Formation mechanism of metal oxido clusters: A complex modelling study using PDF and SAXS

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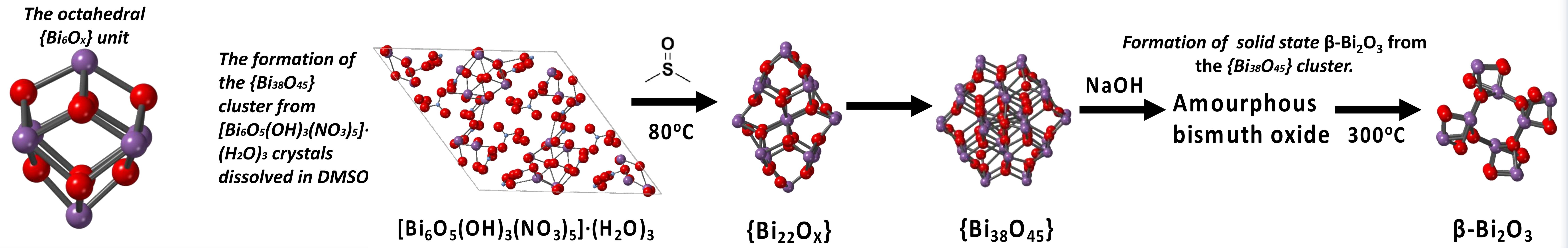
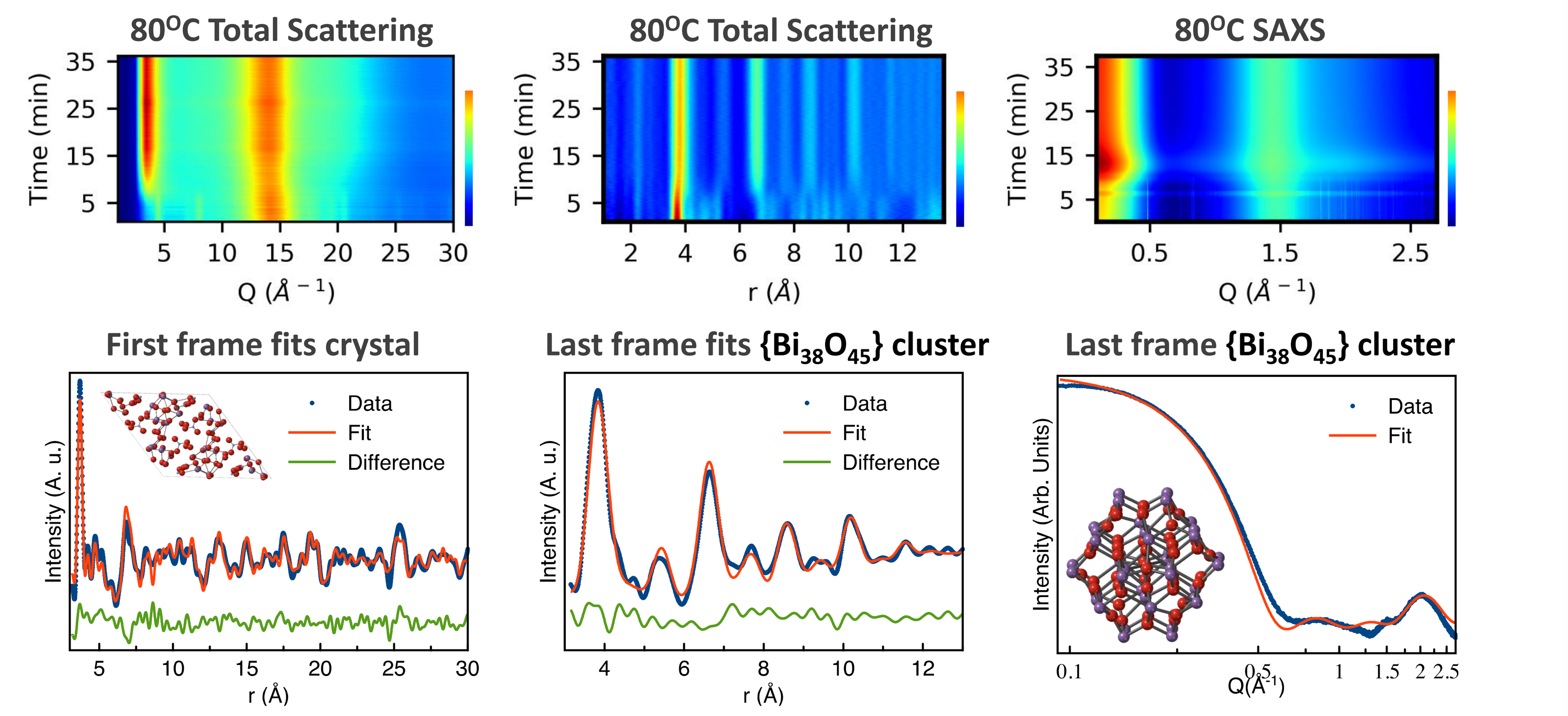
1: Introduction

