Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.
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Supplementary Information: Earth Abundant, Non-Toxic, 3D Printed $Cu_{2-x}S$ with High Thermoelectric Figure of Merit

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X-Ray Diffraction (XRD)

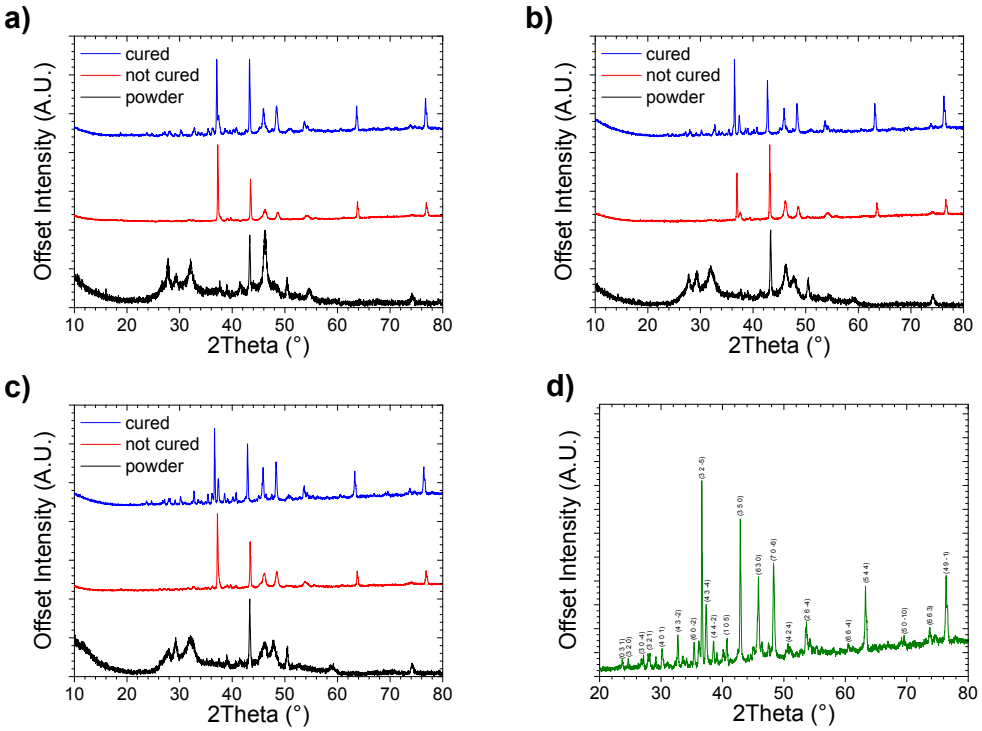
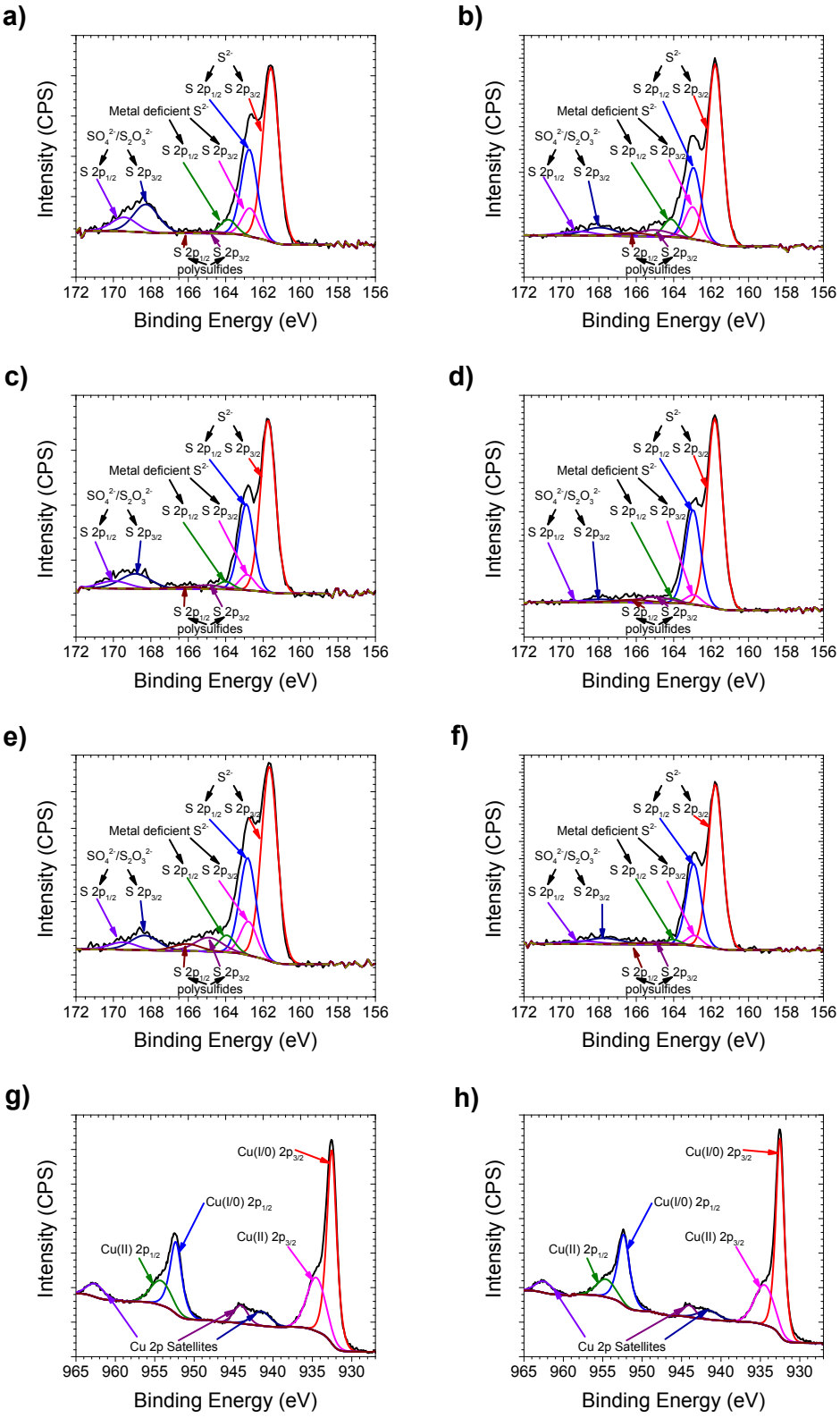
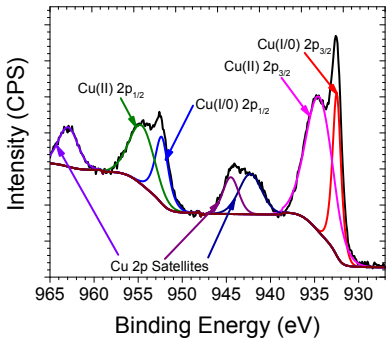


