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Ba$_5$Cu$_8$In$_2$S$_{12}$: a quaternary semiconductor with unique 3D copper-rich framework and ultralow thermal conductivity

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Experimental

Syntheses

All synthetic procedures were performed in an Ar-filled glovebox. Title compound resulted unexpectedly in the course of examining the influence of different ratios of Ba on the Cu/In/S system. It was synthesized from the reaction of Ba, Cu, In and S in the molar ratio 2/5/1/6 in a carbon-coated fused silica tube. The tube was evacuated, sealed, heated to 1273 K in 50 h, held at this temperature for 4 days, after that cooled to 573 K at the rate of 4 K/h and then the furnace was switched off. The product consisted of dark-red bulk crystals. EDX analysis (FESEM, JSM6700F) of several of these crystals led to a composition close to that of "Ba$_5$Cu$_8$In$_2$S$_{12}$", as found later in the Single-crystal X-ray structure determination.

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After numerous explorations on the experimental conditions, the pure phase of $Ba_5Cu_8In_2S_{12}$ was obtained by stoichiometric reaction and quenching at 1173 K. The homogeneous target products were checked by the powder X-ray diffraction (PXRD) data using a Rigaku DMAX 2500 diffractometer with Cu-Kα radiation.

The resulting pure phases of title compounds were ground into a fine powder and subsequently hot pressed around 773 K under a pressure of 100 MPa for 1 h. The obtained pellets had relative densities no less than 98% of the theoretical value.

Property Characterization

The solid-state optical absorption spectrum was performed at room temperature using a Perkin-Elmer Lambda 950 UV–Vis spectrophotometer. The thermal stability analyses were measured on a NETZSCH STA 449C simultaneous analyzer. The thermal conductivity were measured by laser flash techniques with a Netzsch LFA 457 system and calculated using the formula $\kappa = D \times C_p \times d$, where D was the measured thermal diffusivity, C_p was the heat capacity estimated using the Dulong-Petit model ($C_p = 3nR$, where n is the number of atoms per formula unit and R is the gas constant) and d was the sample density.[1] The uncertainty of the thermal conductivity k is estimated to be within 5%, considering the uncertainties for D, C_p and d.

Single-Crystal X-ray diffraction (XRD)

Single-crystal XRD at room temperature was collected on a Mercury CCD diffractometer with Mo Kα radiation. The absorption correction was done,[2] and

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structures were solved by direct methods and refined using the SHELX-97 software.[3] All atoms were refined with anisotropic thermal parameters. Note that the Cu5 atom was refined as split site (e.g., Cu5A, Cu5B and Cu5C) due to the high atomic displacement parameter and the occupancies were refined to 21%, 42%, and 41%, respectively. The coordinates were standardized using *STRUCTURE TIDY*.[4] Crystallographic data and structural refinement details are summarized in Table S1, the positional coordinates and isotropic equivalent thermal parameters are given in Table S2, and important bond distances are listed in Table S3.

Computational Section. Electronic structure calculations are performed using the general potential linearized augmented plan wave (LAPW)[5] method based on density functional theory (DFT),[6] using the Predew-Burke-Ernzerhof of generalized gradient approximation (PBE-GGA)[7] for the exchange and correlation potential. The calculations are performed by using WIEN2k.[8] The k integration over the Brillouin zone was performed by the tetrahedron method[9] using a $5 \times 5 \times 7$ Monkhorst-Pack mesh.
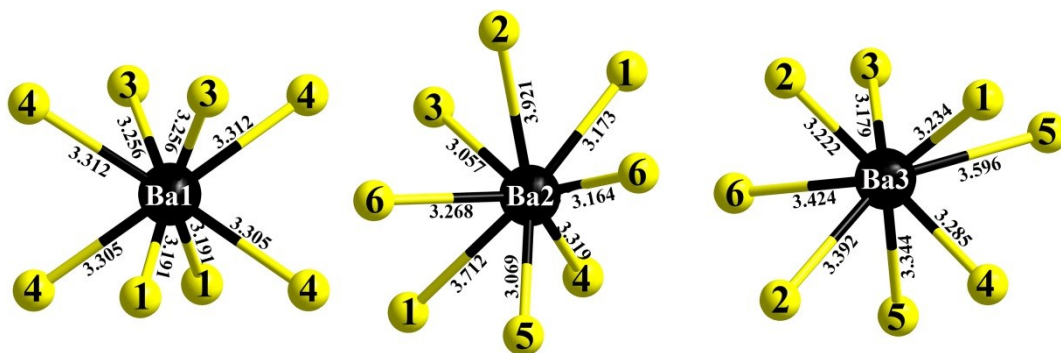
Figure S1. Coordination geometry of Ba atoms with Ba–S distances.
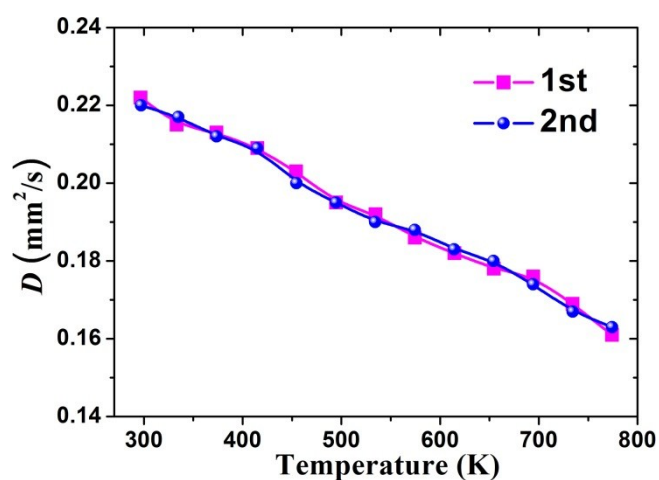

