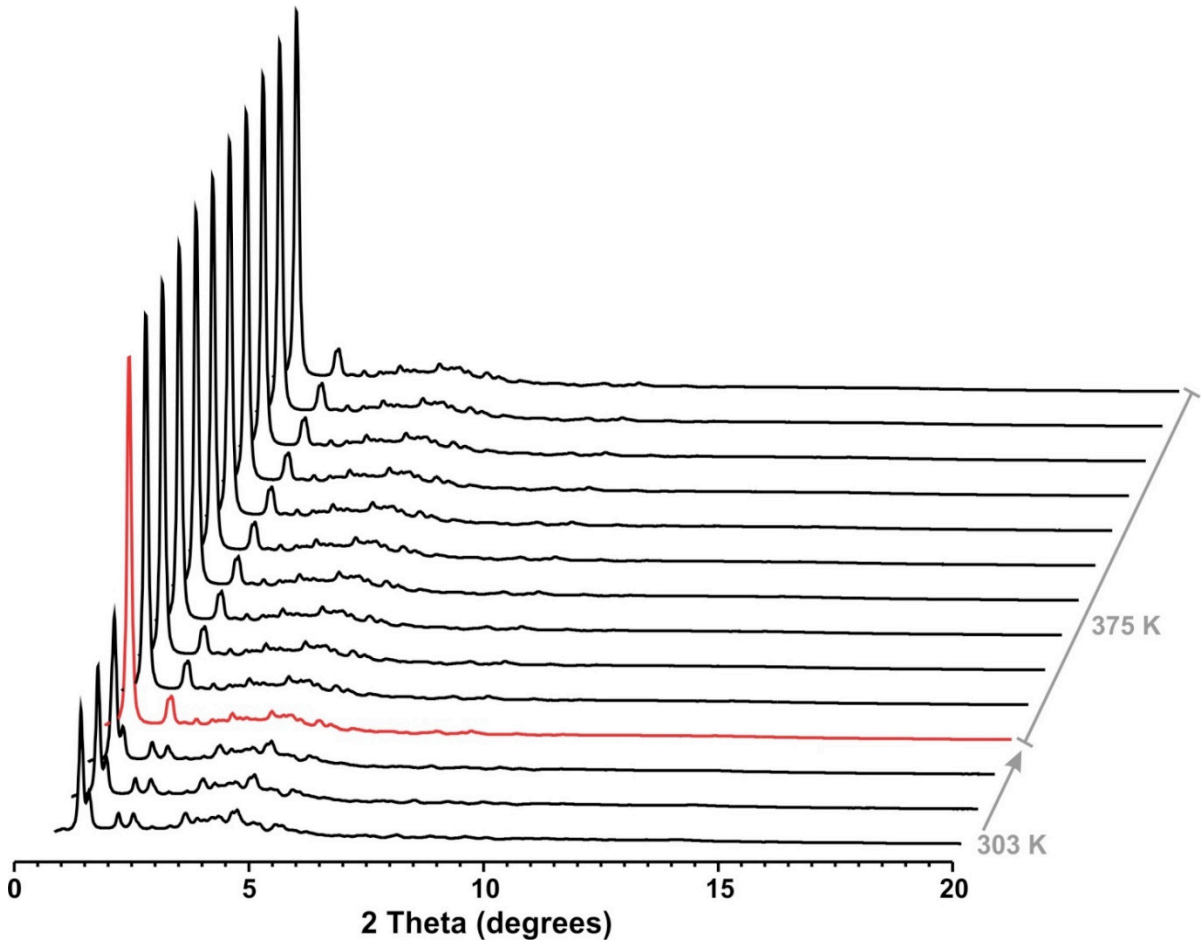

Figure 2. Powder X-ray diffraction patterns collected after dehydration process of the [Y(H_3pptd)]·x(H_2O) material.

