Composition, structure, bonding and thermoelectric properties of “CuT2P3” and “CuT4P3”, members of the T1−x(CuP3)x series with T being Si and Ge
Wang, Peng; Ahmadpour, Faraz; Kolodiazhnyi, Taras; Kracher, Alfred; Cranswick, Lachlan M. D.; Mozharivskyj, Yuriy

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Composition, structure, bonding and thermoelectric properties of “CuT$_2$P$_3$” and “CuT$_4$P$_3$”, members of the T$_{1-x}$(CuP$_3$)$_x$ series with T being Si and Ge†

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Through electron microprobe analysis, X-ray and neutron diffraction, it has been established that “CuT$_2$P$_3$” and “CuT$_4$P$_3$” (T = Si, Ge) adopt the cubic or tetragonally distorted zinc blende structures in which two element mixtures are present on both atomic sites. One site contains the Cu/T mixture while the other site is occupied by T and P. The structure of “CuT$_2$P$_3$” and “CuT$_4$P$_3$” can be derived from that of silicon or germanium, in which the single Si or Ge site is broken into two independent sites by the preferential Cu and P substitution. The phases appear to be members of the extended series with a general formula of T$_{1-x}$(CuP)$_x$. The Cu–P ratio of 1 : 3 provides 4 e$^-$ per atom and optimizes the atomic interactions. Thermoelectric performance of “CuSi$_2$P$_3$”, “CuGe$_2$P$_3$” and “CuGe$_4$P$_3$” was evaluated from low temperatures to 400 K through resistivity, Seebeck coefficient and thermal conductivity measurements. The Ge-containing phases show a metallic-type behaviour and “CuSi$_2$P$_3$” is semiconducting with a narrow band gap. The ZT values are bigger for the Ge-containing phases and reach values of 8.49 × 10$^{-3}$ for “CuGe$_2$P$_3$” and 1.09 × 10$^{-2}$ for “CuGe$_4$P$_3$” at room temperature.

Introduction

Industrial importance of thermoelectric materials lies in their ability to perform cooling/heating when electrical current is applied (Peltier effect) or to generate voltage under a temperature gradient (Seebeck effect). While still suffering from relatively low efficiency, thermoelectric devices offer many advantages over competing technologies in terms of durability, reliability and ease of use. As a result, they find applications in selected fields such as sensors and cooling modules, power generation for remote weather and navigation stations and deep space missions. One of the materials extensively investigated and used for power generation, primarily, for deep-space missions is an (Si, Ge) alloy. Its simple structure (diamond-type) and composition (Si and Ge) provide some advantages such as high stability and good Seebeck voltage. But they also carry a few drawbacks such as a high thermal conductivity and a large band gap, which limit their applications to high temperatures, usually above 800 °C. Optimization of thermal conductivity is achieved through the Si/Ge alloying, besides ultrafine particles of silicon nitride or boron nitride are introduced into the (Si, Ge) matrix to disrupt the phonon propagation. Still, the large band gap (0.66–1.12 eV depending on the Si/Ge ratio) restricted the material’s use to high temperatures.

The (Si, Ge) phases adopt a diamond structure in which tetrahedral bonding around every atom is achieved by having 4 e$^-$ per atom. Similar bonding models are also realized in other semiconductors such as A$^{II}$B$^{VI}$ and A$^{III}$B$^{IV}$. There are also ternary phases with 4 e$^-$ per atom and tetrahedral bonds, but now elements with a larger range of valences and different ratios can be combined to obtain the same electron count, e.g. A$^{II}$B$^{VI}$C$^{V}$ and A$^{III}$B$^{IV}$C$^{V}$. Among these ternary phases, CuSi$_2$P$_3$ and CuGe$_2$P$_3$, discovered back in 1961, were believed to be semiconductors with the bonding features similar to those in the (Si, Ge) alloys. Both CuSi$_2$P$_3$ and CuGe$_2$P$_3$ were found to adopt the zinc blende structure with the Cu/Si or Cu/Ge atoms being mixed on one site. It has also been reported that alloying CuGe$_2$P$_3$ with Ge yields the CuGe$_4$P$_3$ phase with the same structure as CuGe$_2$P$_3$. But now in CuGe$_2$P$_3$, the Cu and P atoms have to be mixed on one site as opposed to the Cu/Ge mixture in CuGe$_2$P$_3$. Similarly, alloying of CuSi$_2$P$_3$ with Si has been reported to produce phases with a general formula of CuSi$_{1-x}$P$_x$ (where x = 1, 2 and 3), but the atomic distribution was not established. All phases regardless of their Si or Ge concentration were found to adopt the cubic zinc blende structure.

The Cu–Si–P and Cu–Ge–P phases may be very attractive in terms of thermoelectric properties as statistical mixtures are likely to reduce their thermal conductivity, and the presence of elements with different electronegativities may decrease the band gap, making these phosphides suitable for power generation at lower temperatures. Through resistivity measurements on a single crystal, CuSi$_2$P$_3$ was found to have a small band gap of 0.0269(1) eV. Surprisingly, CuGe$_2$P$_3$ has reported to possess a large band gap of 0.90(5) eV, which could not be substantiated by other literature data.

