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Credit authorship contribution statement

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Graphical abstracts
Thermoelectric properties of phosphorus-doped van der Waals crystal $\text{Ta}_4\text{SiTe}_4$

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Abstract
Recently, one-dimensional van der Waals crystal $\text{Ta}_4\text{SiTe}_4$ has been reported as a promising low-temperature thermoelectric material. Extraordinarily high power factor has been reported for the one-dimensional $\text{Ta}_4\text{SiTe}_4$ single whisker and two-dimensional (PVDF)/$\text{Ta}_4\text{SiTe}_4$ composite film, but the thermoelectric properties of three-dimensional $\text{Ta}_4\text{SiTe}_4$ polycrystalline bulks have been rarely investigated. In this study, we prepared a series of phosphorus (P)-doped $\text{Ta}_4\text{SiTe}_4$ polycrystalline bulks by using the high-temperature synthesis and cold press method. Their electrical and thermal transport properties along the directions parallel and perpendicular to the pressure were systematically investigated. Upon doping P at the Si-sites to increase the carrier concentration, the electrical conductivity is enhanced while the intrinsic excitation is suppressed, resulting in significantly improved power factor approaching the theoretically optimal value. All $\text{Ta}_4\text{Si}_{1-x}\text{P}_x\text{Te}_4$ bulks possess low lattice thermal conductivities with the values below 1.2 Wm$^{-1}$K$^{-1}$. The weak van der Waals interaction among the $[\text{Si}_2\text{Ta}_8\text{Te}_8]_n$ chains results in the appearance of low-lying optical modes and introduces additional scattering to phonons. A peak thermoelectric figure of merit value of 0.18 is obtained at 300 K for polycrystalline $\text{Ta}_4\text{Si}_{0.995}\text{P}_{0.005}\text{Te}_4$, about double that of pristine polycrystalline $\text{Ta}_4\text{SiTe}_4$.

Key words: thermoelectric, $\text{Ta}_4\text{SiTe}_4$, van der Waals crystal, whiskers
1. Introduction

Thermoelectric (TE) technology has potential applications in converting heat into electricity and solid-state refrigeration [1, 2]. The former application requires the TE materials with high performance above room temperature, called as middle-temperature or high-temperature TE materials, while the latter application requires the TE materials with high performance near or below room temperature, called as low-temperature TE materials. The past several decades have witnessed unprecedented success in developing new middle-temperature and high-temperature TE materials, such as skutterudites [3, 4], half-Heusler alloys [5-7], Cu$_2$Se [8-10], SnSe [11, 12], and MgAgSb [13, 14]. However, the development of new low-temperature TE materials has progressed less rapidly. Currently, the best TE materials applied at low temperature are still commercial Bi$_2$Te$_3$-based compounds developed in 1950s [15, 16]. Although many new low-temperature TE materials, such as Mg$_3$(Bi,Sb)$_2$ [17, 18], BiSb [19-21], CePd$_3$ [22, 23], FeSi [24, 25], YbAl$_3$ [26, 27], and Ag$_2$Se [28, 29], had also been reported, they are still far away the real applications due to the low performance or poor thermal stability.

Recently, one-dimensional van der Waals crystal, Ta$_4$SiTe$_4$, has been reported as a promising low-temperature TE material [30, 31]. Ta$_4$SiTe$_4$ crystallizes in the orthorhombic structure (space group Pbam). As shown in Fig. 1, its crystal structure can be simply regarded as bundles of infinitely extended [Si$_2$Ta$_8$Te$_8$]$_n$ chains connected by van der Waals force. In each [Si$_2$Ta$_8$Te$_8$]$_n$ chain, Ta and Te form two kinds of concentric [Ta$_4$Te$_4$] four-angle stars, which are repeatedly staggered arranged along the c-axis. Si atoms are inserted among these [Ta$_4$Te$_4$] layers forming the one-dimensional [Si$_2$Ta$_8$Te$_8$]$_n$ chain. As a result of such unique structure, Ta$_4$SiTe$_4$ is easily grown into one-dimensional whisker with the length up to several millimeters and the diameter up to several micrometers. Ta$_4$SiTe$_4$ is a semiconductor with a narrow band gap around 0.1 eV [30, 32]. Inohara et al. prepared Ta$_4$SiTe$_4$ whiskers by using the chemical vapor transportation method [30]. They found that the Ta$_4$SiTe$_4$ single whisker has large negative Seebeck coefficient ($S$) around several hundred
μVK\(^{-1}\) and high electrical conductivity (\(\sigma\)) in the order of 10\(^5\) Sm\(^{-1}\) around 300 K along the \(c\)-axis. The calculated power factor \((PF = S^2\sigma)\) for n-type Ta\(_4\)SiTe\(_4\) single whisker along the \(c\)-axis is as high as 80 \(\mu\)Wcm\(^{-1}\)K\(^{-2}\) around 130 K [30], which is double the peak value of commercial n-type Bi\(_2\)Te\(_3\)-based alloys [16].

