Electronic Supplementary Information

Synthesis and surface chemistry of high quality wurtzite- and kesterite-Cu_2ZnSnS_4 nanocrystals using tin(II) 2-ethylhexanoate as new tin source

Grzegorz Gabka,[a] Piotr Bujak,[a]* Maciej Gryszel,[a] Andrzej Ostrowski,[a] Karolina Malinowska,[b] Grazyna Z. Zukowska,[a] Fabio Agnese[c,d], Adam Pron[a] and Peter Reiss[c,e,f]**

[a] *Faculty of Chemistry, Warsaw University of Technology, Noakowskiego 3, 00-664 Warsaw, Poland.*

[b] *Faculty of Chemistry, University of Warsaw, Pasteura 1, 02-093 Warsaw, Poland.*

[c] *Univ. Grenoble Alpes, 38000 Grenoble, France.*

[d] *CEA-INAC-SP2M, Laboratoire d'Etude des Matériaux par Microscopie Avancée.*

[e] *CEA-INAC-SPrAM, Laboratoire d'Electronique Moléculaire, Organique et Hybrid, 17 rue des Martyrs, 38054 Grenoble cedex 9, France.*

[f] *CNRS UMR5819 SPrAM, 38000 Grenoble, France,*

E-mail:peter.reiss@cea.fr.

Experimental

Materials

$CuCl_2\cdot 2H_2O$, sodium oleate (82%), tin(II) 2-ethylhexanoate (92.5%), $Zn(CH_3COO)_2\times 2H_2O$ (98 %), sulfur (99.5%), 1-dodecanethiol (DDT, 98%), oleylamine (OLA, 70%), 1-octadecene (ODE, 90%), 1,2-dichlorobenzene (99%) were supplied by Sigma-Aldrich.

Synthesis of copper(II) oleate[1]

Copper(II) oleate was prepared by reacting $CuCl_2$ with sodium oleate. Sodium oleate (80 mmol, 29.7 g) and $CuCl_2\cdot 2H_2O$ (40 mmol, 6.9 g) were dissolved in a mixed solvent composed of 80 mL of ethanol, 60 mL of water and 140 mL of hexane. The mixture was heated to 70 °C and then kept at this temperature for four hours. The organic layer containing the desired product was washed three times with 30 mL of water in a separatory funnel. After washing, hexane layer was evaporated and the resulting product (copper(II) oleate) was recovered in a form of a green waxy solid.

Characterization

Powder X-ray diffraction patterns were recorded at room temperature on a Bruker D8 Advance diffractometer equipped with a LYNXEYE position sensitive detector, using Cu-Kα radiation (λ = 0.15418 nm). The data were collected in the Bragg-Brentano ($\theta/2\theta$) horizontal geometry (flat reflection mode) between 10° and 70° (2θ) in a continuous scan, using 0.04° steps 960 s/step. The diffractometer incident beam path was equipped with a 2.5° Soller slit, a 1.14° fixed divergence slit, while the diffracted beam was equipped with a programmable antiscatter slit (fixed at 2.20°), a Ni β-filter and a 2.5° Soller slit. The sample holder was rotated with an angular speed of 15 rpm. Data were collected under standard conditions (temperature and relative humidity). TEM analysis was performed on a Zeiss Libra 120 electron microscope operating at 120 kV. High-resolution images were acquired by a FEI Tecnai Osiris (S)TEM microscope operated at 200 kV. The elemental analysis was carried out with a multichannel Quantax 400 EDS system with 125 eV xFlash Detector 5010, Bruker using 15 kV electron beam energy. ^1H NMR spectra were recorded on a Varian Mercury (500 MHz) spectrometer and referenced with respect to TMS and solvents. Raman spectra were recorded on the Nicolet Almega Raman Dispersive Spectrometer, equipped with confocal microscope. Experiments were performed with use of 780 nm excitation line and 1200 lines/mm high resolution gratings. The exposition time was set to 10s; each spectrum averaged from two accumulations. UV-Vis-NIR spectra were registered using a Cary 5000 (Varian) spectrometer. GC-MS analysis was performed on a Gas Chromatograph 7890A Agilent Technologies coupled with tandem mass spectrometer 5975C firm Agilent Technologies equipped with electron impact EI ion source and the single quadrupole mass analyzer. The instrument was controlled and recorded data were processed using MSD Chemstation E. 02.00.493 software package.

Synthesis of wurtzite-CZTS nanocrystals (CZTS-1) *via heating-up*

Wurtzite-CZTS nanocrystals were prepared by thermal decomposition of a mixture of 1.0 mmol (0.63 g) of copper(II) oleate, 0.5 mmol (0.11 g) of $Zn(CH_3COO)_2{\cdot}2H_2O$, 0.5 mmol (0.20 g, 0.16 mL) of tin(II) 2-ethylhexanoate and 3.0 mmol (0.6 g, 0.72 mL) of 1-dodecanethiol in a 50 mL three-necked flask with 15 mL of ODE. First all precursors except for DDT were dissolved in 10 mL ODE at 100 °C under argon flow. Then a solution containing 3 mmol of DDT in 5 mL ODE was added. Color of the mixture changed from green to orange indicating reduction of the copper precursor. The mixture was rapidly heated to 230 °C (when the temperature reached 180 °C the solution became red) and the mixture was kept at this temperature for 3 hours. Upon heating, the color changed gradually from red through brown and finally to black. The mixture was then cooled to room temperature and subsequently chloroform (10 mL) was added. In the next step the reaction mixture was centrifuged and the isolated black precipitate consisting of organic waste and agglomerated particles was separated. The supernatant was treated with 30 mL of acetone leading to the precipitation of the desired fraction of nanocrystals. The nanocrystals were separated by centrifugation (7000 rpm, 5 min) and redispersed in chloroform or methylene chloride.

