SUPPORTING INFORMATION

Experimental and first-principles spectroscopy of Cu_2SrSnS_4 and Cu_2BaSnS_4 photoabsorbers

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Table S 1: PBEsol relaxed lattice parameters of CSTS and CBTS unit cell, percentage difference from experiments given in brackets [1, 2]. CBTS and CSTS crystallise into the same $P3_1$ space group.

PBEsol	a (Å)	c (Å)	α (°)	γ (°)
CSTS	6.249 (-0.65%)	15.364 (-1.34%)	90.00 (0.00%)	120.00 (0.00%)
CBTS	6.337 (-0.46%)	15.580 (-1.63%)	90.00 (0.00%)	120.00 (0.00%)

Table S 2: Lattice parameters of CBTS unit cell relaxed using different functionals, percentage difference from experiments given in brackets [1].

functionals	a (Å)	c (Å)	α (°)	γ (°)
LDA	6.273 (-1.48%)	15.408 (-2.68%)	90.00 (0.00%)	120.00 (0.00%)
LDA+U	6.269 (-1.55%)	15.425 (-2.57%)	90.00 (0.00%)	120.00 (0.00%)
PBE	6.450 (+1.31%)	15.854 (+0.14%)	90.00 (0.00%)	120.00 (0.00%)
PBE+U	6.448 (+1.28%)	15.886 (+0.33%)	90.00 (0.00%)	120.00 (0.00%)
PBEsol	6.337 (-0.46%)	15.580 (-1.63%)	90.00 (0.00%)	120.00 (0.00%)
PBEsol+U	6.333 (-0.54%)	15.6024 (-1.46%)	90.00 (0.00%)	120.00 (0.00%)

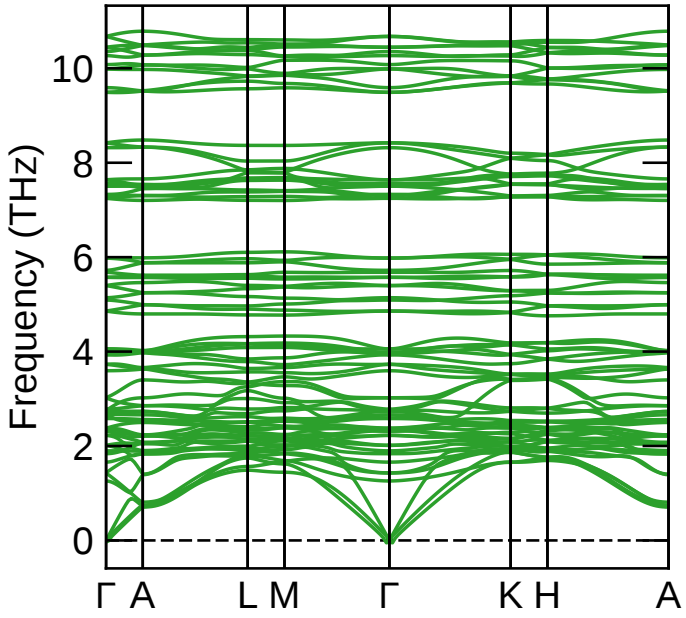

Figure S 1: Phonon band structure calculated with the PBEsol functional.

Table S 3: CBTS Raman peak table

Raman shift (experiment) cm^{-1}	Raman shift (theory) cm^{-1}	Intensity (theory) arb. units	Symmetry (theory)
69	42.5	2096	A
	47.6	1	E
	54.5	0.3	A
	59.2	1	A
	63.0	17	A
	66.6	670	E
81	73.0	2441	E
	74.5	947	E
	79.1	763	A
	80.5	407	E
95	86.4	9110	A
	88.8	672	E
	89.8	672	A
	91.5	454	E
	93.4	0.1	A
	103.1	313	E
	125.2	0.4	A
	127.6	233	E
	135.7	122	A
	136.1	107	E
	140.1	0.5	A
	140.6	19	E
	166.1	687	E
	172.0	515	A
	174.8	0.1	A
	180.9	713	E
182	185.2	3026	E
	189.0	14	A
188	190.4	32020	A
	198.3	102	E
	252.7	4137	E
	255.0	6903	A
255	255.3	279877	A
	265.1	1870	E
	266.2	66449	E
285	267.2	10648	A
	292.9	4371	E
	293.0	4	A
	306.8	11204	E
343	310.4	1114066	A
355	328.3	72594	E
	331.3	11	A
367	340.1	6313	A
	341.1	8	A
	342.2	2682	E
383	353.0	7189	E
409			
453			
463			

