XTe (X = Ge, Sn, Pb) Monolayers: Promising Thermoelectric Materials with Ultralow Lattice Thermal Conductivity and High-power Factor

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Abstract

Motivated by the superior thermoelectric performance of two-dimensional (2D) materials, in this work, we investigate the thermoelectric properties of XTe monolayers (X= Ge, Sn, Pb) by using the first-principles calculation and the Boltzmann transport theory. The calculated results show ultra-low lattice thermal conductivities (κ_L) of XTe (X= Ge, Sn, Pb) as 1.3, 3.6 and 4.3 W/mK at 300 K, respectively. Phonon analyses show that the ultralow κ_L stem from the coexistence of resonant bonding and weak bonding in XTe monolayers, as well as the avoided crossing between the longitudinal acoustic (LA) phonons and the low lying optical (LLO) branches in the Γ -X and Y- Γ high-symmetry paths. In addition, the band structure with “pudding-mold” type results in a high power factor for XTe monolayers. These features lead to high figure of merit (ZT) of XTe monolayers, which can reach more than 1.58 in the case of n-type doping concentration of 10^{19} - 10^{20} cm⁻³ at 900 K, and the GeTe monolayer bears the largest ZT of 4.23. The obtained ZT of XTe monolayers are larger than their bulk counterparts, and even outweigh that of other well-known 2D thermoelectric materials. Therefore, we propose XTe (especially GeTe) monolayers as promising candidates for high-efficient thermoelectric materials.

Keywords: Theoretical simulations; Thermoelectric; Lattice thermal conductivities; Power factor.

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1. Introduction

Nowadays, the energy crisis is one of the greatest challenges facing mankind,^[1] and numerous efforts have been made to develop novel materials for efficient energy conversion and storage.^[2] Notably, thermoelectric materials, which can convert heat into electricity directly without any emissions,^[3] have been a focus of attention as stable, sustainable and inexpensive materials.^[4] The efficiency of thermoelectric material is characterized by the dimensionless figure of merit $ZT = S^2\sigma T/(\kappa_L + \kappa_e)$,^[5] where S , σ , T , κ_L , and κ_e are the Seebeck coefficient, electrical conductivity, absolute temperature, lattice thermal conductivity and electronic thermal coefficient,

electrical conductivity, absolute temperature, lattice thermal conductivity and electronic thermal conductivity, respectively.^[6] Apparently, the high thermoelectric efficiency can be achieved by increasing the power factor ($PF = S^2\sigma$) together with suppressing the sum of thermal conductivity ($\kappa_L + \kappa_e$).^[7] Interestingly, two-dimensional (2D) materials have the favored phonon scattering and stronger electronic transport comparing with their bulks,^[8] resulting in better thermoelectric behaviors.^[9] Using 2D materials in thermoelectric applications therefore is an ideal method to improve the thermoelectric conversion efficiency.^[10]

Bulk XTe (X = Ge, Sn and Pb) have long been studied as thermoelectric materials in the intermediate temperature range.^[11] The three materials have small Seebeck coefficients due to very high carrier density caused by intrinsic X vacancies.^[12] This means that good thermoelectric performance of bulk XTe can only be achieved by carrier and phonon engineering.^[13] For example, by optimizing the p-type doping experimentally, GeTe show the biggest ZT at certain carrier density among bulk XTe, which is up to 1.8.^[13] In addition, bulk PbTe has been researched most extensively in experiments and theory,^[14] but the toxic nature of Pb hinders

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PbTe-based applications into practical level.^[15] Thus, pure bulk XTe have great difficulty in being the state-of-art thermoelectric materials.^[16] On the other hand, the global minimum crystal structures of 2D GeTe, SnTe, and PbTe are first determined by combining evolutionary algorithms with density functional theory,^[17] and it has been reported that monolayer XTe can be experimentally obtained via top-down mechanical or liquid phase exfoliation approach because of the layered crystal structures of bulk XTe.^[18] The obtained 2D SnTe is a ferroelectric material possessing stable in-plane spontaneous polarization with a high transition temperature.^[19] The calculated high ZT of monolayer SnTe show that it has better intrinsic thermoelectric behaviors than its bulk counterpart.^[20]

Fig. 1. Top (a) and side (c) views of GeTe and SnTe monolayers. Top (b) and side (d) views of PbTe monolayer.

