Electronic Supplementary Information

Crystal Structure, Electronic Band Structure and High-Temperature Thermoelectric Properties of Te-Substituted Tetrahedrites $Cu_{12}Sb_{4-x}Te_xS_{13}$ ($0.5 \leq x \leq 2.0$)

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1. Table S1. Single-crystal data collection and structure refinement at 300 K.

Chemical formula	$Cu_{12}Sb_2Te_2S_{13}$ (series S1)
Molar mass ($g.mol^{-1}$)	1678.02
Symmetry	Cubic
Space group	*I-43m*
a (Å)	10.3520(1)
V ($Å^3$)	1108,91(1)
Z	2
ρ ($g.cm^{-3}$)	5.025
Radiation	Mo Kα
θ range	3 – 79.39°
Linear Abs. coeff. μ (mm^{-1})	17.24
Reflection collected	3465
Reflection unique	666
Number of parameters	18
Final *R* value (%)	2.79
S (Goodness of fit)	0.942

2. SEM images and X-ray mapping of the x = 0.61, 1.40 and 1.79 samples (series S1)

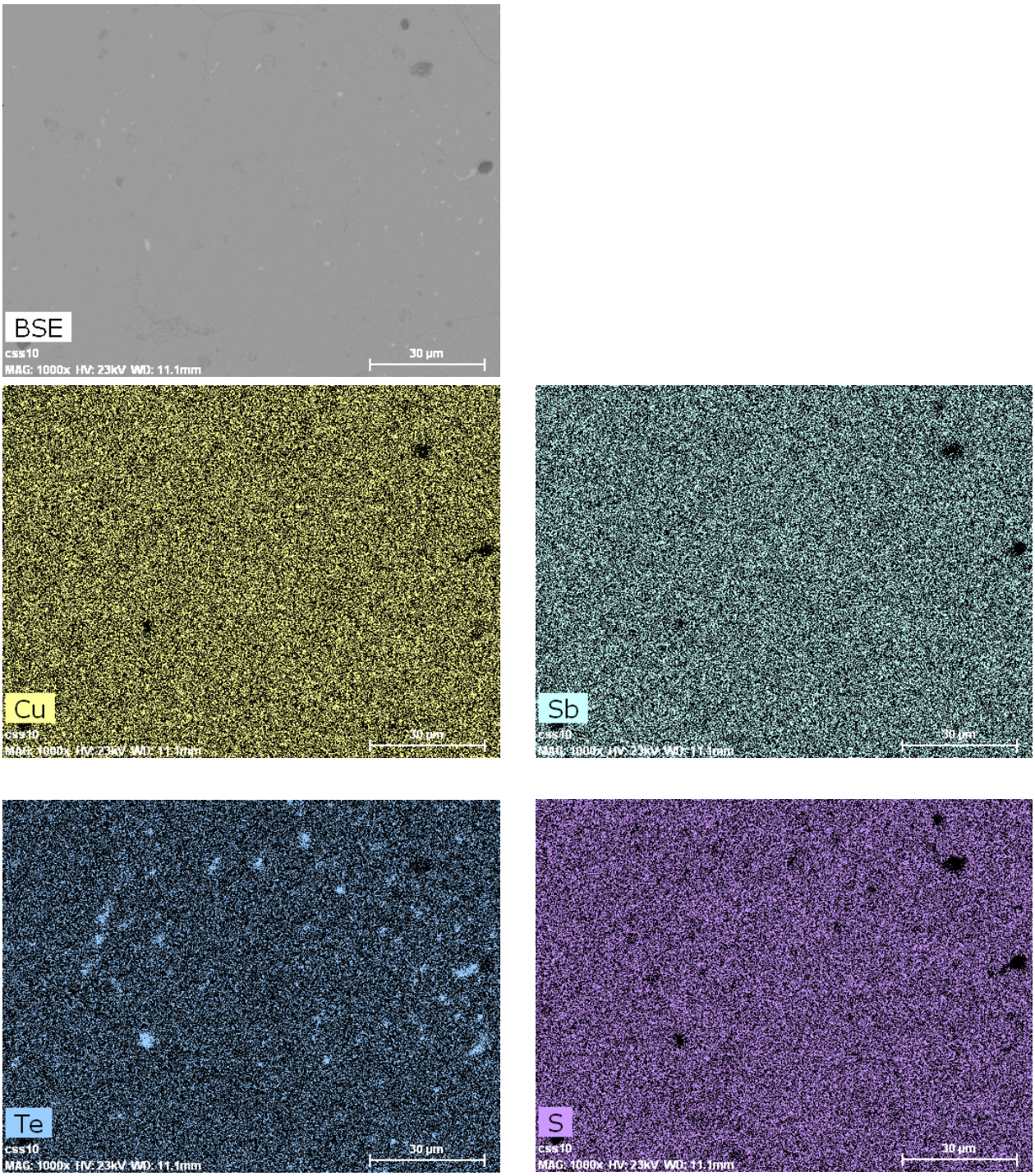

Figure S1. BSE images and X-ray mapping performed on the x = 0.61 sample.

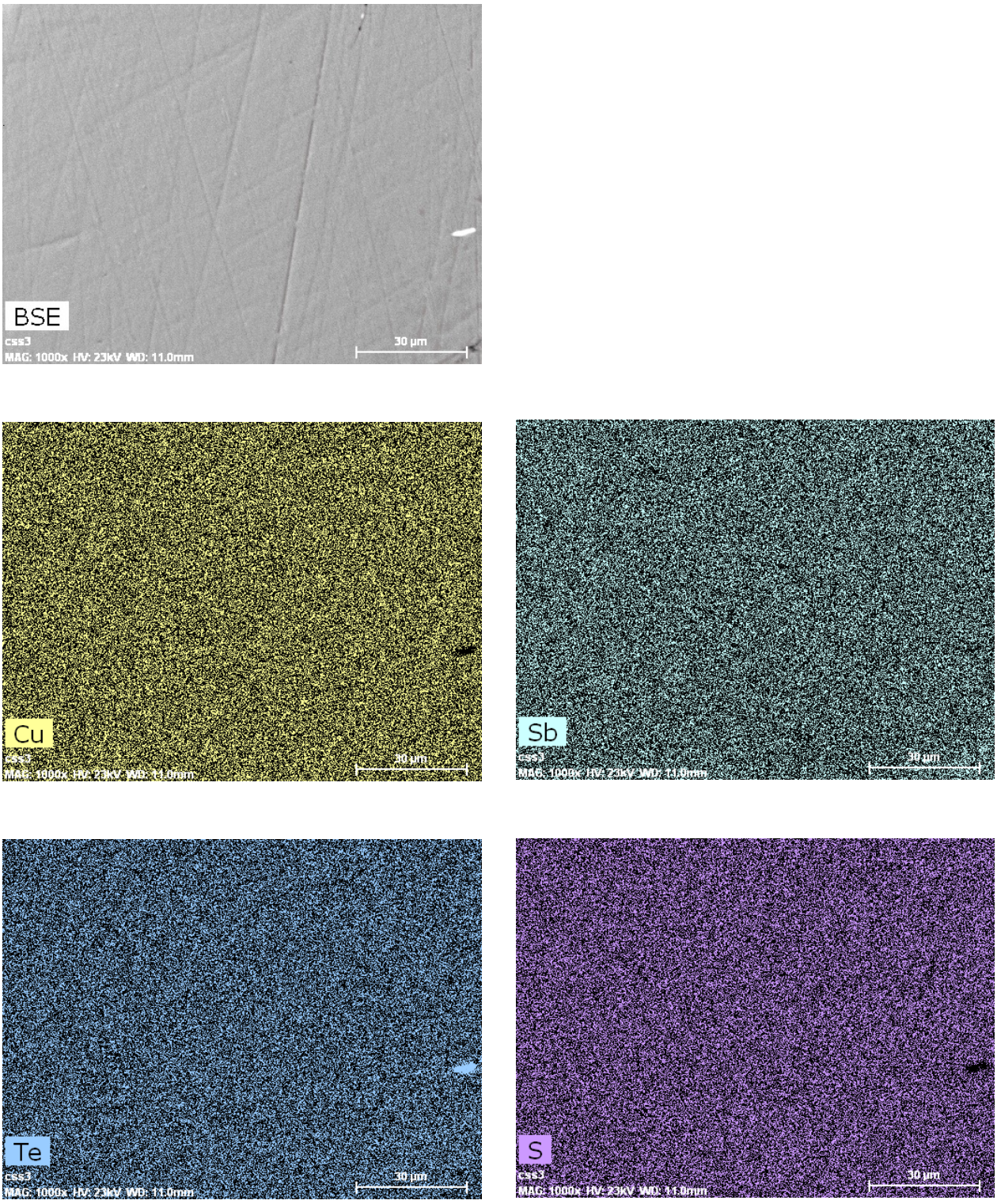

Figure S2. BSE images and X-ray mapping performed on the x = 1.40 sample.