Table S 4: CSTS Raman peak table

Raman shift (experiment) cm^{-1}	Raman shift (theory) cm^{-1}	Intensity (theory) arb. units	Symmetry (theory)
	41.6	45	A
	47.3	46	E
	53.5	402	A
	58.7	0.2	A
66	69.4	3004	E
	70.3	558	E
	71.2	603	A
	73.2	83	E
81	77.7	2914	A
	82.4	730	A
	82.5	443	E
	87.1	854	E
	90.4	16	A
	92.9	544	E
	93.4	2	A
	100.3	236	E
98	111.4	1431	A
	116.6	1001	E
	120.8	17	A
128	128.8	341	E
	141.7	15	A
	141.9	151	E
158	154.9	1536	E
	156.2	341	A
	164.5	1185	A
	164.8	604	E
	170.2	128	A
179	176.0	4051	E
	184.8	3307	A
194	184.9	4145	E
	273.2	2	A
	275.7	3651	E
273	279.7	298577	A
	281.1	600	E
285	283.9	4114	E
	285.6	1676	A
308	310.4	1325	E
	317.3	2807	A
347	317.8	826363	A
	323.5	9492	E
364	340.4	59354	E
	341.1	580	A
377	352.9	15172	A
	353.1	7146	E
	355.2	26	A
	365.2	9773	E
410			
464			