Table 1. The optimized lattice constants (a and b), bandgaps using HSE06 with and without SOC of XTe monolayers.

	Lattice constants (Å)		Bandgaps (eV)	
	a	b	With SOC	Without SOC
GeTe	4.24	4.38	1.08	1.16
SnTe	4.55	4.56	0.89	1.04
PbTe	4.64	4.64	1.01	1.74

Motivated by the excellent thermoelectric performance of 2D materials, we systematically and comparatively studied the intrinsic thermoelectric properties of XTe monolayers, by combining the first-principles calculation and the Boltzmann transport theory. Our results show that XTe monolayers has higher ZT , compared with their bulk counterparts, which suggests that reducing the dimensions of bulk XTe is efficient to achieve better thermoelectric efficiency. To further understand the origin of high thermoelectric conversion efficiency of XTe monolayers, we analyzed a series of related parameters, including the structure, phonon dispersion, lattice thermal conductivity κ_L , the specific heat capacity C , group velocity, phonon scattering rates τ^{-1} , Gruneisen parameters γ , cumulative κ_L , Seebeck coefficient S , electrical conductivity δ , and electronic thermal conductivity k_e . The physical mechanism of the ultralow κ_L of XTe monolayers are then revealed and discussed.

Fig. 2 Phonon dispersions (a) and band structures (b) of XTe monolayers. Red and blue lines express the band structures using HSE06 with and without SOC, respectively. The “pudding mold” in band structures is marked in purple wire frame.

Fig. 3 (a) Lattice thermal conductivity κ_L as a function of temperature for XTe monolayers in the X and Y directions. (b) Frequency resolved phonon group velocity v of the three acoustic branches (ZA, TA, and LA) in the XTe monolayers.

2. Computational details

Density functional theory (DFT)^[21] calculations are carried out by means of the Vienna ab initio simulation (VASP) package^[22] with projector-augmented wave (PAW) potentials.^[23] The exchange-correlation functional is treated by using generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerof (PBE) formulation.^[24] In all calculations, the convergence criteria for the electronic and ionic relaxations are set to 10^{-7} eV and 10^{-3} eV/Å, respectively. K-mesh of $25 \times 25 \times 1$ is used in the Brillouin zone (BZ). To obtain the electronic structures accurately, the Heyd-Scuseria-Ernzerhof (HSE06) hybrid functional is utilized.^[25] Additionally, the spin-orbital coupling effect (SOC) is also considered separately due to the existence of rather heavy elements (Sn, Pb) in our calculations.^[26] A vacuum length of 20 Å is adopted to eliminate the interactions between neighboring layers.^[27] ab initio molecular dynamics (AIMD) simulations^[28] were performed by using the canonical ensemble (NVT)^[29] at 900 K.^[20]

We compute the second-order (harmonic) interatomic force constants (IFCs) using the Phonopy package^[30] and the third-order (anharmonic) IFCs using the thirdorder.py code.^[31] $5 \times 5 \times 1$ supercells and $4 \times 4 \times 1$ supercells with $3 \times 3 \times 1$ k -mesh are adopted for the calculations of second-order harmonic and third-order anharmonic IFCs, respectively. For the anharmonic IFCs calculations, a cutoff radius (r_{cutoff}) of more than 6.0 Å is used. Based on the harmonic and anharmonic IFCs, the κ_L is calculated by solving the phonon Boltzmann transport equation as implemented in the ShengBTE code.^[32] For the convergence of intrinsic κ_L , the phonon sampling k -mesh in the BZ has been tested and we adopted a dense phonon

q-grid of $51 \times 51 \times 1$. The electronic transport parameters are calculated by using the semi-classical Boltzmann theory within the relaxation time approximation with the BoltzTrap2 code,^[33] and a denser $48 \times 48 \times 1$ k -point mesh is used for this calculation. Moreover, 6.10, 6.36 and 6.75 Å are used as the nominal thickness of GeTe, SnTe and PbTe monolayers, respectively.

