Electronic Supplementary Information for

New sustainable ternary copper phosphide thermoelectrics

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Synthetic Protocol: Polycrystalline MgCuP and CaCuP samples were prepared on a 1.3-gram scale by a standard solid state synthetic protocol. Mg powder (99.8%, Alfa Aesar), Ca granules (99.5%, Alfa Aesar), Cu powder (99.9%, Alfa Aesar) and P lump (Red, 99.999%, Alfa Aesar) precursors were used. All sample handling was done inside an argon atmosphere glovebox. In case of MgCuP, the precursors were ground together for about 10 minutes using an agate mortar and pestle. For CaCuP, Cu and P were ground using a mortar and pestle with the Ca granules added to the well-ground mixture. The mixed powders were vacuum sealed into carbon coated quartz ampoules. A stepwise heating profile was used, resting at 200 °C for 3 hours, 600 °C for 3 hours and at 900 °C for 2 hours. The heating rate was 2 °C.min^{-1} and cooling was done at 3 °C.min^{-1} to room temperature. After homogenisation using a mortar and pestle the samples were pressed into disks and vacuum sealed in carbon coated quartz tubes. These were heated at 200 °C for 3 hours and then 900 °C for 24 hours with the same heating and cooling rates as before. Following this, the samples were hot pressed into 13 mm disks using a homebuilt instrument with the graphite dies loaded with

~ 1 gram of powder inside the glovebox. MgCuP (CaCuP) was hot-pressed for 20 minutes at 950 °C (1000 °C) with maximum pressure during heating of 80 MPa. This yielded fully dense samples. Tests on other hot-pressed samples inside vacuum sealed tubes showed that MgCuP is stable up to 900 °C, whilst CaCuP is stable at least up to 1000 °C under these conditions. After hot pressing the disks were annealed inside carbon coated quartz ampoules at 900 °C for 24 hours, using the same heating and cooling profile as above. No mass losses were observed after any of the thermoelectric property measurements (in vacuum for thermal diffusivity and under He for the electrical measurements).

Sample Characterisation: The crystal structures of MgCuP and CaCuP were confirmed from powder diffraction using a Bruker D8 Advance diffractometer. Data were collected in Bragg-Brentano geometry using a monochromated Cu-$K_{\alpha 1}$ beam. Data were recorded between 10°-100° with a total collection time of 4 hours. Rietveld analysis was performed using the Topas V6 software with jEdit used to write input files.[1] Powder diffraction data on unground pieces of the hot-pressed disk were collected using a Malvern Panalytical Empyrean diffractometer, using a non-monochromated Cu-K_{α} beam (Figure S2), on perpendicular directions relative to the hot-pressing direction. SEM measurements were performed on polished (using Al_2O_3 sandpaper down to 1 μm) and fractured surfaces of hot-pressed MgCuP and CaCuP pieces, using a Quanta 650 FEG Scanning Electron Microscope operated at 20 kV in high-vacuum and equipped with an Oxford Instruments X-max^N 150 mm detector for energy dispersive X-ray (EDX) mapping. Backscattered electron images were collected highlighting Cu-rich impurity phases in both samples, and EDX mapping confirmed the approximate composition of the main and impurity phases. X-ray diffraction and SEM on the fractured surfaces confirmed the absence of texturing in the hot-pressed ingots.

Thermal diffusivity (α) and relative heat capacity (C_p) data were collected on hot-pressed disks (parallel to the pressing direction) using a Linseis LFA-1000 Laser Flash instrument. A graphite coating was applied to reduce emissivity errors. Subsequently a bar (8-10 mm length) and square (5-6 mm edges) were cut from the hot-pressed disks. The bars were used for measurement of the

high-temperature Seebeck coefficient (S) and electrical resistivity (ρ) (perpendicular to the pressing direction) using Linseis LSR-3 apparatus with a 4-probe setup. The squares were used to collect Hall data on a homebuilt instrument and were measured in Van der Pauw geometry using an applied AC 1 mA current and magnetic fields between –1 to 1 T, applied perpendicular to the sample. A non-linear response was observed in CaCuP, due to a negative magnetoresistance contribution from the sample consistent with a B^2 behaviour, allowing the Hall voltage (V_H) to be subtracted by simply extracting the linear component of a parabolic fit ($\rho(B) = \rho(0) + bB + cB^2$). MgCuP showed a linear response to field at all temperatures.