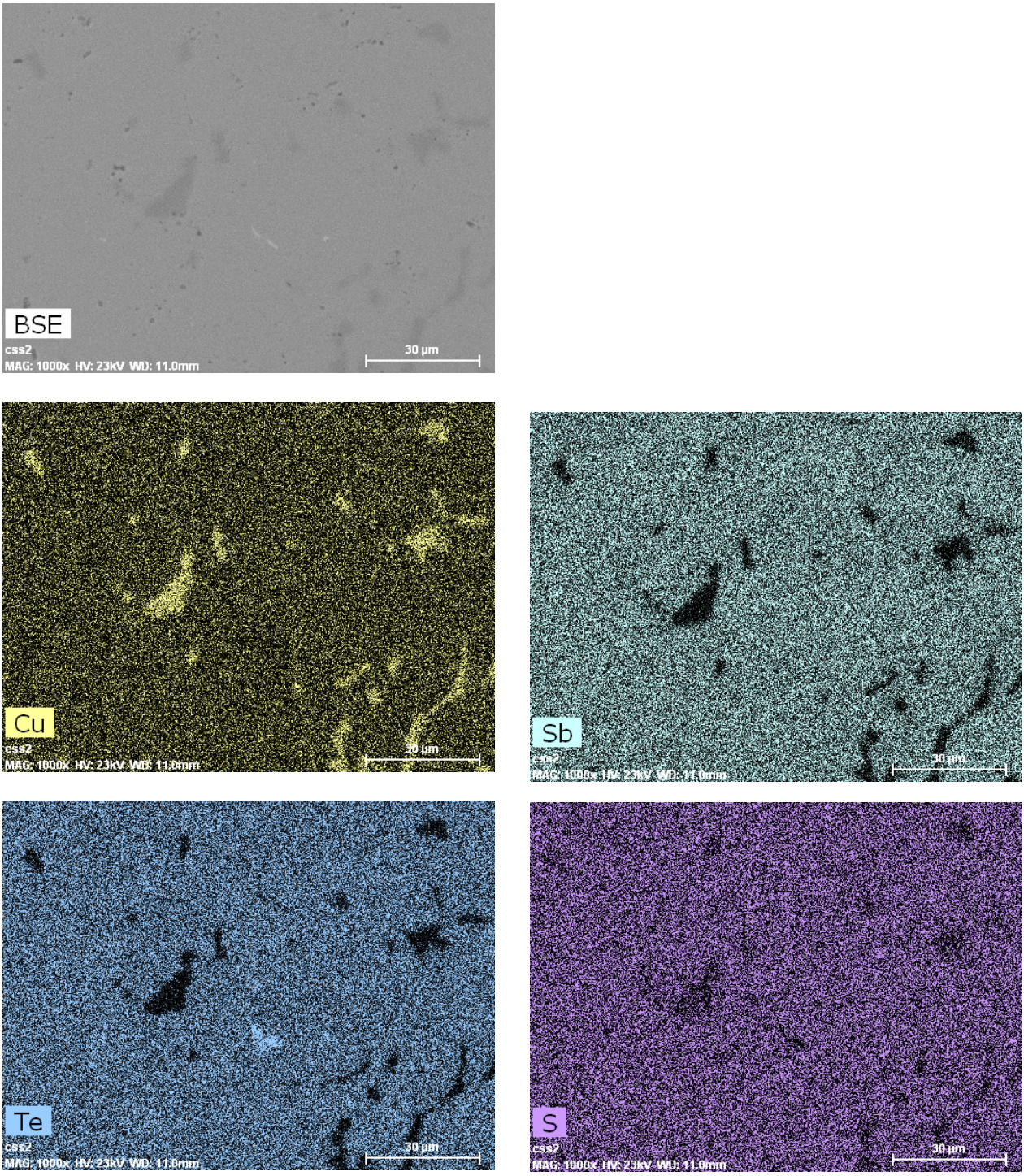

Figure S3. BSE images and X-ray mapping performed on the x = 1.79 sample.