Synthesis of kesterite-CZTS nanocrystals (CZTS-2) *via hot-injection*

All operations were carried out under constant dry argon flow. Copper(II) oleate (1.0 mmol, 0.63 g), $Zn(CH_3COO)_2{\cdot}2H_2O$ (0.5 mmol, 0.11 g) were mixed with 10 mL of ODE in a 50 mL three-neck flask at 100 °C. Then a solution containing 3 mmol of DDT in 5 mL of ODE was added. The mixture was heated to 170 °C until a homogenous orange solution was formed. Then tin(II) 2-ethylhexanoate (0.5 mmol, 0,20 g, 0.16 mL) and sulfur (2.0 mmol, 64 mg) dissolved in 2 mL of oleylamine were quickly injected into the reaction solution. Upon injection the color changed instantly to black. The temperature was raised to 230 °C, and the mixture was kept at this temperature for 30 min. After the mixture was cooled to room temperature, chloroform (10 mL) was added, and the reaction mixture was centrifuged – the isolated black precipitate consisting of organic waste and agglomerated particles was separated. The supernatant was treated with 30 mL of acetone leading to the precipitation of the desired fraction of nanocrystals. The nanocrystals were separated by centrifugation (7000 rpm, 5 min) and then redispersed in chloroform or methylene chloride.

Synthesis of kesterite-CZTS nanocrystals (CZTS-3) *via hot-injection*

The procedure was identical to CZTS-2, however no DDT was added. Copper(II) oleate and $Zn(CH_3COO)_2{\cdot}2H_2O$ were mixed at once with 15 mL of ODE.

Synthesis of kesterite-CZTS nanocrystals (CZTS-4) *via hot-injection*

All operations were carried out under constant dry argon flow. Copper(II) oleate (1.0 mmol, 0.63 g), $Zn(CH_3COO)_2{\cdot}2H_2O$ (0.5 mmol, 0.11 g) and 1-dodecanethiol (2.0 mmol, 0.40 g, 0.48 mL) were mixed with 15 mL 1,2-dichlorobenzene in a 50 mL three-neck flask. The mixture was heated to 150 °C until an orange homogenous solution was formed. Then tin(II) 2-ethylhexanoate (0.5 mmol, 0,20 g, 0.16 mL) and sulfur (2.0 mmol, 64 mg) dissolved in 2 mL of oleylamine were quickly injected into the reaction solution. Upon injection the color changed instantly to black. The temperature was raised to 180 °C (reflux), and the mixture was kept at this temperature for 60 min. After the reaction was complete, the reaction mixture was cooled to room temperature and centrifuged (however usually no solids were isolated in this step). Nanocrystals were precipitated by adding excess methanol and then centrifuged, redispersed in chloroform and precipitated with methanol again in order to remove 1,2-dichlorobenzene completely. Finally nanocrystals were dispersed in chloroform or methylene chloride.

Ligands recovery (for the sample of wurtzite-nanocrystals, CZTS-1)

A colloidal solution of wurtzite-nanocrystals, **CZTS-1** (in 10 mL of chloroform) and 10 mL of conc. HCl were placed in a screw-capped ampoule, which was immersed in an ultrasonic bath for 2h (and shaken every 30 min). Water (20 mL) was next added and the resulting mixture was centrifuged to achieve phase separation – remaining solids were discarded. The organic phase was collected and the aqueous phase was extracted with 15 mL of chloroform. The combined organic layers were washed two times with water, evaporated and dried under reduced pressure affording a black oil.

Ligands recovery (for the sample of kesterite nanocrystals, CZTS-4)

A colloidal solution of kesterite-nanocrystals, CZTS-4 (in 10 mL of chloroform) and 10 mL of conc. HCl were placed in a screw-capped ampoule, which was immersed in an ultrasonic bath for 2 h (and shaken every 30 min). The resulting mixture was centrifuged to achieve phase separation – remaining solids were discarded. The organic phase was washed with water, evaporated and dried under vacuum to afford a black oil. ^{1}H NMR measurements suggested that a long chain alkene is the only organic component of the isolated oil. In order to identify it an additional procedure was performed. The black oil (120 mg) was dissolved in methylene chloride (5 mL) then 20% NaOH (5 mL) was added and the mixture was placed in a screw-capped ampoules under argon atmosphere. The mixture was stirred and heated at 50 °C for 12 h. After cooling to room temperature, the organic phase was diluted with 10 mL of methylene chloride and the mixture was centrifuged to achieve complete phase separation. The resulting organic phase was washed with water, evaporated and dried under vacuum yielding a brown oil. The crude mixture was purified by column chromatography on silica gel using hexane as eluent to give a colorless oil (28 mg).