Table S1: Rietveld refinement results for MgCuP and CaCuP from fits against laboratory powder X-ray diffraction data. The fits are shown in Fig. S1.

		MgCuP	CaCuP
Space group		Pnma (62)	$P6_3/mmc$ (196)
a (Å)		6.5376(1)	4.0596(1)
b (Å)		3.8386(1)	4.0596(1)
c (Å)		7.1745(2)	7.8115(2)
A	x	0.5348(3)	0
	y	1/4	0
	z	0.6788(3)	0
	Occ	1.002(5)	1.009(3)
	B_{eq} (Å^2)	2.15(10)	1.03(4)
Cu	x	0.6285(1)	1/3
	y	1/4	2/3
	z	0.0624(1)	3/4
	Occ	0.997(1)	0.992(1)
	B_{eq} (Å^2)	2.10(4)	1.10(3)
P	x	0.2508(3)	1/3
	y	1/4	2/3
	z	0.1217(2)	1/4
	Occ	1.020(4)	1.012(3)
	B_{eq} (Å^2)	2.15(8)	0.93(5)
R_{wp}		9.60	10.23

Literature lattice parameters:
MgCuP (*a* = 6.532 Å, b = 3.835 Å, c = 7.170 Å)[2]
CaCuP (*a* = 4.055 Å, *c* = 7.803 Å)[3]

