

In-situ EDXRD investigations of the formation of a new polyoxovanadate with composition $[V_{14}Sb_8(C_6H_{15}N_3)_4O_{42}(H_2O)] \cdot 4H_2O$ under solvothermal conditions

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Polyoxovanadates (POVs) modified by heteroatoms (As, Sb or Ge) in the cluster shell are of special interest because such clusters expand and modify the charge density and the coordination ability of the surface. In contrast to As, POVs with Sb or Ge are less explored [1-6]. More or less nothing is known about the crystallization mechanisms of such cluster compounds and hence the successful preparation of a new POV is almost the result of trial-and-error chemistry. *In-situ* energy dispersive X-ray diffraction (EDXRD) investigations may provide important information about the crystallization processes occurring under solvothermal conditions. Recently we investigated for the first time the formation of Ge and Sb modified POVs with compositions $\{C_6H_{15}N_3-H_3\}[V_{14}Ge_8O_{50}]$ and $\{Ni(C_5N_3H_{15})_2\}_2[V_{15}Sb_6O_{42}(H_2O)Ni(C_5N_3H_{15})_2]$ at beamline F3/HASYLAB/DESY in Hamburg [7, 8]. In further *in-situ* EDXRD experiments the crystallization of an Sb POV with composition $[V_{14}Sb_8(C_6H_{15}N_3)_4O_{42}(H_2O)] \cdot 4H_2O$ ($C_6H_{15}N_3=1$ --(2-aminoethyl)piperazine) (**I**) [9] was investigated. The special structural feature of **I** are four Sb-N bonds to 1-(2-aminoethyl)piperazine groups completing the charge-neutral $[V_{14}Sb_8(C_6H_{15}N_3)_4O_{42}(H_2O)]$ clusters. Such linking of organic molecules to the POV clusters was never observed until now (Fig 1).

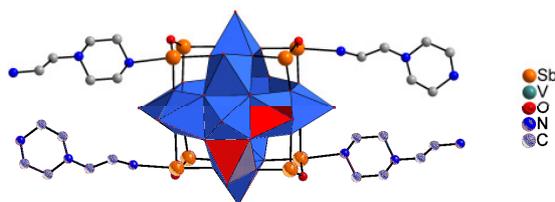


Fig. 1: Spherical cluster of **I** with amine molecules.

For the synthesis of **I** 0.34 mmol Sb_2O_3 and 0.85 mmol NH_4VO_3 were dispersed in 2 mL of a 75 % aqueous solution of 1-(2-aminoethyl)piperazine and heated to 160 – 180 °C in an autoclave with a glass-liner as reaction vessel. The reactions were carried out under stirring conditions. All experiments were performed at F3/HASYLAB/DESY/Hamburg. X-ray diffraction patterns were recorded with acquisition times of 300 s. For the evaluation of the resulting data the program “calf3” was used, which was developed by A. Rothkirch (HASYLAB, DESY). The crystallization kinetics of the formation of **I** were studied as a function of the reaction temperature (Fig. 2; left).

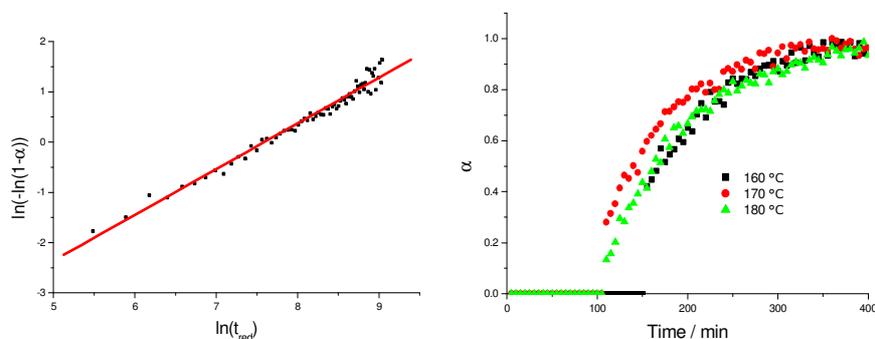


Figure 2: Extent of reaction α for $T = 160 - 180$ °C of the (001) reflection (right); Sharp-Hancock-Plot for the data obtained at 180 °C. The Avrami exponent is obtained from the slope (left).

The kinetic analysis was performed using Sharp-Hancock plots (Fig. 2; left) and established kinetic models (Fig. 3) were used to get hints of the processes occurring in the reaction slurry [10]. The data match well with a diffusion-controlled process at $T = 170^{\circ}\text{C}$ and with the first order reaction at 180°C . For temperatures 170°C and 180°C a good agreement with the models D3, D4 (170°C) and F1 (180°C) is obtained. For $T = 160^{\circ}\text{C}$ no reasonable fit of the experimental data to the model kinetics could be found.

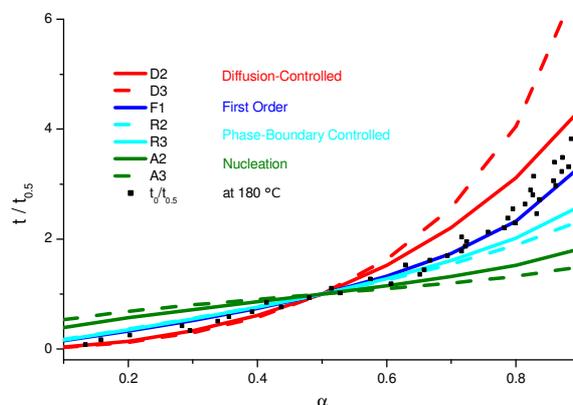


Fig. 3 Comparison of the experimental data with different crystallization mechanisms for $T = 180^{\circ}\text{C}$.

In-situ EDXRD experiments demonstrate that the formation of **I** occurs without crystalline intermediates and/or precursors, i.e., the compound crystallizes in a one-step reaction. The analysis of the crystallization kinetics suggests that different mechanisms dominate at different temperatures, and the values of the Avrami exponents indicate superimposing and/or consecutive mechanisms.

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