CAU

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Direct-space methods for the structure determination of open-framework oxides and coordination polymers

Introduction

Open-framework structures, such as inorganic oxides and coordination polymers, have been extensively studied for their ability to selectively accommodate guest species in their pores and channels. Such materials have applications in heterogeneous catalysis, sorption, separation, and ion exchange. Many of these phases however do not form sufficiently large crystals for structure determination by single crystal X-ray diffraction. Structure determination from X-ray powder diffraction (XPD) is also complicated by the severe overlap problem introduced by the typically large unit cell lengths. We have shown that complicated framework structures with can be solved using direct-space methods if the secondary building units have been identified, even when using low resolution XPD data. In more complex cases charge-flipping can be used in combination with parallel tempering.

Structure Determination

Combining parallel tempering and powder-charge flipping

The structure of the gallogermanate, SU-66,[1] could not be solved by single crystal X-ray diffraction due to small crystal size, nor electron diffraction due to beam damage, and could not be solved from XPD data using conventional methods as 98% of the reflections were overlapping in the data. However, unit cell parameters and space group were determined using selected area electron diffraction and XPD. The cluster type was identified as the Ge_{10} cluster as suggested by IR spectroscopy. The structure of SU-66 was solved by parallel tempering in FOX[2] using low-resolution XPD, and two Ge_{10} clusters as input. Subsequent tests using previously solved structures, confirmed that germanate and zeolite structures built of up to two clusters in the asymmetric unit can be solved using low-resolution XPD data as long as clusters are used as input.
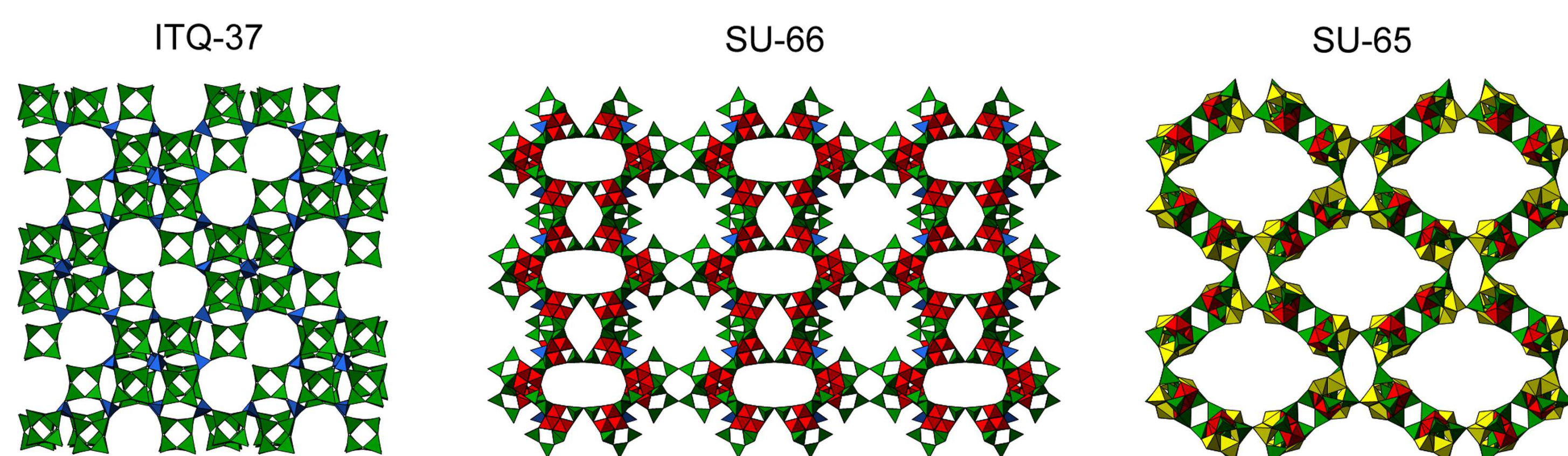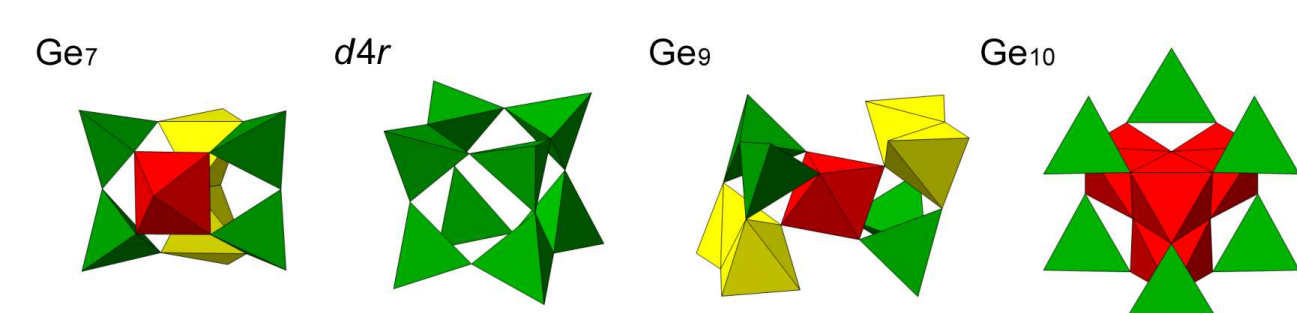

