

## **Zeotype materials based on thioantimonates**

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### **Introduction**

The preparation of non-oxidic open frameworks akin to zeolithes often referred to as zeotype materials is still a challenging issue in solid state chemistry [1]. Structures based on semiconducting materials such as sulfides have attracted particular interest since the initial report from Bedard et al. on open framework thiogermanates and -stannates [2] despite the limitations in stability for practical applications. The number of frameworks with exchangeable alkylammonium cations based on these group (IV) thiometalates, however, emerged to be rather limited. Consequently, thioantimonate(III) building units with their great diversity of coordination geometries were employed in the search for novel framework types [3]. Apart from the cetineite type compounds, which represent rather ionic oxychalcogenides no covalently linked thioantimonate frameworks have been reported to date in which the templating cations can be exchanged.

### **Results**

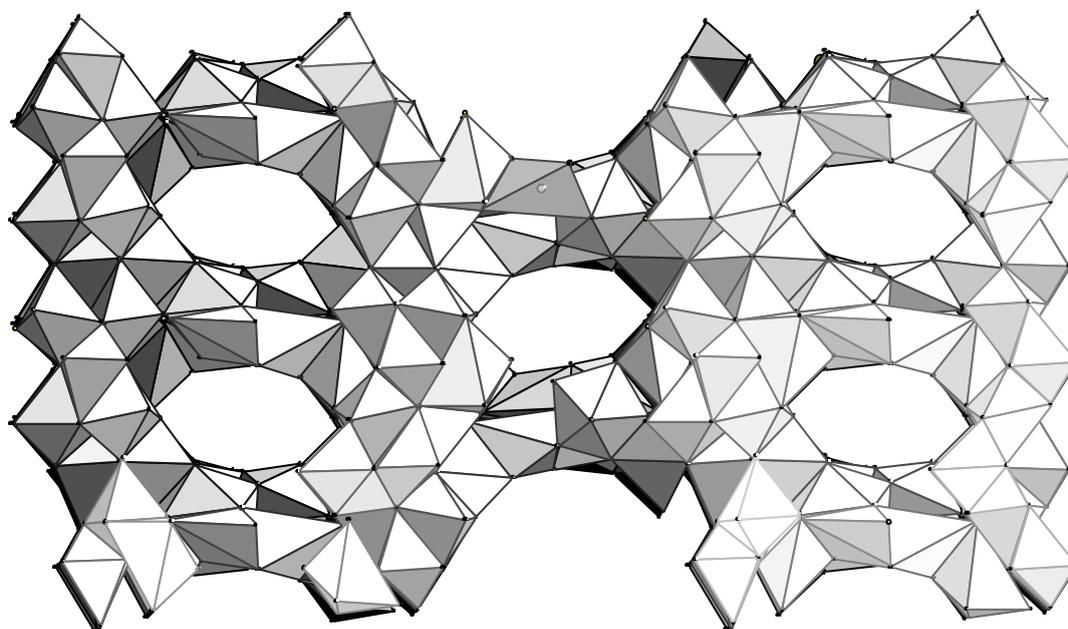
The reaction of antimony and sulfur under solvothermal conditions in the presence of small organic amines yields a number of different thioantimonate frameworks [4]. Within a limited range of conditions for the synthesis we recently obtained a set of novel thioantimonates which have been identified by single crystal and powder diffraction to possess identical frameworks of the composition  $\text{Sb}_{21}\text{S}_{34}^{5-}$ . Needle shaped crystals with this framework type were obtained with methylamine, ethylamine, ethylenediamine, diaminopropane, and ammonia of which five protonated amine molecules are required for charge compensation.

The anionic framework is build up from  $\text{SbS}_3$ -pyramids linked into infinite  $\text{Sb}_4\text{S}_7^{2-}$ -chains running along the c-axis. These chains are interconnected by  $\text{Sb}_5\text{S}_{10}$  units comprising  $\text{SbS}_4$ -trigonal bipyramids resulting in the formation of a 3D-framework exhibiting channels parallel to the c-axis with an approximate free opening of 0.4 nm by 0.7 nm as shown in Fig.1. The positions of the template ions could only be resolved in

the ethylenediamine compound indicating severe disorder for the other cations. Thermogravimetric investigations confirm the stoichiometry with five (monoprotonated) amine molecules. All compounds decompose between 210 °C and 270 °C in a single step under inert atmosphere forming crystalline  $\text{Sb}_2\text{S}_3$ .

The size of the channels and the presumably loose bonding of the amines to this framework prompted us to investigate the possibility of exchanging the organic cations. Refluxing the compounds of ammonium- and methylammonium for several hours in aqueous solutions of various alkali halides and subsequent washing resulted in different degrees of exchange. EDX investigations show a homogeneous distribution of the alkali metal cations within the host crystals. In addition, small shifts of the reflections in the powder patterns after ion exchange indicate some flexibility of the framework.

Fig. 1 Polehedral representation  $\text{Sb}_{21}\text{S}_{34}$  framework; view along the channels running parallel to the c-axis with an open diameter of approximately 0.4 nm by 0.7 nm.



## References

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