3. Results and discussion

3.1 Crystal structures, stability and electronic properties

XTe monolayers can be peeled from the corresponding bulk structures through experimental methods (see Fig. S1(a-b)), such as top-down mechanical, liquid phase exfoliation approach, etc. To accurately assess the exfoliation feasibility of XTe monolayers, we calculate the cleavage energies of XTe monolayers, and these cleavage energies (0.12 to 0.19 Jm⁻²) are lower than that of graphene (0.06 to 0.33 Jm⁻²), as displayed in Fig. S1(c). The structural optimizations (see Figs. 1(a-d)) show that monolayers GeTe and SnTe retain rectangular structures, while PbTe bears a square structure. As listed in Table I, the optimized lattice constants of XTe are in good agreement with previous results within a difference of 1%.^[17]

Fig. 4 (a) Anharmonic scattering rates τ_{ph}^{-1} and (b) Gruneisen parameters γ of XTe monolayers.

The detailed bonding lengths and angles of the optimized XTe monolayers are plotted in Fig. S2. It is interesting to note that, in one monolayer structure, there is a significant difference in the X-Te bonding length, which can induce different types of bonding. The analysis based on Figs. S3 and S4 in the supplemental materials show two types of Sn-Te bonding coexist, one is strong bonding (resonant bonding) and the other is weak bonding.^[20] Fig. 2(a) demonstrates the phonon dispersion relation of XTe monolayers. It can be inferred that the XTe monolayers are dynamically stable since no imaginary frequency occurs in the phonon dispersions.^[34] It is also worth noting that the highest vibration frequency is less than 6 THz in the studied XTe monolayers, which can result in a small vibration range of acoustic branch and a lower phonon group velocity.

According to Fig. 2(a), the phonon dispersions of XTe monolayers display avoided crossing between the longitudinal acoustic (LA) phonons and low lying optical (LLO) branches

in the Γ -X and Y- Γ high-symmetry paths, which is an indicator of low κ_L .^[35] The avoided crossing shares the strong coupling between phonons, and the width of the gap of the avoided crossing stands for the strength of the coupling.^[35] It is obvious that the order of coupling strength is GeTe > SnTe > PbTe, implying that GeTe monolayer may possess lower κ_L than the others. In addition, the AIMD simulations display that the amplitude and period of temperature fluctuation remain largely unchanged in the whole MD process. XTe monolayers remain stable after 4 ps at elevated temperatures along with unchanged structure and little change of bonding length and angle comparing with the corresponding primitive cell (see Fig. S5-S6), indicating that XTe monolayers are thermally stable. We also obtained the linear elastic constants by using the finite distortion method, as listed in Table S1. According to Born-Huang criteria, the elastic constants of XTe monolayers satisfy $C_{11}C_{12} - C_{12}^2 > 0$ and $C_{66} > 0$, confirming that they are mechanically stable. To summarize, the dynamical, thermal and mechanical stability suggest the possibility to fabricate XTe monolayers experimentally.

To study the electronic properties of XTe monolayers, we calculated the band structures using HSE06 with and without SOC, as shown in Fig. 2(b). One can see that XTe monolayers are semiconducting with an indirect band gap, and the detailed bandgaps are listed in Table I, which are in good agreement with previous reports.^[17] Moreover, the SOC effect has an important influence on the bandgaps of XTe monolayers, causing that the conduction bands of XTe under HSE06+SOC are closer to the Fermi level than the corresponding bands of XTe under HSE06, especially for PbTe. This feature indicates that the electrical conductivity increases under the influence of SOC, which further increases the ZT value. Meanwhile, the XTe monolayers possess band structures with a typical shape of “pudding mold” near the band minima in conduction bands and the band maxima in valence bands.^[36] This feature leads to an orbital degeneracy (multiple carrier pockets of a band in the Brillouin zone) and is beneficial for both Seebeck coefficients and electrical conductivities.^[37]

