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Transport properties of binary phosphide AgP₂ denoting high Hall mobility and low lattice thermal conductivity

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Abstract

This study found that polycrystalline AgP₂ shows intrinsic semiconducting electrical conductivity with Hall mobility of 51 cm² V⁻¹ s⁻¹, which is as high as that of Mg₂Si, and lattice thermal conductivity of 1.2 W K⁻¹ m⁻¹, which is as low as that of Bi₂Te₃. First-principles calculations theoretically indicate AgP₂ as an intrinsic semiconductor, and indicate the estimated carrier relaxation time τ as 3.3 fs, which is long for a polycrystalline material. Moreover, the effective mass of hole m* is approximately 0.11 times that of free electrons. These results indicate that long τ and light m* of the carrier are the origins of the high experimentally obtained Hall mobility. Phonon calculations indicate that the Ag atoms in AgP₂ exhibit highly anharmonic phonon modes with mode Grüneisen parameters of more than 2 in the 50–100 cm⁻¹ low-frequency range. The large anharmonic vibrations of the Ag atoms reduce the phonon mean free path. Moreover, the lattice thermal conductivity was found, experimentally and theoretically, to be as low as approx. 1.2 W K⁻¹ m⁻¹ at room temperature by phonon–phonon and grain-boundary scattering.

1. Introduction

Thermoelectric conversion technology can directly convert thermal energy into electrical energy. Thus, because it is difficult to recover energy from low-temperature waste heat in a steam turbine, thermoelectric conversion is attracting attention as a technology to recover energy from low-temperature waste heat. The most widely used thermoelectric materials are Te compounds, such as Bi₂Te₃ [1, 2] and PbTe [3, 4]. However, because of the low earth abundance of Te —approximately the same as that of Pt [5]—alternative materials are needed to replace Te compounds for mass production. In recent years, sulfides [6–8], silicides [9, 10], and half-Heusler [11] compounds have been proposed as alternatives to Te compounds, and are being actively studied worldwide. Moreover, phosphides are gaining increasing attention as a candidate group for new thermoelectric materials. Formation of AgP₂ at Ag-InP junction interfaces has been reported [12]. Moreover, transition metal phosphides are well known as catalysts for various hydrotreatment processes such as hydrogen desulphurization and hydrogen denitrogenation. Actually, Ni, Co, Fe, Mo, and W phosphides have shown promise for use as catalysts [13].

Theoretical calculations have also been conducted for phosphides. First-principles calculations using GGA and HSE06 functional have been performed to elucidate electronic and phonon properties of PdPSeX (X = O, S, Te) and graphene-like boron phosphide monolayers [14, 15]. First-principles calculations have been performed for AlP nanocrystals. Reportedly, the electronic properties approach those of bulk AlP as the nanocrystal size is increased [16].

However, because of their relatively low atomic weight and high speed of sound, many semiconductor phosphides, such as GaP [17] and InP [18], display high lattice thermal conductivity, which limits their application as thermoelectric materials. Recently, phosphides with low lattice thermal conductivity, such as the complex crystal-structured Ag₆Ge₁₀P₁₂ [19] and chain-structured Ag₃SnP₇ [20], have been discovered. In this
In this study, we focused on the binary phosphide AgP₂, which comprises a simpler composition and relatively complex crystal structure.

Figure 1 shows the crystal structure of AgP₂ [21, 22], which displays a P2₁/c space group and monoclinic crystal system. The structure comprises three P(1) and one P(2) atoms that coordinate around Ag to form a tetrahedron (grey tetrahedra in figure 1). Although AgP₂ is a relatively simple binary system, it contains a relatively large number of atoms, namely four Ag (4e sites) and eight P (4e sites) atoms for a total of 12 atoms per primitive cell. Li et al. chemically synthesised AgP₂ nanocrystals [23]. They reported that AgP₂ has a three-fold lower overpotential than that of Ag and is an excellent electrocatalyst for the reduction of CO from CO₂. The synthesis of single crystals and polycrystals of AgP₂ using iodine has also been reported [24]; however, to the best of our knowledge, the physical properties of AgP₂ polycrystals have not been reported to date. In theoretical calculations, J. H. Pöhls et al. reported the phonon bands of AgP₂ in a high-throughput screening study of density functional theory (DFT) calculations for metal phosphides [25]. However, this study focused on NiP₂ and did not discuss the detailed electronic and phonon structures of AgP₂. In this study, we established a method to synthesise polycrystalline samples of AgP₂ and fabricate high-density sintered samples. We also investigated the electronic and phonon properties from both experimental and theoretical aspects.

