Experimental report

12/09/2016

Proposal: 5-22-746 **Council:** 4/2016

Title: Determination of cation arrangement in solid-solution metal-organic frameworks

Research area: Materials

This proposal is a new proposal

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Local contacts: INES PUENTE ORENCH

Samples: ZnCoPF1 - Zn4Co(C17O4H8F6)5
ZnCo(C17O4H8F6)2
ZnCoPF1 - Zn2Co(C17O4H8F6)3

Instrument	Requested days	Allocated days	From	To
D2B	1	1	06/07/2016	07/07/2016

Abstract:

Solid solution metal organic frameworks (MOFs) composed of different metal atoms are of interest because they might exhibit unique and or enhanced properties, compared to their monometallic counterparts. Introduction of a second metal cation during the MOF synthesis is a feasible approach to obtain such type of materials. In the current proposal, we aim at determine the exact atomic arrangement of the metal cations in a series of MOFs prepared with the combination of zinc and cobalt. Our current study has shown that it is possible to incorporate both elements at controllable ratios. Furthermore, depending on the resulting Zn/Co ratio, the crystal structure of the obtained MOF might suffer a structural reorganization that suggests the possibility of having atomic level control on the metal atoms disposition. The similar atomic number of zinc and cobalt precludes a satisfactory refinement of the atomic positions and occupancies with the use of exclusively X-ray diffraction. Thus, powder neutron diffraction will be crucial in the ultimate characterization of these materials.

EXPERIMENTAL REPORT

Proposal: 5-22-746

Instrument: D2B

Schedule: From 06/07/2016 to 07/07/2016

Users: Celia Castillo Blas and Felipe Gándara Barragán

Local Contact: Inés Puente Orench

- Experiment:

According to the proposal, we carried out high-resolution powder diffraction measurements to solid-solution metal-organic frameworks, with the aim of refining the position and occupancy of the different cations that are forming the materials. Three different samples were analyzed, and the measurements were carried out at room temperature for the three of them, with a wavelength of 1.59416 nm. Two additional measurements at low temperature were also collected for one of the samples, since our previous X-ray diffraction analysis indicated that a crystallographic phase transition takes place for this sample. The exposure time of each experiment was 4 hours. All experiments are summarized in *Table 1*.

Number experiment	Material Name	Composition	Temperature/K
1	ZnCo_12	$C_{17}H_8O_4F_6Zn_{0.6}Co_{0.4}$	50
2	ZnCo_12	$C_{17}H_8O_4F_6Zn_{0.6}Co_{0.4}$	150
3	ZnCo_12	$C_{17}H_8O_4F_6Zn_{0.6}Co_{0.4}$	300
4	ZnCo_110	$C_{17}H_8O_4F_6Zn_{0.2}Co_{0.8}$	300
5	ZnMn	$C_{17}H_8O_4F_6Zn_{0.5}Mn_{0.5}$	300

- Results:

The obtained neutron diffraction patterns are summarized in *figure 1*. In the case of the temperature study of the ZnCo_12 sample, we observe the same phase transition as the one by single crystal X-ray diffraction at low temperature, based on the difference in peak intensities. Further data analysis is currently being carried out to determine whether there is any structural domain due to the arrangement of the metal cations within the crystal structure.

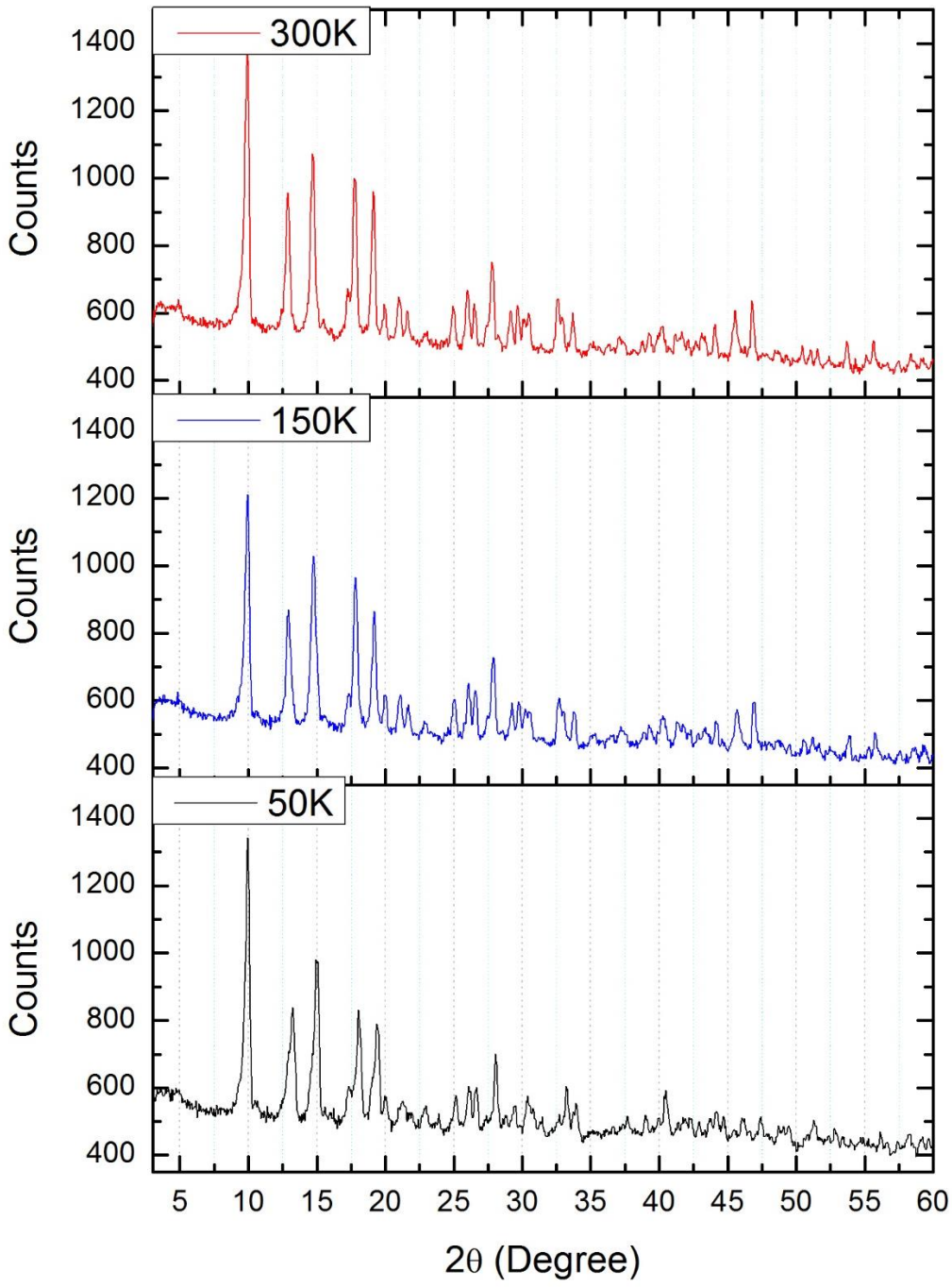

Figure 1. ZnCo_12 neutrons diffraction patterns compared.

The ZnCo_110 neutron diffraction pattern is in agreement with the single crystal X-ray diffraction data. As in the previous case, further data analysis is being carried out to determine the possible presence of structural domains.

As for the ZnMn material, the neutron diffraction pattern is also in agreement with the single crystal X-ray data.