Supporting Information

Doping and thermoelectric properties of the zero-dimensional inorganic halide perovskite derivative, $Cs_3Cu_2I_5$

Ceyla Asker,[a] Candida Pipitone,[b] Federica Ursi,[b] Kan Chen,[a] Antonio Gaetano Ricciardulli,[c] Eugenio S. Suena Galindez,[a] Sally Luong,[a] Paolo Samorì,[c] Mike Reece,[a] Antonino Martorana,[b] Francesco Giannici,[b] and Oliver Fenwick.*[a]

* Corresponding author

[a] School of Engineering and Materials Science, Queen Mary University of London, Mile End Road, London E1 4NS, UK.

E-mail: o.fenwick@qmul.ac.uk

[b] Dipartimento di Fisica e Chimica, Università di Palermo, viale delle Scienze, Ed. 17, 90128 Palermo, Italy.

[c] University of Strasbourg, CNRS, ISIS UMR 7006, 8 allée Gaspard Monge, 67000 Strasbourg, France.

Density measurement

The density of materials was determined by the Archimedes principle. A pellet was first weighed in air and then in water by an el d the density was calculated.

Figure S1. An electronic balance for the density measurements of $Cs_3Cu_2I_5$ pellet. The pellet is suspended on a metal arm and submerged in water for the measurement to enable density measurement by Archimedes' principle.

Table S1. The average density and standard deviation of pristine and doped materials calculated from three distinct measurements.

Materials	0% doped	2% doped	5% doped	10% doped	15% doped
Density(g/cm^3)	4.47	4.48	4.45	4.39	4.37
Standard deviation	0.04	0.02	0.03	0.03	0.04

Electrical conductivity measurement geometry

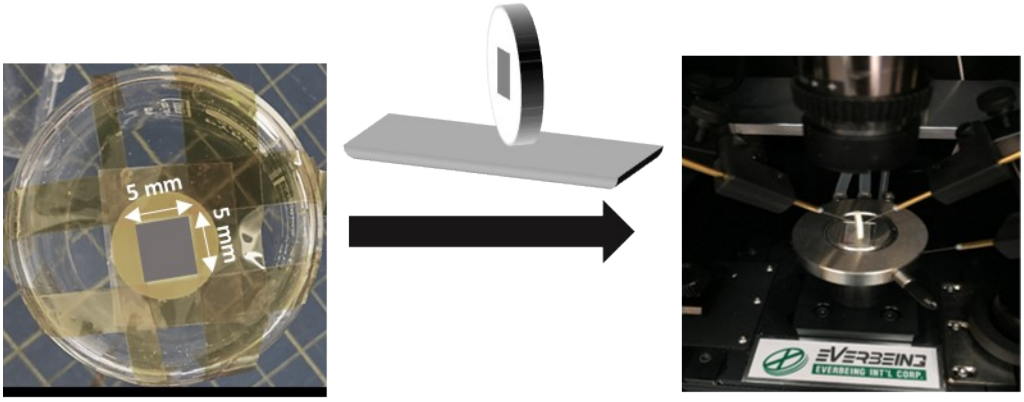

Figure S2. Measurement geometry of bulk resistivity of pellets by a 2-point electrical measurement. Large contacts are first made on each side of the pellet. Electrical connection is made by turning the sample on its edge and contacting with a probe station.

Seebeck measurement principle

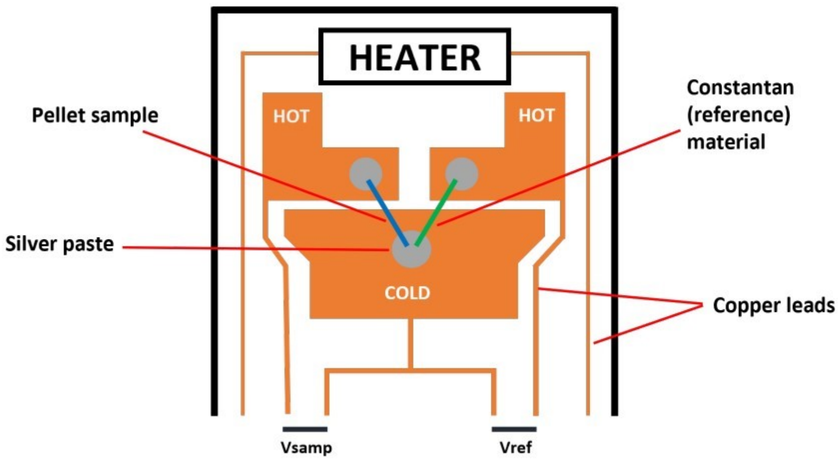

Figure S3. MMR Seebeck Measurement System. The arrangement of the Ba-doped pellet and reference material (constantan) relative to the hot- and cold-contacts.