2. Experimental and computational conditions

2.1. Experiment details

In our first synthesis of AgP₂, we attempted direct reaction synthesis in which the starting materials Ag and P are enclosed and heated in a quartz tube. However, in the direct reaction method, unreacted white phosphorus precipitated. The sample burned in air. We were unable to obtain the AgP₂ phase. Therefore, AgP₂ was synthesised by a chemical vapour phase transport method using iodine as the transport agent. The starting materials were Ag (99.9%, Kojundo Chemical Laboratory Co., Ltd.), P (99.9999%, Rare Metallic Co., Ltd.), and 2.56 × 10⁻⁴ mol I₂ (99.9%, Fuji Film Wako Pure Chemicals Co., Ltd.). The mass of P was set at 0.4 g to prevent the quartz glass tube from exploding due to the vapour pressure of phosphorus. The mixture of starting materials was vacuum-sealed in a quartz tube (thickness, 1.8 mm; diameter, 8.5 mm; length, 10 cm) at a pressure of <5 × 10⁻⁵ Torr. Polycrystalline AgP₂ was obtained by heating the quartz tube containing the sample at 600 °C for 8 h. The polycrystalline AgP₂ pellets were sintered at 400 °C for 15 min under 300 MPa pressure using the hot-press method.

The crystal structure was characterised using powder x-ray diffractometry (XRD; SmartLab, Rigaku Co., Ltd.) with Cu-Kα radiation. Scanning electron microscopy–energy dispersive x-ray spectroscopy (SEM-EDS; TM3030plus; Hitachi, Ltd.) was used for elemental analysis of the samples.

The Seebeck coefficient S and thermal conductivity κ at 7–340 K were measured by the steady-state two-probe method using a physical property measurement system (PPMS, Qantum Design Co., Ltd.). The electrical resistivity from 3 to 340 K and Hall coefficient RH from 50 to 300 K were measured by the four-probe method, using the AC transport option in PPMS. The RH was determined from the slope of the straight line attained by measuring the Hall voltage against the magnetic field in the range of ±5 T (see figure S1 in the Supporting Information (available online at stacks.iop.org/MRX/9/055901/mmedia)). A silver paste was used to adhere the electrode to the sample.
2.2. Computational methods

The $E$–$k$ relationship, density of state, force on the cell, and total energy of AgP$_2$ were calculated using OpenMX [26]—a software package based on DFT, norm-conserving pseudopotentials, and optimised pseudoatomic basis functions. The exchange-correlation potential was calculated using the GGA-PBE functional [27]. The $k$-path of the first Brillouin zone was obtained using See-kpath [28]. The pseudo-atomic orbital basis functions were Ag7.0-s3p2d2f1 and P7.0-s3p2d2f1, each denoting the element, cutoff radius (Bohr units), and specification of optimised orbitals, respectively. The grid of $k$-points for the primitive cell was $16 \times 18 \times 14$, and that for the supercell ($2 \times 2 \times 2$ primitive cell) was $4 \times 5 \times 3$. The quasi-Newton method [29–34] was used for structural relaxation calculations, and the atomic positions and lattice parameters were optimised without applying any constraints until the force on the atoms was $<10^{-6}$ Ha Bohr$^{-1}$. The symmetry of the crystal before and after structural relaxation was analysed using Spglib [35], which confirmed that the space group did not change after structural relaxation. For all calculations, we set an energy cutoff of 500 Ryd for numerical integration.