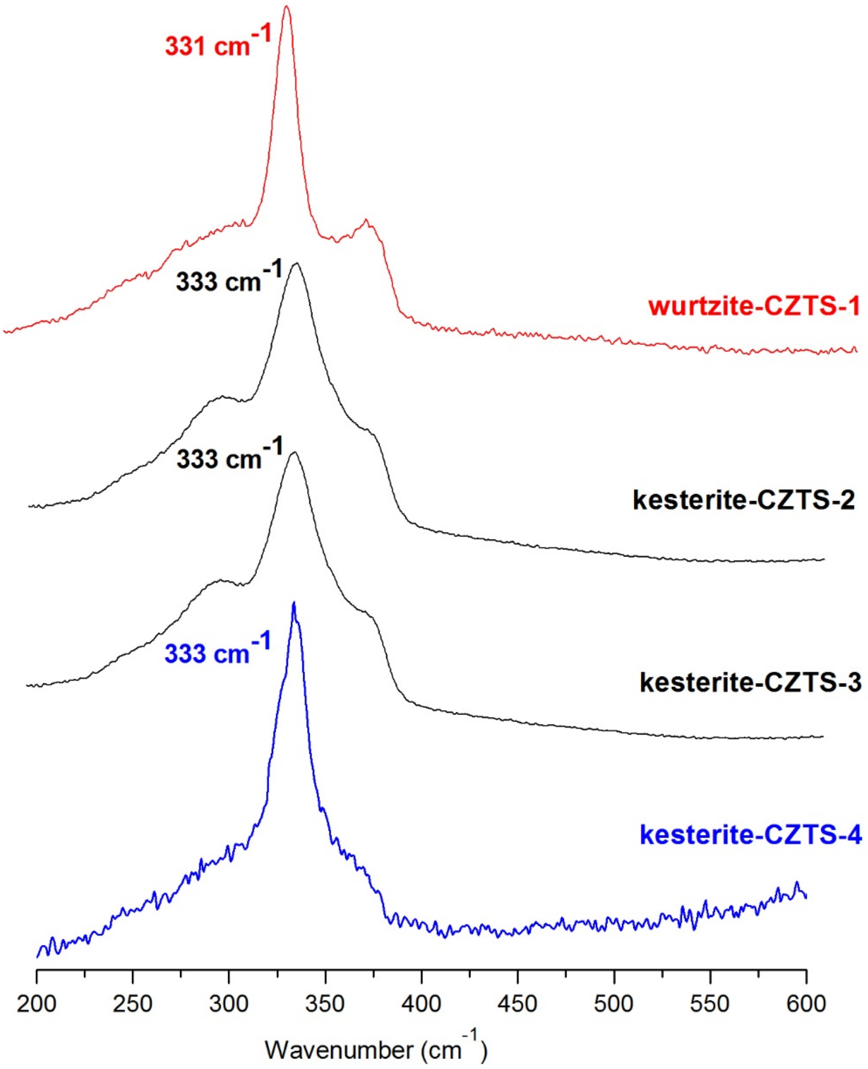


Fig. S1 Raman spectra of the obtained wurtzite (**CZTS-1**) and kesterite (**CZTS-2,3,4**) nanocrystals. The peaks at 331/333 cm^{-1} and 375 cm^{-1} are characteristic of CZTS.[2] No peaks of impurity phases such as $Cu_{2-x}S$ (475 cm^{-1}), ZnS (351 and 274 cm^{-1}), Cu_2SnS_3 (318, 348, and 295 cm^{-1}) or SnS_2 (315 cm^{-1}) are observed.[3]

