TEM Characterization of Quaternary Cu_2ZnSnS_4 Nanocrystals

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1. INTRODUCTION

I_2-II-IV-VI_4 semiconductors are widely studied materials as light absorbers in alternative solar cells. Cu_2InGaS_4 (CIGS) is a very promising material (solar efficiencies around 20%), but In and Ga are expensive components. Currently a large effort is made to replace CIGS. Among the candidate systems, Cu_2ZnSnS_4 (CZTS) has drown significant interest: it has band-gap suitable for solar-harvesting applications, it shows p-type conductivity and a high absorption coefficient. Moreover, it only consists of inexpensive, non-toxic and earth-abundant materials: it does not contain indium whose natural resources are supposed to become scarce in the near future[1].

One of the challenges in the synthesis of colloidal CZTS nanocrystals is the control of internal structure and composition. Due to the reduced size, powder x-ray diffraction peaks are broad and are not really suitable for a detailed structure determination.

Electronic and optical properties are deeply related to structure, which is crucial for applications[2]. Transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM) are unique tools for understanding the internal structure at the nanoscale. Here we apply advanced TEM techniques, such as HRSTEM-HAADF, HR-TEM, STEM-EELS, STEM-EDX in order to solve the crystal structure

2. RESULTS

2.1 Experimental Section

Cu_2ZnSnS_4 nanocrystals were synthesized to investigate nucleation and growth processes during a heating-up method. Precursors were added in a high boiling point organic solvent. During the initial heating stage (110°C, 30 min) nanoparticles with a diameter of about 10 nm were forming, with an initial composition of $Cu_{3.1}Zn_{1.5}S_4$. During the final heating stage (280°C), after 10 minutes the situation got stable: the composition got constant at $Cu_{2.1}Zn_{1.14}SnS_4$, with size practically unchanged with respect to the initial nanoparticles.

TEM characterization was performed *ex-situ*. HRTEM and STEM-HAADF images were obtained using a FEI Titan[3] Ultimate 80-300 kV transmission electron microscope operated at 200 kV equipped with CEOS image and probe Cs correctors, with a Gatan Orius 2kx2k camera and a Fischione HAADF detector. HRTEM images were compared with simulations using JEMS[3] software. STEM-HAADF images were compared with simulations from the Kirkland code TEMSIM[4]. STEM-EELS was performed on a FEI Titan 80-300 kV transmission electron microscope equipped with CEOS probe Cs corrector and a Gatan Tridiem GIF energy filter. Spectra were deconvoluted using Hyperspy[5]. STEM-EDX was carried out on a dedicated FEI Osiris with SuperX detector; spectra were analyzed and quantified using Bruker Esprit 1.9 software.

After purification with antisolvent-solvent dispersion cycles, Cu_2ZnSnS_4 nanocrystals were deposited by drop casting on a PELCO 1824 Ultrathin (<3 nm) carbon film on a holey carbon support film. Sample preparation is fundamental in order to obtain contamination-free STEM images and useful EELS spectra: in facts, organic ligands present on nanocrystal surface in order to avoid the formation of aggregates in the solution are detrimental for STEM imaging.

2.2 HR-TEM and HRSTEM-HAADF

Sizes of nanocrystals has been determined by comparing HRTEM and STEM-HAADF images. STEM-HAADF is sensible to chemical contrast, the signal being dependent on the atomic number Z; it is then possible to observe the sites occupied by the heavier atoms (Sn) in the structure, and distinguish then between kesterite (space group I-4), stannite (space group I-42m) or pre-mixed Cu-Au (PMCA, space group P-42m) structures, which show different characteristic “bright” motifs. The latter (PCMA) structure was the one found when nanocrystals were showing the good direction for phase identification (111).

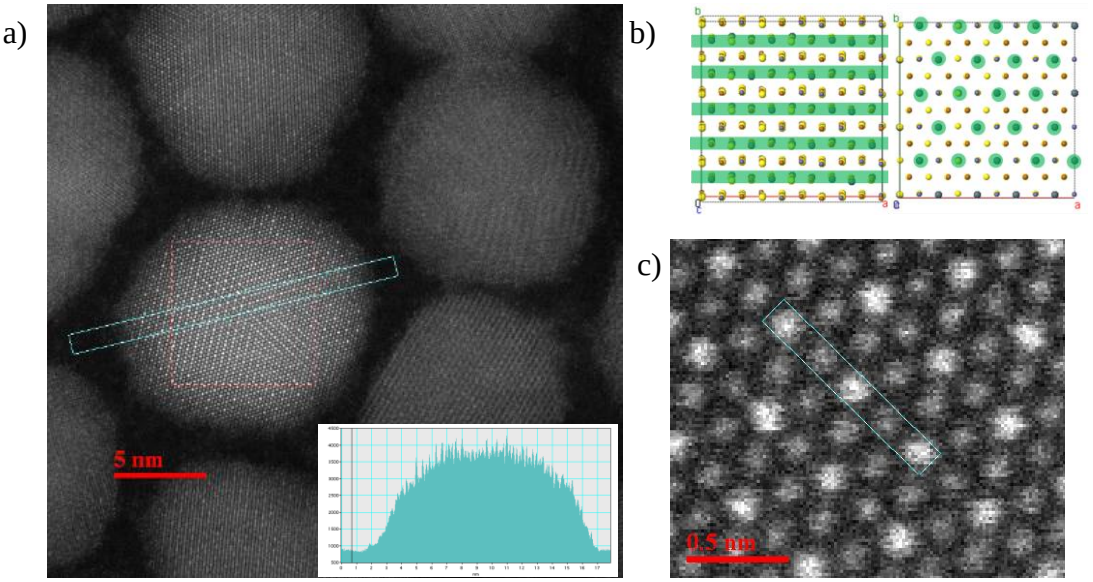

Figure 1. a) STEM-HAADF image of nanocrystals and intensity profile. b) In green, motif drawn by Sn atoms in kesterite (left) and in PCMA (right) structure. c) Zoom on selected nanocrystal area.

2.3 STEM-EELS and STEM-EDX results

It was not possible to obtain atomic resolution information from STEM-EELS experiments in order to confirm the previous observation. Nevertheless, they allowed to state the homogeneity of different elements into single nanocrystals at the nanometric scale.

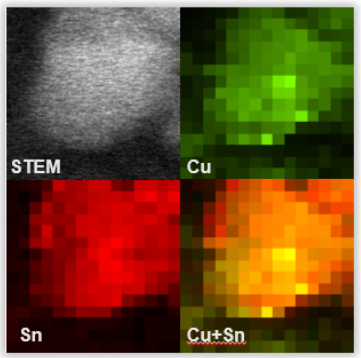

Figure 2. Chemical mapping from EELS spectroscopy

STEM-EDX was used in order to analyze and 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.

3. CONCLUSION

Combination of HR-TEM and HR-STEM revealed PMCA structure for synthesised nanocrystals. Compositional homogeneity was explored by STEM-EELS and STEM-EDX, evidencing no segregation effects or core/shell-like structure.

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