Metal oxides of bismuth and its oxido clusters in solution have attracted much attention with potential applications ranging from antibacterial agents to photocatalysis.[1] However, the chemical processes involved in the cluster formation are not well understood: While the molecular structures of various clusters have been solved by single crystal diffraction, it is much more challenging to study structures of such clusters directly in solution.

Bismuth oxido clusters exist in a range of sizes, most of them built up by simple or edge-sharing octahedral $\{Bi_6O_x\}$ units[2]. Here, we use in situ X-ray total scattering with PDF analysis to study the formation of a $\{Bi_{38}O_{45}\}$ cluster starting from $[Bi_6O_5(OH)_3(NO_3)_5]\cdot(H_2O)_3$ crystals dissolved in DMSO.[3]
The PDF analysis gives unique insight into the structural rearrangements on the atomic scale. By combining with Small Angle X-ray Scattering, SAXS, we furthermore investigate the size, morphology and size dispersion of the clusters taking place in the process. The two techniques complement each other, allowing us to follow the cluster chemistry as it takes place.



2: *In situ* PDF and SAXS studies

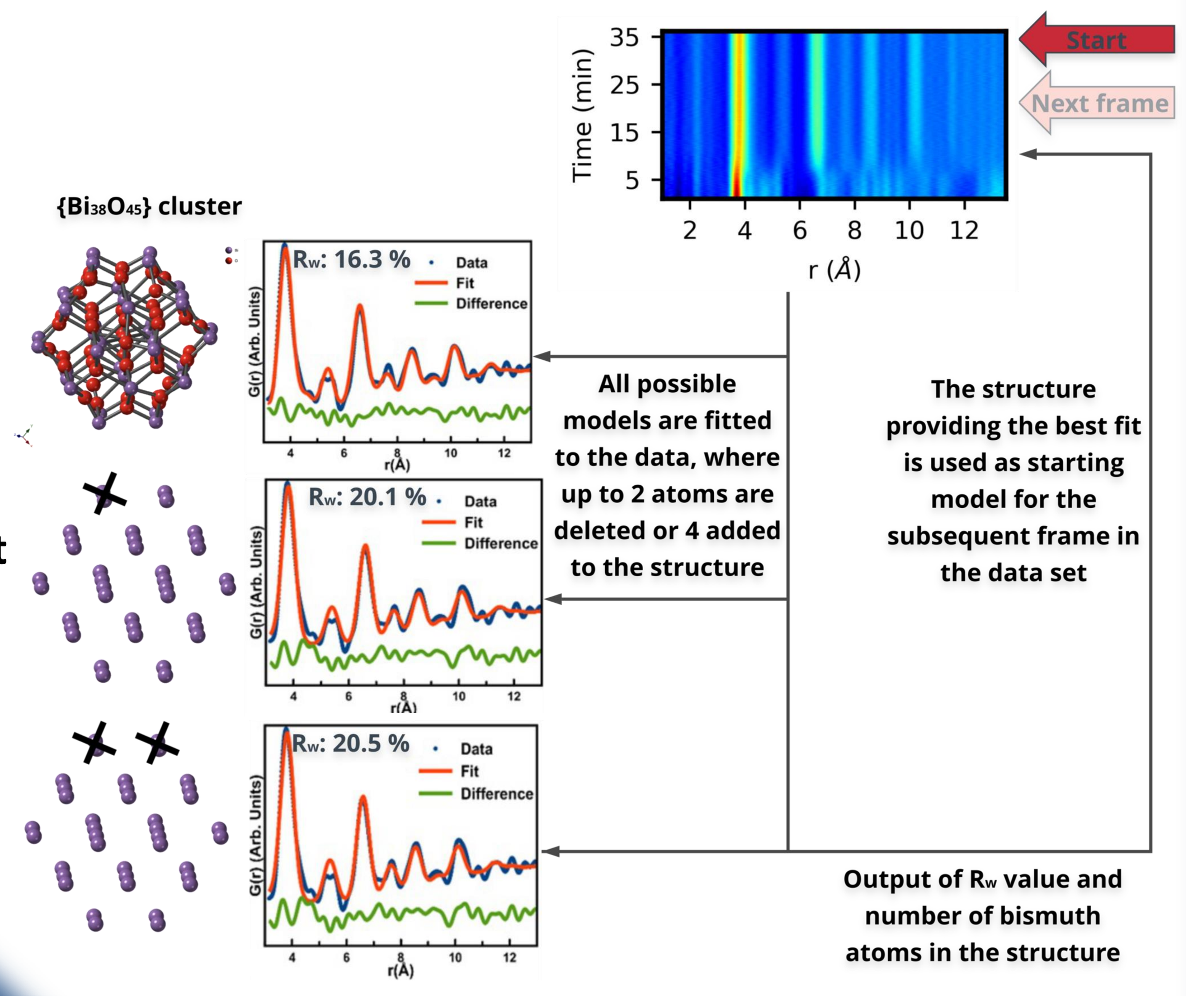


In situ PDF and SAXS studies show:

- Crystalline material in the beginning of the reaction, which can be fitted with $[Bi_6O_5(OH)_3(NO_3)_5]\cdot(H_2O)_3$
- Formation of a nano-sized cluster, which can be fitted with the $\{Bi_{38}O_{45}\}$ structure in the last frame.