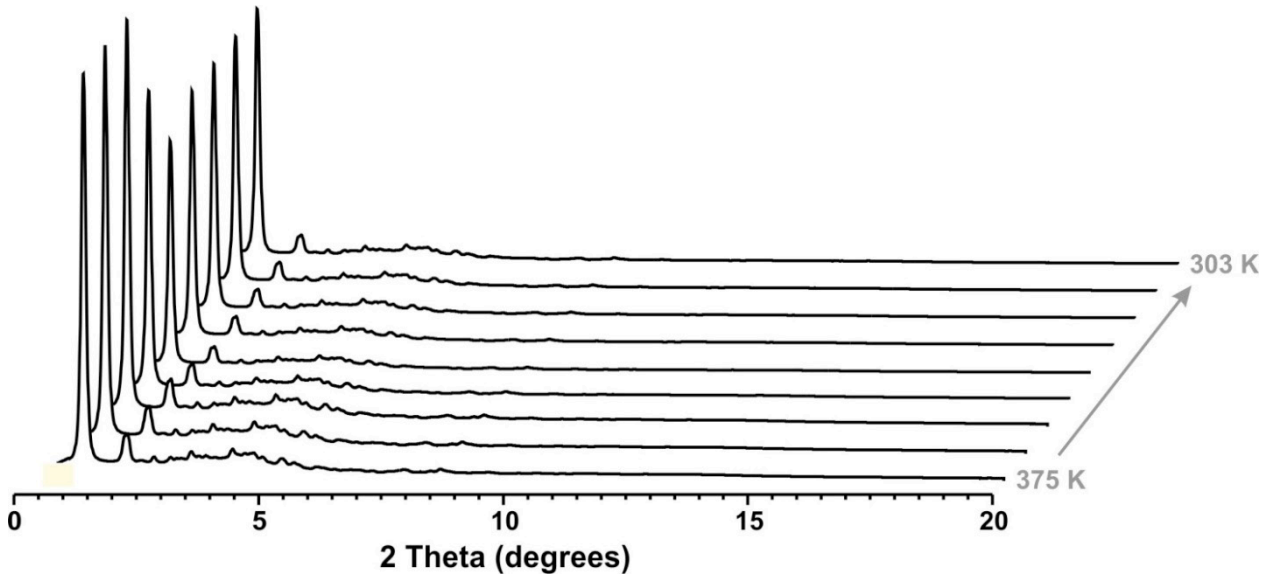

Figure 3. Powder X-ray diffraction patterns of the dehydrated [Y(H_3pptd)] material collected when the experimental temperature was decreased from 375 to 303 K.