The electronic properties were calculated using the electron transport code BoltzTraP [36], based on the Boltzmann transport theory. The electrical conductivity $\sigma$ and Seebeck coefficient $S$ can be expressed by equation (1):

$$\sigma(T) = K_0, \quad S(T) = -\frac{1}{|e| T} K_0,$$

$$K_n = \int \eta(E, T) (E - \mu)^n \left(-\frac{\partial f_E}{\partial E}\right) dE$$

where $e$ is the elementary charge, $T$ is the absolute temperature, $K_n$ is the transport coefficient, $\eta(E, T)$ is the spectrum conductivity at energy $E$ and temperature $T$, $\mu$ is the chemical potential, and $f_E$ is the Fermi–Dirac distribution function. The Fourier completion factor was set to 13, and the total number of $k$-points used for the transport coefficient approximated 50000. In the calculation of the Seebeck coefficient temperature dependence, the Fourier completion factor was set to 25 because numerous $k$-points are required when the chemical potential is located in the gap.

The phonon properties were calculated using ALAMODE [37]. A $2 \times 2 \times 2$ supercell of a structurally relaxed AgP$_2$ primitive cell was constructed, and the second- and third-order interatomic force constants (IFCs) were calculated using the supercell method. The atomic displacements used in the IFC calculations were 0.04 and 0.08 Å for the second- and third-order IFCs, respectively.

We calculated the phonon–phonon scattering intensity $\Gamma_\mu$ and phonon lifetime $\tau_\mu$ using equation (2):

$$\Gamma_\mu(\omega) = \frac{\pi}{2N} \sum_{q', q''} \hbar \frac{|\Phi_3(-q', \mu, q'')|^2}{8\omega_q\omega_{q'}\omega_{q''}} \Delta(-q + q' + q'') \times [n_{q'} + n_{q''} + 1] \delta(\omega_q - \omega_{q'} - \omega_{q''}) - 2(n_{q'} - n_{q''}) \delta(\omega_q - \omega_{q'} + \omega_{q''})],$$

$$\tau_\mu = \frac{\hbar}{2\Gamma_\mu(\omega)}$$

where $N$ is the number of all phonon modes, $\omega_q$ represents the harmonic phonon frequency at $q$, $\Phi_3$ is the third-order IFC, and $n$ is the Bose–Einstein distribution function.

Finally, we calculated the lattice thermal conductivity $\kappa_{\text{lat}}$ by solving the Boltzmann transport equation, assuming a relaxation time approximation, using equation (3):

$$\kappa^m_{\mu n}(T) = \frac{1}{V N_q} \sum_q C_q(T) n^m_q v^\mu_q v^n_q \tilde{\tau}_q$$

where $\mu$ and $\nu$ are the elements of the lattice thermal conductivity tensor, $T$ is the absolute temperature, $V$ is the unit cell volume, $N_q$ is the number of phonon modes at $q$, $C_q$ is the specific heat, and $v_q$ is the phonon group velocity.

3. Results and discussion

3.1. Synthesis of polycrystalline AgP$_2$

Figure 2 shows the XRD spectra of the powdered and hot-pressed AgP$_2$ samples. These spectra are in good agreement with the XRD spectra calculated from the crystal structure of AgP$_2$, indicating that we successfully obtained a single-phase sample. The lattice constants calculated from the XRD spectra of the hot-pressed sample were $a = 6.227(6)$ Å, $b = 5.060(5)$ Å, and $c = 7.81(1)$ Å, all of which are within 0.2% of the literature values [21]. The peak intensity was different from that observed in the simulation, suggesting that the sample was slightly oriented. The SEM–EDS compositional analysis revealed a 1:1.9(1) Ag:P ratio, which was near-identical—within the error range—to the preparation composition.
3.2. Transport properties of hot-pressed AgP₂

Figure 3(a) shows the temperature dependence of the electrical resistivity of hot-pressed AgP₂. The heat flow and current direction were in-plane same direction of pellet for all measurements. The electrical resistivity $\rho$ decreases exponentially with increasing temperature, indicating that AgP₂ is an Arrehenius-type semiconductor. The electrical resistivity at 300 K is 24.9 m$\Omega$m, which is relatively high. The electron thermal conductivity estimated from the Wiedemann–Franz law is almost zero, and thus, the contribution of electronic thermal conduction can be neglected.