Figure S3 is a representation of the holder for the measurement of Seebeck coefficient. The 10% Ba-doped pellets were placed on the holder, along with the constantan reference wire with a diameter of 300 µm, to the hot- and cold-reservoirs. Silver paste was used for the electrical and thermal contact between the reservoirs. The holder was then mounted in a vacuum chamber and the temperature allowed to stabilise. During the measurement, the temperature difference between hot and cold reservoirs was about 1 °C. The data points in the main text are taken from the average of five measurements and the error bars are the standard deviation. In the MMR system, two values of V_{samp} and V_{ref} are recorded for two electrical power values of P_1 and P_2 supplied to the heater, and the Seebeck coefficient of the sample is given by

$$S_{samp} = S_{ref} \frac{[V_{samp}(P_1) - V_{samp}(P_2)]}{[V_{ref}(P_1) - V_{ref}(P_2)]}$$

Thermal conductivity measurement and uncertainty

The thermal conductivities were calculated by multiplying diffusivity, heat capacity at each temperature point and the pellet's density, $\kappa = DC_p\rho$. To calculate the error in the result at a certain temperature for each material, the fractional uncertainties of each variable (D, C_p and ρ) were added together as shown below:

$$\frac{\delta_\kappa}{\kappa} = \sqrt{\left(\frac{\delta_D}{D}\right)^2 + \left(\frac{\delta C_p}{C_p}\right)^2 + \left(\frac{\delta_\rho}{\rho}\right)^2}$$

