New sustainable ternary copper phosphide thermoelectrics†

Robert J. Quinn, Callum Stevens, Hector Leong, Andrew D. Huxley and Jan-Willem G. Bos

The thermoelectric performance of ACuP (A = Mg and Ca) with abundant elements and low gravimetric density is reported. Both systems are p-type doped by intrinsic Cu vacancy defects, have large power factors and promising figures of merit, reaching $zT = 0.5$ at 800 K. This demonstrates that copper phosphides are a potential new class of thermoelectric materials for waste heat harvesting.

Thermoelectric generation is a promising source of renewable energy that uses a temperature gradient to produce power. Despite the obvious attraction of converting waste heat into useful electricity, widespread application has been hindered by the absence of cost-effective thermoelectric materials.1,2

The efficiency of a thermoelectric material increases with its figure of merit, $zT = (S^2/ρk)T$. Here, $S$ is the Seebeck coefficient (voltage response to a temperature gradient), $ρ$ is the electrical resistivity, $k$ is the thermal conductivity, which has electronic ($k_e$) and lattice vibration ($k_{lat}$) components, and $T$ is the absolute temperature.

Here, we present the thermoelectric properties of two promising ACuP (A = Mg, Ca) copper phosphide materials. These unexplored compositions reach figures of merit, $zT = 0.5$ at 800 K and have peak power factors, $S^2/ρ = 1.5–1.75$ mW m$^{-1}$ K$^{-2}$, suited to power generation from waste heat. Dense disks are stable on the bench in ambient conditions and show reproducible cycling performance up to 800 K under a He atmosphere. Mg, Ca, Cu and P are all abundant elements making the ACuP phosphides a more sustainable choice than Bi, Pb and Te containing thermoelectric materials. Another beneficial feature is the low gravimetric densities of 4.3 g cm$^{-3}$ (A = Mg) and 4.0 g cm$^{-3}$ (A = Ca). This is comparable to the low-weight thermoelectric Mg$_3$(Si/Sm) alloys (2–3.5 g cm$^{-3}$) and much lower than Bi$_2$Te$_3$ (7.7 g cm$^{-3}$), PbTe (8.2 g cm$^{-3}$) or intermetallic compositions.

Metal phosphides are currently attracting wider interest as potential thermoelectric materials,3 inspired by the success of Zintl phases based on Sb,4 and the realisation that despite the low atomic mass of P, complex crystal structures can still have low $κ_{lat}$, while small electronegativity differences support good electrical properties. Recently investigated phosphides include cage-like tetrahedrite Ag$_6$Ge$_{10}$P$_{12}$ with $zT = 0.7$ at 750 K,5,6 layered CaZn$_2$P$_2$ and YbCuZnP$_2$ materials with $zT = 0.6$ at 973 K for YbCuZnP$_2$,7–9 the clathrate Ba$_9$Cu$_{14}$Ge$_6$P$_{26}$ with $zT = 0.6$ at 800 K,10 Zn$_{1–x}$Cu$_x$P$_3$ with $zT = 0.25$ at 673 K,11 and tetragonal Cd$_3$P$_2$ with $zT = 0.9$ at 673 K.12,13 We have recently reported a related silver phosphide, CaAg$_{1–x}$P (x = 0.1), containing corner- and edge-sharing AgP$_3$ square pyramids, achieving a highest $zT = 0.4$ at 800 K.14

The crystal structures of MgCuP and CaCuP are illustrated in Fig. 1 and are both distinct from CaAg$_{1–x}$P. MgCuP is orthorhombic (space group Pnma) and has a structure consisting of Cu$_4$ tetrahedra and Mg$_3$P$_2$ square pyramids linked by corner and edge sharing.15 Both tetrahedra and square pyramids are distorted from their ideal geometries. In the $b$ direction, the

---

(a) MgCuP

(b) CaCuP

Fig. 1 Crystal structures of (a) MgCuP and (b) CaCuP. Mg = orange, Ca = turquoise, Cu = blue and P = red. In MgCuP, edge linked Cu$_4$P$_4$ tetrahedra form chains aligned in the $b$ direction.