Figure 3(b) shows the $\ln\rho$–$T^{-1}$ plot. The plot is linear at temperatures $>80$ K, indicating that AgP₂ is an Arhenius-type semiconductor. At high temperatures $>480$ K, the slope increases, indicating that the excitation of carriers with higher activation energy occurs. The estimated activation energies ($E_a$) in the temperature range 80–480 K and at temperatures $>480$ K are 46 and 249 meV, respectively. This suggests that the activation energy corresponds to thermal excitation from the valence band to the impurity level and from the valence band to the conduction band. A possible impurity level is the loss of a small amount of P. Calculations of the electronic densities of state with a 1.6% loss of P show that a sharp impurity level-derived density of state occurs at the upper edge of the valence band. (See figure S2 in the Supporting Information). We evaluated thermal stability using high-temperature measurements of $\rho$ and Seebeck coefficient $S$, and SEM-EDS measurements, which revealed AgP₂ as destabilized around 680 K, resulting in P desorption. The section of Supporting Information describing thermal stability of AgP₂ presents important details.

Figure 4 shows the temperature dependence of the Hall coefficient $R_H$ of AgP₂. $R_H$ is positive across all temperature ranges, indicating that the major carrier of AgP₂ is a hole. As the temperature increases, the $R_H$ decreases exponentially. This qualitatively explains the electrical resistivity results. Assuming a single carrier model, the activation energy estimated from the temperature dependence of $R_H$ is $\sim 43$ meV, which is in good agreement with the $E_a$ estimated from figure 3(b). This corresponds to an exponential increase in the carrier concentration due to thermal excitation from the upper valence band to the impurity level in the 50–300 K temperature range. The Hall mobility of AgP₂, estimated from the Hall coefficient and electrical resistivity, is $\sim 51$ cm$^2$ V$^{-1}$ s$^{-1}$ at 300 K. This value is comparable to that of polycrystalline Mg$_2$Si [38].

Figure 5(b) shows the lattice thermal conductivity $\kappa_{\text{lat}}$–$T^{-1}$ plot. The $\kappa_{\text{lat}}$ of AgP₂ at 300 K is as low as 1.2 W K$^{-1}$ m$^{-1}$. Surprisingly, this value is lower than that of Ag$_6$Ge$_{10}$P$_{12}$ [19], which has a complex crystal structure containing as many as 28 atoms in the basic unit cell, and is comparable to the lattice thermal conductivity of Bi$_2$Te$_3$ [39]. At temperatures $>152$ K, the plot is linear, and phonon–phonon scattering is dominant at relatively low temperatures. This implies that the probability of the phonon–phonon scattering of AgP₂ is high at relatively low temperatures.

The experimental results revealed that AgP₂ is a phosphide with both high Hall mobility and low lattice thermal conductivity. In this study, we investigated the electron and phonon transport properties of AgP₂ using first-principles calculations to theoretically clarify the origin of the high Hall mobility and low lattice thermal conductivity.
Figure 3. (a) Temperature dependence of the electrical resistivity for hot-pressed AgP₂ and (b) ln ρ – T⁻¹ plot of AgP₂: PPMS (solid black circles) and RZ2001i (open circles).

Figure 4. Temperature dependence of the Hall coefficient R_H for hot-pressed AgP₂.
3.3. Theoretical transport properties of AgP₂

3.3.1. Electronic properties

Figure 6(a) shows the E–k relationship for AgP₂. The origin of the energy coincides with the chemical potential at 300 K, as calculated from first-principles calculations. The modified chemical potential $\mu_{\text{Exp}}$ was determined from the chemical potential at 300 K, where the calculated and experimental Seebeck coefficients agree (see figure S3 in the Supporting Information). The slight shift in the position of the chemical potential, compared to the first-principles calculation, suggests the presence of some defects in the AgP₂ sample. This is possibly an impurity level caused by a defect in the P atom, based on the results of figure 3(b) and S2 (Supporting Information). Thus, $\mu_{\text{Exp}}$ is located in the forbidden band, and AgP₂ is an intrinsic semiconductor. The band gap $E_g$ estimated from the E–k relationship is 498 meV, which is almost twice the activation energy ($E_a = 249 \text{ meV}$) estimated from the slope of the $\ln\rho - T^{-1}$ plot [figure 3(b)] at high temperatures (>480 K). At the upper end of the valence band, the band at the Y₂ point has the highest energy, and this band contributes the most to the electrical conduction of AgP₂.