To understand such unusual variations in physical properties, establish atomic rearrangement and evaluate thermoelectric
The larger compositional deviations for the CuP composition (Fig. 1) and pointed at a possible peritectic solidification of the main phase along the CuP–T binary phases, only a limited substitution of P in the Cu metal (the Cu/T–P binary phases at the chemical prospective. Analysis of the Cu–T, Cu–P and Cu–Si systems obtained by different techniques are summarized in Table 4. The refined compositions of CuGeP₁ₓ were determined by neutron powder diffraction for the CuSi₁₋ₓPₓ samples, microprobe data obtained from both the lines scans and random spots yielded the average compositions of Cu₉₋₀(₂ Pain 0.75) and Cu₉₋₀(₂ Pain 0.75), respectively. The simple, one-site mixtures of Cu/Ge for Cu₉₋₀(₂ Pain 0.75) (“CuGeP₁,”) and Cu/G for Cu₉₋₀(₂ Pain 0.75) (“CuGeP₁,”) could not be substantiated. Also from the Cu₉₋₀(₂ Pain 0.75) composition, it can be concluded that germanium has to be present, although in different amounts, on both sites. Additionally, the line scans across the matrix in CuGeP₁ and CuGeP₁ revealed significant variations in the composition (Fig. 1) and pointed at a possible peritectic solidification of the main phase along the CuP₁ line and away from the other compositions. These compositional variations are consistent with the X-ray powder diffraction data. The larger compositional deviations for “CuGeP₁,” were determined by the CuGeP₁ composition, as compared to those for “CuGeP₁,” suggest flatter liquidus and solidus surfaces for the Ge-richer sample.

The microprobe results served as a starting point for the satisfactory refinement of “CuGeP₁,” and “CuGeP₁,” from the single crystal data. Table 1 summarizes the refinement results for the different structural models of “CuGeP₁,”. The second column features the model in which the Cu concentration derived from the microprobe analysis was used as reference and Cu/Ge and Ge/P mixtures were assumed on individual sites. The Cu/Ge ratio on the 4a site was fixed, while the Ge/P ratio on the 4c site was allowed to vary. The resulting composition of Cu₉₋₀(₂ Pain 0.75) is close to the microprobe composition of Cu₉₋₀(₂ Pain 0.75), thus validating the proposed structural model. While mixtures of three elements on each site are possible, the X-ray diffraction techniques employed by us cannot differentiate between two and three element mixtures.

A similar approach was used for refining the occupancies in “CuGeP₁,”. The resulting composition of Cu₉₋₀(₂ Pain 0.75) was relatively close to the Cu₉₋₀(₂ Pain 0.75), formula obtained from the microprobe analysis. Because of the similar X-ray scattering powers of Si and P but different scattering powers of Cu and Si, the P amount was kept constant on one site and the Cu/Si ratio was refined for the other site to yield Cu₉₋₀(₂ Pain 0.75), and Cu₉₋₀(₂ Pain 0.75) for “CuSiP₁,” and “CuSiP₁,”, respectively. The Cu₉₋₀(₂ Pain 0.75) formula deviates somewhat more from the microprobe composition of Cu₉₋₀(₂ Pain 0.75) as compared to the similar results for the Ge-containing phases. The refinement results are given in Tables 1 and 2.

Neutron powder diffraction for the CuSi₁₋ₓPₓ and CuGeP₁ samples provided an additional check for the proposed structural models. The refined compositions of Cu₉₋₀(₂ Pain 0.75) and Cu₉₋₀(₂ Pain 0.75) are in good agreement with those obtained from the microprobe analysis and the single-crystal X-ray diffraction. Compositions obtained by different techniques are summarized in Table 4.

**Results and discussion**

**Composition and site occupancies**

The electron microprobe analysis on the hot-pressed CuSi₁₋ₓPₓ sample yielded the Cu₉₋₀(₂ Pain 0.75) composition, which while coming close to the loading composition of CuSi₁₋ₓPₓ deviated significantly from it. A structural model, in which one site is occupied by the Cu/Si mixture and the other only by P atoms, could not be substantiated. The most probable atomic arrangement is the one in which Si is present also on the P site.