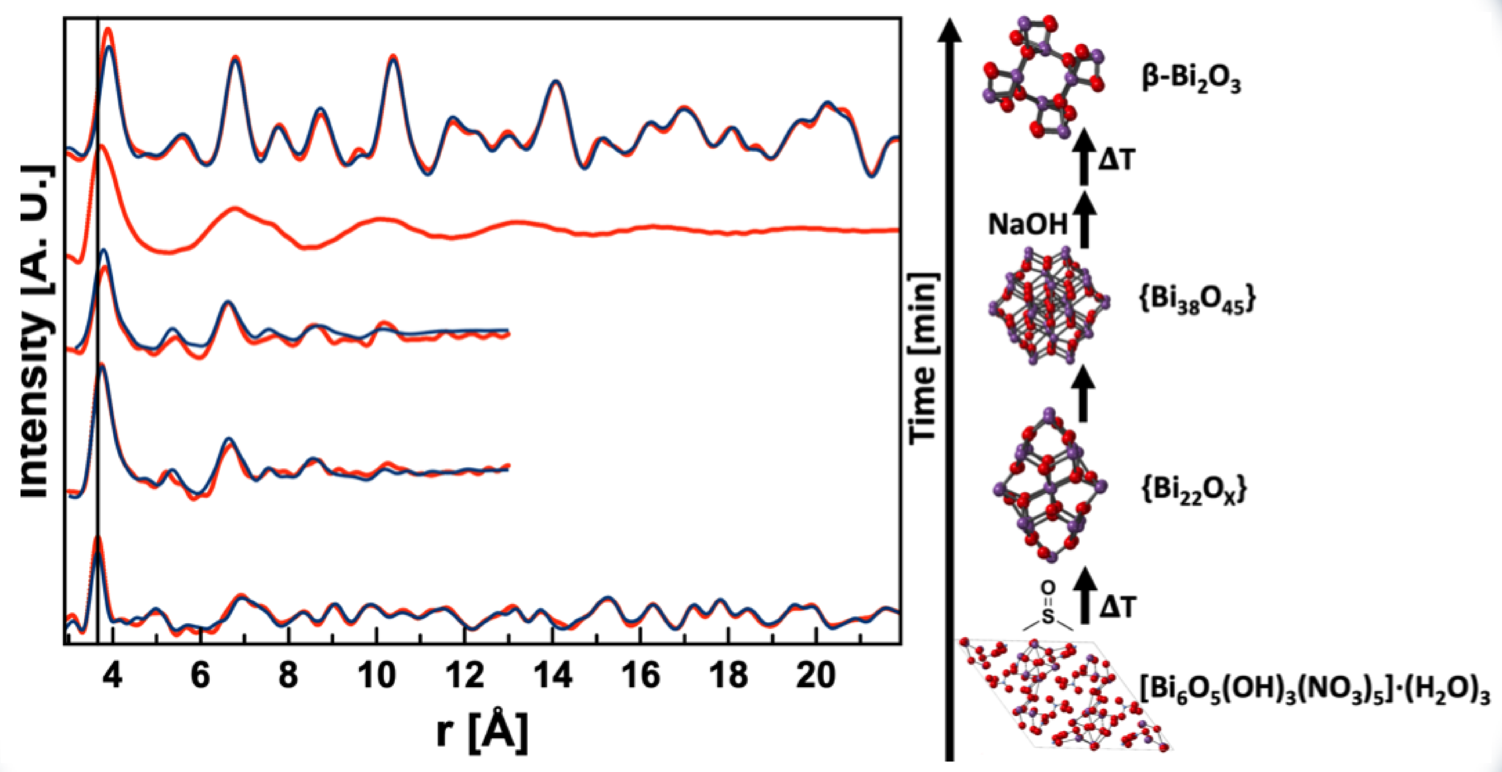
3: Modelling of timeresolved PDFs: Elucidating the intermediate structure

- A structure for the intermediate clusters is elucidated based on the known $\{Bi_{38}O_{45}\}$ cluster structure.
- Bi atoms are removed or added to the structure until the best fit is obtained.



