Application Note SMX041

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SMX041 - Observing a temperature-induced phase transition of $Cu(ta)_2$, a MOF, with XtaLAB Synergy-ED

Introduction

Metal-Organic Frameworks (MOFs) present challenges in structural determination due to their porous structure. Disordered solvent in the pores gives rise to an increase in background while also not contributing to Bragg diffraction. This represents a challenging signal-to-noise situation for single-crystal structure determination.

Coupled to this, to fully understand MOF behaviour and activity, it is often necessary to remove solvent from the pores, or observe structural changes as a consequence of heating the sample. This can give rise to a loss of crystallinity, particularly for larger crystals of suitable size for single-crystal X-ray diffraction (SC-XRD). For this reason and also due to difficulty in growing large enough crystals for SC-XRD, many MOF researchers are accustomed to using powder X-ray diffraction (PXRD) for the majority of their structural analysis.

With the emergence of 3D ED/MicroED and integrated electron diffractometers such as the XtaLAB Synergy-ED[2], MOF samples do not need to be so large and samples typically used for PXRD are generally also suitable for single-crystal analysis with 3D ED/MicroED. This significantly extends the classes of framework materials amenable to single-crystal structure determination without involved and often unsuccessful crystallization protocols. Studying these samples at different temperatures is also desirable to understand phase transitions and their effects on pore shape and volume.

Catena-(hexakis(m-1,2,3-triazolato)-tri-copper(ii)), or $Cu(ta)_2$, has previously been characterised with SC-XRD and PXRD by Grzywa et al[1]. In their paper, two phases were structurally characterised: α-$Cu(ta)_2$, a tetragonal form; and β-$Cu(ta)_2$ a cubic form. Only α-$Cu(ta)_2$ was observed with SC-XRD in the original work, whereas the high-temperature β-phase was only observed with PXRD. Here, we sought to confirm the α to β phase transition with single-crystal diffraction on the same grain using 3D ED/microED and compare our results to that of Grzywa et al. A brief comparison is shown in Figure 2.

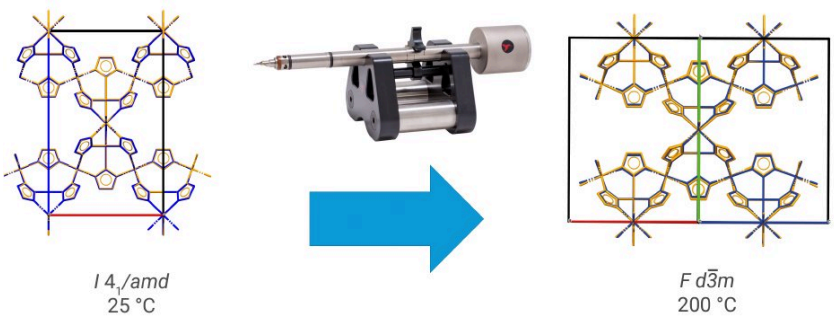

Figure 2: The phase transition observed for $Cu(ta)_2$ with X-rays (orange) and electrons (blue)

Experimental

While the α-form is accessible at ambient conditions, the β-form is only accessible over 120°C. To achieve this sample temperature in situ, the Hummingbird Scientific's MEMS biasing/heating sample holder was used.

This holder allows a tilt range of ±75° whilst giving the option to heat samples up to 1100°C and also apply an electrical bias. The holder silicon chips as a sample substrate, containing electron-transparent silicon nitride membranes for sample observation, which are resistively heated by an on-chip heating structure.

A sample of $Cu(ta)_2$ was prepared with gentle grinding and loaded onto an SiN heating chip mounted on the Hummingbird sample holder. The sample holder was then loaded into the XtaLAB Synergy-ED and a suitable crystalline grain of approx. 400 nm was found for data collection (Figure 3).

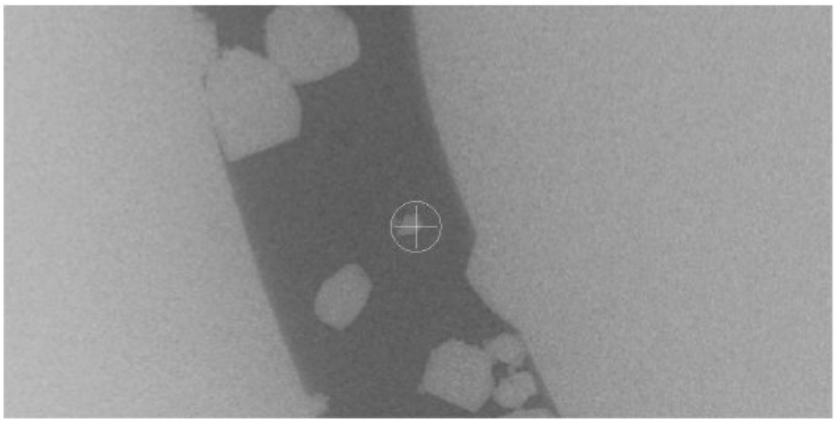

Figure 3: The sample grain used for data collection at both room temperature and 200°C

A data collection, one 60° (-30° to +30°) scan, was then carried out at 25°C in order to obtain a structure of the α-phase. The sample was then heated to 200°C in under a minute and the data collection was repeated using the same grain to obtain the structure of the β-phase.

