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Supporting Information

Visualization and deconvolution of carrier kinetics within grains of $Cu_2ZnSnS_{4-x}Se_x$ using ultrafast diffuse reflectance microscopy

Maha Sharif[1,2], Xiao Ma[1,2], Elham Ghadiri[1,2]

[1]Department of Chemistry, and [2]Center for Functional Materials, Wake Forest University, Winston-Salem 27109, North Carolina, United States

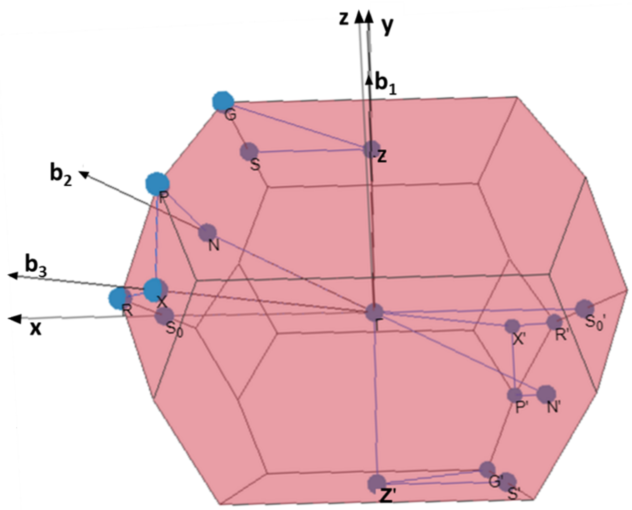
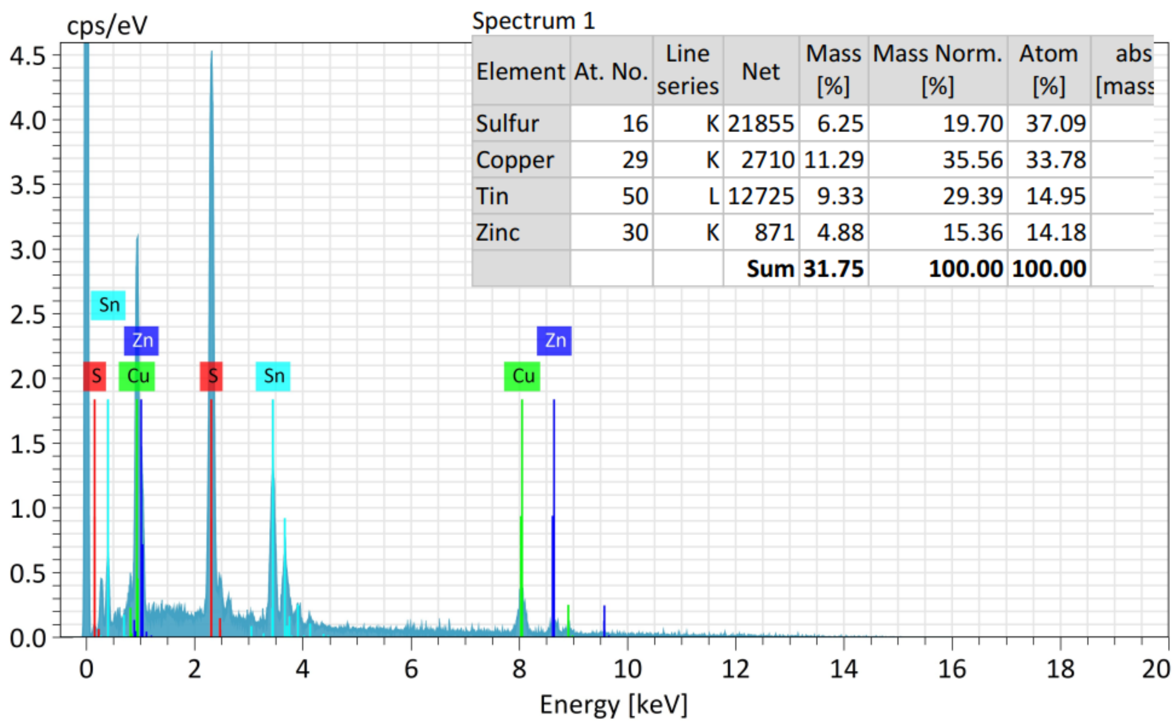


Fig. S1. Enlarged Brillouin zone for Kesterite CZTS generated by Seek-path[1].