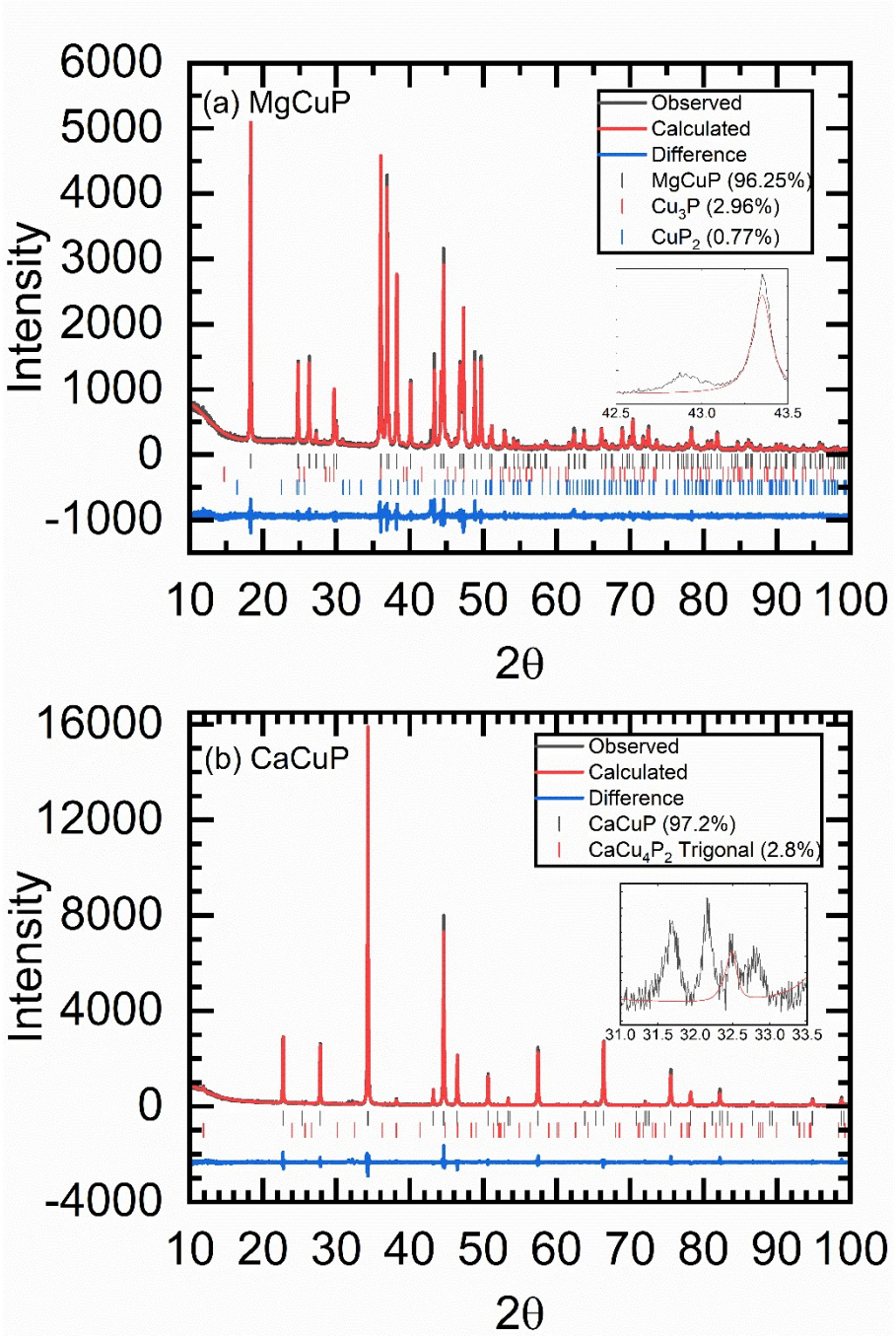

Figure S1: Rietveld fits to X-ray powder diffraction data collected on (a) MgCuP and (b) CaCuP, confirming both phases crystallise as reported in the literature.[2, 3] MgCuP contains low levels of Cu_3P (~3 wt%) and CuP_2 (~0.8 wt%), with one further unindexed diffraction peak (see inset). CaCuP contains ~3 wt% of trigonal $CaCu_4P_2$ and a small amount of another unindexed impurity phase (see inset). There is no evidence for preferred orientation, consistent with a random distribution of powder particles. This suggests that these materials do not have a strong preferred growth direction (e.g. forming as platelets).