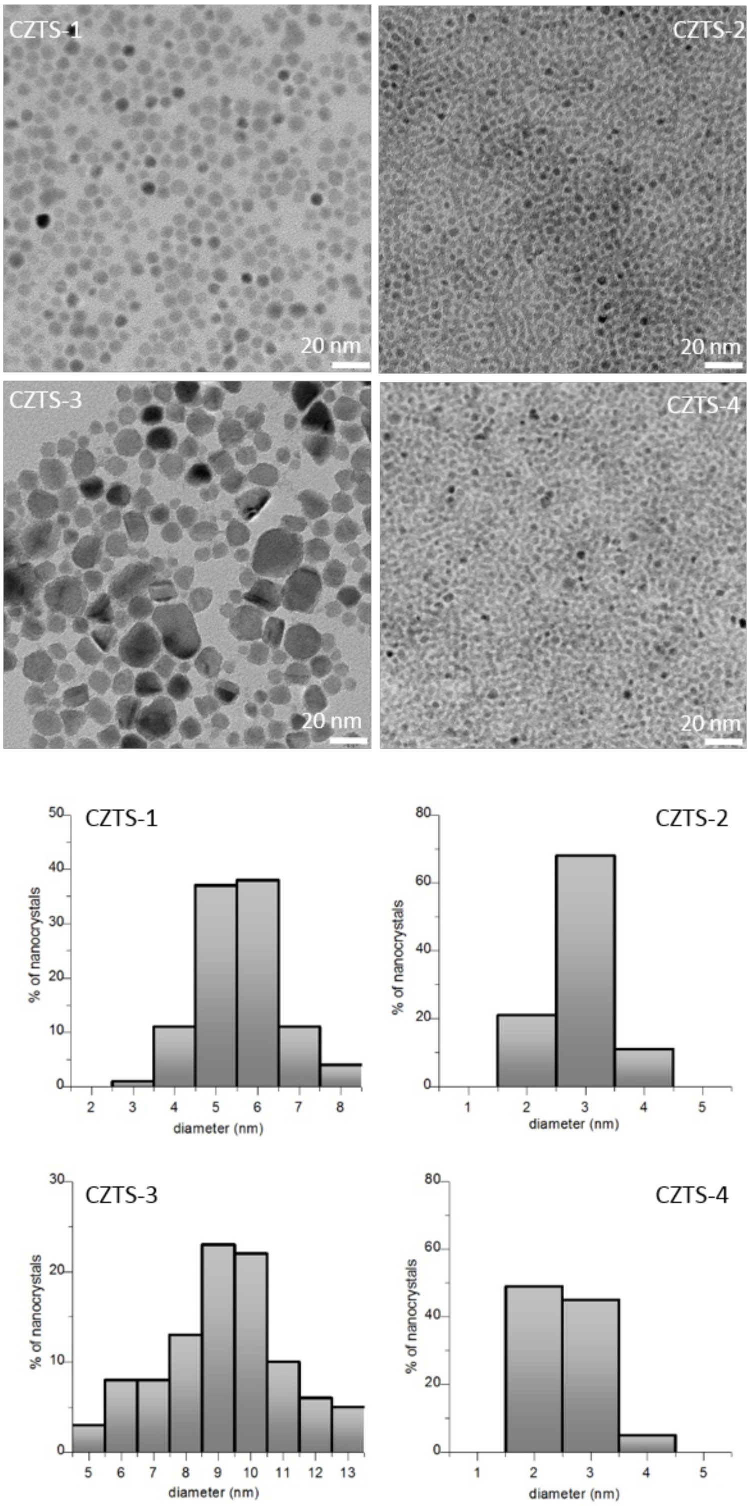


Fig. S2 TEM images of **CZTS** nanocrystals **1-4** and corresponding size histograms.

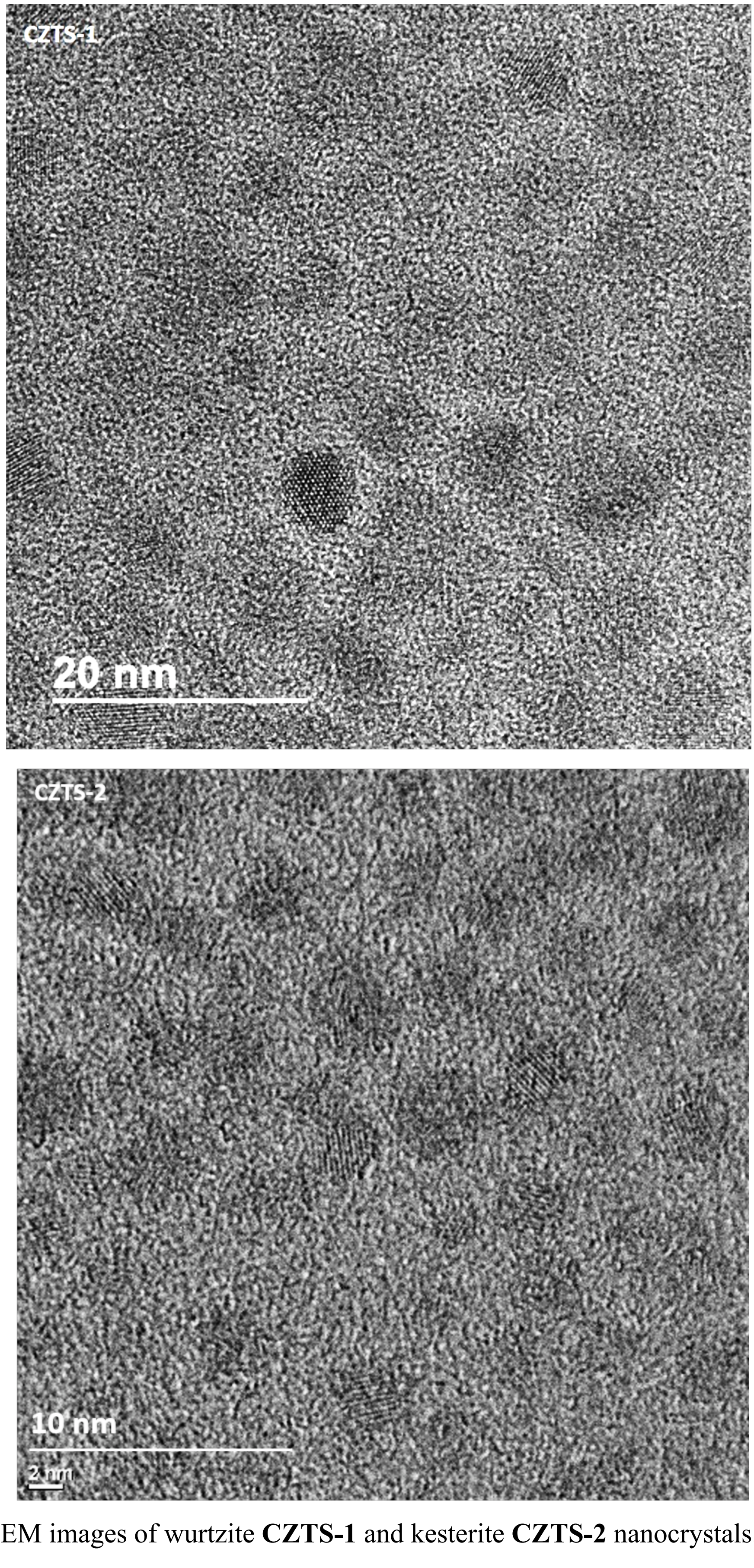


Fig. S3 HRTEM images of wurtzite **CZTS-1** and kesterite **CZTS-2** nanocrystals.