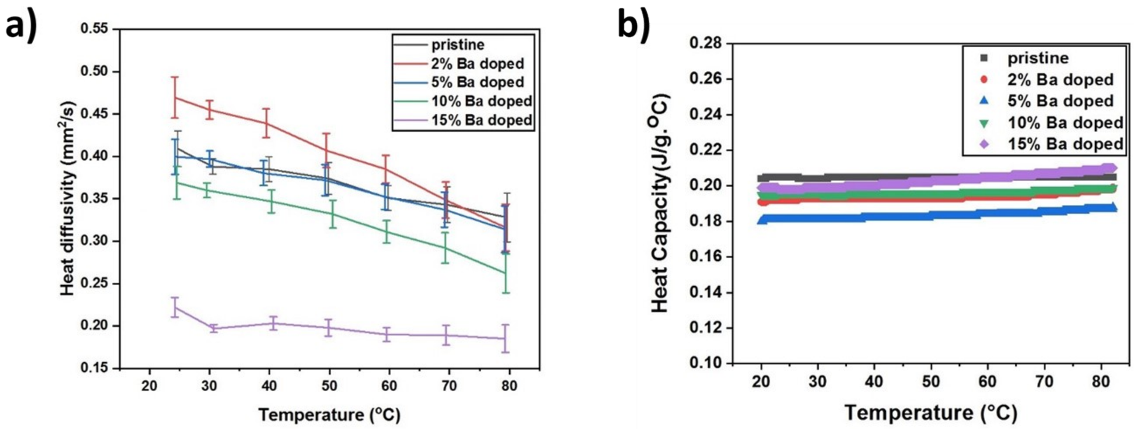

Figure S4. a) Thermal diffusivity, and b) heat capacity of Ba doped pellets

X-ray photoelectron spectroscopy

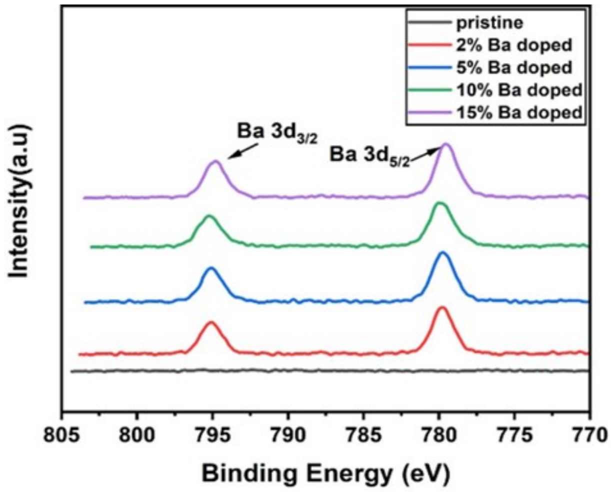

Figure S5. Ba3d XPS spectra of pellets with different dopant concentrations

The Ba 3d high-resolution spectrum is shown in Figure S5. No peaks were obtained for the pristine (undoped) material. For the doped ones, the peaks at ~ 780 eV and ~ 795 eV are assigned to Ba $3d_{5/2}$ and Ba $3d_{3/2}$ respectively.

	Name	Peak BE	FWHM eV	Area (P) CPS.eV	Atomic %	Q
	I3d5	623.11	3.06	490410.55	46.41	☑
	Cs3d5	728.28	3.04	282708.14	25.13	☑
	Ba3d5	784.29	3.10	78123.85	6.91	☑
	C1s	288.74	3.64	61992.58	0.00	☐
	O1s	535.30	3.89	29064.72	0.00	☐
	Cu2p1	955.08	0.00	51.41	0.00	☐
	Cu2p3	935.74	4.55	118777.79	21.55	☑

Table S1. XPS atomic ratio determination of 5% Ba doped pellet

Table S2 Results of the Rietveld refinement of the X-ray diffraction (XRD) data of $Cs_3Cu_2I_5$ as a function of Ba-loading (original data in Figure 3 of main paper). Digits in parentheses denote the uncertainty. Relative uncertainty on the minority trace phases is ~10%.

$Cs_3Cu_2I_5$, space group *Pnma*					CsI, space group *Pm-3m*	$CsCu_2I_3$, space group *Cmcm*
	a	b	c	Volume	**CsI w/w %**	**$CsCu_2I_3$ w/w %**
0%	10.1744(3)	11.6524(3)	14.3608(4)	1702.6(1)	0.7	1.9
2%	10.1746(2)	11.6527(3)	14.3604(3)	1702.60(9)	1.4	0.7
5%	10.1723(3)	11.6498(3)	14.3584(4)	1701.5(1)	0.6	2.6
10%	10.175(1)	11.654(1)	14.359(1)	1702.7(4)	3.4	2.6
15%	10.1751(3)	11.6528(3)	14.3617(4)	1702.83(9)	9.2	0.5