2. Table S2. Atomic coordinates, site occupancies and equivalent atomic thermal displacement parameters (Å^2).

Site	Atom	*x*	*y*	*z*	s.o.f	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
12*d*	Cu1	0.5	0	0.25	0.25	0.0192(3)	0.0192(3)	0.0256(5)	0	0	0
12*e*	Cu2	0	0	0.2168(3)	0.25	0.0737(1)	0.0737(1)	0.0185(1)	0	0	-0.052(1)
8*c*	Sb	0.26391(4)	0.26391(4)	0.26391(4)	0.1667	0.0124(2)	0.0124(2)	0.0124(2)	-0.0008(1)	-0.0008(1)	-0.0008(1)
24*g*	S1	0.8855(1)	0.8855(1)	0.3622(2)	0.5	0.0141(4)	0.0141(4)	0.0110(6)	0.001(4)	0.001(4)	-0.011(5)
2*a*	S2	0	0	0	0.04167	0.0174(1)	0.0174(1)	0.0174(1)	0	0	0

3. Table S3. Refined bond distances and bond angles from single-crystal XRD data at room temperature. Data obtained by Pfitzner *et al.* and Makovicky and Skinner on single-crystals of the ternary compound have been added for comparison.

Composition	$Cu_{12}Sb_2Te_2S_{13}$	$Cu_{12}Sb_4S_{13}$	$Cu_{12.3}Sb_4S_{13}$
Cu1 – S1 (×4)	2.33508	2.3133(8)	2.311(4)
Cu2 – S1 (×2)	2.25911	2.264(2)	2.246(7)
Cu2 – S2	2.16048	2.249(2)	2.250(6)
Cu2 – Cu2 (×4)	3.05538	3.180(3)	3.186(8)
Cu2 – Sb/Te (×2)	3.47533	3.4090(4)	3.386
Sb/Te – S1 (×3)	2.45991	2.438(1)	2.452(4)
S1 – Cu1 – S1 (×2)	112.55	106.37(4)	105.45(15)
S1 – Cu2 – S1	91.24	96.6(1)	96.04(25)
S2 – Cu2 – S1 (×2)	134.38	131.70(7)	131.98(10)
Sb/Te – Cu2 – Sb/Te	170.48	174.6(1)	175.2
S1 – Sb/Te – S1 (×3)	96.67	95.87(4)	95.70(10)