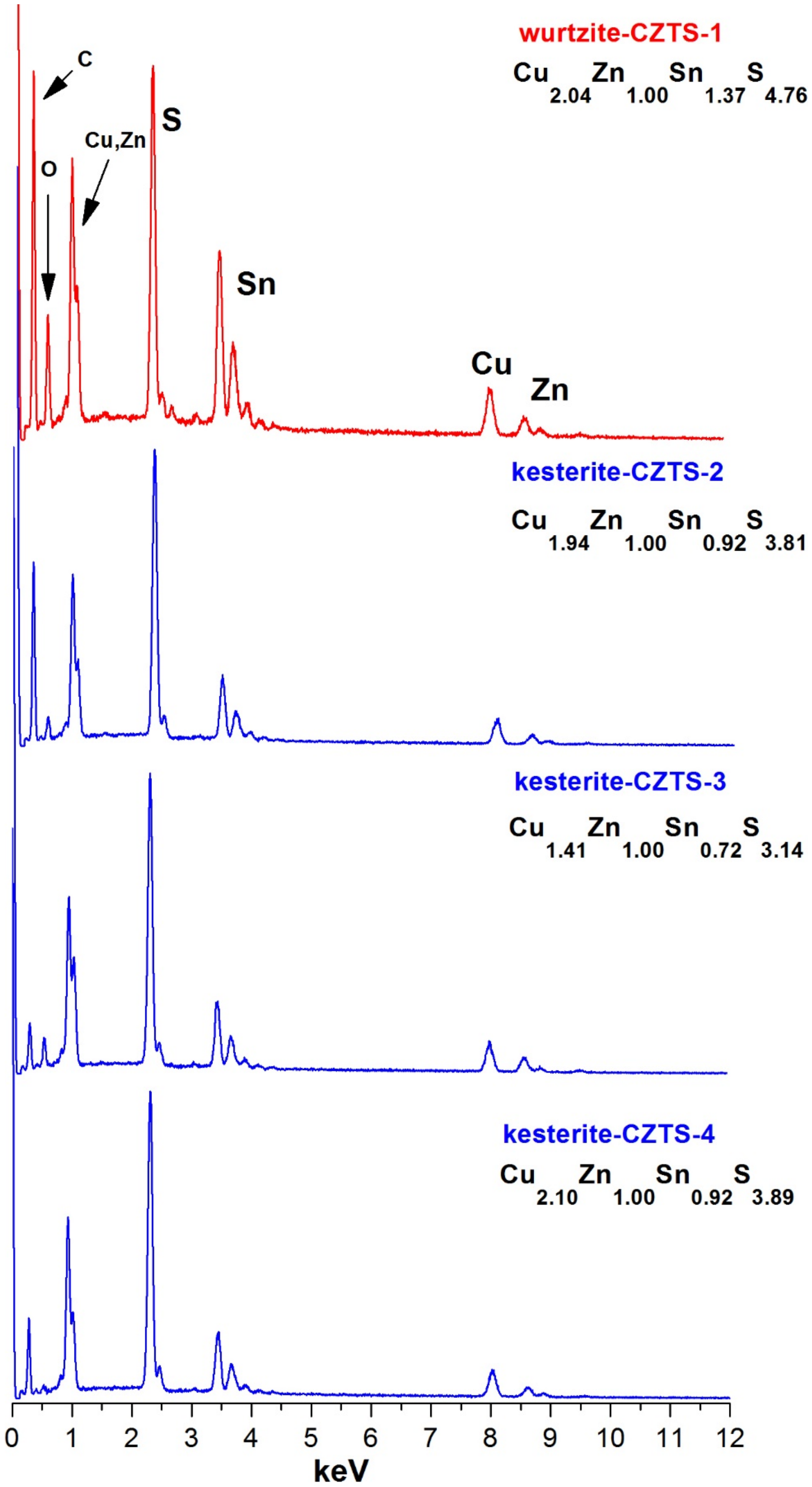


Fig. S4 Energy-dispersive spectra of **CZTS** nanocrystals of batches **1-4**.