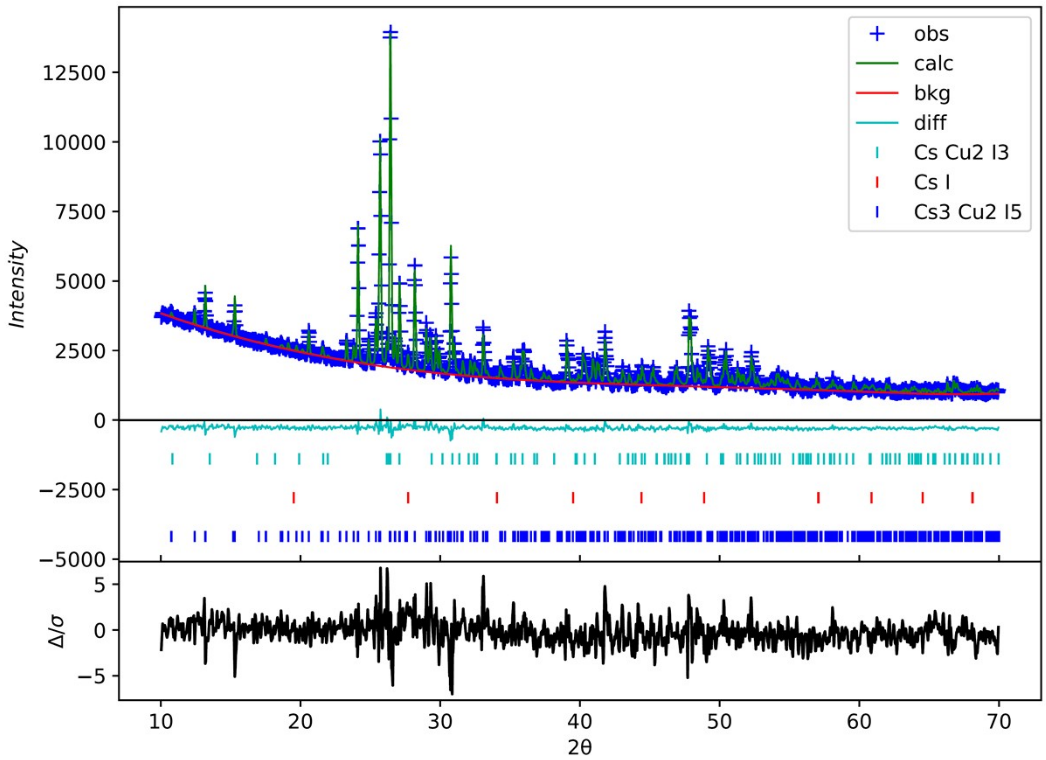

Figure S6 Results of the Rietveld refinement for the undoped $Cs_3Cu_2I_5$ material.

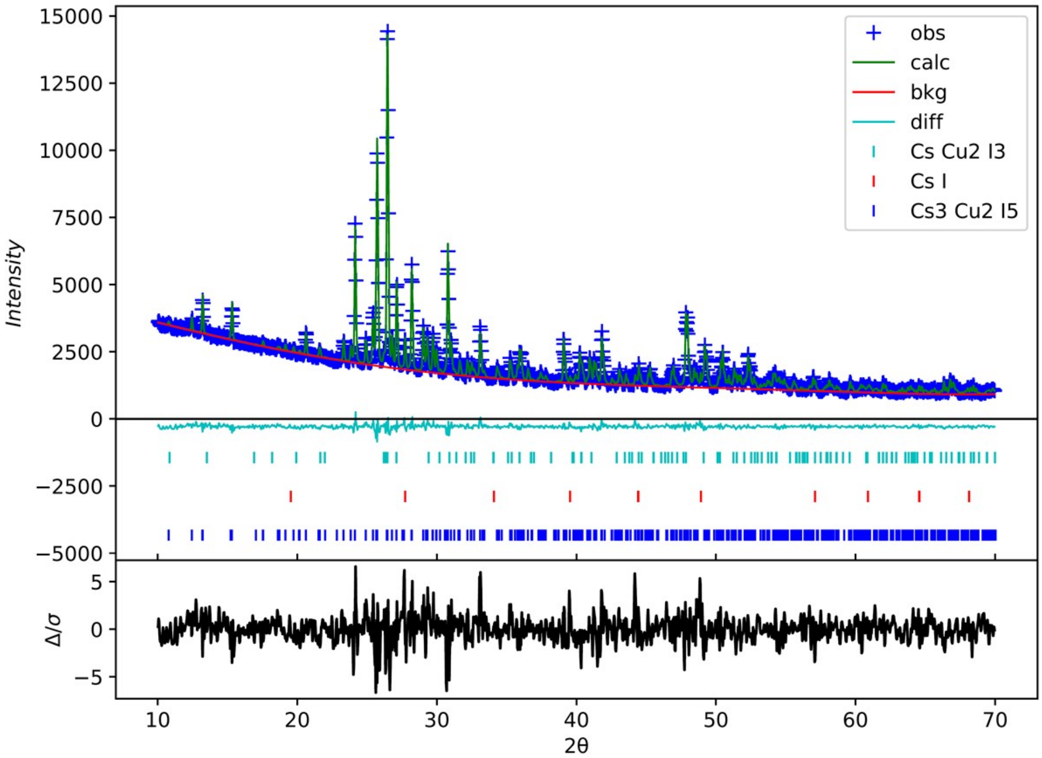

Figure S7 Results of the Rietveld refinement for the $Cs_3Cu_{2(1-x)}Ba_xI_5$ (*x=0.02*) material.