Although the one-dimensional Ta\(_4\)SiTe\(_4\) single whiskers demonstrate extraordinarily high \(PF\), they are very difficult to be directly fabricated into cooling device and used in solid-state refrigeration due to the small sizes. The one-dimensional Ta\(_4\)SiTe\(_4\) whiskers need to be made into two-dimensional films or consolidated into three-dimensional bulks to satisfy the real applications. Via compositing Ta\(_4\)SiTe\(_4\) whiskers with polyvinylidene fluoride (PVDF), a \(PF\) of 5.7 \(\mu\)Wcm\(^{-1}\)K\(^{-2}\) at 300 K has been obtained in two-dimensional (PVDF)/Ta\(_4\)SiTe\(_4\) conformal composite film, which is superior to most flexible organic–inorganic TE composites reported previously [32]. However, the TE properties of three-dimensional Ta\(_4\)SiTe\(_4\) polycrystalline bulks have been rarely investigated. The chemical vapor transportation method can obtain high quality Ta\(_4\)SiTe\(_4\) single whisker, but it is not suitable to prepare the Ta\(_4\)SiTe\(_4\) polycrystalline bulks because of the low yield and plentiful byproducts. In this study, we prepare a series of phosphorus (P)-doped Ta\(_4\)SiTe\(_4\) polycrystalline bulks by high-temperature synthesis and cold press method. The effect of P-doping on the electrical transport properties and the origin of low \(\kappa\) in three-dimensional Ta\(_4\)SiTe\(_4\) bulks are systematically investigated. A maximum \(zT\) of 0.18 is achieved for Ta\(_4\)Si\(_{0.995}\)P\(_{0.005}\)Te\(_4\) at 300 K along the direction perpendicular to the pressure, which is about two times of that of pristine Ta\(_4\)SiTe\(_4\).

2. Results and discussion

Fig. 2a presents the room-temperature X-ray diffraction patterns for the Ta\(_4\)Si\(_{1-x}\)P\(_x\)Te\(_4\) (\(x=0, 0.005, 0.01, \) and 0.02) powders prepared by high-temperature synthesis. The main diffraction peaks can be indexed belonging to the Ta\(_4\)SiTe\(_4\) phase (space group, Pbam, PDF #88-1616). Several weak diffraction peaks appear around 2\(\theta\) = 13.2°, corresponding to the existence of a very tiny amount of secondary phase TaTe\(_2\). The X-ray diffraction patterns of all Ta\(_4\)Si\(_{1-x}\)P\(_x\)Te\(_4\) samples are quite similar,
indicating that the structure symmetry is not changed upon doping P. Fig. S1 plots the lattice parameters obtained from the Rietveld refinement. They are almost unchanged upon doping P, which is reasonable considering the similar atomic radiiuses between P and Si. In addition, Fig. S2 shows that the P-doped samples possess better crystallinity than the pristine Ta₄SiTe₄.

Because of the inherent one-dimensional crystal structure, the Ta₄Si₁₋ₓPₓTe₄ whiskers prefer to be oriented along the c-axis. Fig. 2b shows the microstructure of the as-prepared Ta₄SiTe₄. Most of them exist in the form of thin plates consisting of numerous one-dimensional whiskers. The diameter of the whiskers is in the order of hundreds of nanometers. The high-resolution TEM image shown in Fig. 2c clearly shows that the Ta₄SiTe₄ single whisker is well crystalized. No obvious lattice distortions, dislocations, or amorphous phases are observed. The selected area electron diffraction (SAED) pattern in the inset of Fig. 2c proves that Ta₄SiTe₄ crystallizes in an orthorhombic structure, being consistent with the XRD measurement. Based on the fast Fourier transformation (FFT) image, the (110) plane spacing (d₁₁₀) in Ta₄SiTe₄ is estimated to be around 9.3 Å, which is close to the value of 9.1 Å obtained from the lattice parameters.

The as-prepared one-dimensional Ta₄Si₁₋ₓPₓTe₄ whiskers must be consolidated into three-dimensional bulks before the real application. Spark plasma sintering (SPS) is a common method to obtain the dense bulks. We try to use SPS to consolidate the as-prepared Ta₄Si₁₋ₓPₓTe₄ whiskers, but the content of secondary phase TaTe₂ is always significantly increased in the sintered bulks (Fig. S3). This might be related to the weak van der Waals force among the [Si₂Ta₈Te₈]ₙ chains. Thus, we use cold press instead of SPS to consolidate the as-prepared Ta₄Si₁₋ₓPₓTe₄ whiskers. The relative densities of obtained bulks are about 88%. As shown in Fig. 2d, there are many nano-sized pores inside the samples, which are responsible for their low relative densities. The scanning electron microscope (SEM) image with EDS mapping (Fig. 2e) performed on the obtained Ta₄Si₀.₉₈P₀.₀₂Te₄ bulk indicates that Ta, Si, Te, and P are homogeneously distributed. No P-containing enrichments are detected inside the sample, which can be inferred that P is doped into the lattice instead of forming
secondary phase.

