In-situ EDXRD Investigations on the Formation of the Thioantimonate [Fe(tren)]Sb_4S_7 and it's Transformation into [Fe(tren)]$FeSbS_4$

B. Seidlhofer, E. Antonova, J. Wang, D. Schinkel, and W. Bensch

Institute of Inorganic Chemistry, University of Kiel, Max-Eyth-Straße 2, 24118 Kiel, Germany

The interesting properties and potential applications of thiometallates as e.g. photoconductors, catalysts, ion exchangers etc. attract an increasing number of scientists in the fields of chemistry, material sciences and catalysis. Many interesting compounds are obtained by trial-and-error procedures because the fundamental reaction mechanisms are not well understood. Analyzing the recipes given in the literature there is no obvious relation between the reaction conditions and product formation. This observation is not surprising taking into account the complex nature of the heterogeneous reactions occurring under solvo-/hydrothermal conditions. In-situ energy dispersive X-ray diffraction (EDXRD) is an appropriate method to investigate such reactions under real conditions. The main goal is to acquire information about the crystallization kinetics and reaction mechanisms. Here we present the results of in-situ EDXRD experiments on the formation of the thioantimonate [Fe(tren)]Sb_4S_7 (**I**) and it's transformation into [Fe(tren)]$FeSbS_4$ (**II**) being a mixed-valent Fe^{II}/Fe^{III} compound with an protein-analogous $[2Fe^{III}\text{-}2S]^{2+}$ cluster [1, 2].

The in-situ EDXRD investigations were conducted with 0.3 mmol $FeCl_3$, 0.3 mmol Sb and 0.9 mmol S in 2 mL of 50 – 100% tren (tren = tris-(2-aminoethyl)amine). To monitor the influence of the temperature, experiments were done between 140 and 180 °C. All experiments were performed at beamline F3/HASYLAB/DESY in Hamburg. More details about the setup of the experimental station F3 can be found in reference [3].

The two different Fe containing thioantimonates [Fe(tren)]Sb_4S_7 and [Fe(tren)]$FeSbS_4$ (Fig. 1) can be obtained adjusting the tren concentration. **I** crystallizes with amine concentrations between 50 and 90 % and **II** between 70 and 100 %. In the intermediate concentration range (70 – 90 %) both compounds coexist.

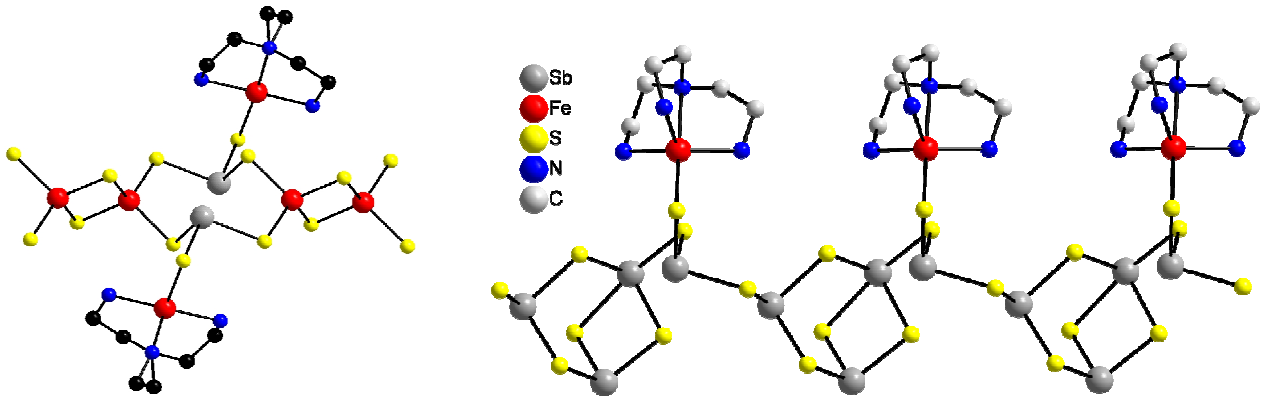

Figure 1: Structures of [Fe(tren)]$FeSbS_4$ (left) and [Fe(tren)]Sb_4S_7 (right).