Ge7   d4r   Ge9   Ge10

ITQ-37   SU-66   SU-65

Figure 1 *Clusters common in open-framework germanates (top). Crystal structures of ITQ-37 (left), SU-66 (center) and SU-65 (right) as solved by FOX.*

Structure determination was not successful for SU-72 which contains three Ge_7 clusters in its asymmetric unit. The incorrect solutions produced by FOX consistently placed the Ge_7 clusters in approximately correct positions, but had incorrect orientations. The incorrect model used as input in Superflip[3] to define the initial structure factor phases. Superflip managed to solve the structure only when such a model was used as input.
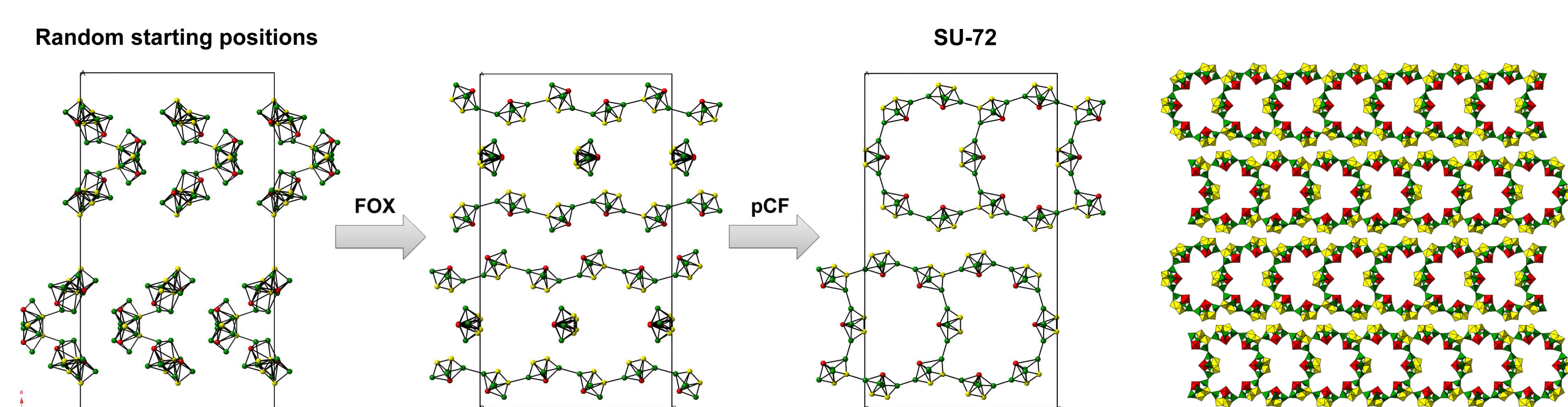

Random starting positions   SU-72

FOX   pCF

Figure 2 *Structure determination of SU-65 with FOX and then powder charge-flipping.*

Framework Dynamics

In situ structure dynamics investigation of SU-65

The structure of SU-65 was originally solved using single crystal diffraction data collected on beamline I19 at Diamond Light Source. Due to problems introduced by the small crystal size and beam damage, an adequate data set was obtained after three trips to Diamond. Later it was discovered that the structure of SU-65 could easily be solved using low-resolution XPD data collected within 9 minutes on an in-house diffractometer, using parallel tempering and two Ge_7 clusters.