Figure 6(b) shows the electrical conductivity $\sigma^{-1}$ of AgP₂ obtained from the E–k relationship. The $\sigma^{-1}$ decreases exponentially from the band edge to the forbidden band, with a $\sigma^{-1}$ value of $1.22 \times 10^{16} \Omega^{-1} \text{ m}^{-1} \text{ s}^{-1}$ at $\mu_{\text{Exp}}$. Compared to the electrical resistivity $\rho$ at 300 K, the carrier relaxation time $\tau$ is estimated at $\sim 3.3 \text{ fs}$. This value is relatively long for a polycrystalline material [40].

Based on the obtained carrier relaxation time $\tau$ and experimental Hall mobility $\mu_H$, we estimated the effective mass $m^*$ of holes in AgP₂ at 300 K using equation (4):

$$\mu_H = \frac{e\tau}{m^*}$$

where $e$ is the elementary charge. The effective mass of holes $m^*$ in AgP₂ at 300 K was estimated to be 0.11 $m_0$, while the effective mass of free electrons is $m_0$. This indicates that the effective mass of carriers in AgP₂ is much lighter than that of free electrons. Thus, the large Hall mobility of AgP₂ was attributed to the relatively long carrier relaxation time and small effective mass of AgP₂.

Figure 7 shows the highest occupied molecular orbital (HOMO) at the Y₂ point. At this point, the Ag 4d orbitals and P(1) 3p orbitals are dominant. Because P(2) has no orbitals at the Y₂ point, the conduction hole at this point is understood to propagate on the Ag–P(1) network.

The electronic structure and electronic transport properties of AgP₂ were investigated using first-principles calculations. AgP₂ is an intrinsic semiconductor and exhibits a high Hall mobility comparable to that of Mg₃Si. This is due to its relatively long relaxation time (3.3 fs) and small effective carrier mass (0.11 $m_0$). The carrier conduction is dominated by hole conduction through a network of Ag 4d orbitals and P(1) 3p orbitals.

3.3.2. Phonon properties

Figures 8(a) and (b) show the phonon dispersion relations and partial densities of state of the constituent atoms of AgP₂. The phonon dispersion relation is colour-mapped for each phonon mode according to the value of the mode Grüneisen parameter. The optical phonon modes occur in the low-frequency region ($\sim 60 \text{ cm}^{-1}$),
suggesting that the scattering probability of phonon–phonon scattering at the Brillouin zone boundary is high at room temperature. This qualitatively supports the experimental results for $\kappa_{\text{lat}} - T^{-1}$. A relatively large anharmonic phonon mode with $\gamma > 2$ occurs in the 50–100 cm$^{-1}$ frequency range. This mode has a small energy dispersion and a slight gap in the 90–100 cm$^{-1}$ frequency region. From the partial densities of state of the phonons, the contribution of the Ag atom to the phonon mode is dominant in the frequency region below 100 cm$^{-1}$, indicating that the highly anharmonic phonon mode with small energy dispersion in the 50–100 cm$^{-1}$ region originates from the Ag atom. The phonon mode of the Cu atom in CuP$_2$, which has the same crystal
structure as AgP₂, was reported by Ji et al. [41] to display a large-mode Grüneisen parameter and high anharmonicity, and the phonon mode of the Ag atom in AgP₂ is similar.

To clarify the origin of the anharmonic phonon mode of the Ag atoms in AgP₂, we calculated the difference in electron density in real space and investigated the bonding state. The difference in electron density was calculated by subtracting the electron densities of the isolated Ag and P atoms from the electron density of the AgP₂ crystal.