For the “CuGeP₁,” and “CuGeP₁,” samples, microprobe data obtained from both the lines scans and random spots yielded the average compositions of Cu₉₋₀(₂ Pain 0.75) and Cu₉₋₀(₂ Pain 0.75), respectively. The simple, one-site mixtures of Cu/Ge for Cu₉₋₀(₂ Pain 0.75) (“CuGeP₁,”) and Cu/P for Cu₉₋₀(₂ Pain 0.75) (“CuGeP₁,”) could not be substantiated. Also from the Cu₉₋₀(₂ Pain 0.75) composition, it can be concluded that germanium has to be present, although in different amounts, on both sites. Additionally, the line scans across the matrix in CuGeP₁ and CuGeP₁ revealed significant variations in the composition (Fig. 1) and pointed at a possible peritectic solidification of the main phase along the CuP₁ line and away from the other compositions. These compositional variations are consistent with the X-ray powder diffraction data. The larger compositional deviations for “CuGeP₁,” as compared to those for “CuGeP₁,” suggest flatter liquidus and solidus surfaces for the Ge-richer sample.

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**Structure and boundaries of the T₄₃₄(CuP₁ₓ) phases**

Based on the microprobe and diffraction results, we propose a structural model in which one site is occupied by a Cu/T mixture and the other one by a T/P mixture (T = Si and Ge, Fig. 2). While a three-component mixture on each site cannot be excluded, no unique way to partition the three elements on the two sites can be proposed based on the experimental techniques employed by us. Besides, a significant three-component mixture is unlikely from the chemical prospective. Analysis of the Cu–T, Cu–P and T–P binary phases, only a limited substitution of P in the Cu metal (the maximum of 3.5 at% at 700 °C) has been observed. Additionally,
Table 2 Crystallographic data and structure refinements for single crystals from the CuSi,P₃, CuGe,P₃ and CuGe,P₃ samples at 293 K, MoKα₁ radiation, STOE IPDS II diffractometer

<table>
<thead>
<tr>
<th>Loading composition</th>
<th>Cu₃Si,P₃</th>
<th>Cu₃Ge,P₃</th>
<th>Cu₆Ge₂,P₃</th>
<th>Cu₆Ge₄,P₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>R indices (all data)</td>
<td>0.076(4)</td>
<td>0.12(1)</td>
<td>0.056 × 0.225 × 0.251</td>
<td>0.056 × 0.225 × 0.251</td>
</tr>
<tr>
<td>Space group</td>
<td>F4m</td>
<td>F₄m</td>
<td>F₄m</td>
<td>F₄m</td>
</tr>
<tr>
<td>Lattice parameters/Å</td>
<td>a = 3.695(1) (β = 90°)</td>
<td>a = 5.241(2)</td>
<td>a = 5.393(2)</td>
<td>a = 5.445(1)</td>
</tr>
<tr>
<td>c = 5.225(1)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>V/Å³</td>
<td>71.35(3)</td>
<td>143.96(8)</td>
<td>156.89(8)</td>
<td>161.44(7)</td>
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<tr>
<td>Z</td>
<td>2</td>
<td>4</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Completeness to max. 2θ (%)</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Data/restraints/parameters</td>
<td>98/0/6</td>
<td>48/0/5</td>
<td>51/0/5</td>
<td>55/0/6</td>
</tr>
<tr>
<td>Final R indices [I &gt; 2σ(I)]</td>
<td>R₁ = 0.0118, wR₂ = 0.0187</td>
<td>R₁ = 0.0086, wR₂ = 0.0150</td>
<td>R₁ = 0.0104, wR₂ = 0.0248</td>
<td>R₁ = 0.0058, wR₂ = 0.0120</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>1044</td>
<td>1046</td>
<td>1108</td>
<td>1054</td>
</tr>
<tr>
<td></td>
<td>98 [Rint = 0.0410]</td>
<td>48 [Rint = 0.0793]</td>
<td>51 [Rint = 0.0790]</td>
<td>55 [Rint = 0.0422]</td>
</tr>
<tr>
<td>Space group</td>
<td>P(2)</td>
<td>P(2)</td>
<td>P(2)</td>
<td>P(2)</td>
</tr>
<tr>
<td></td>
<td>P/Si(2)</td>
<td>P/Si(2)</td>
<td>P/Si(2)</td>
<td>P/Si(2)</td>
</tr>
<tr>
<td>Atom W yckoff symbol Occupancy</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu/Si(1)</td>
<td>2a</td>
<td>0.28/0.72(1)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>P(2)</td>
<td>2d</td>
<td>1.00</td>
<td>0</td>
<td>1/2</td>
</tr>
<tr>
<td>Cu/Si(1)</td>
<td>4a</td>
<td>0.271/0.729(7)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>P/Si(2)</td>
<td>4c</td>
<td>0.75/0.25</td>
<td>1/4</td>
<td>1/4</td>
</tr>
<tr>
<td>Cu₁₁Ge₃Si₃P₁₉₀₃ (Cu₃Ge₃P₃)</td>
<td>Cu/Ge(1)</td>
<td>4a</td>
<td>0.295/0.705</td>
<td>0</td>
</tr>
<tr>
<td>P/Ge(2)</td>
<td>4c</td>
<td>0.798/0.202(8)</td>
<td>1/4</td>
<td>1/4</td>
</tr>
<tr>
<td>Cu₁₃Ge₄Si₃P₃₂₇₃₂ (Cu₃Ge₄P₃)</td>
<td>Cu/Ge(1)</td>
<td>4a</td>
<td>0.238/0.762</td>
<td>0</td>
</tr>
<tr>
<td>P/Ge(2)</td>
<td>4c</td>
<td>0.642/0.358(3)</td>
<td>1/4</td>
<td>1/4</td>
</tr>
</tbody>
</table>