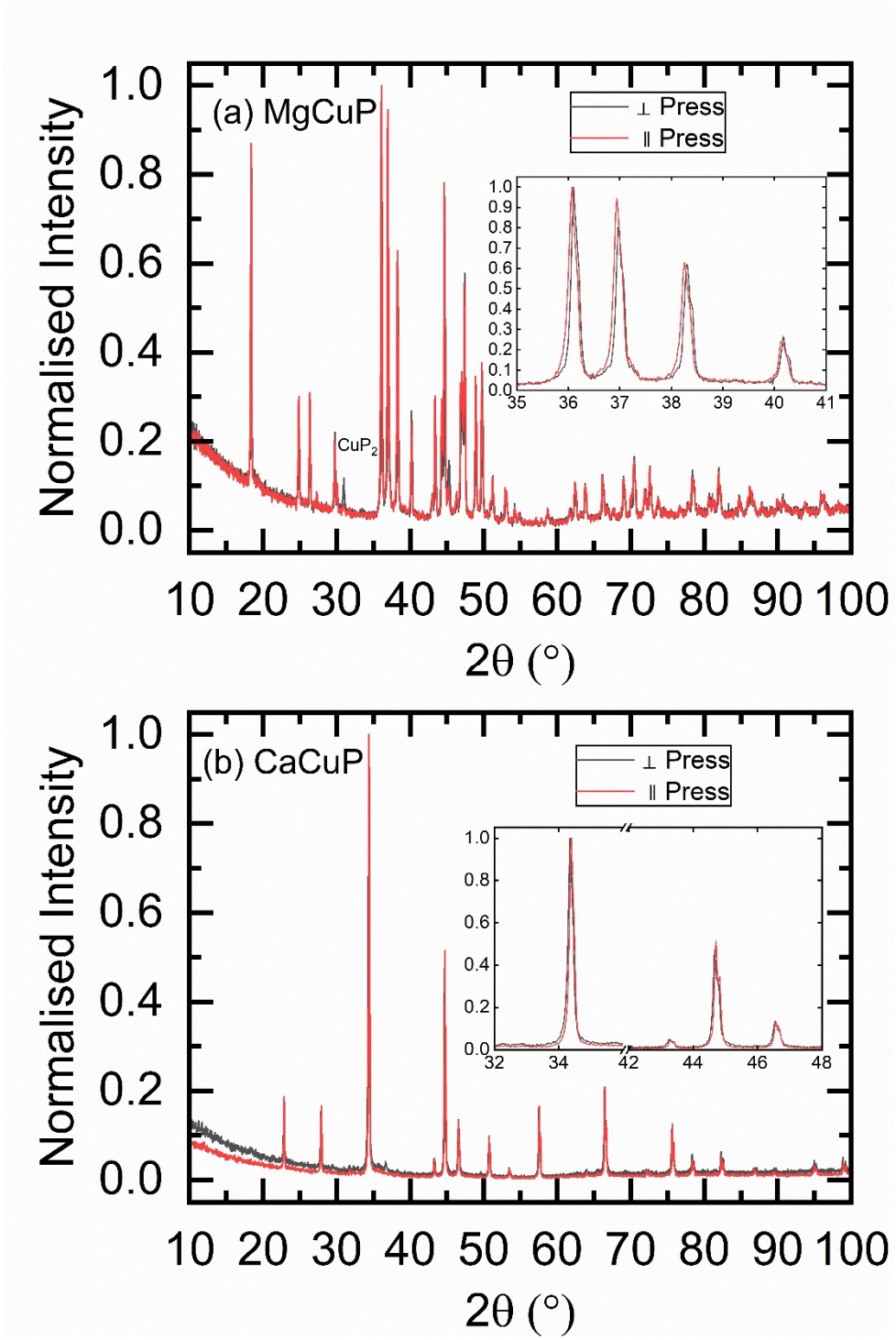

Figure S2: X-ray powder diffraction data on hot-pressed disks for (a) MgCuP and (b) CaCuP collected on faces perpendicular and parallel to the pressing direction. The two patterns overlap with negligible differences in peak intensities, confirming the absence of texturing in the hot-pressed disks.