6: From building blocks to materials

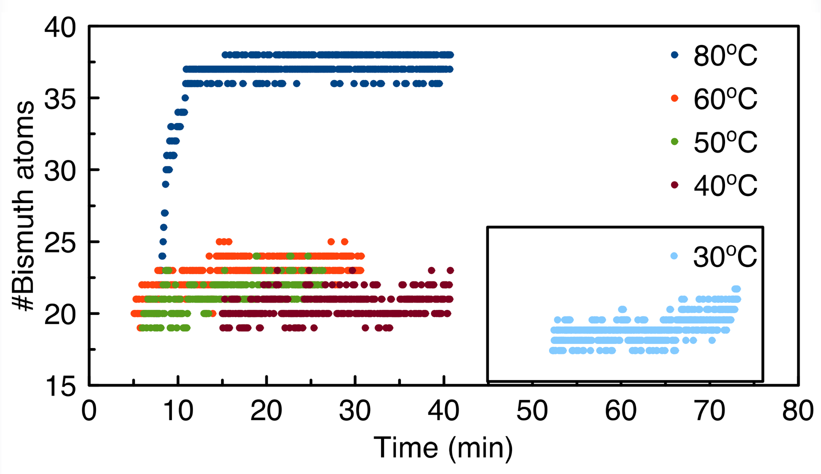
- The $\{Bi_{38}O_{45}\}$ cluster is synthesized by dissolving $[Bi_6O_5(OH)_3(NO_3)_5]\cdot(H_2O)_3$ in DMSO and the reaction goes through an intermediate of 19 - 23 bismuth atoms