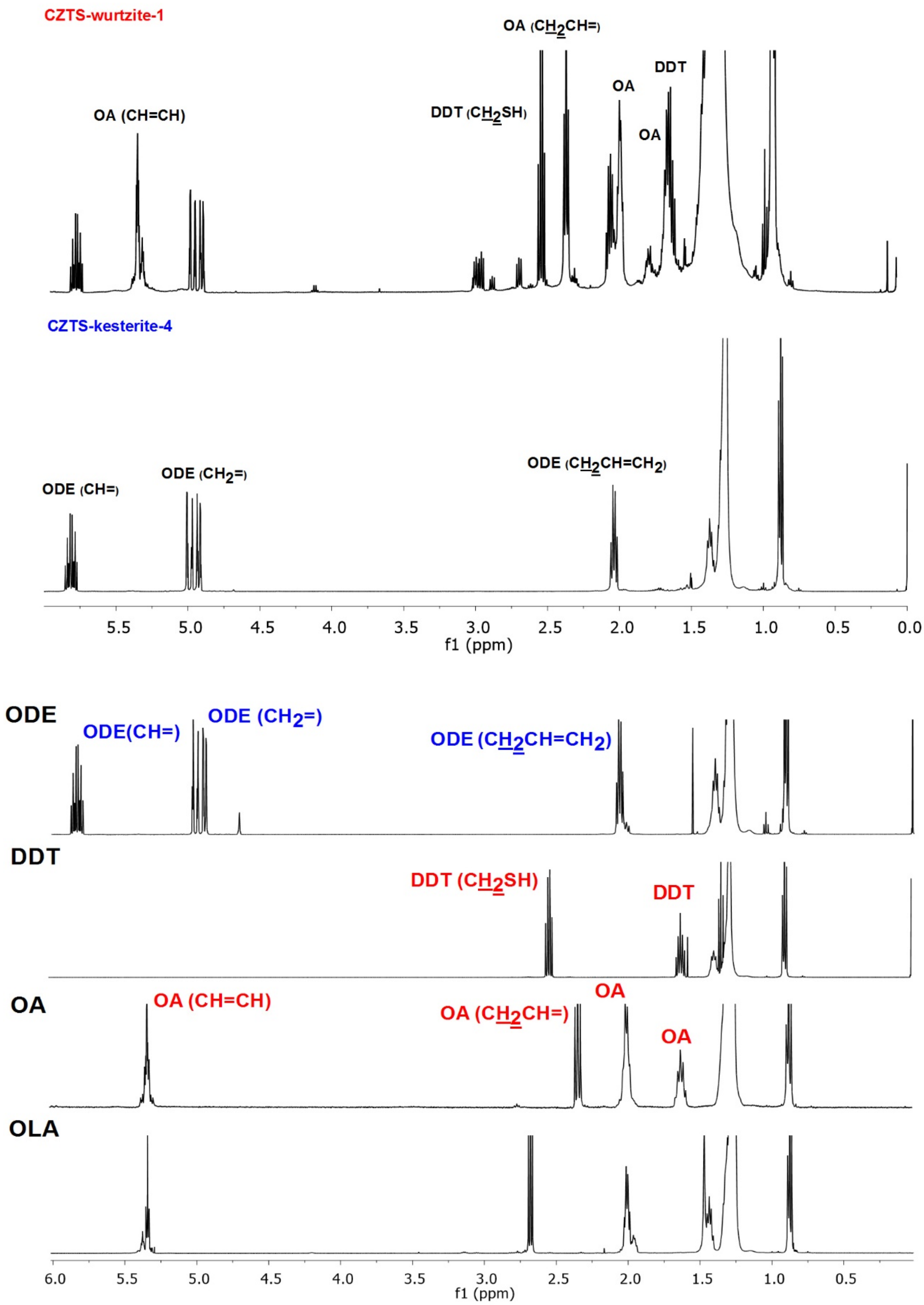


Fig. S5 ^{1}H NMR spectra of organic residue from wurtzite-**CZTS-1** and kesterite-**CZTS-4** nanocrystals, 1-octadecene (ODE), 1-dodecanethiol (DDT), oleic acid (OA), oleylamine (OLA), recorded in $CDCl_3$.

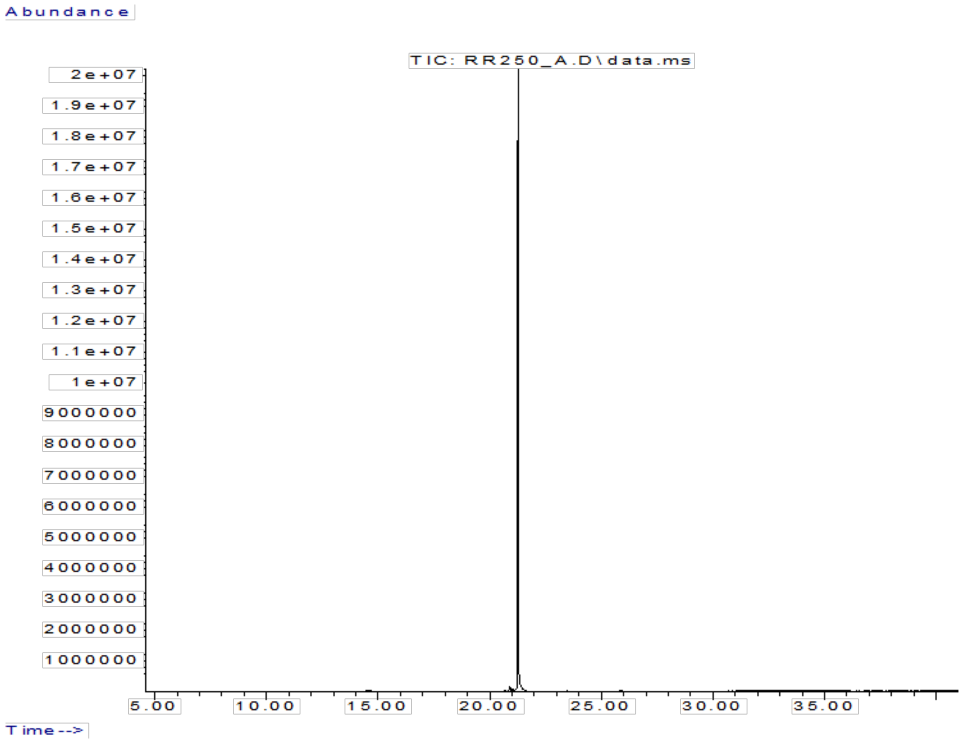


Fig. S6 a) GC chromatogram of organic residue from kesterite-**CZTS-4** nanocrystals.