Fig. 3a and 3b show the measured electrical conductivity (\(\sigma\)) and Seebeck coefficient (\(S\)) for Ta\(_4\)Si\(_{1-x}\)P\(_x\)Te\(_4\) \((x=0, 0.005, 0.01, \text{ and } 0.02)\) polycrystalline bulks measured along the directions perpendicular (\(\perp\)) and parallel (\(/\!/\)) to the pressure. The \(S\) values are similar in the entire measured temperature range, but the \(\sigma\) values along the direction perpendicular to the pressure are much higher than those along the direction parallel to the pressure. The strong anisotropy of \(\sigma\) is originated from the one-dimensional character of Ta\(_4\)Si\(_{1-x}\)P\(_x\)Te\(_4\) whiskers. On one hand, the band structure of Ta\(_4\)SiTe\(_4\) shows anisotropic character as the effective masses along \(\Gamma\)-\(X\) \((1.69 \, m_0)\) and \(\Gamma\)-\(Y\) \((1.37 \, m_0)\) directions are much larger than that along the \(\Gamma\)-\(Z\) \((0.14 \, m_0)\) direction [32]. On the other hand, the presence of fewer interfaces along the direction perpendicular to the pressure will introduce weaker scattering to electrons. These two aspects simultaneously contribute to the higher \(\sigma\) values along the direction perpendicular to the pressure. Likewise, the negative \(S\) values indicate that electrons are the dominate carriers. The peak |\(S\)| for pristine Ta\(_4\)SiTe\(_4\) is 215 \(\mu\text{VK}^{-1}\) at 200 K, which is lower than that for the Ta\(_4\)SiTe\(_4\) single whisker reported by Inohara et al.[30] (Fig. S4). The Ta\(_4\)SiTe\(_4\) single whisker was fabricated by the crystal growth in a vapor phase, while the Ta\(_4\)SiTe\(_4\) bulks were prepared by the solid reaction method with many pores and/or defects. These two fabrication methods might lead to the differences in actual chemical compositions and defects and thus different TE properties.

Above 200K, the \(\sigma\) for pristine Ta\(_4\)SiTe\(_4\) increases dramatically with increasing temperature, showing a typical semiconducting transport behavior. This is consistent with the existence of a narrow spin-orbit band gap around 0.1 eV in Ta\(_4\)SiTe\(_4\) [30, 32]. As a result of this band gap, the intrinsic excitation is easily to occur below room temperature, which is responsible for the appearance of peak values in the \(S\) curves. Since the valence band maximum and conduction band minimum of Ta\(_4\)SiTe\(_4\) are asymmetric with different density of states [30], its band gap \(E_g\) can be estimated by the Goldsmid-Sharp relation [33]

\[
E_g = 2e|S_{\text{max}}|T_{\text{max}} \tag{1}
\]
where \( e \) is the elementary charge, \( |S_{\text{max}}| \) is the peak value of Seebeck coefficient, and \( T_{\text{max}} \) is the corresponding temperature of \( |S_{\text{max}}| \). The \( E_g \) values are estimated to be 0.08-0.09 eV for all \( \text{Ta}_4\text{Si}_{1-x}\text{P}_x\text{Te}_4 \) samples, close to the theoretical band gap (0.1 eV).

The \( \sigma \) for the pristine \( \text{Ta}_4\text{SiTe}_4 \) polycrystalline bulk is \( 0.86 \times 10^4 \, \text{Sm}^{-1} \) at 300 K. This value is much lower than that of the \( \text{Ta}_4\text{SiTe}_4 \) single whisker along the \( c \)-axis reported by Inohara et al. [30], about \( 5 \times 10^4 \, \text{Sm}^{-1} \) at 300 K. It is because that a lot of grain boundaries among the bulk sample will introduce extra scatterings to the carriers. In addition, the existence of nano-sized pores is also responsible for the low \( \sigma \) obtained in polycrystalline bulk. Upon doping P at the Si-sites, the absolute value of \( S \) is reduced, while the \( \sigma \) is increased in the entire measured temperature range. For the \( \text{Ta}_4\text{Si}_{0.98}\text{P}_{0.02}\text{Te}_4 \), the \( \sigma \) is \( 3.0 \times 10^4 \, \text{Sm}^{-1} \) at 300 K, which is about 2 times higher than that of the pristine \( \text{Ta}_4\text{SiTe}_4 \). Correspondingly, below 300 K, the Seebeck coefficients \( S \) decreases with increasing P content. The \( S \) is \(-114 \, \mu\text{VK}^{-1} \) at 300 K, about 30% lower than that for the pristine \( \text{Ta}_4\text{SiTe}_4 \). Furthermore, with the increase of P doping content, the \( T_{\text{max}} \) rises from 200 K for the pristine \( \text{Ta}_4\text{SiTe}_4 \) to 320 K for \( \text{Ta}_4\text{Si}_{0.98}\text{P}_{0.02}\text{Te}_4 \), indicating that the intrinsic excitation is effectively suppressed.