3.2 Lattice thermal conductivity of XTe monolayers

Based on the 2nd and 3rd IFCs, the κ_L of XTe monolayers can be calculated by solving the phonon Boltzmann transport equation (PBTE),^[38] as plotted in Fig. 3(a). The κ_L of XTe monolayers decreases as T increases, following a $1/T$ dependence. This phenomenon can be explained by the intrinsic phonon-phonon scattering enhancement with increasing T in crystalline materials.^[39] As expected, GeTe monolayer has the lowest κ_L among the three materials, and the κ_L of all the XTe monolayers are comparable with that of the 2D SnSe (3.0 W/mK)^[40] at 300 K. We calculated the cumulative κ_L of XTe monolayers (see Fig. S7), and it can be seen that κ_L is dominated by phonons with low frequencies (<1.5 THz for GeTe, <3.7 THz for SnTe and <4.3 THz for PbTe). More evidence can be found in Table S2, which reveals that κ_L of XTe monolayers mainly come from the acoustic

phonons, and the contribution from the optical phonons is less than 30%.

Thermal conductivity is closely related to the specific heat capacity C , group velocities v and phonon relaxation time τ_{ph} .^[41] To further identify the origin of the ultralow κ_L in the three materials, we analyzed the corresponding C , v and τ_{ph}^{-1} . The detailed expressions for C , v_i and τ_{ph}^{-1} can be found in the supplemental materials. The C of monolayers GeTe, SnTe and PbTe are 3.84×10^5 , 3.87×10^5 and 4.16×10^5 Jm⁻³ K⁻¹ at 300 K, respectively, which are comparable with that of 2D KAgSe with a high ZT (2.08),^[36] indicating that XTe monolayers have the desired C for 2D materials with high thermoelectric performance. The ZA branch of the XTe monolayers is a quadratic phonon branch with frequencies depending on the wave vectors.^[41] As exhibited in Fig. 3(b), for XTe monolayers, the group velocity v of the ZA branch is smaller than that of the LA and TA branches due to the nonlinear dispersion of the ZA branch near the Γ point. Moreover, the group velocities v share similar feature of distribution and their maximums are about 4 km s⁻¹, exhibiting that the XTe monolayers have low v and advantages in inducing low κ_L comparing with the well-known 2D thermoelectric materials such as KAgSe, Pb₂Se₃, α -CuSCN, and SnSe, et al., as listed Table S3. Then, we analyze the anharmonic scattering rate τ_{ph}^{-1} , which is reciprocal to the phonon relaxation time τ_{ph} . High scattering rates indicate strong phonon scattering, which lowers τ_{ph} , and thus decreases the lattice thermal conductivity. As shown in Fig. 4(a), XTe monolayers exhibit high three-phonon scattering rates and the scattering rate of GeTe is larger than that of the other two structures, resulting in the lowest τ_{ph} in GeTe. To quantitatively measure the anharmonicity of XTe monolayers, the mode Grüneisen parameters (γ) are calculated. A large Grüneisen parameter indicates strong anharmonicity in a system. Fig. 4(b) reveals that the acoustic and low-frequency optical phonon branches (0-5 THz) of XTe monolayers both own huge $|\gamma|$, suggesting that the low-frequency acoustic phonons are able to strongly couple with optical phonons. We also calculate the average $|\gamma|$ of XTe monolayers, as listed in Table S3. The corresponding results are 3.21, 2.67 and 2.65, respectively, which are much larger than that of other 2D materials with low thermal conductivity such as KAgSe,^[36] Pb₂Se₃,^[37] SnSe,^[42] α - and β -CuSCN,^[35] which further corroborates the strong anharmonicity and low τ_{ph} in XTe monolayers. The desired C , low v , large $|\gamma|$ and low τ_{ph} therefore can be explained based on the fact that the coexistence of weak bonding and resonant bonding in XTe monolayers structures, ensuring that XTe monolayers exhibit ultralow κ_L .