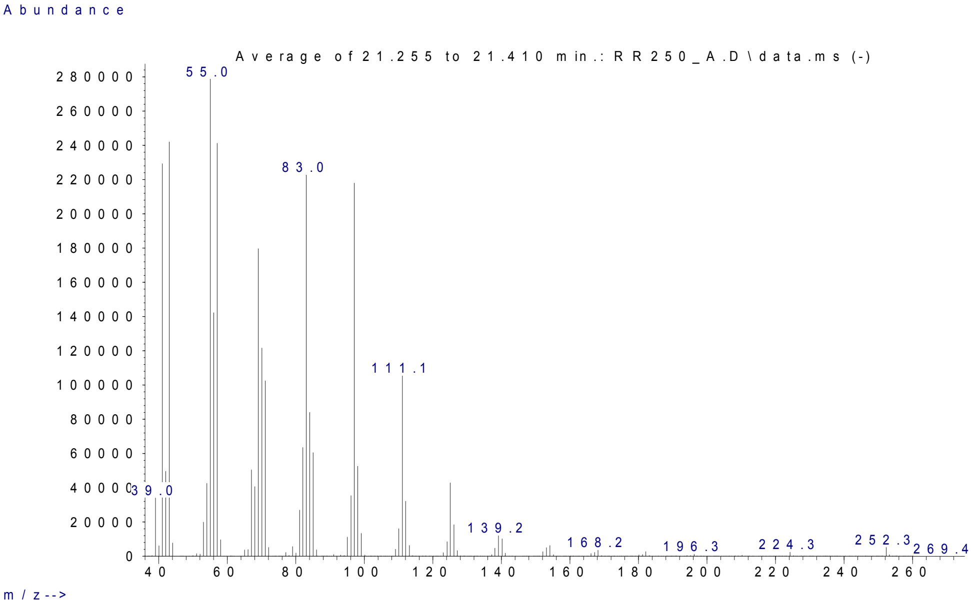


Fig. S6 b) EI-MS spectrum of organic residue from kesterite-**CZTS-4** nanocrystals.

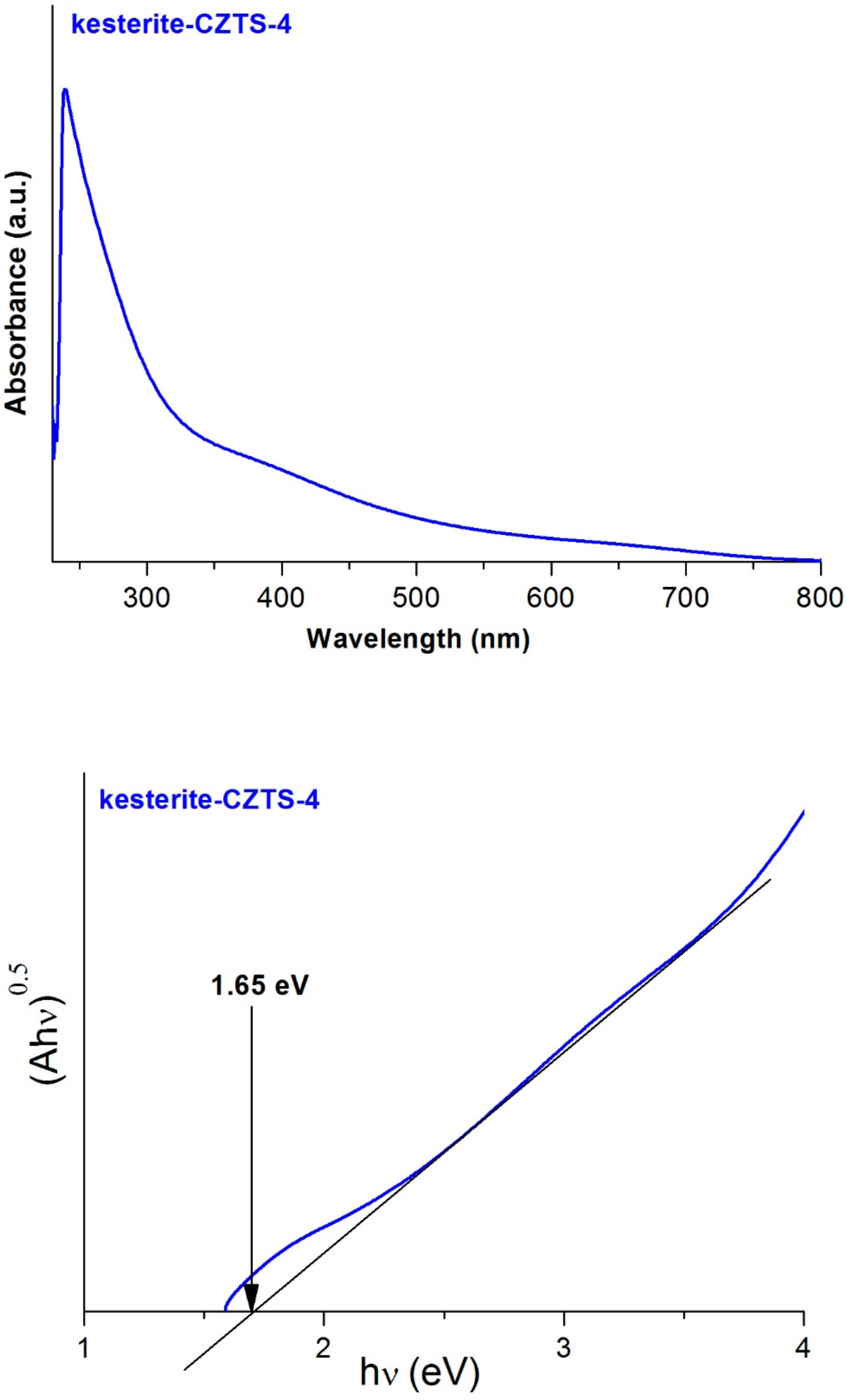
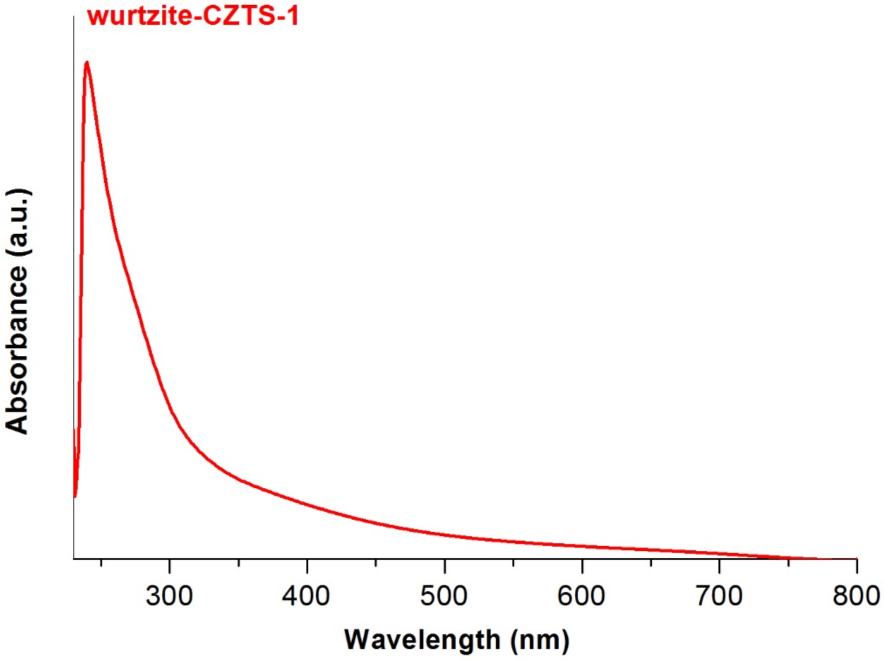