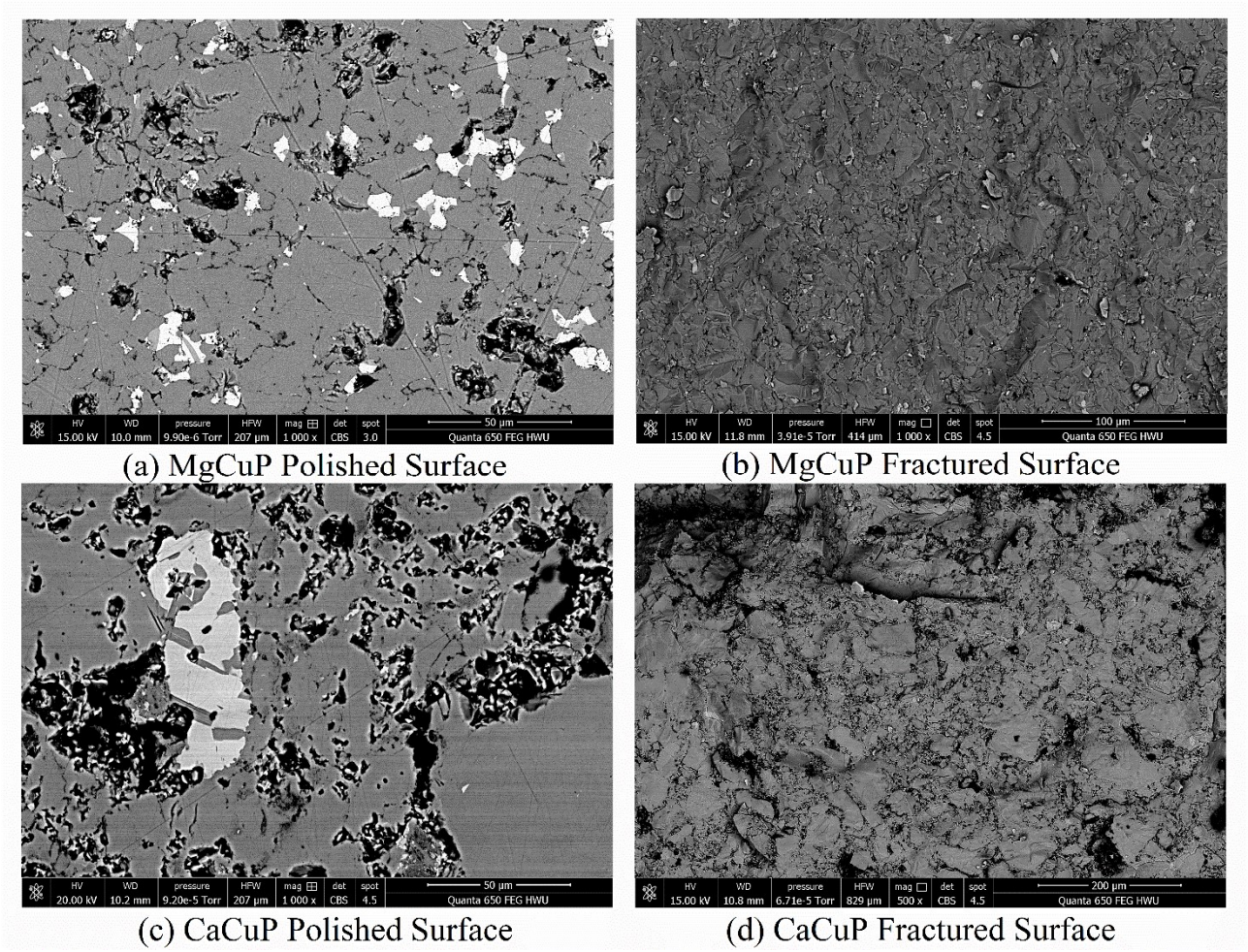

Figure S3: SEM-BSE images for polished and fractured surfaces of MgCuP and CaCuP (after LFA measurement). In MgCuP (a), brighter regions contain only Cu (~75%) and P (~25%) confirmed by EDX mapping and arise due to the presence of Cu_3P and CuP_2 impurities observed by diffraction (Fig. S1). In CaCuP, the bright region contains increased amounts of Cu relative to Ca and P, consistent with the $CaCu_4P_2$ impurity observed by diffraction. The fractured surfaces (b and d) do not show any evidence of preferred growth, consistent with the absence of texturing from the XRD data in Fig. S2.