Figure S1. XRD of ball milled powders, not cured printed samples and cured printed samples of a) $Cu_{1.97}S$, b) $Cu_{1.98}S$ and c) $Cu_{2.00}S$. d) A representative Miller index labelled sample (cured $Cu_{1.97}S$) using crystallographic open data base file 9015068.

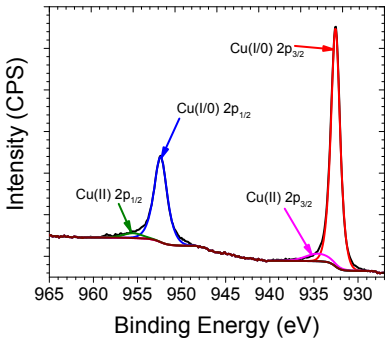
X-Ray Photoelectron Spectroscopy (XPS)



i)


Intensity (CPS)
Binding Energy (eV)
965 960 955 950 945 940 935 930
Cu(I/0) 2p3/2
Cu(II) 2p3/2
Cu(II) 2p1/2
Cu(I/0) 2p1/2
Cu 2p Satellites

j)


Intensity (CPS)
Binding Energy (eV)
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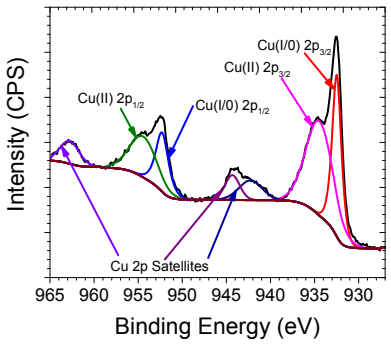
Cu(I/0) 2p1/2
Cu(II) 2p1/2
Cu(II) 2p3/2

k)


