Controlling Nucleation and Crystal Growth of a Distinct Polyoxovanadate Cluster: An *In-Situ* EDXRD Study under Solvothermal Conditions

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Polyoxovanadates (POVs) are of interest due to their versatile properties and potential applications covering the wide range form medicine to catalysis [1]. Especially POVs modified by integration of heteroatoms like As, Sb or Ge are attractive because such heteroatoms expand the cluster shell, varies the charge density and the coordination ability of the surface can be altered.

Recently we investigated the nucleation and crystal growth of Sb modified POV with compositions $[V_{14}Sb_8(C_6H_{15}N_3)_4O_{42}(H_2O)]\cdot 4H_2O$ (I) $\{V_{14}\}$ [2], $(C_6H_{17}N_3)_2[V_{15}Sb_6(C_6H_{15}N_3)_2O_{42}(H_2O)]\cdot 2.5H_2O$ (II) $\{V_{15}\}$ [3] and $\{C_6H_{15}N_3\}_4[V_{16}Sb_4O_{42}]\cdot 2H_2O$ (III) $\{V_{16}\}$ [3] ($C_6H_{15}N_3$=1-(2-aminoethyl)-piperazine) at beamline F3/HASYLAB/DESY in Hamburg (Fig. 1).

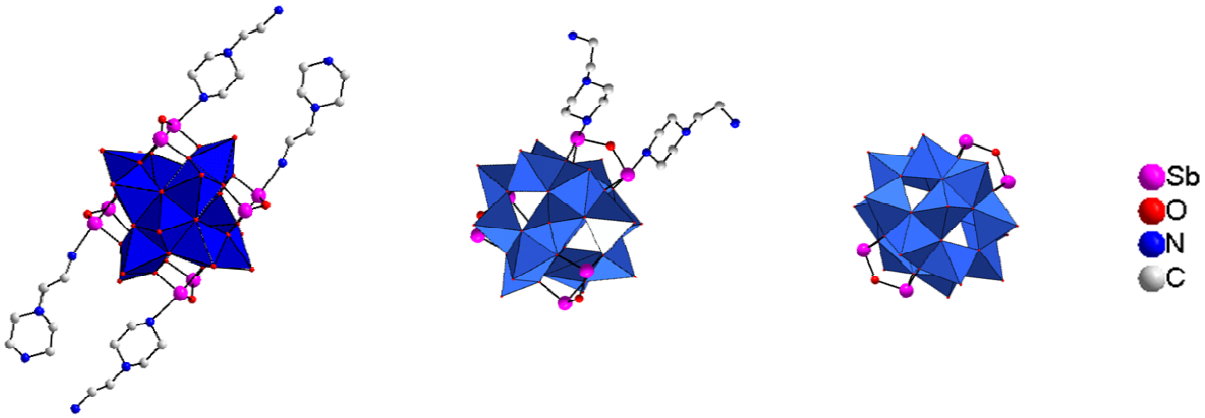

Fig. 1: Important structural motifs in compounds **I** (left), **II** (middle) and **III** (right).

Interestingly the change of the concentration of the amine led to the formation of these three different POVs in a narrow window while using the identical molar ratio of NH_4VO_4 and Sb_2O_3 under stirring conditions (T: 150-170 °C). This is in contrast to the results obtained under static conditions were different educt ratios, reaction temperatures and amine concentrations were necessary. In Figure 2 the results of the in-situ studies are schematically summarized. The formation of the POV with the largest number of reduced V centers $\{V_{16}\}$ (**III**) requires the highest amine concentration while at lower concentrations the other two compounds are formed [4]. Applying an amine concentration of 77.5% first reflections of **II** ($\{V_{15}\}$) appeared followed by reflections of compound **I** ($\{V_{14}\}$) at later reaction times when no further growth of reflection intensities of **II** could be detected (Fig. 3, right). This observation indicates that the amine concentration is not high enough for further nucleation, crystallization and growth of **II** but suitable for nucleation and growth of **I**.

Increasing the reaction temperature during the formation of one compound leads to a reduction of the induction period, which is shown in Figure 3, left.