Table 3 Atomic and isotropic temperature (U) parameters for Cu₃Si₃P₃, Cu₆Ge₃P₃, Cu₁₂Ge₃P₃ and Cu₆Ge₄P₃, from single-crystal diffraction data

<table>
<thead>
<tr>
<th>Atom</th>
<th>Wyckoff symbol</th>
<th>Occupancy</th>
<th>x/a</th>
<th>y/b</th>
<th>z/c</th>
<th>U/Å²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu₃Si₃P₃</td>
<td>Cu/Si(1)</td>
<td>2a</td>
<td>0.28/0.72(1)</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>P(2)</td>
<td>2d</td>
<td>1.00</td>
<td>0</td>
<td>1/2</td>
<td>3/4</td>
<td>0.0091(5)</td>
</tr>
<tr>
<td>Cu₆Ge₃P₃</td>
<td>Cu/Si(1)</td>
<td>4a</td>
<td>0.271/0.729(7)</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>P/Si(2)</td>
<td>4c</td>
<td>0.75/0.25</td>
<td>1/4</td>
<td>1/4</td>
<td>1/4</td>
<td>0.0081(4)</td>
</tr>
<tr>
<td>Cu₁₂Ge₃P₃</td>
<td>Cu/Ge(1)</td>
<td>4a</td>
<td>0.295/0.705</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>P/Ge(2)</td>
<td>4c</td>
<td>0.798/0.202(8)</td>
<td>1/4</td>
<td>1/4</td>
<td>1/4</td>
<td>0.0109(5)</td>
</tr>
<tr>
<td>Cu₆Ge₄P₃</td>
<td>Cu/Ge(1)</td>
<td>4a</td>
<td>0.238/0.762</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>P/Ge(2)</td>
<td>4c</td>
<td>0.642/0.358(3)</td>
<td>1/4</td>
<td>1/4</td>
<td>1/4</td>
<td>0.0114(2)</td>
</tr>
</tbody>
</table>

Table 4 Composition of the Tᵥ₋₁(Cu₃P₃) phases obtained by different techniques

<table>
<thead>
<tr>
<th>Sample</th>
<th>Electron microprobe</th>
<th>X-Ray single crystal</th>
<th>Neutron powder</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu₃Si₃P₃</td>
<td>Cu₃Si₃Si₂Si₂P₂P₂</td>
<td>Cu₃Si₃Si₂Si₂P₂P₂</td>
<td>Cu₃Si₃Si₂Si₂P₂P₂</td>
</tr>
<tr>
<td>Cu₃Si₃P₃</td>
<td>No data</td>
<td>No data</td>
<td>No data</td>
</tr>
<tr>
<td>Cu₃Ge₃P₃</td>
<td>Cu₃Ge₃Ge₂Ge₂P₂P₂</td>
<td>Cu₃Ge₃Ge₂Ge₂P₂P₂</td>
<td>Cu₃Ge₃Ge₂Ge₂P₂P₂</td>
</tr>
<tr>
<td>Cu₃Ge₄P₃</td>
<td>No data</td>
<td>No data</td>
<td>No data</td>
</tr>
</tbody>
</table>

Table 5 Crystallographic data and structure refinements for single crystals from the CuSi,P₃, Cu₆Ge₃P₃ and Cu₆Ge₄P₃ samples at 293 K, MoKα₁ radiation, STOE IPDS II diffractometer

inability to prepare CuSi₃P₃ and CuGe₃P₃, in which P will have to be present on the Cu/T site, precludes existence of substantial three-component mixtures.

According to the proposed model, increase in the T content on going from “CuT₃P₃” to “CuT₄P₃” leads to a bigger population of T on the two sites, while the P : Cu ratio remains close to
3 : 1 (according to the microprobe results, P : Cu = 2.92(3) for “CuSiP" and P : Cu = 2.83(6) for “CuGeP," and P : Cu = 2.83(9) for “CuGeP")). The distribution of the elements on the two sites and the ratios between them allow us to view the compounds as members of the extended series with a general formula T_{1-x}(CuP)₂ (T = Si and Ge). If the series were fully continuous, the end members on the T-rich side would be pure silicon and germanium (x = 0), while the other end member would be a binary CuP (x = 1), which is unknown. Since CuSiP₃ and CuGeP₃ could not be prepared under our experimental conditions, the largest value of x has to be smaller than 0.5. Further studies will have to be undertaken to map finer boundaries of the T₁₋ₓ(CuP)₂ series.