Intensity (CPS)
Binding Energy (eV)
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Cu(II) 2p3/2
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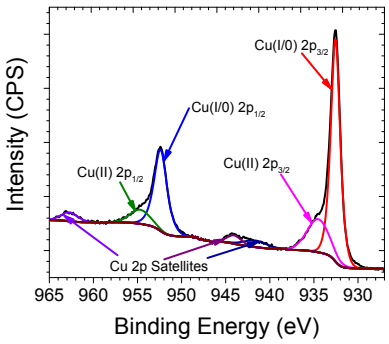
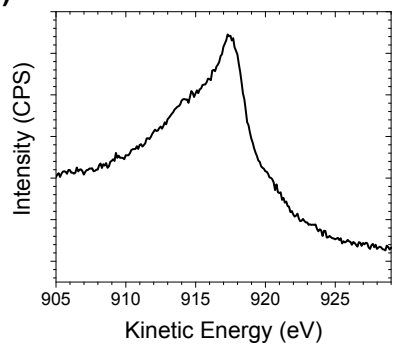
Cu(I/0) 2p1/2
Cu 2p Satellites

l)


Intensity (CPS)
Binding Energy (eV)
965 960 955 950 945 940 935 930
Cu(I/0) 2p3/2
Cu(I/0) 2p1/2
Cu(II) 2p1/2
Cu(II) 2p3/2
Cu 2p Satellites

m)


Intensity (CPS)
Kinetic Energy (eV)
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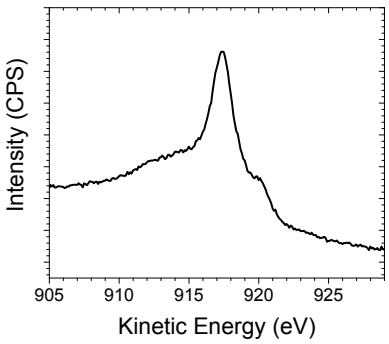
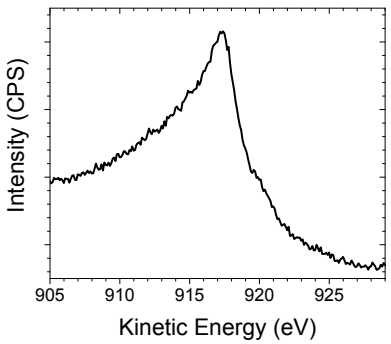
n)


Intensity (CPS)
Kinetic Energy (eV)
905 910 915 920 925

o)


Intensity (CPS)
Kinetic Energy (eV)
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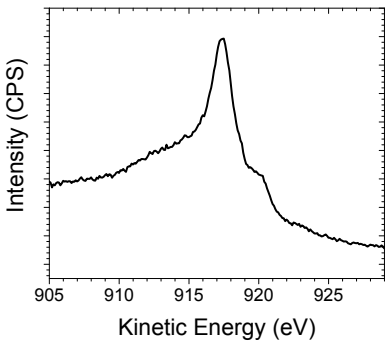
p)