The temperature dependence of power factor (PF) for \( \text{Ta}_4\text{Si}_{1-x}\text{P}_x\text{Te}_4 \) \((x=0, 0.005, 0.01, \text{and} 0.02) \) polycrystalline bulks is presented in Fig. 3c. With the increase of the doped P content, the power factor \( PF \) firstly shows a tendency of increasing and then decreasing. The peak \( PF \) for pristine \( \text{Ta}_4\text{SiTe}_4 \) is just 2.5 \( \mu\text{Wcm}^{-1}\text{K}^{-2} \), which is much lower than that for the \( \text{Ta}_4\text{SiTe}_4 \) single whisker along the \( c \)-axis reported by Inohara et al. [30]. As mentioned above, the numerous grain boundaries among the whiskers and nano-sized pores are responsible for the low \( PF \) for the polycrystalline bulk. Upon doping P, a maximum \( PF \) value of 5.6 \( \mu\text{Wcm}^{-1}\text{K}^{-2} \) is achieved at 275 K for \( \text{Ta}_4\text{Si}_{0.995}\text{P}_{0.005}\text{Te}_4 \). The enhancement in \( PF \) for the doped samples can be attributed to the substantial improvement in \( \sigma \) and the well-maintained high \( S \). In addition, the \( PF \) values along the direction perpendicular to the pressure are much higher than those along the direction parallel to the pressure.

Since P has one more outermost electron than Si, doping P in \( \text{Ta}_4\text{SiTe}_4 \) should introduce extra electrons and increase the carrier concentration. This can be confirmed
by the measured Hall carrier concentration \( n_H \) along the direction perpendicular to the pressure. As shown in Fig. 3d, the \( n_H \) monotonically rises with increasing the dopant’s content. When \( x = 0.02 \), the \( n_H \) reaches \( 2.5 \times 10^{20} \text{ cm}^{-3} \) at 300 K, which is around three times that of the pristine Ta$_4$SiTe$_4$. The \( n_H \) increment is more obvious at low temperatures. Fig. S5 shows the calculated band structures of Ta$_4$SiTe$_4$ and Ta$_4$Si$_{0.875}$P$_{0.125}$Te$_4$. They are very alike near the conduction band maximum, except that the Fermi level in P-doped Ta$_4$SiTe$_4$ shifts into the conduction band. This indicates that doping P in Ta$_4$SiTe$_4$ scarcely modifies the band structure. Likewise, the existence of finite density of states at Fermi energy is responsible for the weak temperature dependence of \( n_H \) at low temperatures shown in Fig. 3d. Furthermore, the higher \( n_H \) is also responsible for the suppressed intrinsic excitation mentioned above because higher temperature is required to excite more minority carriers (holes) to compensate the majority carriers (electrons).

In thermoelectrics, single parabolic band (SPB) model is often used to analyze the electrical transports. However, as showing in Fig 3e and 3f, the data of pristine Ta$_4$SiTe$_4$ sample obviously deviate off the lines predicted by the SPB model at 200 K and 250 K. Thus, we use a two-band model considering both the contributions from electrons and holes to analyze the electrical transports of the Ta$_4$Si$_{1-x}$P$_x$Te$_4$ samples. The details about this two-band model derivation are described in Supporting Information. This is a rough model, but it can provide a simple understanding of how the TE properties of Ta$_4$SiTe$_4$ can be optimized by adjusting carrier concentrations. Based on this two-band model, the \( S \) and \( PF \) can be expressed as [34]

\[
S = S_e + \frac{k_b}{e} \sigma_e \left( \frac{\lambda_h + \lambda_e + 5 + \eta_g}{\sigma_e} \right),
\]  

(2)

and

\[
PF = PF_e \left[ 1 + \frac{\alpha_h}{\sigma_e} \left( 1 - 2 \frac{k_b}{e} \frac{\lambda_h + \lambda_e + 5 + \eta_g}{|S_e|} \right) \right],
\]  

(3)

where \( k_b \) is the Boltzmann constant, \( e \) is the elementary charge, \( \lambda_e (\lambda_h) \) represents the scattering parameter of electron (hole) with a value of -1/2 for acoustic-mode lattice scattering, \( \sigma_e (\sigma_h) \) represents the electron (hole) electrical conductivity, and \( S_e (PF_e) \) represents the Seebeck coefficient (power factor) calculated by the traditional SPB
model.