Both datasets were processed in the same way and structures were solved and refined with Olex2 using scattering factors appropriate for electron diffraction.

Results

The results from data collections on the XtaLAB Synergy-ED are summarised next to the equivalent data from the 2012 Grzywa paper in Tables 1 and 2.

Table 1. Comparison of parameters for X-ray and ED structures for both forms.

Parameter	α-X-ray	α-ED	β-X-ray*	β-ED
a (Å)	11.8447 (7)	11.8(5)	17.4416(15)	17.4(3)
c (Å)	18.9782(13)	18.9(5)	-	-
Resolution (Å)	0.74	0.90	0.93	0.90

R_{int} (%)	17.13	53.73	-	43.89
R_1 (%)	4.75	16.65	-	13.85
R_p (%)	-	-	4.64	-
wR_2 (%)	5.84	45.87		42.63
R_{wp} (%)	-	-	-7.32	-

* Data from PXRD

Table 2: Comparison of bond lengths for X-ray and ED structures for both forms

Bond	**α-SCXRD**	**α-ED**	**β-PXRD**	**β-ED**
Cu1-N1	2.19	2.20	2.18	2.11
Cu1-N3	2.02	2.03	-	-
Cu1-Cu2	3.79	3.79	3.78	3.78
Cu1-Cu1	6.33, 5.92	6.31,5.92	6.17	6.17
Cu2-Cu2	7.59	7.57	7.55	7.55
Cu2-N2	2.04	2.11	2.32	2.11
Cu2-N4	2.35	2.42	-	-

The asymmetric units for the structures obtained are shown in Figure 4 with labelled atoms and the structures overlaid with those from the Grzywa study are shown in Figure 5 and 6. As can clearly been seen in both the numerical data and the structural overlays, the data from single-crystal electron diffraction are in very good agreement with the X-ray data previously reported.

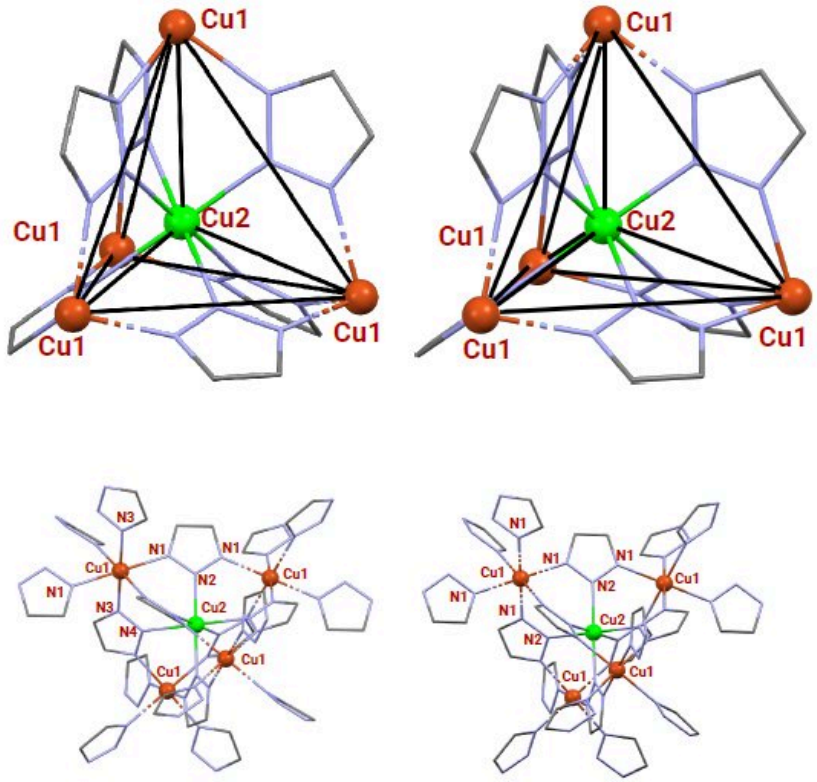

Figure 4: Numbering schemes for: Non-bonding Cu-Cu distances for the α-form (top left) and β-form (top right); and Cu-N distances for the α-form (bottom left) and
β-form (bottom right).