Intensity (CPS)
Kinetic Energy (eV)
905 910 915 920 925

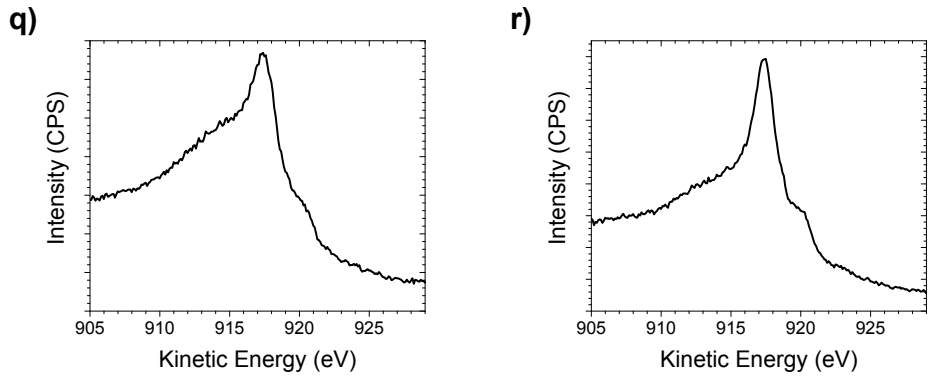
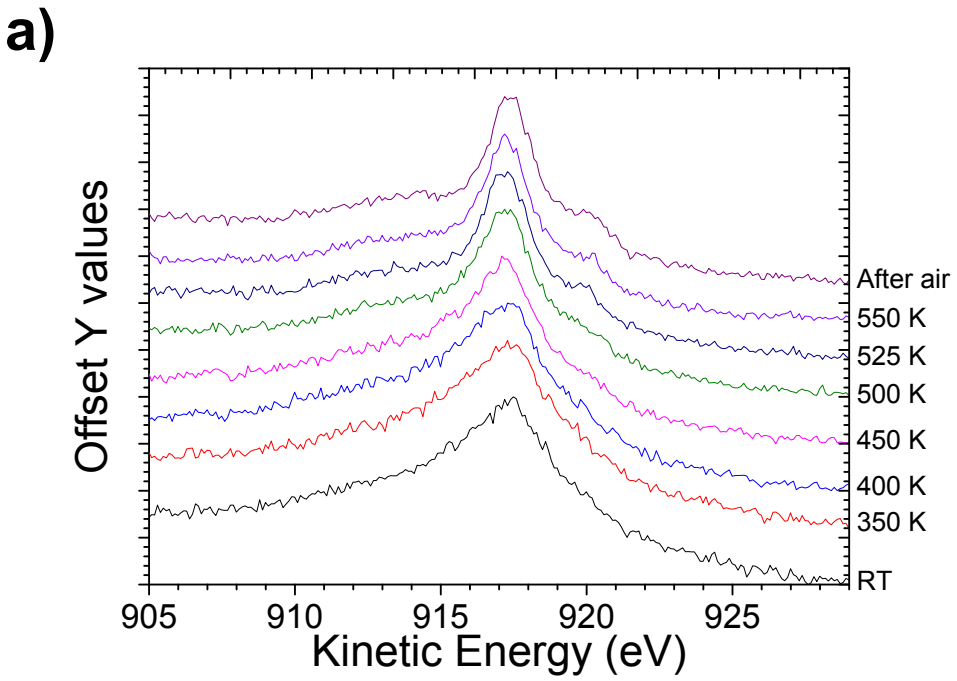


Figure S2. XPS analysis of printed $Cu_{2-x}S$ samples, where the left column (a, c, e, g, i, k) have been printed on a hot plate in air at 413 K and the right column (b, d, f, h, j, l) have had a curing step at 550 K in a He atmosphere. a-f) are fitted Sulphur 2p data, g-l) are fitted Copper 2p data, whilst m-r) are Cu Augers. a,b,g,h,m,n) are $Cu_{1.97}S$, c,d,I,j,o,p) are $Cu_{1.98}S$ and e,f,k,l,q,r) are $Cu_{2.00}S$.



b)

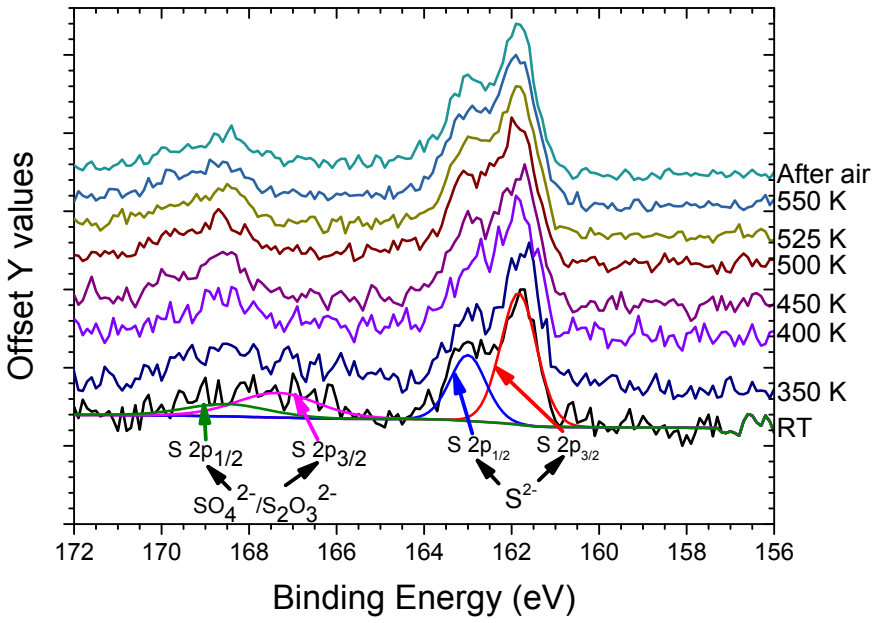


Figure S3. XPS data of the a) the Cu Auger region and b) the S 2p region of printed $Cu_{1.98}S$ sample at increasing temperatures in a vacuum.