The carrier concentration dependences of $S$ and $PF$ calculated by using the two-band model are shown in Fig. 3e and 3f (solid lines). $S$ shows an inflection at low carrier concentration range, instead of monotonously increasing with decreasing the carrier concentration predicted by the SPB model (dashed lines). Therefore, a sharper peak of $PF$ is obtained in two-band model, which illustrates that narrow gap semiconductors like Ta$_4$SiTe$_4$ are more sensitive to the carrier concentration. In the high carrier concentration range, the lines predicted by the two-band model are overlapped with those predicted by the SPB model. This is caused by the weakened intrinsic excitation and negligible contribution from the minority carriers to the electrical transports. The experimental data of Ta$_4$Si$_{1-x}$P$_x$Te$_4$ at 200 K and 250 K roughly fall around these curves, proving that the two-band model is more suitable to analyze the electrical transport properties of the present narrow band gap Ta$_4$Si$_{1-x}$P$_x$Te$_4$ samples. The optimal carrier range for Ta$_4$Si$_{1-x}$P$_x$Te$_4$ is around $5 \times 10^{19}$ cm$^{-3}$ at 200 K and $8 \times 10^{19}$ cm$^{-3}$ at 250 K. The $n_H$ for the Ta$_4$Si$_{0.995}$P$_{0.005}$Te$_4$ is already close to these optimal values.

Fig. 4a shows the thermal conductivity ($\kappa$) for Ta$_4$Si$_{1-x}$P$_x$Te$_4$ ($x$=0, 0.005, 0.01, and 0.02) polycrystalline bulks measured along the directions parallel and perpendicular to the pressure. The $\kappa$ values along the direction perpendicular to the pressure are much higher than those along the direction parallel to the pressure. Likewise, the $\kappa$ of all samples are below 1.2 Wm$^{-1}$K$^{-1}$ in the entire measured temperature. Below 70 K, the $\kappa$ quickly increases with increasing temperature till reaching a plateau. Around 250 K, the pristine Ta$_4$SiTe$_4$ shows an abrupt $\kappa$ increment again. Upon doping P, the magnitude of $\kappa$ increment above 250 K is gradually weakened and the corresponding temperature is shifted to the higher temperature. Alike the $S$ variations shown in Fig. 3b, these abrupt $\kappa$ increments above 250 K can be also attributed to the intrinsic excitation. The generation and recombination processes of thermally excited electron-hole pairs can conduct part energy from the hot end to the cold end (named as bipolar thermal conductivity), which would also contribute to the total $\kappa$. Doping P can suppress the intrinsic excitation and then shift its occurring
temperature to higher temperatures, being consistent with the scenario shown in Fig. 4a.

The carrier thermal conductivity ($\kappa_c$) can be calculated by the equation $\kappa_c = L\sigma T$, where $L$ is Lorenz constant. Below the intrinsic excitation temperature, $L$ can be estimated by single parabolic band model, with the results shown in Fig. S6a. By subtracting the carrier thermal conductivity $\kappa_c$ from the measured $\kappa$, the $\kappa_L$ for Ta$_4$Si$_{1-x}$P$_x$Te$_4$ samples were calculated and plotted in Fig. S6b. Herein the data above 200 K are not included due to the appearance of extra bipolar thermal conductivity. Since the $\sigma$ of all Ta$_4$Si$_{1-x}$P$_x$Te$_4$ samples are relatively low, the measured $\kappa$ is mainly dominated by $\kappa_L$. The $\kappa_L$ slightly increases with increasing P-doping content, which might be related to the better crystallinity of P-doped Ta$_4$SiTe$_4$ samples (Fig. S2).

Beyond the nano-sized pores, the low $\kappa_L$ observed in the present Ta$_4$Si$_{1-x}$P$_x$Te$_4$ bulk samples should be originated from their intrinsic crystal structure and chemical bonding. In order to obtain a better understanding to the low $\kappa_L$, the phonon spectrum of Ta$_4$SiTe$_4$ was calculated and shown in Fig. 4b. The phonon dispersions in the $ab$-plane ($\Gamma$-$X$ and $\Gamma$-$Y$ directions) are much flatter than that along the $c$-axis ($\Gamma$-$Z$ direction). The average sound velocity ($v_{\text{avg}}$) values derived from the phonon dispersions are 1007 ms$^{-1}$, 1471 ms$^{-1}$, and 2304 ms$^{-1}$ along the $\Gamma$-$X$, $\Gamma$-$Y$, and $\Gamma$-$Z$ directions, respectively. This scenario is consistent with the weak van der Waals interaction among the [Si$_2$Ta$_8$Te$_8$]$_n$ chains but the strong covalent bond inside the [Si$_2$Ta$_8$Te$_8$]$_n$ chains inside the crystal structure of Ta$_4$SiTe$_4$. Such anisotropy is responsible for the different $\kappa$ values along different directions in the Ta$_4$Si$_{1-x}$P$_x$Te$_4$ bulks (Fig. 4a). In addition, the low-lying optical phonon modes with the starting energy of 0.58 THz are found in the calculated phonon spectrum. These low-lying optical phonon modes are related to the rotation of the neighboring [Si$_2$Ta$_8$Te$_8$]$_n$ chains along the reverse directions in the $ab$-plane, with the schematic shown in Fig. 4c. Based on the phonon dispersions, the heat capacity ($C_p$) of pristine Ta$_4$SiTe$_4$ was calculated. As shown in Fig. 4d, the calculated $C_p$ curve agrees well with the measured one. The low-lying optical phonon modes can explain why the calculated and measured $C_p/T$ vs. $T^2$ curves significantly deviate off the straight line at low
temperature, which is the ideal case considering only the electronic item and Debye item.