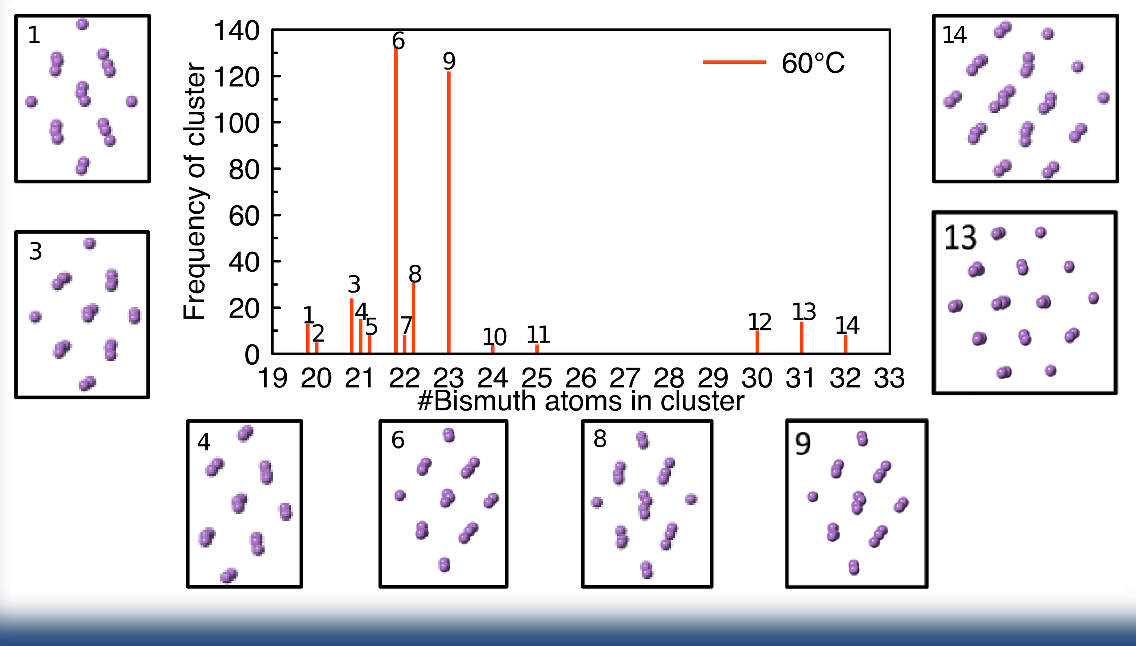
- The intermediate is found from permutations of the $\{Bi_{38}O_{45}\}$ structure and analyzed with complex modelling.
- The $\{Bi_{38}O_{45}\}$ cluster can be used for synthesis of the photocatalytically active β-Bi_2O_3.

4: Cluster modelling reveals intermediate

- The analysis confirms the $\{Bi_{38}O_{45}\}$ cluster as product and reveals an intermediate containing 19 – 23 bismuth atoms