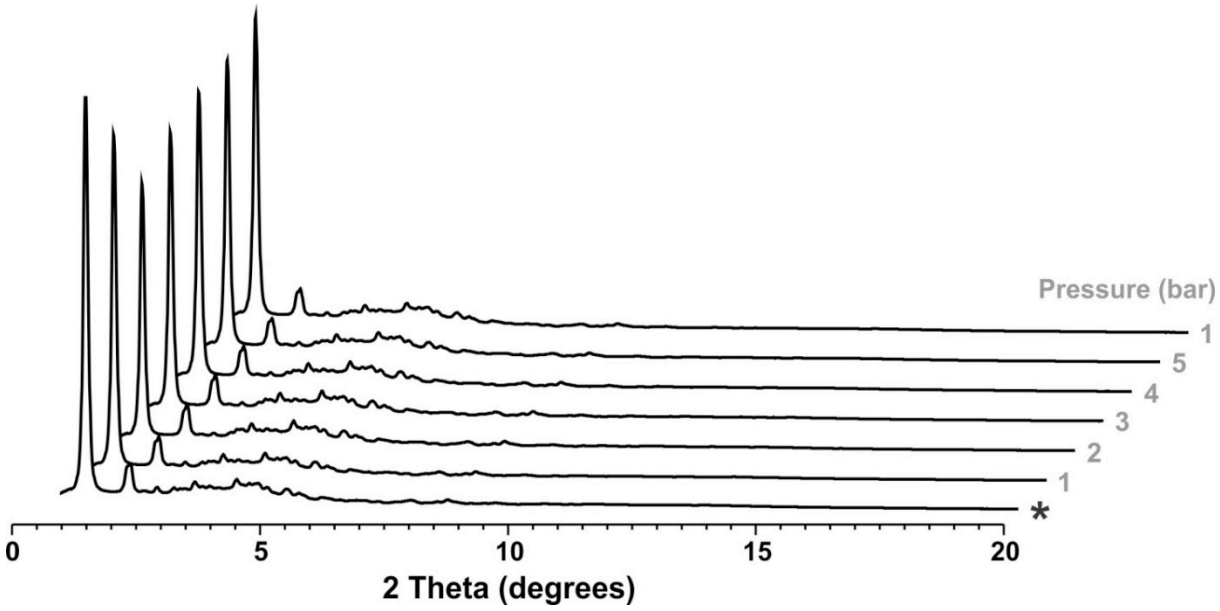

Figure 4. Powder X-ray diffraction patterns (PXRD) collected for the dehydrated [Y(H_3pptd)] material at 303 K by using different CO_2 flow pressures. The PXRD pattern of [Y(H_3pptd)], collected before the pressure studies, is denoted with an asterisk (*).

Decreasing the temperature for 273 K it is not detected, once again, any structural alteration (Figure 5). At that temperature it was evaluated the effect of different pressures in [Y(H_3pptd)]. As describe above for the measurements performed at 303 K the structure of the material does not suffer any modification (Figure 6).

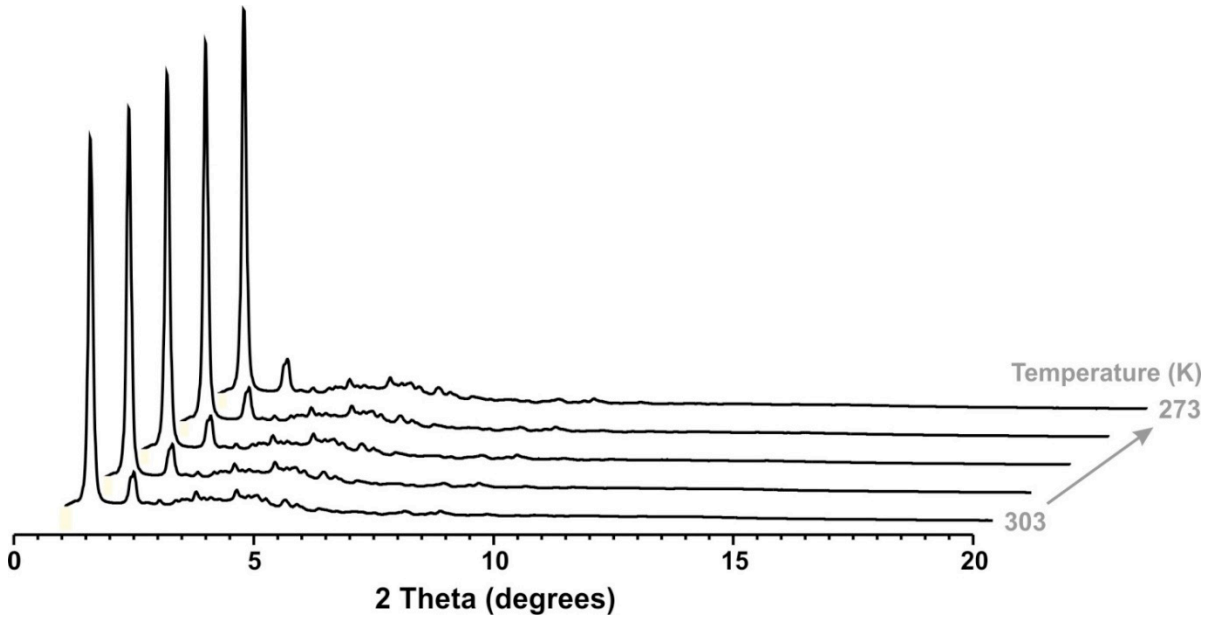

Figure 5. Powder X-ray diffraction patterns of the dehydrated [Y(H_3pptd)] material collected when the experimental temperature was decreased from 303 to 273 K.