Spectrum 1

Element	At. No.	Line series	Net	Mass [%]	Mass Norm. [%]	Atom [%]	abs [mass
Sulfur	16	K	21855	6.25	19.70	37.09	
Copper	29	K	2710	11.29	35.56	33.78	
Tin	50	L	12725	9.33	29.39	14.95	
Zinc	30	K	871	4.88	15.36	14.18	
			Sum	**31.75**	**100.00**	**100.00**	

Fig. S2. Energy dispersive spectrum (EDS) for Cu_2ZnSnS_4.

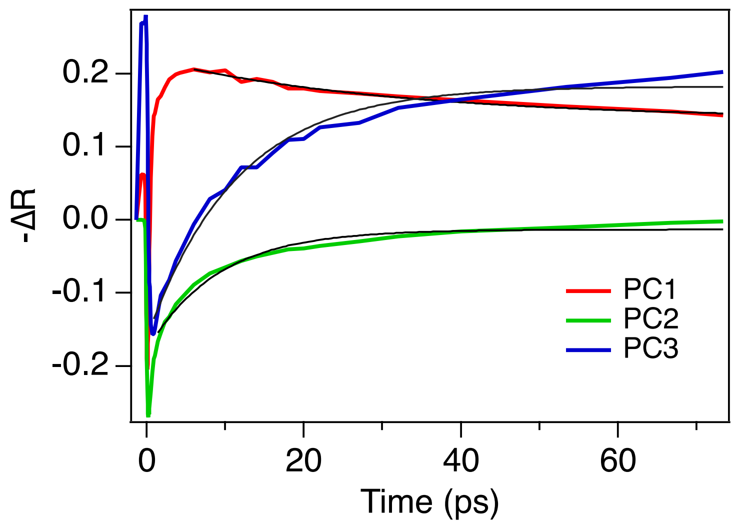


Fig. S3. Representative principal components of the TAS extracted from TAM images. PCs are fitted with single exponential functions and the fitting parameters are provided in the supporting table 1.

Supporting Table S1. Parameters of exponential function fit to TAS PC components extracted from TAM images shown in Fig. 3 and S.

	Y0	**A1**	**τ_1 (ps)**
PC1	0.14 ± 0.00	0.08 ± 0.00	31.25±4.71
PC2	-0.01 ± 0.00	-0.17 ± 0.00	8.25±0.68
PC3	0.18 ± 0.01	-0.34± 0.01	11.37±0.62

Calculation of laser fluence, and carrier density

The absorbtion coefficient *α* of CZTS was estimated using equation S1, as suggested by Bindu *et al.*[2]:

$$\alpha = \frac{\ln \frac{100}{T\% + R\%}}{d} \qquad (S1)$$

According to Fig. 1c at 460 nm, the Transmittance% (T%) of the sample is 1.1 % and the Reflectance% (R%) is 28.3 %. The thickness *d* of the CZTS film for which the optical absoption responses are provided in Fig. 1c, was measured by the cross section under SEM.