Figure S2. Thermal conductivity (*D*) as a function of the temperature for a hot-pressed polycrystalline sample of **1** during two thermal cycles.

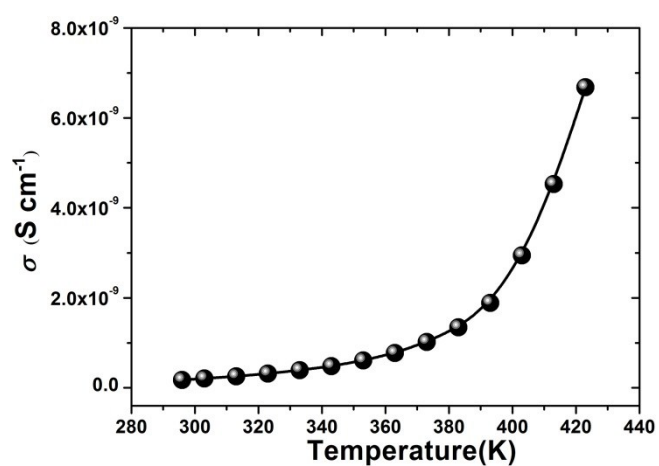**Figure S3.** Electrical conductivity (σ) as a function of temperature for **1** using a K2500-5RSLP Variable Temperature Hall Measurement System.
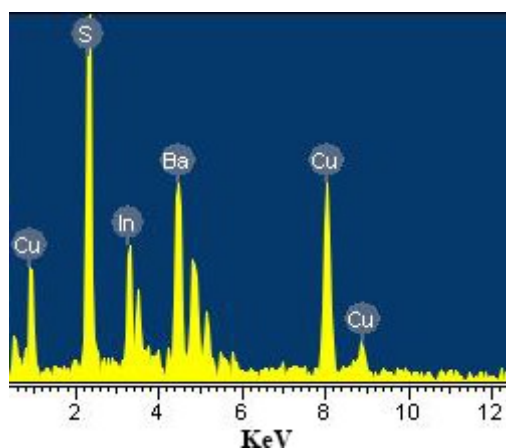
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Figure S4. EDX results for **1**.

Point-1				Point-2			
Element	Weight%	Atomic%	Formula	Element	Weight%	Atomic%	Formula
S K	21.42	44.66	12.11	S K	21.26	44.47	12.01
Cu K	28.12	29.58	8.02	Cu K	27.96	29.51	7.96
In L	12.55	7.31	1.98	In L	12.83	7.49	2.02
Ba L	37.91	18.45	5	Ba L	37.95	18.53	5
Total	100.00			Total	100.00		
Point-3				Point-4			
Element	Weight%	Atomic%	Formula	Element	Weight%	Atomic%	Formula
S K	21.33	44.47	12.13	S K	21.03	44.11	11.86
Cu K	28.35	29.83	8.14	Cu K	28.11	29.75	8.01
In L	12.68	7.38	2.02	In L	12.88	7.54	2.03
Ba L	37.64	18.32	5	Ba L	37.98	18.60	5
Total	100.00			Total	100.00		
Point-5							
Element	Weight%	Atomic%	Formula				
S K	21.55	44.88	12.17				
Cu K	27.94	29.36	7.96	Average formula:			
In L	12.59	7.32	1.99				
Ba L	37.92	18.44	5	$Ba_5Cu_{8.01(4)}In_{2.01(2)}S_{12.05(6)}$			
Total	100.00						

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Table S1. Crystallographic data and refinement details for $Ba_5Cu_8In_2S_{12}$.