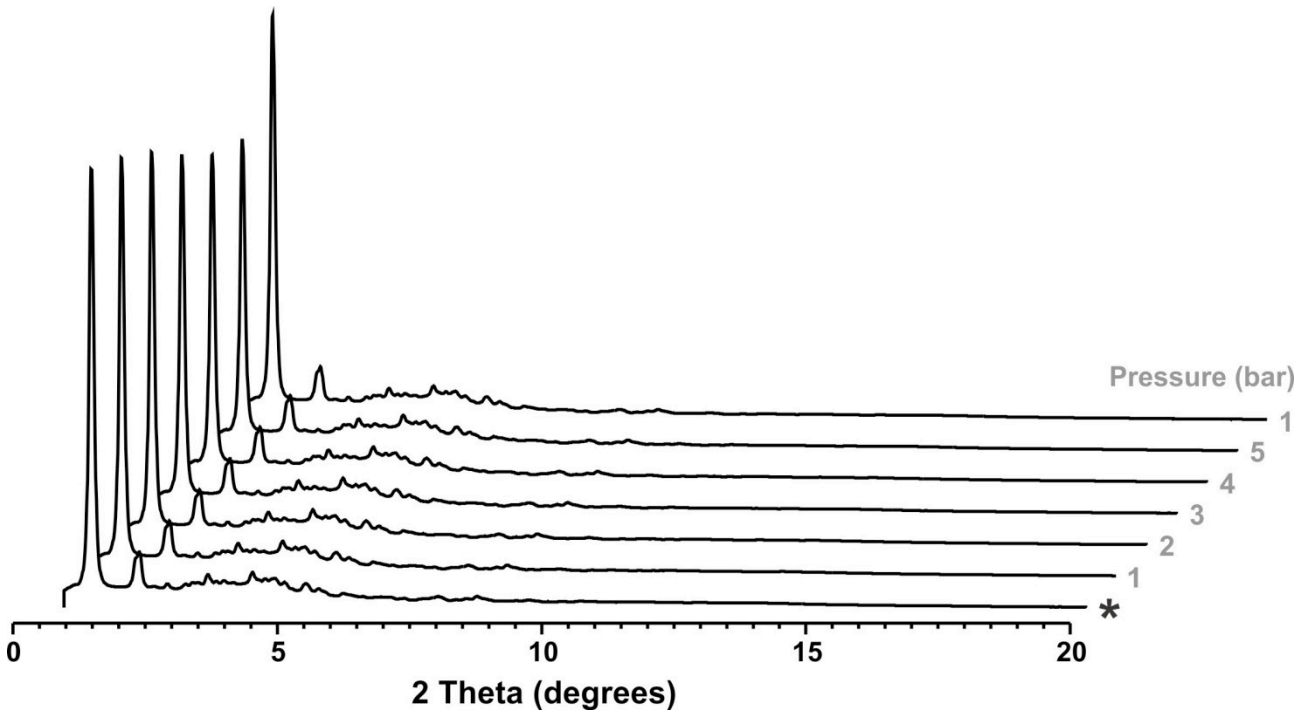

Figure 6. Powder X-ray diffraction patterns (PXRD) collected for the dehydrated [Y(H_3pptd)] material at 273 K by using different CO_2 flow pressures. The PXRD pattern of [Y(H_3pptd)], collected before the pressure studies, is denoted with an asterisk (*).

Conclusions:

The effect of the dehydration process of the [Y(H_3pptd)]·x(H_2O) material as well as the influence of different CO_2 flow pressures were investigated by high-resolution synchrotron powder X-ray diffraction, in order to gain insight on the stability and robustness of the structure of [Y(H_3pptd)]·x(H_2O). These investigations involved different two main tasks: i) evacuation of the solvent molecules of the studied

material using a He flow; and ii) variation of the CO_2 flow pressures (1, 2, 3, 4 and 5 bar) at 273 and 303 K. The collected data suggest that structural modifications indeed occurs in the structure of $[Y(H_3pptd)]\cdot x(H_2O)$ after the dehydration process, affording another crystalline phase. This new phase is highly robust and stable when different CO_2 flow pressures were tested at distinct temperatures (273 and 303 K).

In short, we consider that this experiment was very successful with all the results being already compiled in Dr- Sérgio Vilela PhD thesis. In addition, we are at the moment writing up a manuscript for publication which will contain most of these results.

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