In terms of atomic arrangements, the T₁₋ₓ(CuP)₂ structures could be viewed as derived from the diamond structures of silicon or germanium via symmetry reduction and introduction of Cu atoms on one site and P atoms on the other site. While the Ge-containing phases and “CuSiP” keep the cubic zinc blende structure (F₄m₃ space group), “CuSiP” adopts a tetragonally distorted version of it (I₄m2). The relationship between the two unit cells can be presented by the following matrix transformation:

\[
\begin{pmatrix}
1/2 & 1/2 & 0 \\
-1/2 & 1/2 & 0 \\
0 & 0 & 1
\end{pmatrix}
\begin{pmatrix}
\tilde{a} \\
\tilde{b} \\
\tilde{c}
\end{pmatrix}
= \begin{pmatrix}
\bar{a} \\
\bar{b} \\
\bar{c}
\end{pmatrix}
\]

It is worth noting that the tetragonal distortion disappears as the Si concentration increases. Currently, we do not understand the origin of the tetragonal distortion in the Si-containing phases. It has been also reported that tetragonal “CuSiP" prepared through the iodine transport at 800 °C develops a large superstructure easily detectable through the X-ray diffraction. In contrast, the crystals from “CuSiP" prepared by us at 1000 °C show no superstructure reflections even with a large overexposure on the image plate. Additionally, the TEM analysis (not described here) performed by us on the CuSiP₃ powder indicated no superstructure formation. It can be speculated that the annealing temperature of 1000 °C produces the higher-symmetry lattice, while 800 °C and lower temperatures may yield a lower-symmetry lattice.

**Transport properties**

Temperature dependence of electrical resistivity, Seebeck coefficient and thermal conductivity is given in Fig. 3–5. Room temperature physical properties for “CuSiP," “CuGeP," and “CuGeP" are summarized in Table 5. The presence of small quantities of Ge and Cu₃P is unlikely to change the values of the Seebeck coefficient and thermal conductivity to a significant extent. We found no published data on the electrical resistivity of Cu₃P. Even assuming the resistivity of Cu₃P to be similar to that of Cu, the resistivity of “CuGeP," and “CuGeP," is underestimated by ~2% (1.15 and 0.80 wt% of Cu₃P, respectively) according to the resistivity-mixture rule for a highly conductive dispersed phase. Since the contribution of Ge to electrical conductivity is opposite to that of Cu₃P, the values given in Table 5 are expected to be close to those for pure phases. There are well-pronounced bumps in the resistivity and only small changes in the Seebeck coefficient around
possible to calculate the electronic part of the thermal conductivity dominates the thermal conductivity.

It is found that in all phases lattice contribution significantly. In comparison to the Si$_{1-x}$Ge$_x$ alloys, "CuSi$_x$P$_{3-x}$", "CuGe$_x$P$_{3-x}$", and "CuGe$_x$P$_3$" have much lower electrical resistivity than the intrinsic Si$_{1-x}$Ge$_x$ (\(\rho = 10^{-10} \text{ Ohm cm}\))\(^6\) but the relationship observed by us between the resistivity and germanium content is reverse. In comparison to the Si$_{1-x}$Ge$_x$ alloys, "CuSi$_x$P$_{3-x}$", "CuGe$_x$P$_{3-x}$", and "CuGe$_x$P$_3$" are more conductive (\(\rho = -1.42 \times 10^{-3}\) Ohm cm for the p-type Si$_{0.5}$Ge$_{0.5} + 0.5$ wt\% of B)\(^17\).

The total thermal conductivity of all phases is much lower than the thermal conductivity of pure bulk germanium (58 W K$^{-1}$ m$^{-1}$) or silicon (130 W K$^{-1}$ m$^{-1}$) and is also lower than the thermal conductivity of the Si$_{1-x}$Ge$_x$ alloys (6.28 – 11.74 W K$^{-1}$ m$^{-1}$ for 0.2 < \(x < 0.85\))\(^18\) at room temperature.\(^18\) Using the Wiedemann–Franz law for degenerate conductors, it is also possible to calculate the electronic part of the thermal conductivity (\(k_e = LT/\rho\), with \(L\) being the Lorenz number) and subsequently the lattice thermal conductivity, \(k_l\).\(^19\) While "CuGe$_x$P$_3$" and "CuGe$_x$P$_{3-x}$" can be considered as degenerate conductors (heavily-doped degenerate semi-conductors), "CuSi$_x$P$_{3-x}$" is likely to behave as a non-degenerate semi-conductor for which the Lorenz number is a function of an exponent, \(\lambda\), that is usually unknown.\(^20\) Still, treating "CuSi$_x$P$_{3-x}$" as a degenerate conductor will not alter the lattice contribution significantly. It is found that in all phases the electronic contribution is relatively low and the lattice contribution dominates the thermal conductivity.