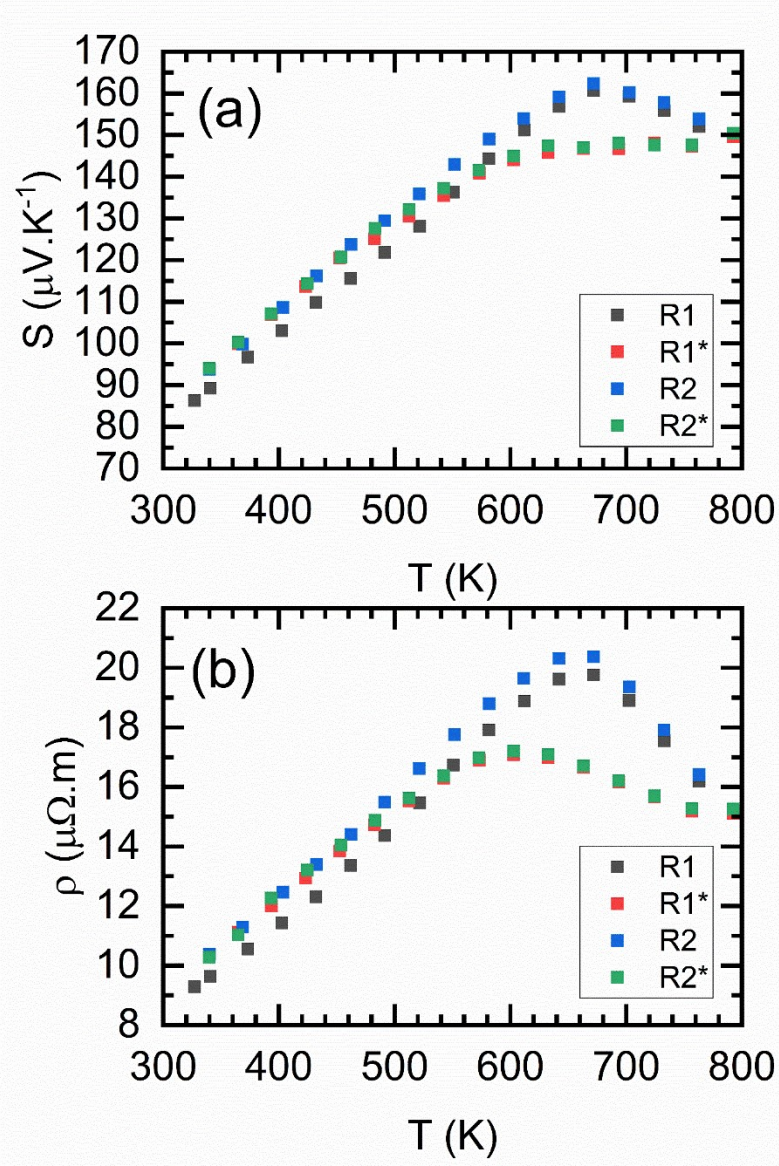

Figure S4: Effect of thermal cycling on MgCuP. Panel (a) shows *S(T)* and (b) shows *ρ(T)*. R1 and R2 are runs with increasing temperature, R1* and R2* are runs with decreasing temperature. Ex-situ X-ray diffraction measurements on samples that were slow-cooled and quenched during the measurement, revealed an increased amount of Cu_3P (7 wt%) and CuP_2 (6 wt%) for the quenched sample, whereas the slow-cooled samples had weight percentages in line with the as-synthesised sample (Fig. S1). This suggests that the hysteretic behaviour may be linked to a reversible phase transformation involving formation of Cu-P and Mg-P phases, although the latter were not observed in diffraction.

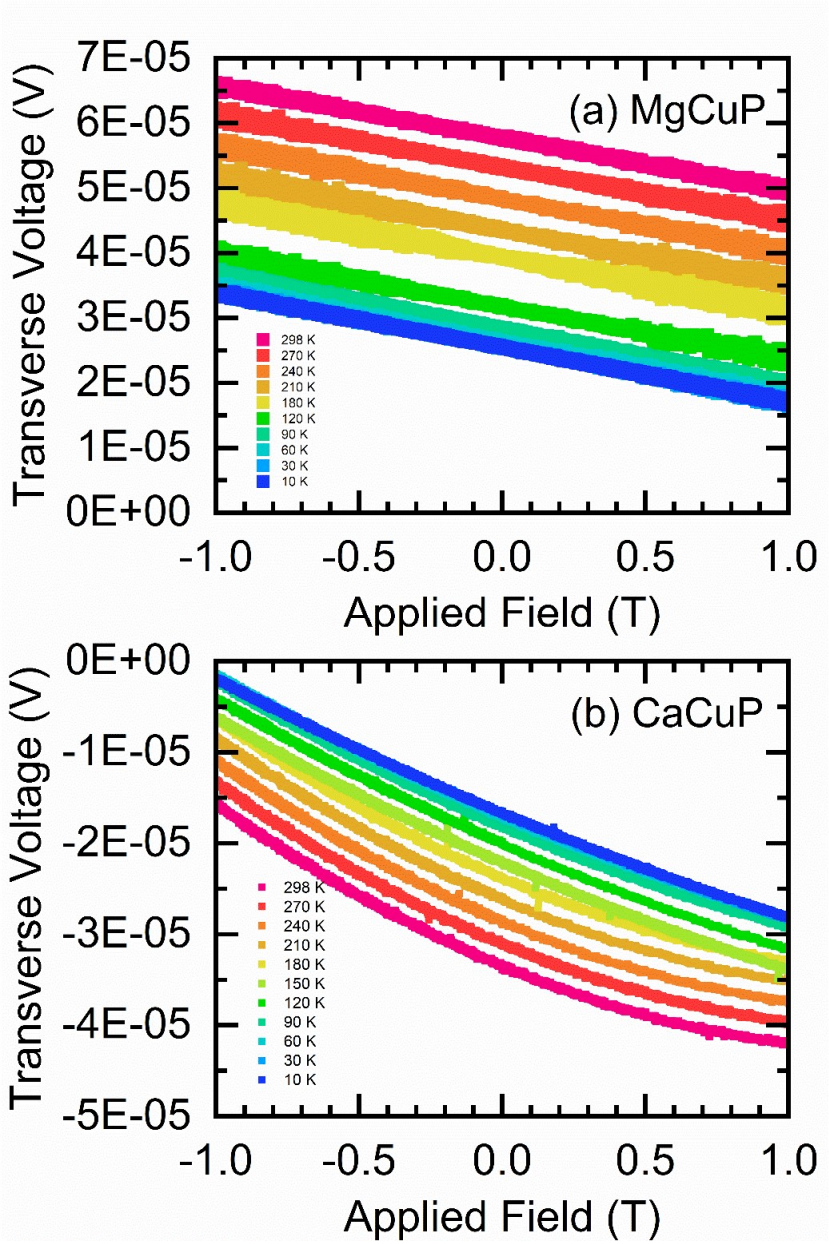

Figure S5: Hall voltage responses for (a) MgCuP and (b) CaCuP. In (a) the 150 K measurement was not recorded due to measurement error. In (b) there is a negative magnetoresistance contribution to the transverse voltage signal.