3.3 Electronic transport properties and figure of merit (ZT)

In addition to ultralow κ_L , excellent thermoelectric materials also need to have high thermoelectric power (Seebeck coefficient S), good electronic transport properties (electrical conductivity σ) and low thermal conductivity contributed by electrons (κ_e).^[43] Fig. 5(a-c) and Fig. S8-S9 show S , electronic

Fig. 5 (a-b) The Seebeck coefficient S , (c-d) the electronic conductivity with respect to the scattering time σ/τ_e , and (e-f) the power factor ($PF = S^2\sigma$) of monolayer GeTe along the X and Y directions as a function of the chemical potential (μ) at different temperatures.

conductivity with respect to the relaxation time σ/τ_e , and PF/τ_e of XTe monolayers as a function of chemical potential (μ) at different temperatures ($T = 300, 500, 700$ and 900 K). To be consistent with the experiment, we take the electronic properties of XTe monolayers under the effect of SOC to calculate the thermoelectric properties. The negative μ represent electron (p-type) doping, and the positive μ means hole (n-type) doping. Similar to κ_L (see Fig. 3(a)), the electronic transport properties of monolayers GeTe, SnTe and PbTe are anisotropic, indistinct anisotropic and isotropic, respectively. Such difference originates from the different electronic energy bands along the X (G-X in high symmetry point path) and Y (G-Y in high symmetry point path) directions presented in Fig. 2(b). It also can be caused by the structural symmetry difference of XTe monolayers.

The peak values of S for XTe monolayers at 300, 500, 700 and 900 K are in the range of 0.53-1.61 mV K⁻¹ (see Table S4), which are larger than that of these high-performance thermoelectric materials Pb₂Se₃ (0.42-0.50 mV K⁻¹ at 300-900 K)^[37] and SnSe (0.53 mV K⁻¹ at 300 K, 0.56 mV K⁻¹ at 600 K and 0.40 mV K⁻¹ at 800 K).^[42] This feature implies that the XTe monolayers are likely to have excellent thermoelectric conversion performance. Moreover, as T increases, the σ/τ_e around 0 eV enhances slightly since the electrons obey the Fermi-Dirac distribution (see red dotted frame in Fig. 5(b)).^[36] It is important to note that, S decreases with increasing carrier doping concentration, while σ/τ_e increases. Thus, we should compute the $PF/\tau_e = S^2\sigma/\tau_e$ based on S and σ/τ_e in order to achieve the maximum ZT. As plotted in Fig. 5(c), the PF/τ_e peak appears at the chemical potential where both S and σ/τ_e are not at their maximum values. The maximum PF/τ_e

increases with increasing T , as temperature increase the number of carriers at the high orbital degeneracy.^[36] The variation of S against μ is basically the same for the electron and hole doping. The smaller electron effective mass causes a higher electron mobility than that of holes in the XTe monolayers,^[20] which leads to smaller σ/τ_e of electrons than that of holes at the same $|\mu|$. Similar to σ/τ_e , PF/τ_e of p-type XTe monolayers is much higher than its n-type counterpart. It is worth noting that GeTe has the biggest PF/τ_e and the lowest κ_L among the three structures, indicating that p-type monolayers GeTe may have the highest thermoelectric conversion efficiency.

To assess to the thermoelectric conversion efficiency, we now derive the power factor from the $PF\sigma/\tau_e$ and calculate the ZT. τ_e can be estimated based on the deformation potential (DP) theory initially proposed by Bardeen and Shockley,^[37] in which only the coupling between the free carrier and longitudinal acoustic phonon modes is considered. More accurate calculation of τ_e needs to consider the effects of other phonon modes and ionized impurities with screening.^[37] Recent studies show that, to agree with the experiment quantitatively, the constant relaxation time approximation should introduce some deviations in the calculation of the electrical transport properties and Lorenz ratio. Moreover, Ref.^[37] also shows that the electron relaxation time should be temperature-dependent. Smaller constant relaxation time should be used at higher temperatures. As a conservative estimate, here we set τ_e to 10 fs at each temperature according to Ref.^[31] in which τ_e is in the range of 10-300 fs in heavily doped 2D semiconductors. Then, the maximum PF of XTe monolayers are calculated, as listed in Table S4. The PF of XTe monolayers at both 300 and 900

K are comparable to that of some promising thermoelectric materials with high PF , such as Pb_2Se_3 ($1.61 \text{ mW m}^{-1} \text{ K}^{-2}$ at 300K and $2.97 \text{ mW m}^{-1} \text{ K}^{-2}$ at 900 K)^[37] and $SnSe$ ($3.12 \text{ mW m}^{-1} \text{ K}^{-2}$ at 300 K and $9.83 \text{ mW m}^{-1} \text{ K}^{-2}$ at 900 K),^[44] suggesting that monolayers also have high PF .