	SU-65	SU-65ht
Space group	I2/a	I2/a
a (Å)	16.78	16.00
b (Å)	25.48	20.70
c (Å)	29.34	29.36
β (°)	94.5	90.0
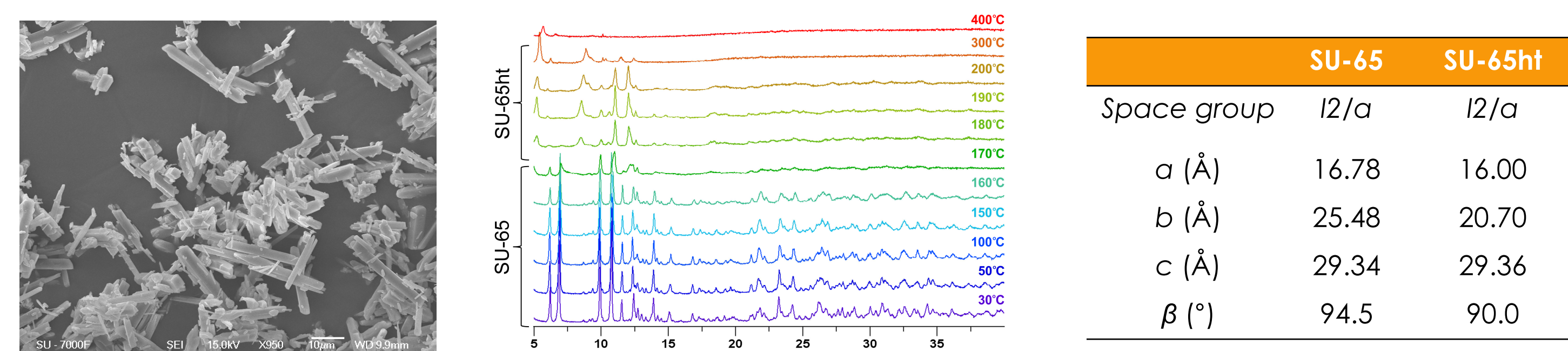
Figure 3 *SEM micrograph of SU-65 crystals (left). In situ XPD in vacuum showing the transformation of SU-65 into SU-65ht (center). Unit cell parameters of SU-65 compared to SU-65ht (right)*

In situ XPD with an in-house diffractometer showed that the unit cell suddenly changes at 170°C under vacuum. The unit cell parameters and original space group were determined by rotating electron diffraction. The high temperature phase (SU-65ht) has a unit cell volume that is 22% smaller than SU-65, primarily due to shortening of the *b*-axis. A model was created preserving the topology of SU-65 and based on the unit cell parameters determined by rotation electron diffraction, space group confirmed by XPD, and distance least squares geometry optimization. Due to the rather low quality of the XPD pattern of SU-65ht Rietveld refinement has not yet been performed.

SU-65   SU-65ht

Δ vacuum

SU-65ht observed

SU-65ht calculated

Figure 4 *Structure of SU-65 (left) and model of SU-65ht (center). The observed XPD and calculated XPD pattern of SU-65ht based on the model (right).*

