TEM Characterization of Quaternary Cu_2ZnSnS_4 Nanocrystals

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Controlling structure and composition in synthesis of colloidal CZTS nanocrystals is challenging and crucial for applications. Electronic and optical properties are deeply related to structure. Transmission electron microscopy is a unique tool for understanding ordering at nanoscale. Here we apply advanced *ex-situ* TEM techniques such as HRSTEM-HAADF, HR-TEM, STEM-EELS, STEM-EDX to solve the crystal structure.

Cu_2ZnSnS_4 nanocrystals were synthesized with a heating-up method: during the initial heating stage (110°C, 30 min), 10 nm diameter nanoparticles were formed, having an initial composition of $Cu_{3.1}Zn_{1.5}S4$. During the final heating stage (280°C), after 10 minutes composition got constant at $Cu_{2.1}Zn_{1.14}SnS_4$ with size practically unchanged with respect to the initial nanoparticles.

Size of nanocrystals has been determined by comparing HRTEM and STEM-HAADF images. STEM-HAADF being sensible to chemical contrast, it is possible to observe the sites occupied by heavier atoms (Sn) and distinguish between kesterite (space group I-4) , stannite (I-42m) or PMCA (P-42m) structures. The latter was the one observed.
STEM-EELS experiments allowed to state the homogeneity of different elements into single nanocrystals at nanometric scale. STEM-EDX was used to quantify the compositional homogeneity between different nanocrystals and confirm the elemental distribution inside single nanocrystals.
No observation of segregation or core/shell like structuring was found, suggesting the formation of homogeneous nanocrystals.