Table 2. Calculated maximum ZT of GeTe, SnTe and PbTe monolayers at 900 K. ZT of some well-known 2D thermoelectric materials are also included for comparison.

Materials	$ZT_{\max}$	Materials	$ZT_{\max}$
Bulk GeTe ^a	0.8	Monolayer InP_3 ^d	2.1
Bulk SnTe ^a	0.4	Monolayer $\delta\text{-Cu}_2\text{Se}$ ^e	1.3
Bulk PbTe ^a	1.7	Monolayer GeTe (this work)	4.23
Bulk Bi_2Te_3 ^b	0.8	Monolayer SnTe (this work)	1.87
Bulk SnSe ^c	2.0	Monolayer PbTe (this work)	1.58

^a Ref¹¹, ^b Ref⁴⁶, ^c Ref⁴², ^d Ref⁴¹, ^e Ref³¹.

Fig. 6 (a) Calculated electronic conductivity κ_e and (b) figure of merit (ZT) as a function of chemical potential μ at different temperatures for monolayer GeTe along the X and Y directions.

Before evaluating the ZT of XTe monolayers, we explore κ_e by using the obtained σ and the Wiedemann-Franz law: $\kappa_e = L\sigma T$, where $L = 1.5 \times 10^{-8} \text{ W } \Omega \text{ K}^{-1}$ is the Lorenz number.^[45] The obtained results show that κ_e increases with temperature, as demonstrated in Fig. 6(a) and Figs. S6-S7. Based on the PF , κ_L , and κ_e presented above, the ZT of XTe monolayers can be estimated. Fig. 6(c-d) and Figs. S6-S7 show that monolayers GeTe and SnTe have anisotropic ZT , while that of PbTe is isotropic. It can be seen that the ZT of XTe monolayers reaches the maximum up to 1.58 in the case of 0.5-0.6 eV (n-type doping concentration of 10^{19} - 10^{20} cm^{-3}) at 900 K. More importantly, the ZT of GeTe is the highest among the three materials. We also made a comparison about ZT , as listed in

Table 2. Whether it is a bulk material or a 2D thermoelectric material, XTe has competitive ZT , suggesting that XTe monolayers, (especially GeTe) are very promising candidates for thermoelectric applications.

4. Conclusions

In summary, we study the crystal structures, electronic properties, phonon and electronic transport properties of XTe monolayers based on the density functional theory and Boltzmann transport theory. Our results demonstrate that the XTe monolayers are dynamically, thermally and mechanically stable, suggesting that fabricating XTe monolayers is feasible in the experiment. Additionally, the XTe monolayers with low Young's modulus and shear modulus have weak bonding and resonant bonding, which slows down the phonon transport and result in ultralow κ_L . Based on the formula $\kappa_L = \frac{1}{V} \sum_i C_i v_i^2 \tau_i^{ph}$, we further analyzed the underlying physics for the ultralow κ_L . The PF of XTe monolayers at 900 K are much larger than that of conventional thermoelectric materials, such as Pb_2Se_3 , $SnSe$ and so on. The ZT of XTe monolayers at different temperatures were estimated and that of monolayers GeTe can reach 4.23. These results qualify XTe monolayers, especially GeTe monolayer, as promising candidates for building outstanding TE devices.

Associated content

Supplemental materials

The detailed expressions for C , v_i and τ_i in ShengBTE; views of XTe bulk; Cleavage energies; views of XTe monolayers; the total and partial density of states; ELF; AIMD calculations; young' modulus; shear modulus; elastic constants; cumulative κ_L ; contribution rates to κ_L ; attice thermal conductivity κ_L , specific heat capacity C , maximum value of group velocities $v_{\max}$ and average Grüneisen parameters $|\gamma|$; Seebeck coefficient S , the transport coefficients; power factor PF ; κ_e and figure of merit (ZT).

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Supporting information

Not applicable.

Conflict of interest

There are no conflicts to declare.

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