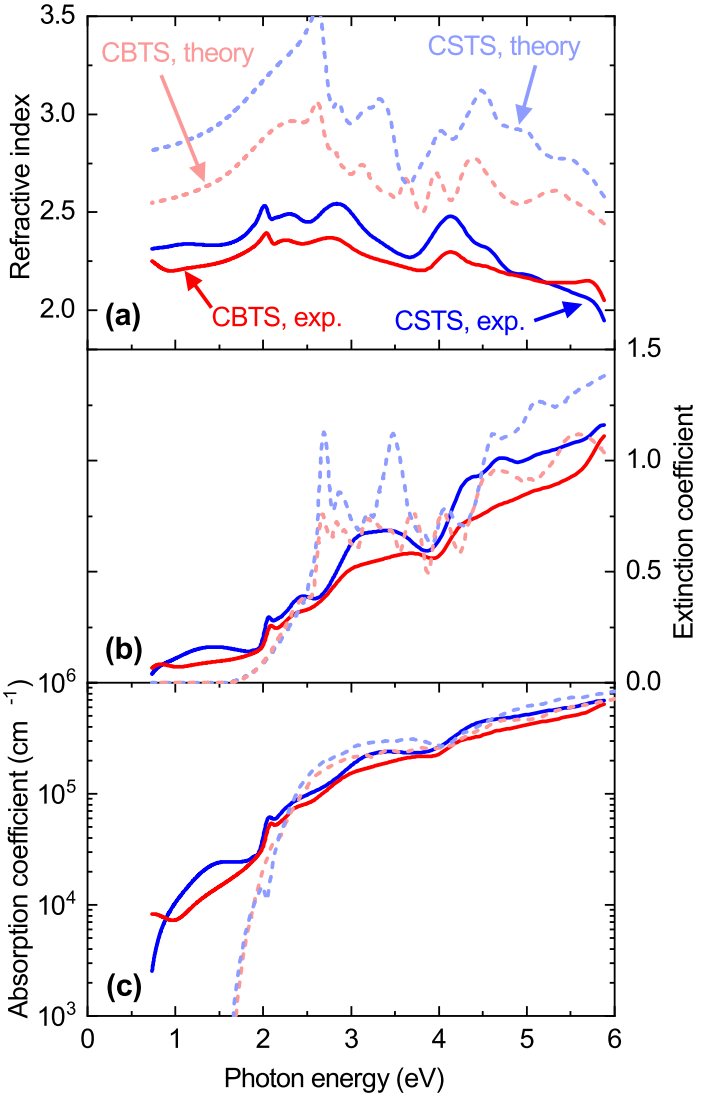

Figure S 2: Measured (solid lines) and calculated (dashed lines) optical properties of CBTS (red) and CSTS (blue). (a): Refractive index n; (b): extinction coefficient κ; (c) absorption coefficient α on a logarithmic scale.

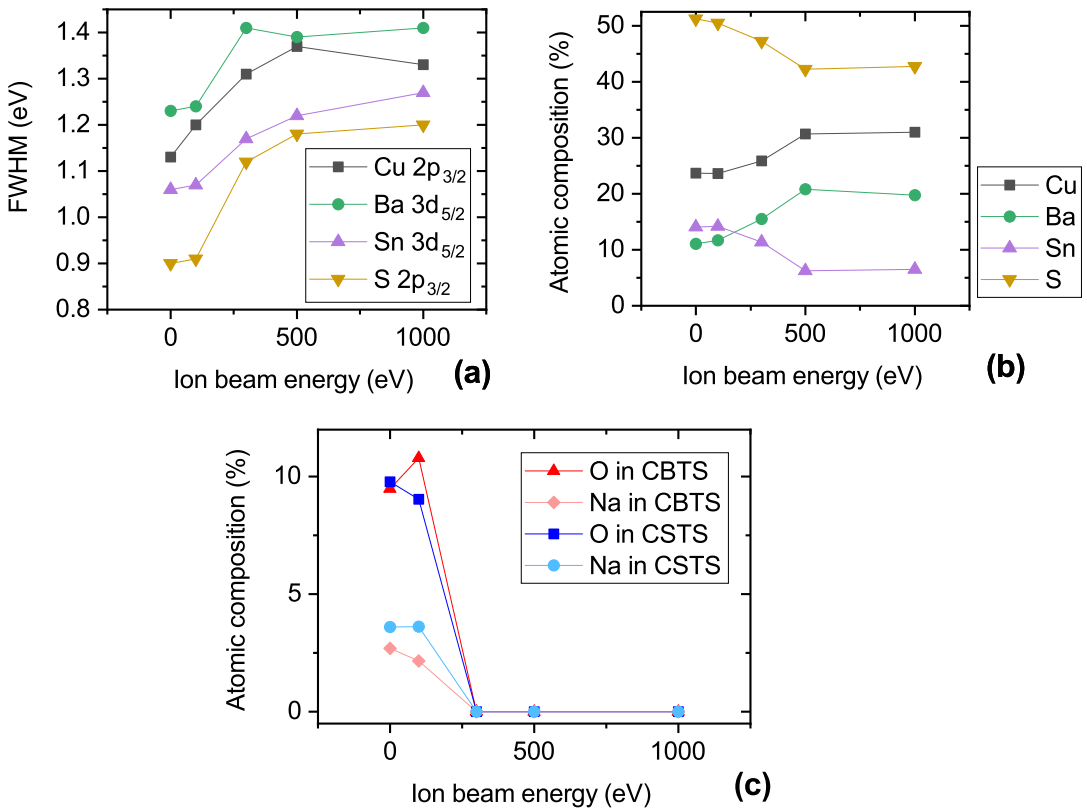

Figure S 3: (a): Full width at half maximum of various XPS core level peaks as a function of the energy of the Ar^+ ion beam used to clean the surface of the sample. (b): XPS-measured atomic composition of the CBTS surface (O and Na excluded) as a function of ion beam energy. Note the preferential loss of SnS already at low energies. (c): XPS-measured O and Na atomic composition in CBTS (expressed as fraction of the total Cu + Ba +Sn + S + O + Na composition) as a function of ion beam energy. For ion beam energies above 300 eV, both elements are below the detection limit.