Formula	$Ba_5Cu_8In_2S_{12}$
Formula weight	1809.38
Temperature(K)	293(2)
Crystal system	Monoclinic
Crystal color	Dark-red
Space group	$C\,2/c$ (No.15)
a (Å)	14.584(2)
b (Å)	16.369(2)
c (Å)	10.509(2)
α (deg.)	90
β (deg.)	100.14(2)
γ (deg.)	90
V (Å^3)	2469(5)
Z	4
D_c (g·cm^{-3})	4.87
GOOF on F^2	1.13
R_1, wR_2 ($I > 2\sigma(I)$) [a]	$R_1 = 0.048$, $R_2 = 0.079$
R_1, wR_2 (all data)	$R_1 = 0.057$, $R_2 = 0.084$
Largest diff. Peak / hole (e·Å^{-3})	1.76/-1.26

[a]$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$

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Table S2. Atomic coordinates and equivalent isotropic displacement parameters of

$Ba_5Cu_8In_2S_{12}$.

Atom	Symmetry	x	y	z	$U_{(eq)}(Å^2)$*	Occu.
Ba1	4e	0	0.00079(6)	0.25	0.0162(3)	1
Ba2	8f	0.26154(6)	0.01105(5)	0.57285(7)	0.0219(2)	1
Ba3	8f	0.35377(6)	0.2251(4)	0.32646(7)	0.0194(2)	1
Cu1	8f	0.1073(2)	0.19129(9)	0.3655 (2)	0.0231(4)	1
Cu2	4e	0	0.5143(2)	0.25	0.0287(6)	1
Cu3	8f	0.1606(2)	0.3675(2)	0.1470(2)	0.0292(4)	1
Cu4	4e	0	0.3314(2)	0.25	0.0404(7)	1
Cu5A	8f	0.0052(2)	0.4183(10)	0.4526(2)	0.014(4)	0.17(2)
Cu5B	8f	0.0088(3)	0.4338(3)	0.0104(5)	0.025(2)	0.42(2)
Cu5C	8f	0.0201(5)	0.4067(4)	0.4657(7)	0.026(2)	0.41(2)
In	8f	0.0976(6)	0.17607(5)	0.0111(8)	0.0173(2)	1
S1	8f	0.3225(2)	0.3889(2)	0.1520(3)	0.0164(7)	1
S2	8f	0.4196(2)	0.1812(2)	0.0576(3)	0.0196(7)	1
S3	8f	0.1732(2)	0.1204(2)	0.2191(3)	0.0186(7)	1
S4	8f	0.0604(2)	0.1108(2)	0.5160(3)	0.0186(7)	1
S5	8f	0.1402(3)	0.3245(2)	0.3634(3)	0.0285(8)	1
S6	8f	0.3883(2)	0.0187(2)	0.3580(3)	0.0200(7)	1

*$U_{(eq)}$ is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

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Table S3. Selected bond lengths (Å) of $Ba_5Cu_8In_2S_{12}$.

bond	length (Å)	bond	length (Å)
Cu1–S3	2.272(4)	Ba1–S1×2	3.190(4)
Cu1–S4	2.255(4)	Ba1–S3×2	3.257(4)
Cu1–S5	2.232(4)	Ba1–S4×2	3.305(4)
Cu2–S6×2	2.142(4)	Ba1–S4×2	3.311(4)
Cu3–S1	2.377(4)	Ba2–S1	3.172(4)
Cu3–S2	2.396(4)	Ba2–S1	3.712(4)
Cu3–S5	2.449(4)	Ba2–S2	3.921(4)
Cu3–S6	2.573(4)	Ba2–S3	3.057(4)
Cu4–S5×2	2.180(4)	Ba2–S4	3.318(4)
Cu5–S2	2.345(4)	Ba2–S5	3.068(4)
Cu5–S6	2.369(4)	Ba2–S6	3.162(4)
Cu5–S6	2.506(5)	Ba2–S6	3.269(4)
Cu5A–Cu5B	0.534(2)	Ba3–S1	3.235 (4)
Cu5A–Cu5C	0.303(2)	Ba3–S2	3.221(4)
Cu5B–Cu5C	0.689(9)	Ba3–S2	3.392(4)
In–S1	2.476(4)	Ba3–S3	3.178(4)
In–S2	2.445(4)	Ba3–S4	3.285(4)
In–S3	2.444(4)	Ba3–S5	3.345 (4)
In–S4	2.510(4)	Ba3–S5	3.596(4)
		Ba3–S6	3.423(4)

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