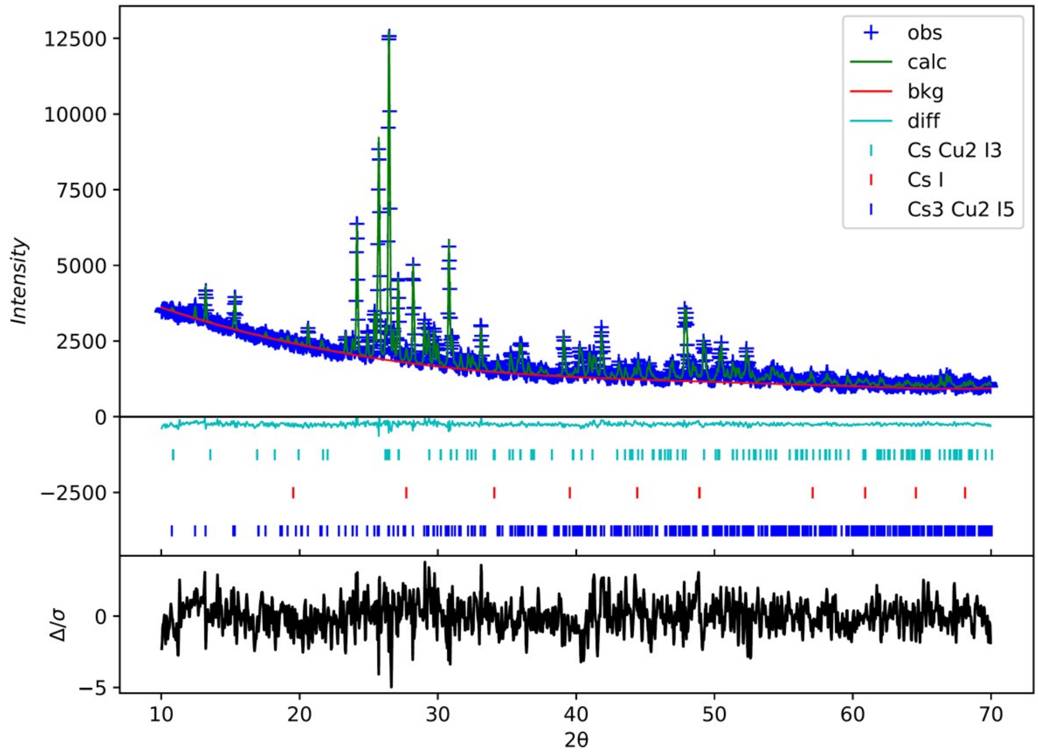

Figure S8 Results of the Rietveld refinement for the $Cs_3Cu_{2(1-x)}Ba_xI_5$ (*x=0.05*) material.