Figure 9 shows a two-dimensional colour map of the difference electron density distribution near the P(1)–Ag–P(1)–Ag and P(1)–Ag–P(2) bonds in AgP₂. The Ag–P bonds are ionic because of the polarity from the difference electron density between the bonds. P(1)–Ag–P(1)–Ag is a quadrupole, while P(1)–Ag–P(2) comprises a dipole-like charge polarity. In addition, the polarity from the difference electron density between the Ag–P(2) bonds is larger than that between the Ag–P(1) bonds, suggesting that the bonding strength of the latter is weaker than that of the former. These results indicate that the bonding around the Ag atoms is strongly anisotropic. The difference electron density between the P–P bonds is concentrated at the centre of the two atoms, which is a typical covalent bond (Figure not shown). AgP₂ is a crystal with a mixture of ionic and covalent bonds, and the strong anisotropy of the bonds around the Ag atoms is suggested to be the origin of the large anharmonic vibration of the Ag atoms.
To compare the anharmonicity of the phonon structure of AgP₂ with that of other materials, the mean-square displacement (MSD) of the constituent atoms, relaxation time of phonon–phonon scattering, and phonon group velocity were compared with those of CuP₂ [42], which has the same crystal structure, and InP [43], which constituent atoms are close in atomic weight. The calculation conditions for the phonon properties of CuP₂ and InP are listed in table S1 in the Supporting Information.

Figures 10(a)–(c) show the temperature dependence of the MSD of the constituent atoms in AgP₂, CuP₂, and InP, respectively. The MSD increases monotonically with increasing temperature, and the scattering cross-section in phonon–phonon scattering also increases. In AgP₂, the MSD of the Ag atoms at 300 K is between 1.6- and 1.7-fold larger than the that of the P atoms. Notably, the MSD of the Cu atoms in CuP₂ is approximately 1.5-fold larger than that of the P atoms, but not as large as that of the Ag atoms in AgP₂. This indicates that the scattering cross-section of the Ag atoms in AgP₂ is larger than that of the Cu atoms in CuP₂. The MSD of In in InP is approximately 1.1-fold larger than that of P, and the In atoms in InP do not vibrate as much against P as do the Ag atoms in AgP₂.

Figures 11(a)–(c) respectively show the phonon relaxation time \( \tau_{q_1} \), absolute value of the phonon group velocity \( |v_q| \), and mean free path (MFP) of phonon–phonon scattering in the three-phonon processes of AgP₂, CuP₂, and InP (see equation (3) for definitions of \( \tau_{q_1} \) and \( v_q \)). The temperature of the Bose–Einstein distribution is 300 K, while the maximum \( \tau_{q_1} \) is \( \sim 500 \) ps, which is relatively short. The overall decrease in \( \tau_{q_1} \) compared to that of CuP₂, which has the same crystal structure, indicates that the scattering probability in phonon–phonon scattering is smaller than that of CuP₂. This is qualitatively consistent with the MSD results in figure 10, in which the Ag atoms in AgP₂ present a larger phonon scattering cross-section than do the Cu atoms in CuP₂. The overall relaxation time is shorter than that of InP, indicating that AgP₂ exhibits a large phonon–phonon scattering probability. The phonon group velocity in AgP₂ is shifted to a lower speed than that in CuP₂, attributed to the difference in the atomic weights of Ag and Cu. The highest phonon group velocity in InP is relatively close to that of AgP₂, indicating that the phonon group velocity in AgP₂ is not particularly slow. The frequency distribution of the phonon MFP in AgP₂ is shifted to a much shorter MFP than that in CuP₂, which is caused by the high phonon–phonon scattering probability of the Ag atoms in AgP₂ and the lower phonon group velocity due to the relatively heavy atomic weight of the Ag atoms.

Figure 12 shows the temperature dependence of the lattice thermal conductivity of AgP₂. Following Matthiessen’s rule, the average values of the lattice thermal conductivities in the a-, b-, and c-axes were calculated using equation (5):

\[
\frac{3}{\kappa_{\text{lat Ave}}} = \frac{1}{\kappa_{\text{lat a}}} + \frac{1}{\kappa_{\text{lat b}}} + \frac{1}{\kappa_{\text{lat c}}}
\]

(5)

where \( \kappa_{\text{lat Ave}} \) is the average lattice thermal conductivity along the a, b, and c axes, \( \kappa_{\text{lat a}} \), \( \kappa_{\text{lat b}} \), and \( \kappa_{\text{lat c}} \) are the respective lattice thermal conductivities along the a, b, and c axes.

