

Supporting Information

Observation of Antisite-Related Defects in $\text{Cu}_2\text{ZnSnS}_4$ by Transmission Electron Microscopy

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SI 1. CZTS nanocrystals synthesis and sample preparation

CZTS nanocrystals were prepared by hot injection method as previously described.¹ Briefly, 1.5 mmol Copper (II) acetylacetonate, 0.75 mmol zinc acetylacetonate hydrate and 0.75 mmol tin (IV) bis(acetylacetonate) dichloride were dissolved in 10 mL of oleylamine to achieve a stoichiometric ratio Cu:Zn:Sn of 2:1:1. An excess of sulphur dissolved in oleylamine was added at 225 °C in an Ar atmosphere and left for 30 min. The mixture was then cooled to ~80 °C and centrifuged using a mixture of toluene and isopropanol to precipitate the material which was then dried. The resulting powder was annealed in a 3 cm vacuum sealed quartz tube at 550 °C for two hours with a heating rate of 10 °C/min and was then cooled naturally to room

temperature. Figure S1 illustrated CZTS nanoparticles powder before and after annealing in quartz tube. TEM samples were prepared by crushing and dispersing the powder in ethanol and depositing a drop of solution onto a holey carbon film. After drying, the films were examined by TEM, either in a Philips EM430 TEM, or in a JEOL 200ARM fitted with aberration correction on the pre-specimen lenses.

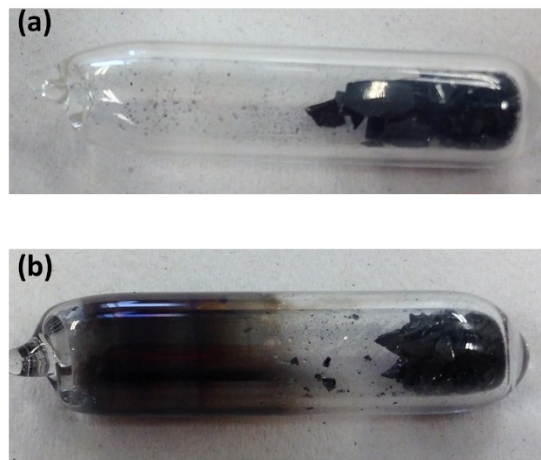


Figure S1. Picture of a quartz ampule used for annealing as-grown CZTS nanoparticles under vacuum at 550 °C. (a) Before annealing, and (b) after annealing.

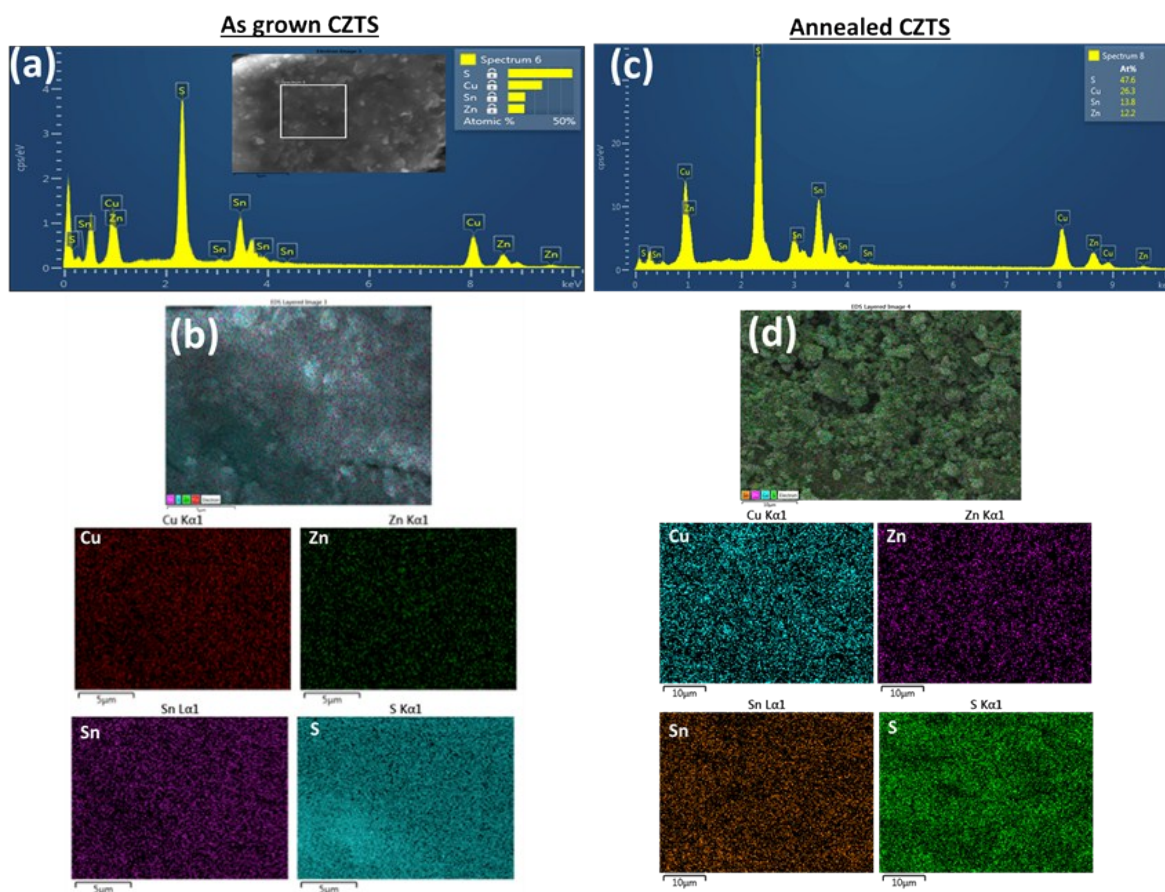


Figure S2. EDX/SEM and elemental mapping of as-grown (a, b) and annealed CZTS nanocrystals (c, d), respectively.