---

† Electronic supplementary information (ESI) available. See DOI: https://doi.org/10.1039/d2cc03154j
CuP₄ tetrahedra are linked by edge sharing, while in the a and c directions only corner sharing is present. This gives rise to quasi 1D copper phosphide chains (Fig. 1a) with short Cu–Cu bond distance ~2.70 Å, comparable to ~2.54 Å in elemental Cu. This difference in connectivity is reflected in the calculated bandstructure with dispersive electronic bands along the chain direction and flat bands in the other directions. CaCuP₄ has a layered hexagonal structure (space group P6₃/mmc) consisting of [CuP]₂⁻ planes, with flatter bands for transport across the Ca²⁺ layers. Both compositions have comparable calculated indirect electronic bandgaps, $E_g = 1.1–1.2 \text{ eV}$.¹⁷

Successful synthesis (protocol is outlined in the ESI†) of these samples was confirmed by X-ray powder diffraction. Rietveld fits are shown in Fig. S1 (ESI†), and the main crystallographic data is summarised in Table S1 (ESI†). Both samples contain low levels of impurities. In case of MgCuP₂, Cu₃P (≈ 0.8 wt%) were identified as impurity phases. For CaCuP₄, ~3 wt% of the trigonal form of CaCuP₂ was observed alongside a second very small weight fraction of unidentified impurity. As shown below, both materials are p-type semiconductors with high levels of doping. Most commonly this is caused by small transition metal deficiencies.¹⁴ Rietveld fitting of site occupancies confirms the presence of in-gap states that reduce the effective bandgap.

The thermoelectric properties of ACuP are shown in Fig. 2. Both samples have a positive $S(T)$ indicating p-type conduction (Fig. 2a). The linear temperature dependence reveals high levels of doping and degenerate semiconducting behaviour. Above 670 K, $S(T)$ for MgCuP begins to decrease, suggesting the emergence of n-type carriers.¹⁹ These reduce $S = (\sigma_p S_p + \sigma_n S_n)/\sigma$, through the opposing sign of the hole and electron Seebeck coefficients, $S_{pn}$. Here, $\sigma_{pn}$ are the p-type and n-type contributions to the electronic conductivity $\sigma = \frac{1}{\rho}$, where $\rho$ is the electrical conductivity. The observation of n-type carrier effects above 670 K is unexpected given the large $E_g$ generated from recombination.²³ The fitted exponents $q = 0.9 (A = Ca)$ and $q = 0.8 (A = Mg)$ are indicative of low levels of structural disorder, consistent with the nearly stoichiometric ACuP composition from Rietveld analysis. With increasing temperature, both samples attain similar $\kappa - \kappa_{el}$, which is due to the emergence of $\kappa_{bi}$ for MgCuP. The differences in electronic and thermal transport largely end up cancelling each other out, with $zT$ of both samples being quite similar as shown in Fig. 2f, increasing from $zT_{300K} = 0.1$ to $zT_{700K} = 0.5$. Extrapolating to higher temperatures, $zT$ for CaCuP will continue to increase while MgCuP would inevitably decrease due to n-type carrier effects.

$k(T)$ due to a larger electronic contribution $\kappa_{el} = LT/\rho$ (Fig. 2d). Here, $L$ is the Lorenz number which is estimated from $S(T)$ using an empirical relation.²² For MgCuP, $k(T)$ increases rapidly above 670 K due to the presence of both p- and n-type carriers, resulting in a bipolar contribution $\kappa_{bi} = \sigma_p \sigma_n (S_p - S_n) T/\rho$.²³ This effect only occurs for materials with hole and electron currents in a thermal gradient and is linked to heat generated from recombination.²³ The $\kappa_{lat}$ shown in Fig. 2e (log-log scale) was estimated by subtracting $\kappa_{el}$, which gives a good estimate in the single carrier regime. At 340 K, CaCuP has a substantially larger $\kappa_{lat} = 3.9 \text{ W m}^{-1} \text{ K}^{-1}$ compared to 2.5 W m⁻¹ K⁻¹ for MgCuP. Both samples have a $\kappa_{lat} \sim T^{-q}$ dependence. Here, $q = 1$ is expected for defect-free crystalline materials, $q = 0.5$ is typical of alloyed systems, whilst glasses have $q < 0.21$. The fitted exponents $q = 0.9 (A = Ca)$ and $q = 0.8 (A = Mg)$ are indicative of low levels of structural disorder, consistent with the nearly stoichiometric ACuP composition from Rietveld analysis. With increasing temperature, both samples attain similar $\kappa - \kappa_{el}$, which is due to the emergence of $\kappa_{bi}$ for MgCuP. The differences in electronic and thermal transport largely end up cancelling each other out, with $zT$ of both samples being quite similar as shown in Fig. 2f, increasing from $zT_{300K} = 0.1$ to $zT_{700K} = 0.5$. Extrapolating to higher temperatures, $zT$ for CaCuP will continue to increase while MgCuP would inevitably decrease due to n-type carrier effects.