A rare example of a porous layered coordination polymer

Direct-space methods are very suitable for the structure determination of metal-organic frameworks (MOFs) and coordination polymers as the organic linker molecules present in the framework are usually known and are often rigid. However due to the overlapping of reflections, determination of the space group can be difficult. The extinction symbol for a novel aluminium-based 4,4'-sulfonyldibenzoate coordination polymer, CAU-11,[4] appeared to be either *Pn--*, *Pna-*, *Pnc-*, or *Pnn-*. Through an Edisonian approach the structure of CAU-12 was solved in the space group *Pna2₁* using one aluminium atom and one linker molecule as input for FOX. The crystal structure consists of layers containing lozenge-shaped channels. CAU-11 is a rare example of a porous layered coordination polymer having a specific BET surface area of 350 m²g⁻¹ and a micropore volume of 0.17 cm³g⁻¹.
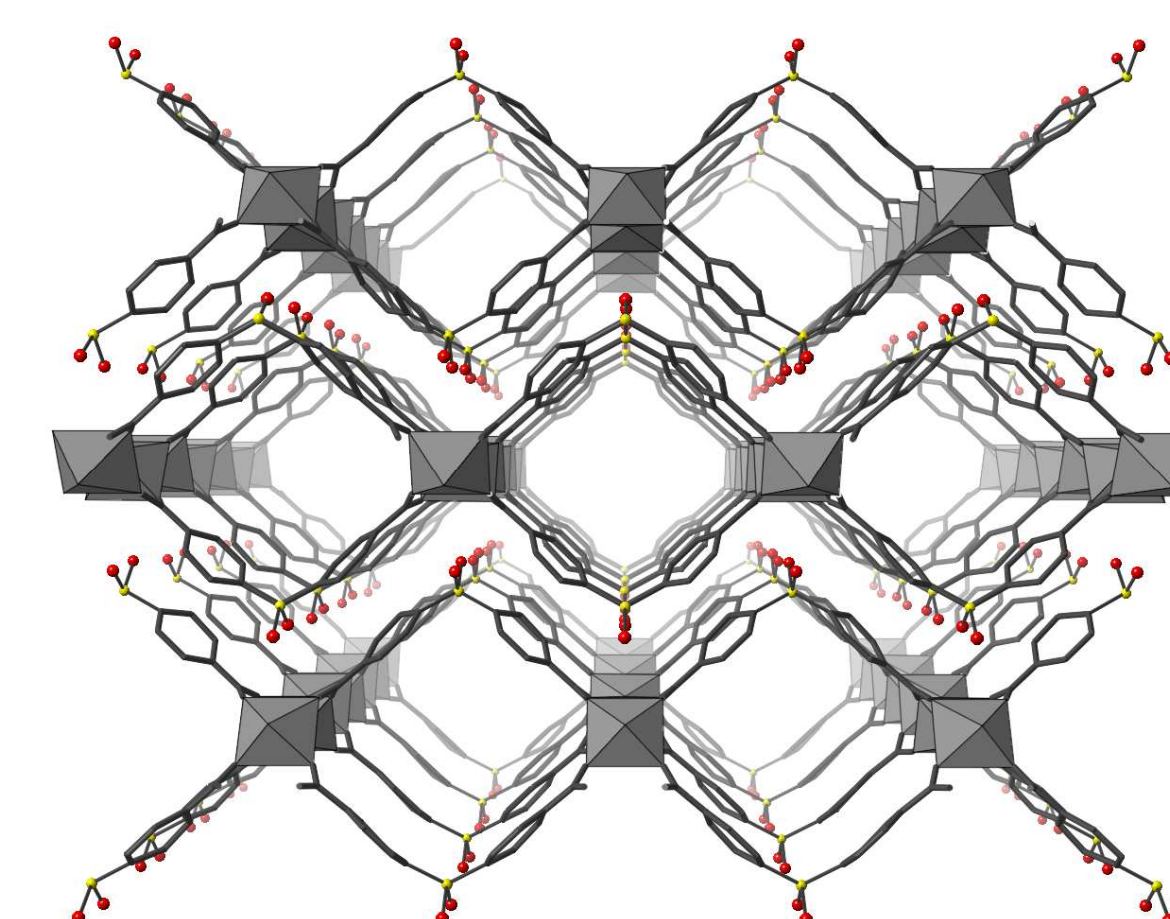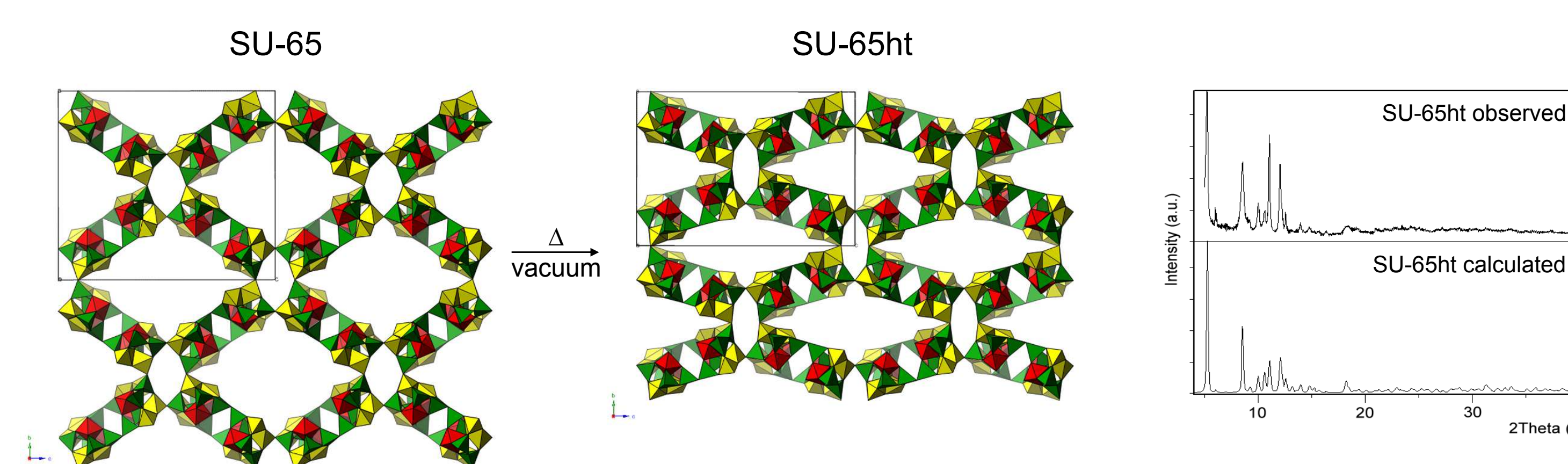

Figure 5. *Crystal structure of CAU-11*

References

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