Scanning Electron Microscopy (SEM)

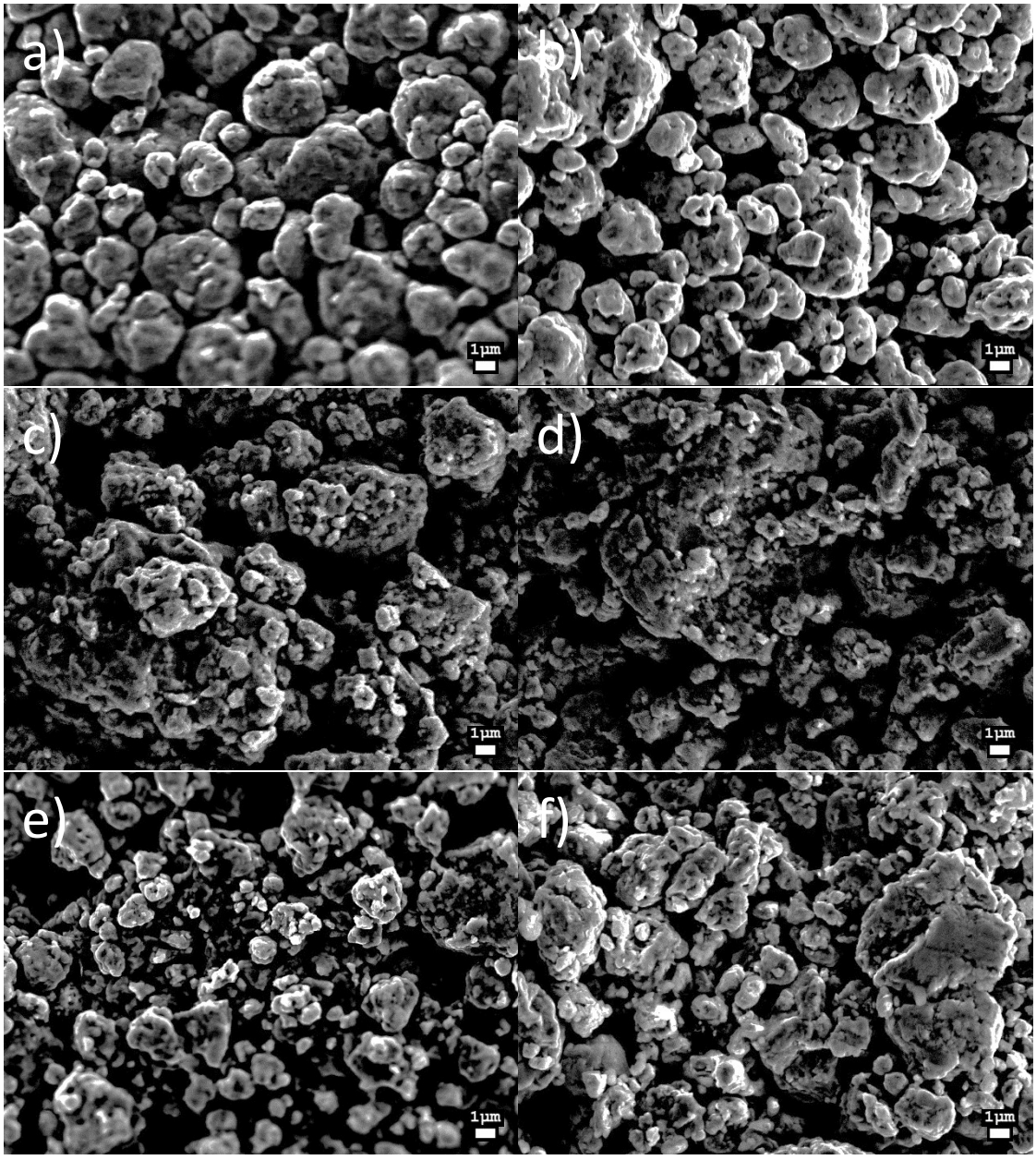


Figure S4. SEM of printed $Cu_{2-x}S$ samples where a, c and e have been printed on a hot plate in air at 413 K and b, d and f have had a further curing step at 550 K in a He atmosphere, a,b) $Cu_{1.97}S$ c,d) $Cu_{1.98}S$ and e,f) $Cu_{2.00}S$.