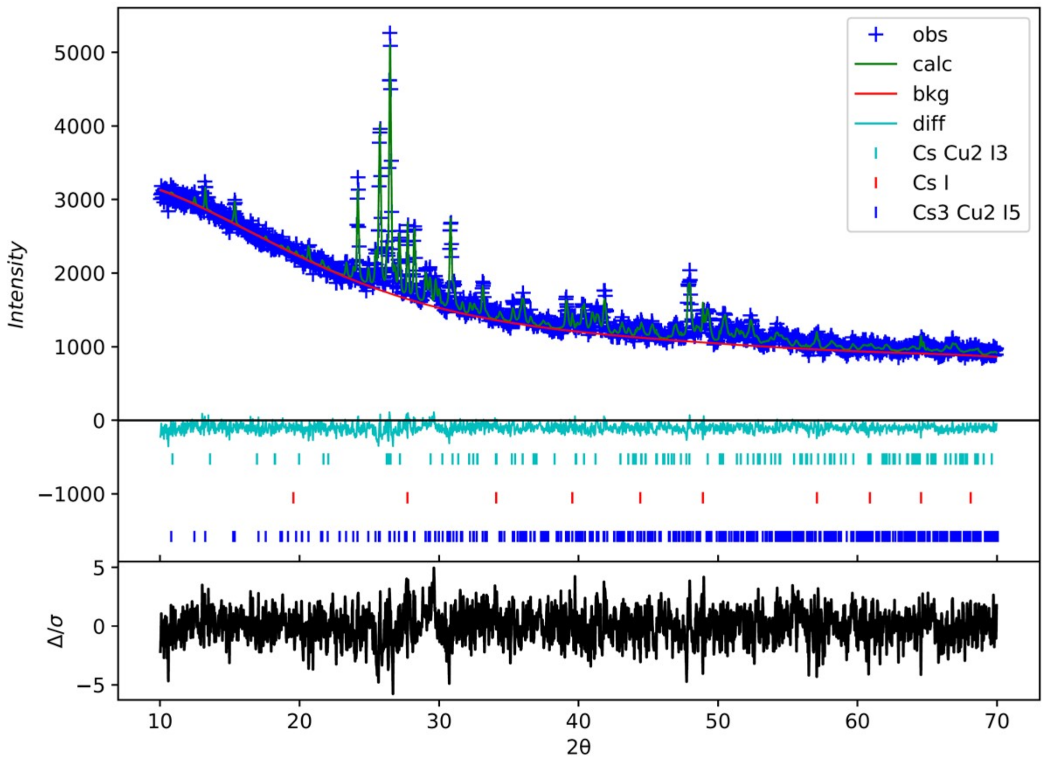

Figure S9 Results of the Rietveld refinement for the $Cs_3Cu_{2(1-x)}Ba_xI_5$ (*x=0.10*) material.

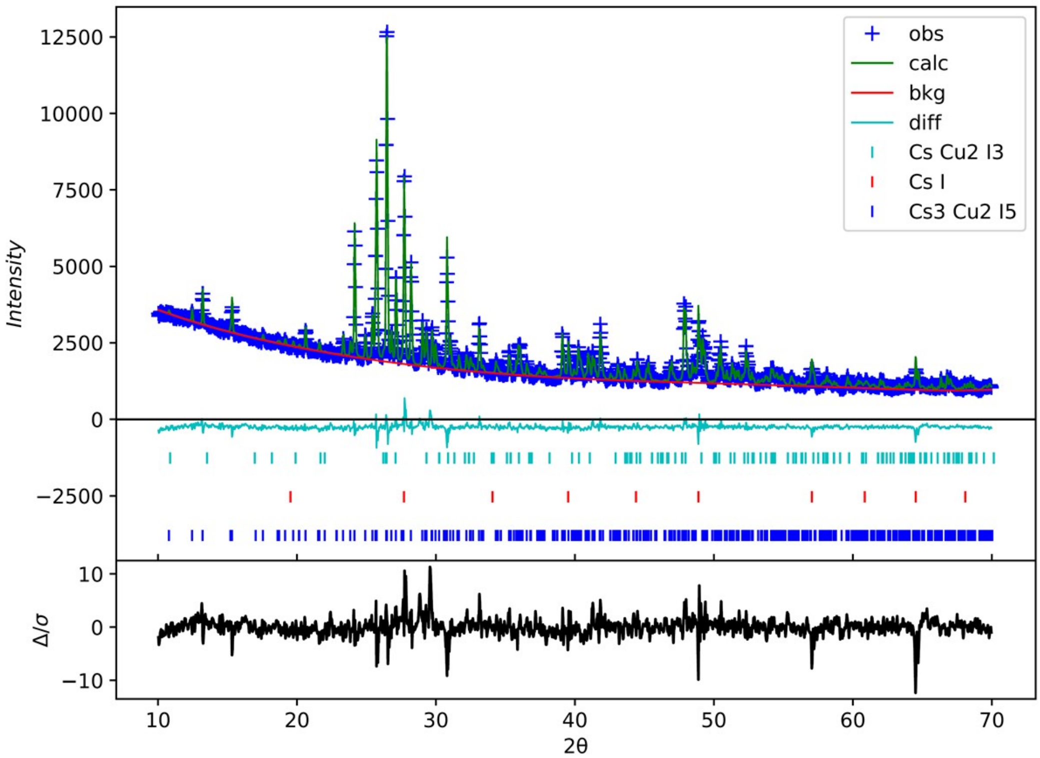

Figure S10 Results of the Rietveld refinement for the $Cs_3Cu_{2(1-x)}Ba_xI_5$ (*x=0.15*) material.