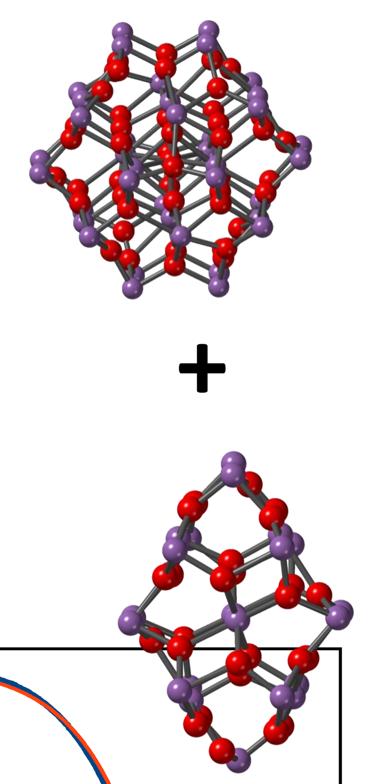


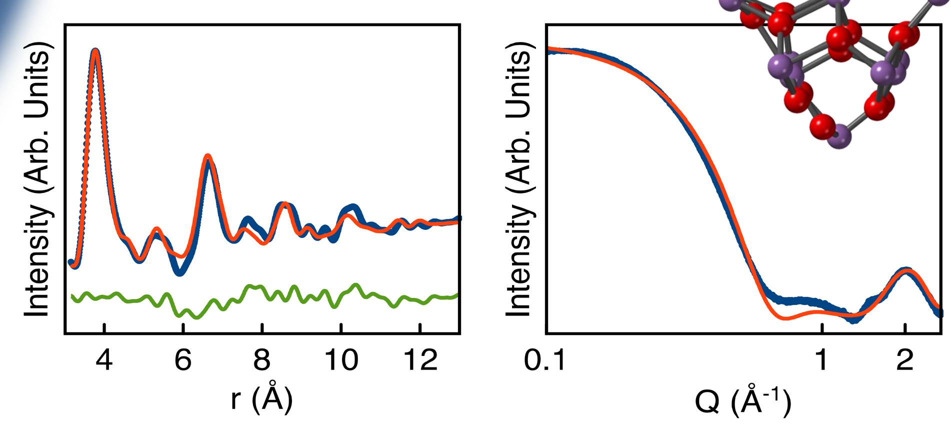
- The structure output from the analysis all follow the same building block principle.



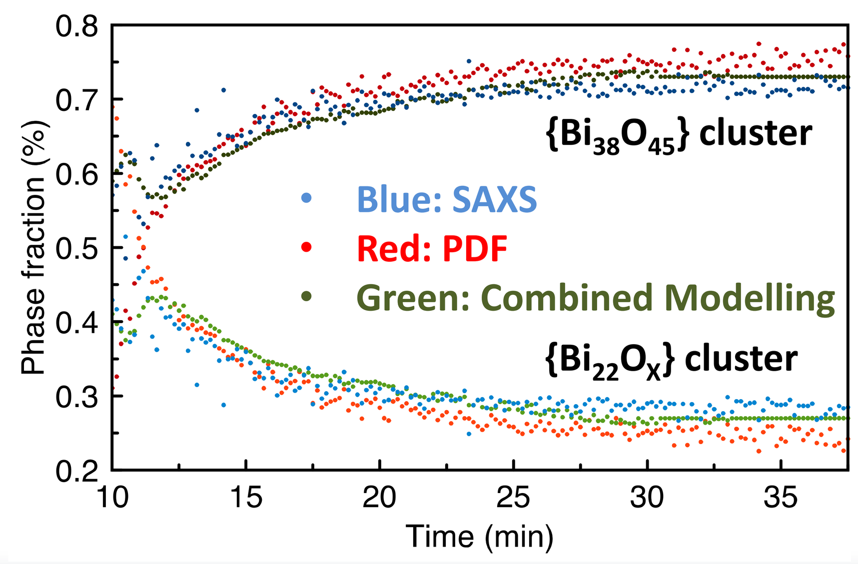
5: Two-phase refinement with complex modelling

- The $\{Bi_{38}O_{45}\}$ cluster found from the last frame.
- The $\{Bi_{22}O_X\}$ cluster found from permutations.





- Timeresolved fits reveal increasing $\{Bi_{38}O_{45}\}$ phase fraction.



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[1] M. Schlesinger, et. al, Dalton T 42 (2013), 1047-1056
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