**Fig. 2** Temperature dependence of (a) $S(T)$, (b) $\rho(T)$, (c) $S^2/\rho(T)$, (d) $k(T)$, (e) $\kappa_{el}(T)$ and (f) the figure of merit, $zT$ for MgCuP (black) and CaCuP (red) between 300–800 K.
A possible explanation for the observation of n-type carrier effects in MgCuP is found in the heat-cool cycling in the electrical property measurements. MgCuP shows an unusual stable hysteretic effect where \( S(T) \) and \( \rho(T) \) are substantially reduced between 550–800 K on cooling (Fig. S4, ESI†). This suppression does not affect \( S^2/\rho(T) \), which is identical for the heat-cool runs. The sample did not lose mass or discouler and post measurement X-ray diffraction yielded an unchanged heat-cool runs. The sample did not lose mass or discolour and the ACuP materials Hall measurements were carried out as described in the ESI† (Fig. S5 and S6). Both compositions have constant Hall carrier concentrations (\( n_H \)) between 10–300 K (Fig. 3), as expected for degenerate semiconductors. The obtained values are \( n_H = 2.4 \times 10^{20} \text{ cm}^{-3} (A = \text{Mg}) \) and \( n_H = 1.6 \times 10^{20} \text{ cm}^{-3} (A = \text{Ca}) \). This corresponds to Cu vacancy concentrations of \( \sim 1\% \) assuming a single 4s\(^1\) electron is removed per Cu. This is in line with the diffraction results that indicate a slight deficiency on the Cu-site. A recent report on thin-film CaCuP has a similar \( n_H \sim 1.2 \times 10^{20} \text{ cm}^{-3} \), but a lower \( n_H \sim 36 \text{ cm}^{-2} \text{ V}^{-1} \text{ s}^{-1} \) compared to \( 100 \text{ cm}^{-2} \text{ V}^{-1} \text{ s}^{-1} \) in this work.\(^{25}\)

Density of states effective mass, \( m_{\text{DoS}}^* \), values were determined using the single parabolic band (SPB) model.\(^{26}\) \( m_{\text{DoS}}^* \) is an important fundamental electronic parameter that determines the magnitude of \( S \) and is linked to the total orbital and valley degeneracy (\( N_e \)) and band mass (\( m_e^* \)) of the carriers. The obtained values are \( m_{\text{DoS}} = 1.7m_e^* (A = \text{Mg}) \) and \( m_{\text{DoS}} = 1.0m_e^* (A = \text{Ca}) \). The larger \( m_{\text{DoS}}^* \) for MgCuP is consistent with the published bandstructure.\(^{17}\) MgCuP has a single band at the valence band maximum (VBM), which occurs at the \( \Gamma \)-point (\( N_e = 1 \)). Using the published anisotropic band masses \( m_{\Gamma - \text{VBM}}^* = 6.3m_e^* \) and \( m_{\Gamma - \text{VBM}}^* = 0.15m_e^* \), yields \( m_{\text{DoS}}^* = 1.8m_e^* \). This average value is in good agreement with \( m_{\text{DoS}}^* = 1.7m_e^* \) from the SPB model. For CaCuP, the VBM also occurs at the \( \Gamma \)-point but there are two bands present (\( N_e = 2 \)).\(^{17}\) The experimental \( m_{\text{DoS}}^* = 0.63m_e^* \) is therefore much lower than the value for MgCuP. Using the published \( m_{\Gamma - \text{VBM}}^* \) and \( m_{\Gamma - \text{VBM}}^* \) values,\(^{17}\) yields \( m_{\text{DoS}}^* = 0.2m_e^* \) and \( m_{\text{DoS}}^* = 0.4m_e^* \). These low values are in line with the low SPB value, confirming that the holes are indeed much lighter in CaCuP.