The dimensionless figure-of-merit, \(ZT\), as a function of temperature for three materials is given in Fig. 6. The \(ZT\) value is bigger for the Ge-containing phases due to their lower electrical resistivity, with "CuGe$_x$P$_3$" having the highest \(ZT\). Although the room temperature \(ZT\) values are relatively low, the steep upward trend suggests that much higher values can be achieved at elevated temperatures. Future studies on these phases will explore their transport properties above room temperature.

![Fig. 6](image)

**Fig. 6** Dimensionless figure-of-merit, \(ZT\), as a function of temperature for "CuSi$_x$P$_{3-x}$", "CuGe$_x$P$_{3-x}$", and "CuGe$_x$P$_3$".

**Electronic structure of CuSi$_x$P$_3$ and CuGe$_x$P$_3$**

Electronic structure calculations were performed to understand bonding features, stoichiometry and electrical conductivity of the "Cu$_x$T$_{1-x}$P$_3$" and "CuT$_x$P$_3$" phases. Calculated density of states, DOS, (Fig. 7) for the hypothetical, ordered structures of CuSi$_x$P$_3$ and CuGe$_x$P$_3$ are quite similar with one feature being significantly distinct: presence of a small band gap of 0.04 eV in CuSi$_x$P$_3$ and its closure in CuGe$_x$P$_3$. Such difference can be related to the stronger bonding involving the Si orbitals, which brings down the bonding states and pushes up the antibonding states, thus, opening the band gap. Similar densities of states can be assumed for "CuSi$_x$P$_3" and "CuGe$_x$P$_3". While the DOS calculations agree reasonably well with the electrical resistivity measurements that yielded a small band gap of 0.053 eV for the "CuSi$_x$P$_3" phase (Table 5) and metallic-type behaviour for the Ge-containing ones, the calculations do not account for the statistical mixtures that are likely to influence the electrical resistivity. Nevertheless, the claim by Berger et al. that "CuGe$_x$P$_3" has a band gap of 0.90(5) eV\(^15\) could neither be substantiated by our calculations nor by the resistivity measurements.

![Fig. 7](image)

**Fig. 7** Calculated densities of states (DOS) for ordered CuSi$_x$P$_3$ and CuGe$_x$P$_3$.

It is interesting to understand the reasons for the band gap contraction in CuSi$_x$P$_3$ and closure in CuGe$_x$P$_3$ as compared to pure Si and Ge. The calculation performed for the high-pressure modification of GeP with the zinc blende structure\(^21\) reveal a band gap of ~1 eV for the electron count of 4 e$^{-}$ per atom (see ESI†). While the Ge : P ratio in CuGe$_x$P$_3$ is different from being equiatomic as in GeP, it is unlikely that a different Ge : P ratio...
leads to the closure of the band gap. A substantial contribution of the Cu states, primarily from the d orbitals, just below the Fermi level indicates that the Cu atoms are responsible for the metallic behaviour. Similar arguments can be applied to explain the DOS features of CuSi$_4$P$_3$.

The tetrahedral environment around each atom in CuSi$_4$P$_3$ and CuGe$_4$P$_3$ and the 4 e$^-$/per atom count are expected to result in the scenario where all the bonding states are populated and antibonding states are empty. The calculated COHP curves for CuGe$_4$P$_3$, between Cu1, Ge1 atoms and the site 2 atoms prove that the interactions are indeed optimized for the 4 e$^-$/per atom count (Fig. 8). Thus, significant deviations from the Cu : 3P ratio is energetically unfavourable as a lower electron count diminishes bonding interactions whereas a larger electron count results in the population of antibonding states. The lower limit for the Cu : 3P ratio is likely to be around 2.8, as both Ge-phases are found to have this ratio (Cu : P = 2.83(6) for “CuGe$_4$P$_3$”, Cu : P = 2.83(9) for “CuGe$_4$P$_3$” and Cu : P = 2.91(3) for “CuSi$_4$P$_3$”). Such Cu : P ratios yield a lower than 4 e$^-$/per atom count and render the phases p-type conductors (in agreement with the Seebeck coefficient).

The samples were sealed in the evacuated silica tubes 15 cm $\times$ 1.5 cm, and CuGe$_4$P$_3$ phases could not be obtained. Also, all samples contained some unreacted phosphorus. To remove white phosphorus condensed from vapours, the tube end containing the sample was heated to 400 $^\circ$C in a horizontal tube furnace while the other end was cooled by a wet towel. After the white phosphorus had re-condensed at the cold end, the tube was removed from the furnace and air-cooled.

The Si-containing samples were always solids (powders) at the annealing temperatures, and the Ge-containing ones were liquids at and above 800 $^\circ$C. While none of the heat treatments could yield 100% pure samples, annealing at 1000 $^\circ$C for 72 h was found to produce the most homogeneous samples with the lowest amount of impurities and, thus, was chosen as a synthetic route. Still, the CuSi$_4$P$_3$ sample annealed at 1000 $^\circ$C contained large quantities of CuSi (Table 1). Interestingly, the Ge-containing samples showed significant compositional variations as discussed above.