The temperature strongly influences the crystal growth of **I**. Both the induction time and reaction rate increase with temperature (Fig. 2 left). At 140 and 160 °C evaluation of the data indicates that diffusion plays the key role whereas at 180 °C nucleation seems to dominate.

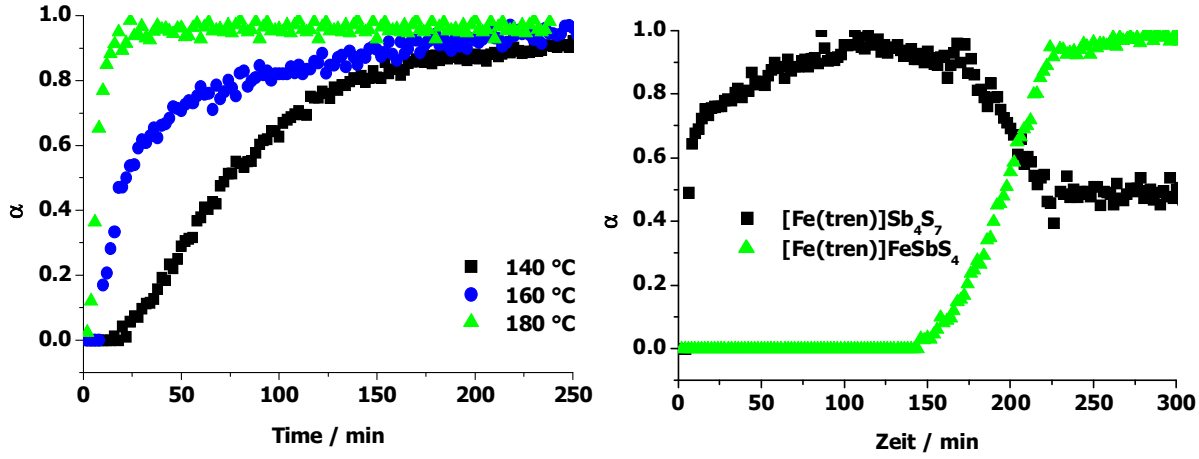

Figure 2: Evolution of the normalized area of the (002) reflection of **I** depending on T (left) and evolution of the normalized areas of the (002) reflections of **I** and **II** (concentration of tren = 80 %, T = 160 °C) (right).

An increase of the amine concentration lowers the induction time and the reaction rates of **I** and **II**. Applying 80 % tren (Fig. 2 right) **II** starts to grow after about 140 minutes, while **I** is decomposed until the growth of **II** is finished. Above about 220 min. the compounds coexist. A phase pure material **I** with 80 % tren solution can only be obtained stopping the reaction after about 130 min.

A change of the reaction mechanism depending on the amine concentrations is also observed. For concentrations where only **I** is crystallizes, the growth seems to follow a first order mechanism. In the regime where both compounds coexist the growth of **I** is mainly diffusion and that of **II** nucleation controlled. At higher concentrations, where only **II** appears, phase-boundary control seems to dominate.

The present example shows one of the problems of solvothermal syntheses: phase purity of the products can only be achieved by variation of several reaction parameters. In addition, the results obtained for 80 % tren solution suggest that thioantimonate compounds may be used as sources for the synthesis of new compounds, i.e., one compound can be transformed to another one like **I** into **II** in the present system.

References

[1] M. Schaefer, R. Stähler, R. Kiebach, C. Näther, and W. Bensch, Z. Anorg. Allg. Chem. **630**, 1816 (2004).

[2] R. Kiebach, W. Bensch, R.-D. Hoffmann, and R. Pöttgen, Z. Anorg. Allg. Chem. **629**, 532 (2003).

[3] L. Engelke, M. Schaefer, M. Schur, and W. Bensch, Chem. Mater. **13**, 1383 (2001).