Besides the grain boundary scattering, point defect scattering, and phonon-phonon Umklapp scattering, the low-lying optical phonon modes would introduce additional phonon resonant scattering to interrupt phonon transports. In order to understand the respective contributions of different scattering mechanisms to thermal transports, the $\kappa_L$ of Ta$_4$SiTe$_4$ below 100 K along the directions parallel and perpendicular to the pressure are analyzed by the Debye-Callaway model [35, 36]

$$\kappa_L = \frac{k_b}{2\pi^2v_{avg}} \left( \frac{2\pi k_b T}{\hbar} \right)^3 \int_0^{\Theta_D/T} \tau_C \frac{x^4 e^x}{(e^x-1)^2} dx , \quad (4)$$

where $x = \hbar \omega/k_b T$ is the reduced phonon energy, $\hbar$ is the reduced plank constant, $\omega$ is the phonon frequency, and $\tau_C$ is phonon relaxation time. $\tau_C$ is given by [35, 36]

$$\tau_C^{-1} = \frac{v_{avg}}{i} + A\omega^4 + B\omega^2 T e^{\Theta_D/T} + \frac{C_1 \omega^2}{(\omega_{E1}^2 - \omega^2)^2} + \frac{C_2 \omega^2}{(\omega_{E2}^2 - \omega^2)^2} , \quad (5)$$

where the terms on the right of Eqn. 5 represent grain boundary scattering (B), point defect scattering (PD), phonon-phonon Umklapp scattering (U), and phonon resonant scattering (RES), respectively. $i$ is the grain size, $\Theta_D$ is Debye temperature, and $\omega_{Ei}$ ($i = 1, 2$) is the resonant frequency. $A$, $B$, and $C_i$ ($i = 1, 2$) are parameters related to point defect scattering, grain boundary scattering, and phonon resonant scattering, respectively. Based on the calculated phonon spectrum, the $v_{avg}$ values of 2304 ms$^{-1}$ (sound velocity along $\Gamma$-Z direction) and 1239 ms$^{-1}$ (the average sound velocity along $\Gamma$-X and $\Gamma$-Y directions) are used to fit the $\kappa_L$ along the directions perpendicular and parallel to the pressure, respectively. The $\Theta_D$ value is set as 125 K, which is derived from the cut-off frequency of longitudinal acoustic phonon branches (2.6 THz) of Ta$_4$SiTe$_4$. As shown in Fig. 4e and 4f, the fitted $\kappa_L$ curves agree well with the experimental data. The related fitting parameters are listed in Table S1. The fitted $\omega_E$ values are around 0.65 THz and 1.05 THz, corresponding to those shown in the phonon dispersions.

The fitting results shown in Fig. 4e and 4f suggest that the contribution on $\kappa_L$ reduction from grain boundary scattering along the direction parallel to the pressure is much higher than that along the direction perpendicular to the pressure. This is
reasonable because more interfaces along the direction parallel to the pressure will introduce stronger scattering to phonons, thereby yielding lower lattice thermal conductivity. In addition, the contribution on $\kappa_L$ reduction from phonon resonant scattering along the direction parallel to the pressure is also higher than the other direction. This is also reasonable since the low-lying optical phonon modes are mainly related to the rotation of the neighboring $[\text{Si}_2\text{Ta}_8\text{Te}_8]_n$ chains along the reverse directions in the $ab$-plane.

Based on the measured $S$, $\sigma$, and $\kappa$, the $zT = S^2\sigma T/\kappa$ of $\text{Ta}_4\text{Si}_{1-x}\text{P}_x\text{Te}_4$ ($x = 0, 0.005, 0.01$ and $0.02$) polycrystalline bulks are calculated. The $zT$ values along the direction parallel to the pressure are much lower than those along the other direction. Upon doping P at the Si-sites, the $zT$ is greatly enhanced. A peak $zT$ of 0.18 is obtained at 300 K for $\text{Ta}_4\text{Si}_{0.995}\text{P}_{0.005}\text{Te}_4$ along the direction perpendicular to the pressure. This value is about double that of pristine $\text{Ta}_4\text{SiTe}_4$. For comparison, Fig. 5b summarizes the $zT$ values of typical low-temperature TE materials. The $zT$ of present P-doped $\text{Ta}_4\text{SiTe}_4$ is much lower than the commercial $\text{Bi}_2\text{Te}_3$-based alloys, $\text{Mg}_3(\text{Bi},\text{Sb})_2$, and $\text{BiSb}$ [2, 19], but it is comparable with those of $\text{CePd}_3$, $\text{FeSi}$, and $\text{YbAl}_3$ [22, 25, 26]. Further increasing the $zT$ of $\text{Ta}_4\text{Si}_{1-x}\text{P}_x\text{Te}_4$ polycrystalline bulks can be expected if the whiskers inside the bulks can be highly oriented.