Fig. S7 Room temperature UV-vis-NIR spectrum of chloroform dispersion of kesterite-**CZTS-1** nanocrystals and the corresponding $(Ah\nu)^{0.5}$ *vs* hν curve (where A = absorbance, h = Planck's constant and ν = frequency) derived from spectrum.



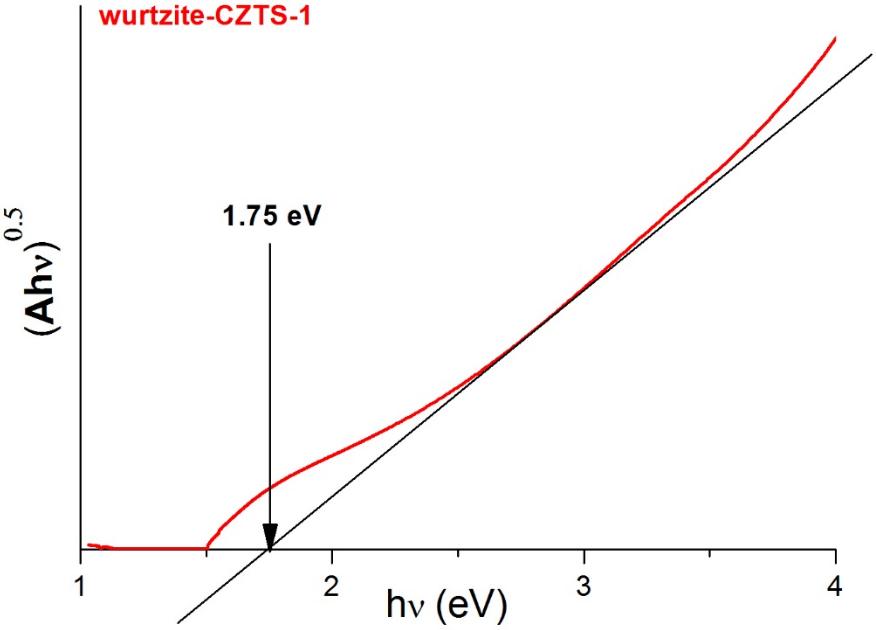


Fig. S8 Room temperature UV-vis-NIR spectrum of chloroform dispersion of wurtzite-**CZTS-1** nanocrystals and the corresponding $(Ah\nu)^{0.5}$ *vs* hν curve (where A = absorbance, h = Planck's constant and ν = frequency) derived from spectrum.

References

(1) J. Park, K. An, Y. Hwang, J.-G. Park, H.-J. Noh, J.-Y. Kim, J.-H. Park, N.-M. Hwang, T. Hayeon, *Nat. Mater.,* 2004, **3**, 891-895.

(2) X. Lin, J. Kavalakkatt, K. Kornhuber, S. Levcenko, M. C. Lux-Steiner, A. Ennaoui, *Thin Solid Films*, 2013, **535**, 10-13.

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