5. High-temperature PXRD patterns of the x = 0.61 (a) and 1.79 (b) samples (series S1)

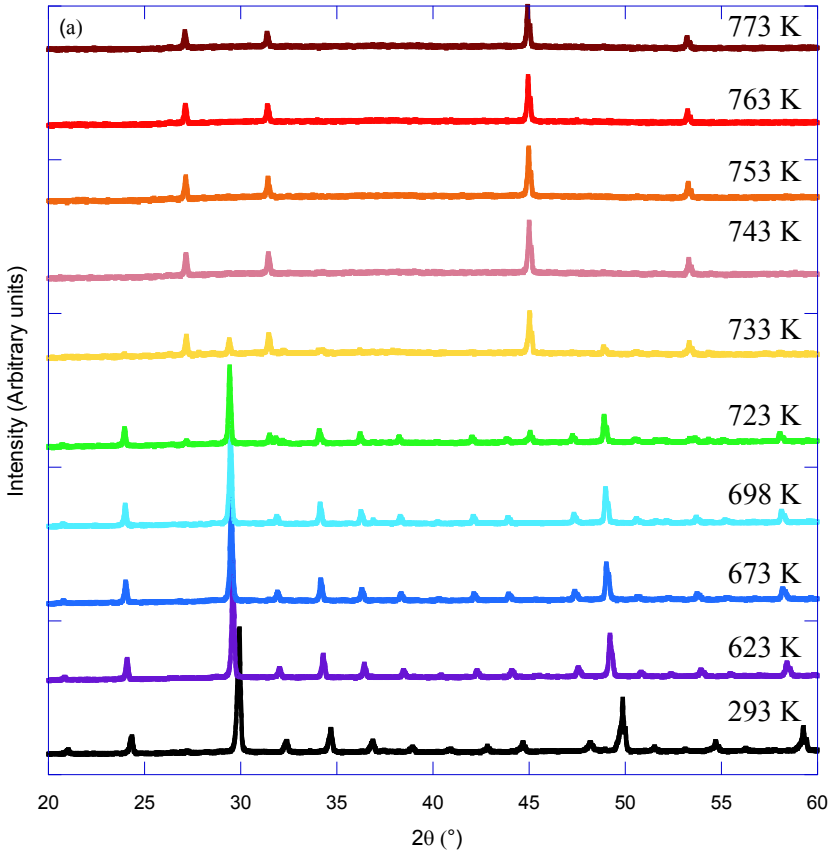

Figure S4. High-temperature PXRD spectra of the x = 0.61 sample.

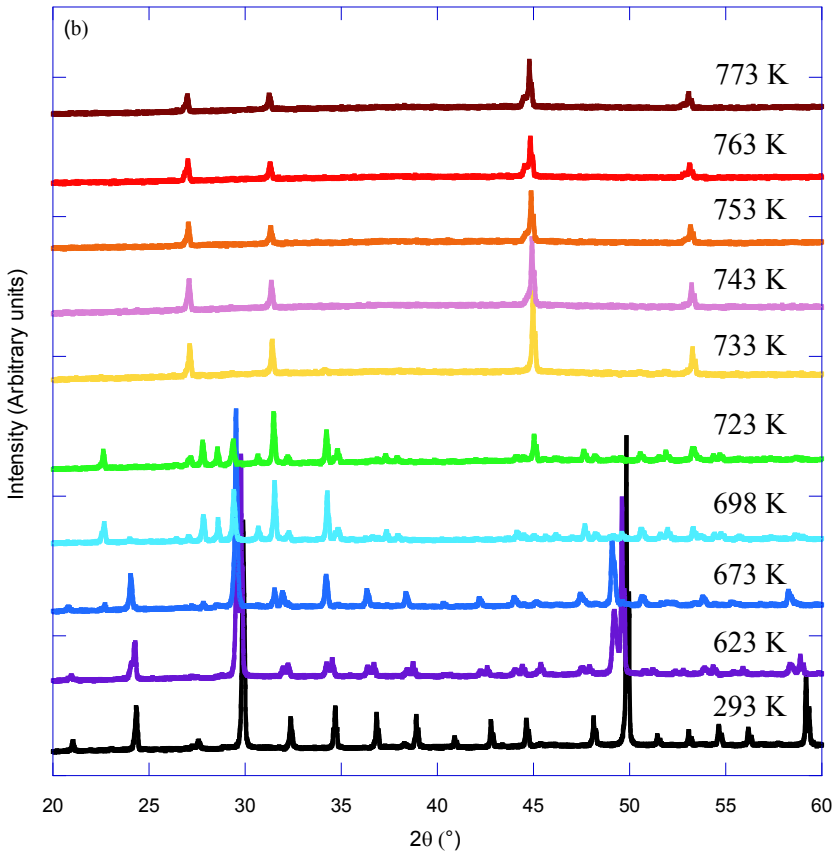

Figure S5. High-temperature PXRD spectra of the x = 1.79 sample.

6. Temperature dependence of the specific heat of the x = 0.80 sample (series S1)

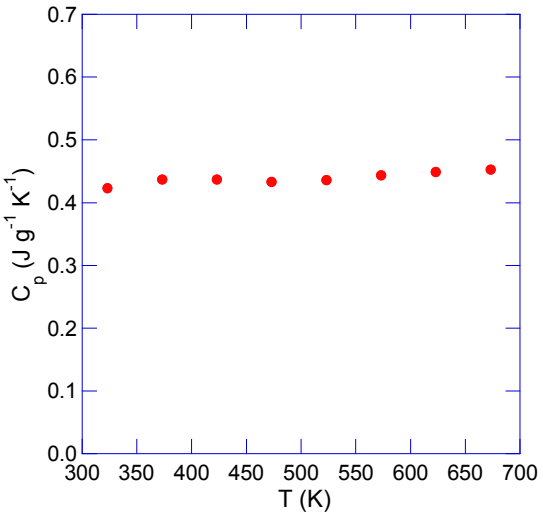

Figure S6. Temperature dependence of the specific heat C_p of the x = 0.80 sample.