The lattice thermal conductivity of single-crystal AgP₂ obtained from theoretical calculations is 1.80 W K⁻¹ m⁻¹ at 300 K. This is an extremely low value comparable to that of single-crystal Bi₃Te₃ [39]. The theoretical temperature dependence of the lattice thermal conductivity, assuming grain-boundary and phonon–phonon scattering for a particle size of 300 nm, well-reproduces the experimental value of \( \kappa_{\text{lat}} \) for AgP₂. This indicates that the average size of the effective grain boundary for phonons is \( \sim 300 \) nm. Both experimental and theoretical results indicate that the large phonon scattering due to the anharmonic vibrations of the Ag atoms and the decrease in the phonon group velocity associated with the relatively large atomic weight are the origins of the low lattice thermal conductivity of AgP₂.

4. Conclusions

In this study, a polycrystalline sample of binary phosphide AgP₂ was synthesised by the chemical vapour transport method to obtain single-phase polycrystalline AgP₂, which was then hot-pressed into a high-density sintered compact. The as-synthesised polycrystalline AgP₂ has a high Hall mobility \( \mu_H \) of 51 cm² V⁻¹ s⁻¹ at 300 K, which is comparable to that of Mg₂Si, and a low lattice thermal conductivity \( \kappa_{\text{lat}} \) of \( \sim 1.2 \) W K⁻¹ m⁻¹, which is comparable to that of Bi₃Te₃.

To clarify the origin of the high \( \mu_H \) and low \( \kappa_{\text{lat}} \), the electron and phonon transport properties were investigated in detail by first-principles calculations. The results revealed that AgP₂ has a semiconducting electronic structure in which the respective 4d and 3d orbitals of Ag and P dominate the electrical conduction at the Y₂ point in the upper valence band. The carrier relaxation time of AgP₂ is 3.3 fs at 300 K, which is relatively long for a polycrystalline material, and its effective mass hole is 0.11-fold lighter than that of free electrons. The high \( \mu_H \) of AgP₂ is attributed to the relatively long carrier relaxation time and small effective mass.
Phonon calculations revealed that AgP$_2$ exhibits highly anharmonic phonon modes in the low-frequency region (50–100 cm$^{-1}$), with small energy dispersion from the Ag atoms and a mode Grüneisen parameter $>2$. Compared to CuP$_2$, which has the same crystal structure, and InP, which has the same atomic weight of the constituent elements, AgP$_2$ exhibits a shorter phonon relaxation time and lower group velocity. The $\kappa_{lat}$ obtained from the theoretical calculations well-reproduced the experimental values, assuming phonon–phonon interactions.
scattering and grain-boundary scattering by 300 nm grains. It is theoretically clarified that the high scattering probability of phonon–phonon scattering due to the large anharmonic vibration of Ag atoms is the origin of the low $\kappa_{\text{lat}}$ of AgP$_2$. AgP$_2$ shows high potential as a thermoelectric material, but because it is an intrinsic semiconductor, its carrier concentration is low. To use AgP$_2$ as a thermoelectric material, it is necessary to dope the carriers by elemental substitution or introduction of defects.

Figure 11. Frequency distribution of the phonon properties at each phonon mode: (a) Phonon relaxation time $\tau_q$, (b) absolute value of phonon group velocity $|v_q|$, and (c) phonon mean free path (MFP).
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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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Ethical statement

Not applicable.

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Figure 12. Temperature dependence of the lattice thermal conductivity $\kappa_{lat}$ for AgP$_2$: Experimental $\kappa_{lat}$ for hot-pressed AgP$_2$ (solid black dots), theoretical $\kappa_{lat}$ of single-crystal (SC) AgP$_2$ considering phonon–phonon (ph–ph) scattering obtained from first-principles calculations (blue), and theoretical $\kappa_{lat}$ of polycrystal AgP$_2$ assuming phonon–phonon scattering and grain boundary (GB)-scattering of 300 nm grains (red).
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