Thermal Conductivity

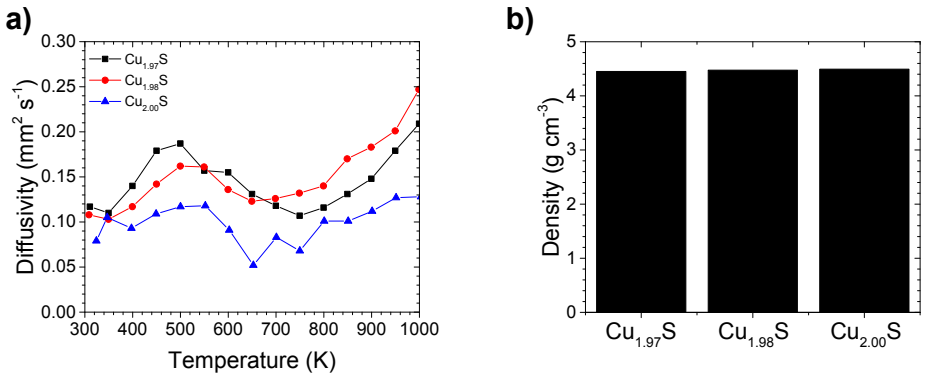


Figure S5. The measured values of the components of thermal conductivity, a) thermal diffusivity, b) density.

ZEM3 Cycling

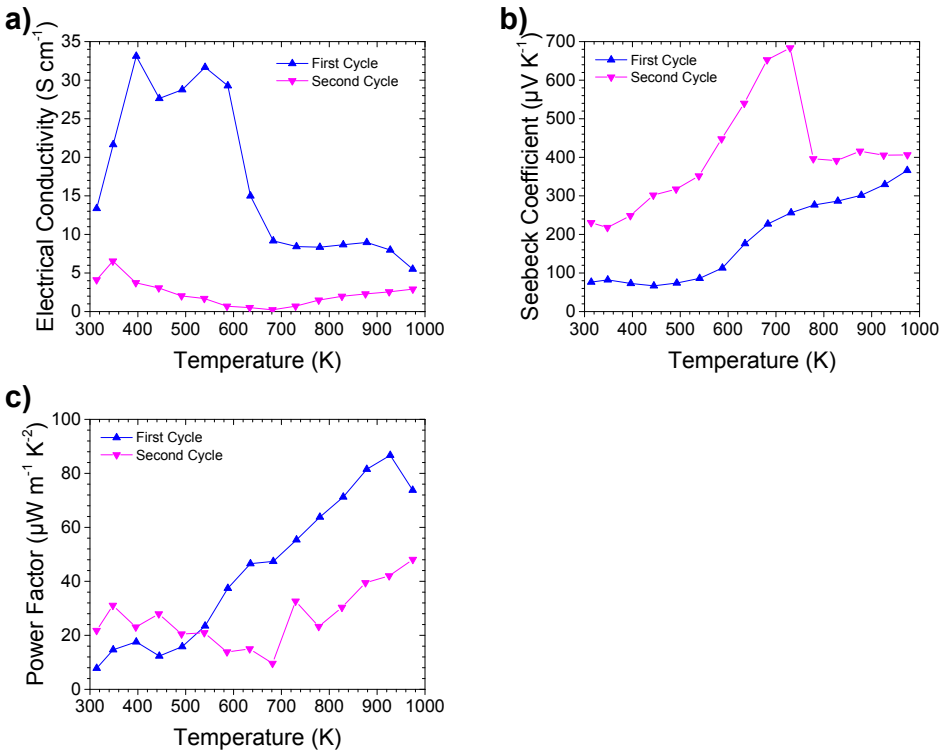


Figure S6. Thermoelectric performance $Cu_{1.98}S$ through two thermal cycles in an ULVAC ZEM3, a) electrical conductivity, b) Seebeck coefficient, c) power factor.