**Hot pressing**

The CuSi$_4$P$_3$ and CuSi$_4$P$_3$ samples were powders and required hot pressing for microprobe analysis and physical property measurements. Since the CuSi$_4$P$_3$ sample contained a significant amount of Cu, Si, we have proceeded with the CuSi$_4$P$_3$ sample only. The CuSi$_4$P$_3$ powder was ground and pre-pressed in a 12 mm graphite die in the argon-filled glove box. The die was transferred in the sealed container to the hot press, where the samples were annealed at 1073 K for 2 h under the pressure of 1 metric ton in an argon atmosphere.

**Microprobe analysis**

Quantitative electron probe microanalysis was performed on the air-cooled CuSi$_4$P$_3$, CuGe$_4$P$_3$ and CuGe$_4$P$_3$ samples employing a JEOL JXA-8200 Superprobe with 20 kV acceleration potential and 20 nA beam current. Pure elements were used as standards for Si, Ge and Cu. Crystals of CuP$_2$ grown through an iodine transport were used as standard for P. The composition of CuP$_2$ crystals was verified from the single-crystal X-ray diffraction data collected on a STOE IPDSII diffractometer. Copper was also calibrated on the CuP$_2$ standard, and results were found to be identical within analytical uncertainty to calibrating on Cu metal.

The 4th order CuK$\alpha$ line ($4\lambda = 6.1674$ Å) overlaps the P K$\alpha$ line used for the analysis of P ($\lambda = 6.1589$ Å), and a linear correction was applied to account for this interference. The correction amounts to 0.2% of the P signal for a Cu : P ratio of 1 : 3. For a single data point this is within analytical uncertainty, but it becomes statistically significant for aggregate data.

**X-Ray powder and single-crystal diffraction**

X-Ray powder diffraction profiles in the 20–100$^\circ$ 29 range were recorded on a PANalytical X’Pert Pro diffractometer with an X’Celerator detector and a CuK$_{α1}$ radiation. The full-profile Rietveld refinement (Rietica program$^{22}$) was used to obtain the lattice constants and to determine impurity concentrations (Table 6). It was found that “CuGe$_4$P$_3$”, “CuGe$_4$P$_3$” and “CuSi$_4$P$_3” adopt the cubic zinc-blende structure (space group, $F\bar{4}3m$) while “CuSi$_4$P$_3$” is tetragonally distorted (space group $I4m2$, Fig. 9).

The air-cooled CuGe$_4$P$_3$ sample showed slight peak broadening, and CuGe$_4$P$_3$ exhibited closely spaced peaks that could be associated at least with three phases (Fig. 10). Lattice constants of “individual” components of “CuGe$_4$P$_3$” could not be reliably refined because of the peak overlap. Compositional inhomogeneity

![Image](https://example.com/image.png)

**Fig. 8** Crystal orbital Hamilton population (COHP) for selected interactions in CuGe$_4$P$_3$.

**Experimental**

**Synthesis**

The starting materials were pieces of Cu (99.9 wt%, Alfar Aesar), Si (99.999 wt%, Alfa Aesar), Ge (99.999 wt%, Alfa Aesar) and a powder of amorphous red phosphorus (99.5 wt%, Cerac Inc.). The copper and silicon or germanium with either 1 : 1, 1 : 2 or 1 : 4 ratios were arc-melted in the argon atmosphere, ground, mixed with the corresponding phosphorus amount to yield CuT$_p$P$_3$ (T = Si, Ge, x = 1, 2 and 4) compositions with a total sample mass of 5 g. The samples were sealed in the evacuated silica tubes 15 cm in length, heated at 4 $^\circ$C h$^{-1}$ for the Si-containing and 50 $^\circ$C h$^{-1}$ for the Ge-containing samples to the target temperatures of 800, 900 or 1000 $^\circ$C, kept at that temperature from 12 to 72 h and air-cooled. Regardless of the annealing temperature and time, the CuSi$_4$P$_3$ and CuGe$_4$P$_3$ phases could not be obtained. Also, all samples contained some unreacted phosphorus. To remove white phosphorus condensed from vapours, the tube end containing the

![Diagram](https://example.com/diagram.png)

**Fig. 10** Reduced X-ray powder diffraction pattern of CuSi$_4$P$_3$ (right) compared with the predictions of the structure refinement (left) and the Rietica simulation (middle).

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face indexing but later optimized against equivalent reflections on the crystal shape that was originally derived from the optical reciprocal sphere. A numerical absorption correction was based on the tetragonal distortion. 