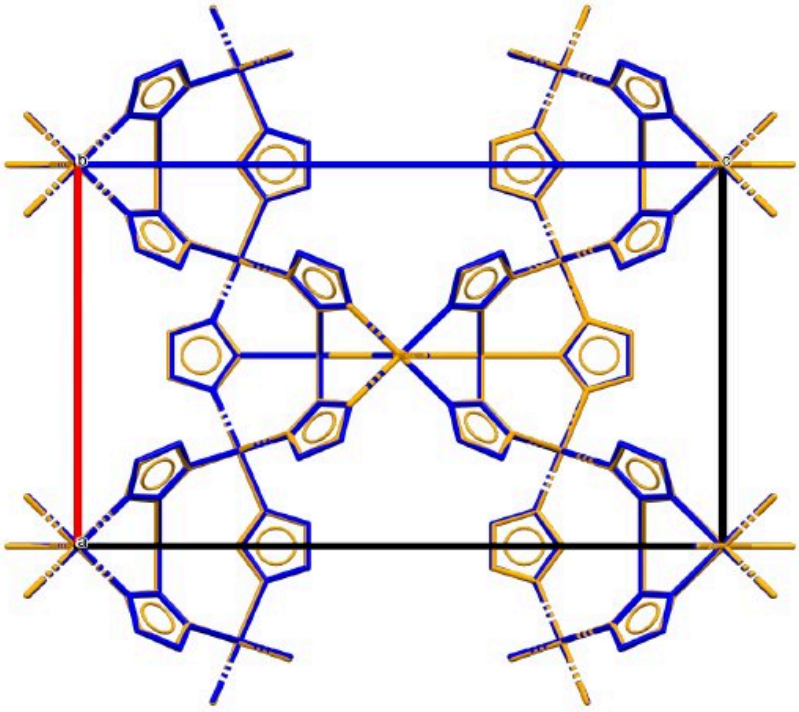

Figure 5: The tetragonal α-form of $Cu(ta)_2$ viewed along the b-axis.

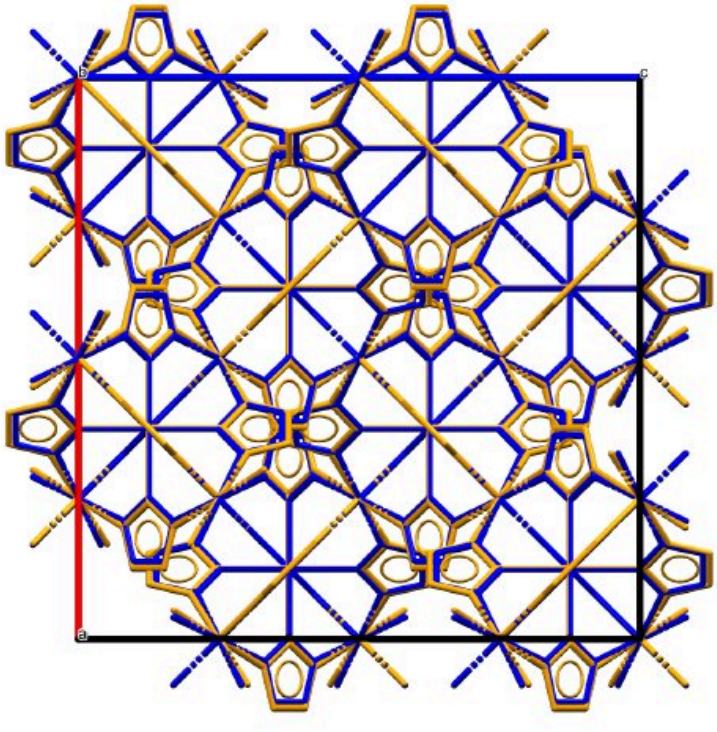

Figure 6: The cubic β-form of $Cu(ta)_2$ viewed along the b-axis.

Conclusions

The Hummingbird Scientific MEMS biasing/heating specimen holder provides XtaLAB Synergy-ED users a simple, turnkey solution for exploration of high temperature structural forms.

In this application note, the value offered by electron diffraction conducted with the XtaLAB Synergy-ED is demonstrated by enabling a single-crystal to single-crystal phase transition of a MOF material to be observed using the same grain with good agreement to prior experimental data.

Acknowledgements

We are grateful to Hummingbird Scientific for providing the unit on which this work was carried out.

References

1. Grzywa et al. *Dalton Trans*., 2012, **41**, 4239
2. Ito et al. *CrystEngComm*, 2021, **23**, 8622-8630

Related products

XtaLAB Synergy-ED

A new and fully integrated electron diffractometer for meas uring submicron crystals, utilizing a seamless workflow fro m data collection to structure determination of crystal struc tures.