3. Conclusion

In this work, a series of P-doped $\text{Ta}_4\text{SiTe}_4$ polycrystalline bulks are prepared by the high-temperature synthesis and cold press method. Doping P at the Si-sites greatly increases the carrier concentration, yielding enhanced $\sigma$ and suppressed intrinsic excitation. A peak $PF$ of 5.6 $\mu\text{Wcm}^{-1}\text{K}^{-2}$ is obtained for $\text{Ta}_4\text{Si}_{0.995}\text{P}_{0.005}\text{Te}_4$, approaching the optimal value predicited by the two-band model. Low $\kappa$ values below 1.2 $\text{Wm}^{-1}\text{K}^{-1}$ have been observed for the $\text{Ta}_4\text{Si}_{1-x}\text{P}_x\text{Te}_4$ bulks. The existence of low-lying optical modes caused by the weak van der Waals interaction among the $[\text{Si}_2\text{Ta}_8\text{Te}_8]_n$ chains is found to be one of the main origins for the low lattice thermal conductivity observed in polycrystalline $\text{Ta}_4\text{SiTe}_4$ bulks. Consequently, $\text{Ta}_4\text{Si}_{0.995}\text{P}_{0.005}\text{Te}_4$ demonstrates a peak $zT$ of 0.18 at 300 K along the direction perpendicular to the pressure, which is about double that of pristine $\text{Ta}_4\text{SiTe}_4$. 
4. Method

4.1 Preparation

$\text{Ta}_4\text{Si}_{1.5-x}\text{P}_x\text{Te}_4$ ($x = 0$, 0.005, 0.01, and 0.02) polycrystalline bulks were prepared by the high-temperature synthesis and cold-press method. High purity Ta powders, Si powders, P chips, and Te shots were weighed with mole ratio of 4 : (1 - $x$) : $x$ : 4. These powders were firstly mixed and ground in a mortar. The mixtures were sealed in evacuated quartz tubes and then heated to 1323 K in 8 h, dwelling at this temperature for 72 h. The products were consolidated by cold-pressing under 300 MPa for 5 min. The relative densities of obtained bulk were about 88%. The bulks were then cut into specified shapes for characterization.

4.2 Characterizations

The phase purity of $\text{Ta}_4\text{Si}_{1.5-x}\text{P}_x\text{Te}_4$ ($x = 0$, 0.005, 0.01, and 0.02) samples were analyzed by the X-ray diffraction (XRD, D8 Advance) with Cu K$_\alpha$ radiation. The microstructures were observed by scanning electron microscope (SEM, ZEISS Supra 55) and Transmission electron microscopy (TEM, JEOL 2100F, Japan). Selected area electron diffraction (SAED) was used to confirm the crystal structure. The $\text{Ta}_4\text{SiTe}_4$-ethanol suspension was fabricated by ultrasonic dispersion. Then, the single $\text{Ta}_4\text{SiTe}_4$ whisker was selected from the suspension to perform the TEM characterization. The Seebeck coefficient ($S$), thermal conductivity ($\kappa$), electrical conductivity ($\sigma$), and Hall coefficient ($R_H$) were measured on a Physical Property Measurement System (PPMS, Quantum Designs) from 5 K to 350 K. The cross-section area of the samples was around 5 mm $\times$ 2 mm and the length was around 2 mm. Fig. S7 shows that the $\kappa$ for $\text{Ta}_4\text{SiTe}_4$ measured by PPMS is comparable with that measured by the laser flash method (LFA 457, Netzsch). Hall coefficients ($R_H$) were measured by sweeping the magnetic field up to 3 T in both positive and negative directions. Hall carrier concentration ($n_H$) and the Hall mobility ($\mu$) were estimated by $n_H = 1/eR_H$ and $\mu = \sigma R_H$, respectively. All TE property characterizations were performed in the direction perpendicular to the cold-pressing direction.