The results also demonstrate that the formation of compound **I** needs the longest t_{ind} which include different steps like dissolution of Sb_2O_3, reduction of V_V to V_{IV} and kinetics of nucleation, whereas compound **III** with the highest amine concentration begins to crystallize within a few minutes.

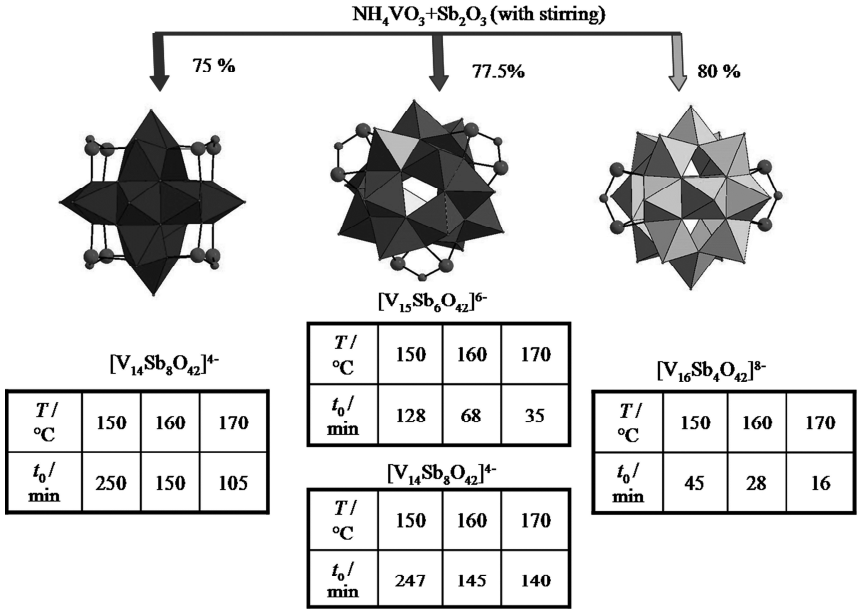

Fig. 2: Schematic summary of in-situ EDXRD investigations on the formation of **I** (left), **II** (middle) and **III** (right).

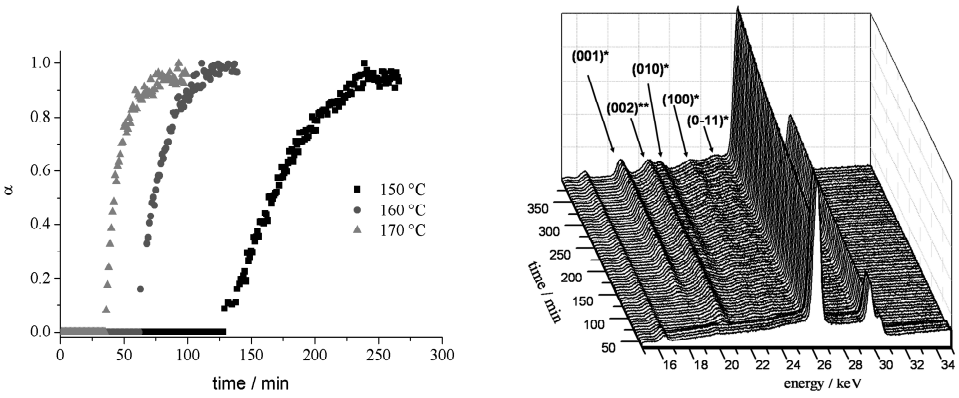

Fig. 3: Extent of reaction α of compound **II** for T=150-170 °C (left); time-resolved *in-situ* EDXRD spectra recorded during the crystallization of **I** (*) and **II** (**).

All experiments were accomplished at F3/HASYLAB/DESY/Hamburg. The resulting data were evaluated with the program “f3tool”, which was developed by A. Rothkirch (HASYLAB, DESY). Established models for crystallization kinetics were used to evaluate the results [5].

The results show the sensitivity of solvothermal syntheses and the results of the *in-situ* EDXRD experiments allow to control crystallization of one of the three different POVs.

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