Copper thioantimonate and copper thioantimonide nanoparticles obtained by hot injection: formation mechanism

Fábio Baum[1]*, Tatiane Pretto[2], Marcos José Leite Santos[1,2]

[1] Universidade Federal do Rio Grande do Sul, PPGCIMAT, Brazil.
[2] Instituto de Química, Universidade Federal do Rio Grande do Sul, Brazil.

[#]Corresponding author: fabio.baum@ufrgs.br

In this work we present a systematic study on the formation mechanism of copper thioantimonate (Cu_3SbS_4) and copper thioantimonide ($CuSbS_2$) nanoparticles synthesized by hot injection. In a three-neck flask, 0.45 mmol of copper chloride I and antimony chloride III and 7 mL of oleylamine were mixed, degassed at 80 °C, and heated to the temperature of reaction (between 200 and 250 °C). In another flask, 1 mmol of elemental sulfur and 3 mL of oleylamine were mixed and heated to 60 °C. The sulfur solution was injected in the copper solution, the reaction was allowed to proceed for 10 minutes and aliquots were taken after 1, 2 and 5 minutes of reaction. The nanoparticles were characterized by UV-VIS-NIR absorption spectroscopy, transmission electron microscopy, Raman spectroscopy, and X-ray diffraction (XRD). The analysis of the XRD patterns and Raman spectra show the formation of Cu_3SbS_4 and $CuSbS_2$ in all reaction conditions, as well as the formation of Sb_2O_3 in temperatures up to 230 °C and metallic antimony at 250 °C. The results clearly show the formation of Cu_3SbS_4 at the beginning of the reaction and, as the reaction progress, it is converted to $CuSbS_2$. In addition this process is found to be faster in higher temperatures. To explain this behavior, we suggest a mechanism where the Sb precursor is oxidized to Sb^{5+} in the sulfidic medium and as the reaction progresses Sb^{5+} is reduced back to Sb^{3+} by oleylamine.

Acknowledgements
The authors thank to CAPES and CNPq for financial support, CMM and CNANO/UFRGS.