The heavier hole mass for MgCuP is reflected in the mobility with \( \mu_H = 29 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1} \) compared to \( \mu_H = 101 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1} \) for CaCuP. Ultimately the higher \( \mu_H \) for CaCuP leads to overall better electronic properties, evidenced by the much larger \( S^2/\rho \) (Fig. 2c). The better electronic properties are confirmed by the weighted mobility, \( \mu_{\text{w}} = \left( m_{\text{DoS}}^* / m_e^* \right)^{1/2} \mu_0 \), that can be readily calculated from the measured \( S(T) \) and \( \rho(T) \) and is shown in Fig. S7 (ESI†).\(^{27}\) Here, \( \mu_0 \) is the mobility in the semiconducting limit (\( n_H \rightarrow 0 \)). Using the \( m_{\text{DoS}}^* \) values from the SPB analysis yields \( \mu_0 = 45 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1} (A = \text{Mg}) \) and \( \mu_0 = 180 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1} (A = \text{Ca}) \) at 350 K. Hence, the hole mobility is 4 times higher in CaCuP. This large hole mobility leads to \( S^2/\rho \) that are leading amongst phosphide thermoelectrics. Fig. 4 shows a comparison of the temperature-averaged power factor (\( S^2/\rho \)) over a 340–670 K gradient for the current best thermoelectric phosphides. MgCuP and many of the other high \( zT^2 \) materials have \( S^2/\rho \approx 1 \text{ mW m}^{-1} \text{ K}^{-2} \), whereas CaCuP approaches 2 mW m\(^{-1}\) K\(^{-2}\). The high hole mobility for CaCuP may also be linked to the negative magnetoresistance (MR) that is observed for this compound (Fig. S5, ESI†). This is largely temperature-independent, reaching values up to \( -15\% \) in 1 T. The observation of negative MR is unusual for non-magnetic semiconductors. Large MR up to high temperatures has been linked...
to topological electronic states in the Weyl semimetal TaP,\textsuperscript{28,29} but the symmetry of CaCuP precludes these exotic topological effects.

To conclude, we report the thermoelectric properties of two unexplored ternary copper phosphide materials. These are characterised by good performance, are based on abundant elements, have low gravimetric densities and good stability both in storage at room temperature and under temperature cycling in inert atmosphere. Further work on these materials and on related (copper) phosphides is of considerable interest. CaCuP has better overall electronic performance due to a better compromise between density of states effective mass ($m^*_\text{DOS}$), which dictates $S$ and high carrier mobilities ($\mu$), which largely controls $\rho$. To the best of our knowledge, CaCuP displays the largest reported $S^2/\rho$ of any phosphide (barring the exceptional values resulting from the quantum thermoelectric Hall effect in TaP)\textsuperscript{28}. At 790 K both materials have $\kappa_{\text{lat}}$ below 2 W m\textsuperscript{-1} K\textsuperscript{-1}, a promising result for compositions with no targeted alloying, suggesting that further improvements in $zT$ can be achieved by atomic substitutions, processing and microstructure control. Currently both materials are over-doped and a method of controlling the p-type doping is required to maximise $S^2/\rho(T)$ and minimise $\kappa(T)$. Our data suggests that the p-type doping is linked to low levels of Cu vacancies in both materials, so control of doping would require minimisation of Cu vacancies. Future investigations need to examine the behaviour of vacancies with temperature. In addition, materials growth from slightly off-stoichiometric compositions is known to affect defect formation energies and should be explored. In the case of MgCuP, investigations of the hysteretic behaviour and n-type doping effects at high temperature are warranted. Combined with our recent report on the thermoelectric performance of CaAg\textsubscript{1-x}P, we believe there is great unexplored potential within the large group of 1:1:1 ternary metal phosphides. From the materials reported here, CaCuP is the strongest contender, due to its better inherent electronic properties.

R. J. Q. and J.-W. G. B. acknowledge the Leverhulme Trust (RPG-2020-177). A. D. H. acknowledges the EPSRC (EP/R013004/1). Jim Buckman is acknowledged for assistance with SEM data collection. Raw data underpinning this work are available from the Heriot-Watt University data repository.\textsuperscript{30}

Conflicts of interest

There are no conflicts of interest to declare.

Notes and references