Table 6 Lattice constants and impurity levels from powder diffraction for the samples annealed at 1000 °C for 72 h followed by air-cooling

<table>
<thead>
<tr>
<th>Sample</th>
<th>Major phase</th>
<th>Space group</th>
<th>Lattice constants/Å</th>
<th>Impurities and amounts (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuSi,P$_3$</td>
<td>&quot;CuSi,P$_3&quot;</td>
<td>$I\overline{4}m2$</td>
<td>$a = 3.70724(3)$ &amp;</td>
<td>Cu,P 0.19(2)%, Si 2.08(4)%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$c = 5.19471(5)$ &amp;</td>
<td></td>
</tr>
<tr>
<td>CuSi,P$_3$</td>
<td>&quot;CuSi,P$_3&quot;</td>
<td>$F\overline{4}m$</td>
<td>$a = 5.24811(6)$ &amp;</td>
<td>Cu,Si 12.8(3)%,</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$a = 5.39598(2)$ &amp;</td>
<td>Cu,P 1.15(2)%, Ge 1.67(2)%</td>
</tr>
<tr>
<td>CuGe,P$_3$</td>
<td>&quot;CuGe,P$_3&quot;</td>
<td>$F\overline{4}m$</td>
<td>$a = 5.454-5.441$</td>
<td>Cu,P 0.80(2)%, Ge 1.99(3)%</td>
</tr>
</tbody>
</table>

Neutron powder diffraction

The room temperature neutron data for the air-cooled CuSi,P$_3$ and CuGe,P$_3$ samples were collected on the NRC's C2 powder neutron diffractometer at Chalk River, Ontario, Canada. C2 consists of a curved 800 wire position sensitive detector covering a range of 80° with angular wire spacing of 0.1002425°. Further details of the C2 diffractometer can be found in Ref. 25 and 26. The powder diffraction pattern for the CuSi,P$_3$ and CuGe,P$_3$ samples were taken in a vanadium sample can over the 2θ range of 38–114° with a wavelength of $\lambda = 1.33037$ Å. The atomic parameters obtained from the corresponding single crystal refinements were used as starting models for the full-profile Rietveld refinements (Rietica program,$^2$ Fig. 11). The same refinement approaches as for the X-ray single crystal data were used for the neutron data. The refinement results are provided in the ESI.$^\dagger$

Physical property measurements

The electrical resistivity, Seebeck voltage and thermal conductivity of "CuSi,P$_3"$, "CuGe,P$_3"$, and "CuGe,P$_3"$ were measured in the 2–400 K (30–400 K for "CuSi,P$_3"$) region on a QD PPMS instrument. The thermal conductivity was measured using the two-probe configuration of the Thermal Transport Option (TTO) of the QD PPMS. The data were collected in the continuous
measurement mode at a cooling rate of 0.2 K min\(^{-1}\). The power and period of the heating pulses were automatically adjusted to create a thermal gradient across the sample of 3% of the ambient temperature. Thermal conductivity was obtained by fitting the time-temperature dependencies of the hot and cold thermometers by the TTO software assuming that the infrared emissivity of the polycrystalline samples is close to 1. Thermally evaporated Al contacts have been used as contact pads for four-probe electrical resistivity measurements. Spring-loaded rhodium-plated Be-Cu pin contacts have been utilized to ensure excellent mechanical and electrical contact with the sample during electrical resistivity measurements. The band gap of 0.053 eV for “CuSi\(_4\)” was determined from the Arrhenius behaviour of the resistivity in the high temperature region assuming one type of charge carriers.

Electronic structure calculations

Tight-binding linear-muffin-tin-orbital calculations using the atomic sphere approximation (TB-LMTO-ASA)\(^2\) were carried out for an idealized CuSi\(_x\)P\(_{1-x}\) and CuGe\(_x\)P\(_{1-x}\) structures with the lattice constants of the corresponding single crystals. The symmetry was reduced to trigonal to allow the following atomic arrangement: 1 Cu atom at 0 0 0; 3 Si/Ge atoms at 1/2 0 1/2; 1/2 1/2 0; 3 P atoms at 1/2 1/2 1/2. To satisfy the overlap criteria of the atomic spheres in the TB-LMTO-ASA method, empty spheres were included into the unit cell. A tetrahedron integration method was included into the unit cell. A tetrahedron integration method was used with a total of 512 points in the irreducible wedge of the Brillouin zone. For comparison, the electronic structure of the GeP binary with the cubic zinc blende structure\(^2\) has been also calculated.

Conclusion

The “CuT\(_4\)” and “CuT\(_3\)” phases (T = Si, Ge) with the zinc blende structure appear to be members of the extended T\(_{14}\)(CuP\(_4\))\(_{14}\) series, in which two-element mixtures, Cu/T and T/P, are present on both atomic sites. The large statistical mixtures significantly reduce the thermal conductivity of “CuT\(_4\)” and “CuT\(_3\)” as compared to pure Si and Ge. However, the thermal conductivity is still relatively large, which in combination with low electrical conductivity does not allow to reach desirable ZT values at room temperature. The Ge-containing phases show metallic-type behaviour while “CuSi\(_4\)” is semiconducting with \(\Delta E = 0.053\) eV. Reduction or closure of the band gap in the ternary phases as compared to Si or Ge is caused primarily by the Cu d-states.

Acknowledgements

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