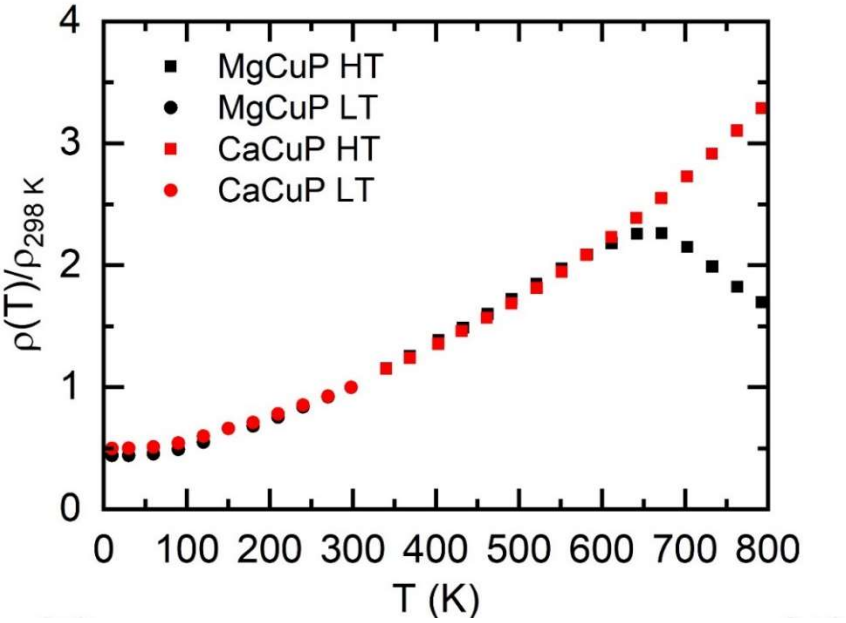

Figure S6: Normalized ρ/ρ_{298K} data between 10-790 K for MgCuP and CaCuP, combining low- and high-temperature data.

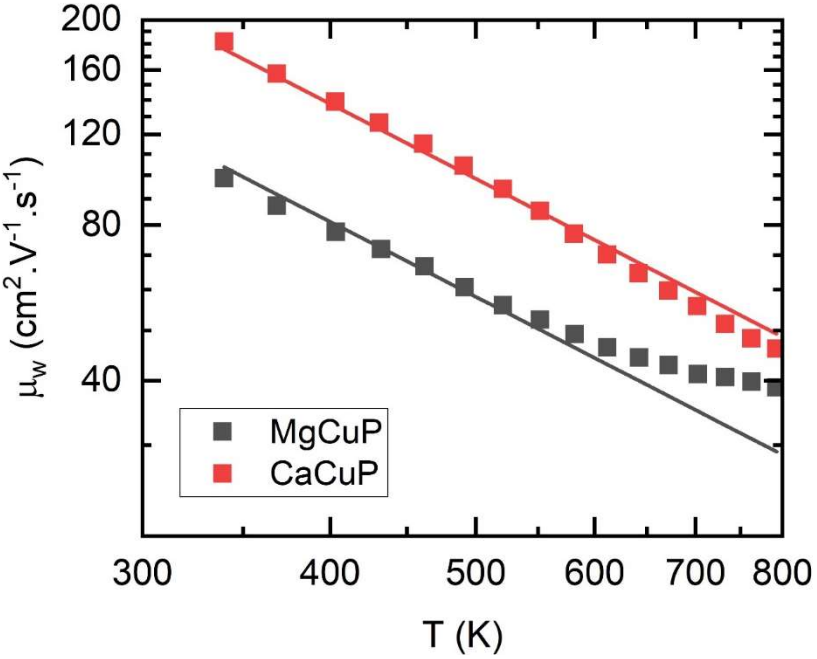

Figure S7: Weighted mobility (μ_w) of MgCuP and CaCuP between 300-800 K. The solid lines are $T^{-1.5}$ guides that would be expected from ideal acoustic phonon scattering behaviour. The upturn for MgCuP is a consequence of the empirical treatment of $S(T)$ and $\rho(T)$ breaking down with the emergence of minority carriers.

References

1. A. A. Coelho, *Journal of Applied Crystallography*, 2018, **51**, 210-218.
2. A. Mewis, *Zeitschrift für Naturforschung B*, 1979, **34**, 1373-1376.
3. A. Mewis, *Zeitschrift für Naturforschung B*, 1978, **33**, 983-986.