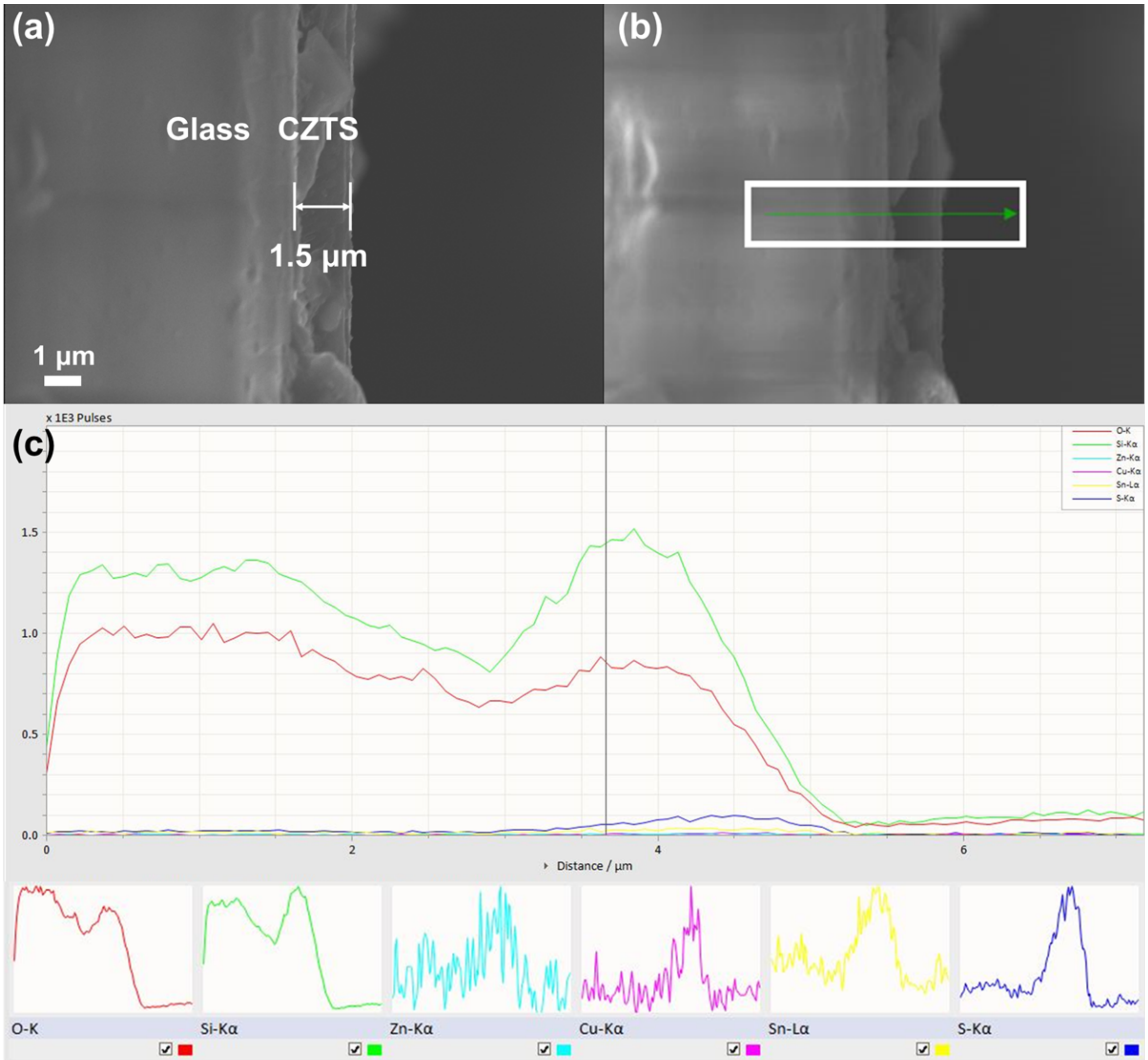


Fig. S4. (a) The corss-section scanning electron microscopy (SEM) image of CZTS film, (b) EDS in line scan mode and (c) corrspoding elemental distribution results across the green arrow shown in Fig. S4b.

Therefore, the absorbtion coefficient $\alpha = 8.1 \times 10^{3} cm^{-1}$ for the CZTS sample at 460 nm.

With a pump power of 1 mW and a beam diameter of 5 μm, the pump fluence was typically 50 $mJ\ cm^{-2}$. With an absorption coefficient of $8.1 \times 10^{3} cm^{-1}$ (calculation shown above) and assuming a photon-to carrier yield of 100% for the CZTS sample, the initial carrier density was estimated $9.4 \times 10^{20} cm^{-3}$ according to equation S2 according to previous reports [3]:

$$density = \frac{F\,\alpha}{h\upsilon} \qquad (S2)$$

Where F and α represent the fluenece and absorption coeffiecient respectively, and $h\upsilon$ is photon energy.

For 600 nm-pump, T% become 5.61% and R% is 27.36%, α become $1.11/d = 7.4 \times 10^{3} cm^{-1}$ and the initial carrier density would become $11.2 \times 10^{20} cm^{-3}$, which is 18.6 % larger than the value for 460 nm-pump.

(1) Hinuma, Y.; Pizzi, G.; Kumagai, Y.; Oba, F.; Tanaka, I. Band Structure Diagram Paths Based on Crystallography. *Comput. Mater. Sci.* **2017**, *128*, 140–184. https://doi.org/10.1016/j.commatsci.2016.10.015.

(2) Bindu, K.; Nair, P. K. Semiconducting Tin Selenide Thin Films Prepared by Heating Se–Sn Layers. *Semicond. Sci. Technol.* **2004**, *19* (12), 1348–1353. https://doi.org/10.1088/0268-1242/19/12/003.

(3) Lv, J.; Liu, A.; Shi, D.; Li, M.; Liu, X.; Wan, Y. Hot Carrier Trapping and It's Influence to the Carrier Diffusion in CsPbBr3 Perovskite Film Revealed by Transient Absorption Microscopy. *Adv. Sci.* **2024**, 2403507. https://doi.org/10.1002/advs.202403507.