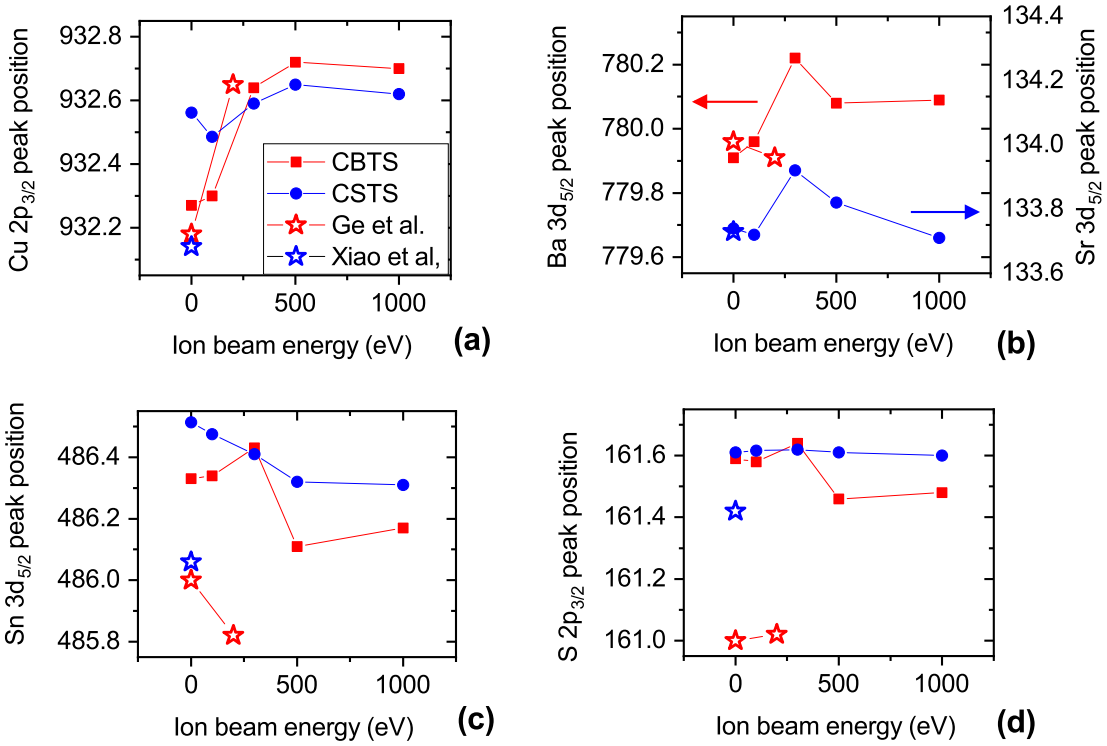

Figure S 4: Energy position of the main core level peaks of CBTS and CSTS as a function of the energy of the Ar^+ ion beam used to clean the surface of the sample. Red (blue) symbols indicate data points for CBTS (CSTS) films. The data points from the present study are shown as full squares and circles. Data points from previous studies (Ref. [3] for CBTS, Ref. [4] for CSTS) are shown as empty stars.

References

[1] Teske C L and Vetter O 1976 *Zeitschrift für anorganische und allgemeine Chemie* **426** 281–287

[2] Teske C L 1976 *Zeitschrift für anorganische und allgemeine Chemie* **419** 67–76

[3] Ge J and Yan Y 2017 *Journal of Materials Chemistry C* **5** 6406–6419

[4] Xiao H, Chen Z, Sun K, Yan C, Xiao J, Jiang L, Hao X, Lai Y and Liu F 2020 *Thin Solid Films* **697** 137828