Table 1. Compositions and atomic ratios of as-grown and annealed CZTS nanocrystals.

Sample	Atomic composition (%)				Atomic Ratios		Composition
	Cu	Zn	Sn	S	Cu/(Zn + Sn)	Zn/Sn	
As-grown	25.8	12.4	12.9	48.9	1.03	0.96	$\text{Cu}_{2.1}\text{Zn}_{1.0}\text{Sn}_{1.0}\text{S}_{3.9}$
Annealed	26.3	12.2	13.8	47.6	1.01	0.88	$\text{Cu}_{2.2}\text{Zn}_{1.0}\text{Sn}_{1.1}\text{S}_{3.9}$

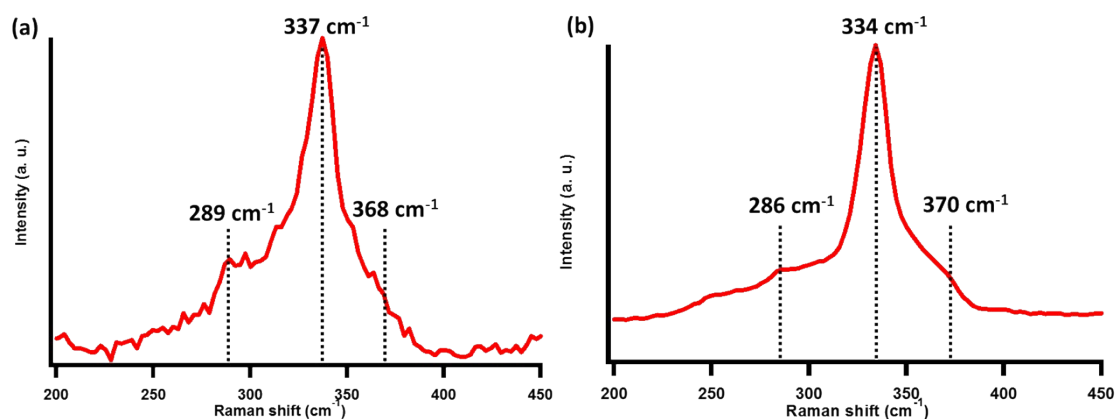


Figure S3. Raman spectra (514 nm excitation) of as-grown (a) and annealed (b) CZTS nanocrystals.

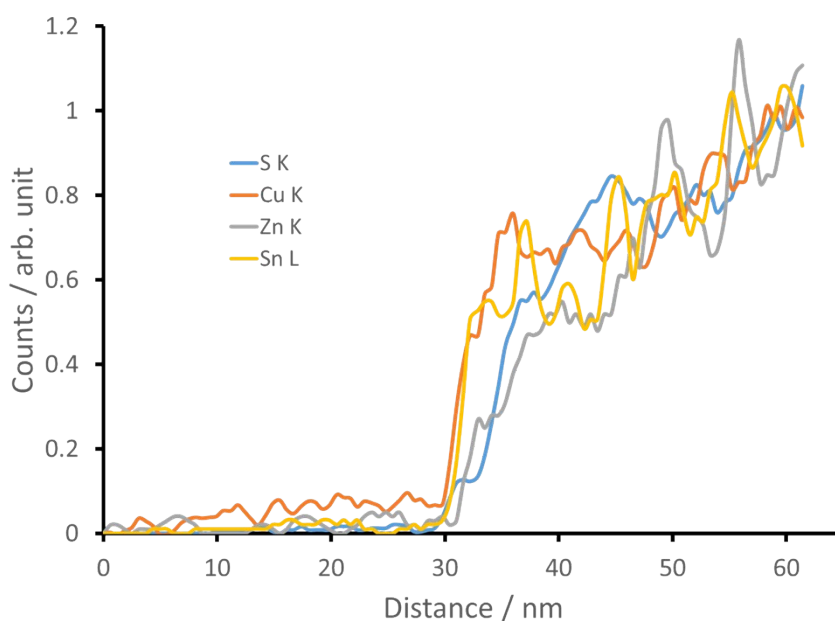


Figure S4. Normalised counts from component elements as function of distance obtained by EDX mapping across a thin edge of a CZTS particle. The counts measured were kept low in order to avoid beam damage (TEM voltage 200kV). Although the profiles suggest a slight depletion of Zn and S near the surface, elemental composition is mostly retained across the region probed.

References

- (1) Hou, B.; Benito-Alifonso, D.; Kattan, N.; Chems, D.; Galan, M. C.; Fermín, D. J. Initial Stages in the Formation of $\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$ Nanoparticles. *Chem. A Eur. J.* **2013**, *19*, 15847–15851.