4.3 Density functional theory calculations
The phonon spectrum of $\text{Ta}_4\text{SiTe}_4$ was calculated by the TDEP method [37]. Ab initio molecular dynamic simulation with an NVT ensemble at 300 K was performed by VASP [38]. A $1\times1\times2$ supercell containing 72 atoms was employed. The PBE functional [39] was used in the simulation with DFT-D3 method describing the van der Waals interaction between the chains [40]. Projector augmented wave (PAW) potentials were used to describe the core–valence interaction [41]. The $\Gamma$ point and a cutoff energy of 300 eV were used. The simulation was run for 80 ps with a time step of 2 fs. The force constants were extracted from the simulation of the last 50 ps. The heat capacity and sound velocity were derived from the phonon calculations. The band structure of the doped $\text{Ta}_4\text{SiTe}_4$ was calculated by the PBE functional [39] with the spin-orbital coupling effect included. We used a $1\times1\times2$ supercell and replaced one Si atom by a P atom. The structure was allowed to relax until the maximal forces were less than 0.01 eV/Å. To make a comparison, the band structure of the undoped structure was calculated employing the $1\times1\times2$ supercell. A $4\times2\times4$ k-point mesh was used in the electronic calculations.

Credit authorship contribution statement

Qing Xu: Investigation, Data Curation, Writing- Original draft, Writing- Review & Editing, Visualization, Validation. Chen Ming: Conceptualization, Investigation, Software, Writing - review & editing. Tong Xing: Writing- Original draft, Writing- Review & Editing, Visualization. Pengfei Qiu: Conceptualization, Methodology, Writing- Original draft, Writing- Review & Editing, Validation, Supervision, Funding acquisition. Jie Xiao: Data Curation. Xun Shi: Writing- Review & Editing, Supervision, Funding acquisition. Lidong Chen: Writing- Review & Editing, Supervision, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this
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References


**Fig. 1.** Crystal structure of Ta₄SiTe₄. The unit cell is indicated by broken lines. The right panel shows the magnification of one [Si₂Ta₈Te₈]ₙ chain.
Fig. 2. (a) Room-temperature powder X-ray diffraction patterns for the $Ta_4Si_{1-x}P_xTe_4$ ($x=0$, 0.005, 0.01, and 0.02). (b-d) Microstructures of as-prepared $Ta_4SiTe_4$ whiskers characterized by SEM and TEM. The inset in (c) shows the selected area electron diffraction pattern performed on the $Ta_4SiTe_4$ whisker. The right panel in (c) is a zoomed image of the square region. (d) SEM images and (e) EDS elemental mapping of the cold-pressed $Ta_4Si_{0.98}P_{0.02}Te_4$. The inset in (d) shows the microstructure of the bulk with high magnification.
Fig. 3. Temperature dependences of (a) electrical conductivity ($\sigma$), (b) Seebeck coefficient ($S$), and (c) power factor ($PF$) for Ta$_4$Si$_{1-x}$P$_x$Te$_4$ ($x$=0, 0.005, 0.01, and 0.02) polycrystalline bulks measured along the directions perpendicular ($\perp$) and parallel ($\parallel$) to the pressure. (d) Hall carrier concentration ($n_H$) measured along the directions perpendicular to the pressure. Carrier concentration dependences of (e) $S$ and (f) $PF$ for Ta$_4$Si$_{1-x}$P$_x$Te$_4$ at 200K and 250K. The blue triangles and red squares are experimental data. The solid lines are calculated using two-band model considering the contribution from the minority carriers. The dashed lines are calculated using SPB model considering only one kind of carrier.
Fig. 4. (a) Temperature dependence of thermal conductivity ($\kappa$) for Ta$_4$Si$_{1-x}$P$_x$Te$_4$ ($x=0$, 0.005, 0.01, and 0.02) measured along the directions perpendicular (⊥) and parallel (∥) to the pressure. (b) Calculated phonon spectrum (left picture) and partial phonon density of states (right picture) for Ta$_4$SiTe$_4$. (c) Sketch map of [Si$_2$Ta$_8$Te$_8$]$_n$ chain motion in the $ab$-plane. The arrows represent the rotation directions. (d) Measured and calculated $C_p$ versus $T$ for Ta$_4$SiTe$_4$. Lattice thermal conductivity ($\kappa_L$) for pristine Ta$_4$SiTe$_4$ below 100 K along the directions (e) perpendicular and (f) parallel to the pressure. The solid lines represent the contribution of different phonon scattering mechanisms to the lattice thermal conductivity, including the Umklapp process scattering (U), grain boundary scattering (B), point defect scattering (PD), and phonon resonant scattering (RES).
Fig. 5. (a) Figure of merit $zT$ versus temperature for $\text{Ta}_4\text{Si}_{1-x}\text{P}_x\text{Te}_4$ ($x=0$, 0.005, 0.01, and 0.02) polycrystalline bulks along the directions perpendicular ($\perp$) and parallel ($//$) to the pressure. (b) Comparison of $zT$ among typical low-temperature TE materials [2, 19, 22, 25, 26].
Highlights

- A series of phosphorus-doped Ta₄SiTe₄ polycrystalline bulks are prepared.
- Doping phosphorus in Ta₄SiTe₄ can enhance the electrical conductivity and power factor.
- Ta₄SiTe₄ polycrystalline bulks possess low lattice thermal conductivity below 1 Wm⁻¹K⁻¹.
- The origins for the low lattice thermal conductivity in Ta₄SiTe₄ bulks are revealed.
Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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