Strong interlayer coupling in two-dimensional PbSe with high thermoelectric performance

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Abstract
It was generally believed that weak van der Waals interactions exist between neighboring layers in the two-dimensional group-IV chalcogenides. Using PbSe as a prototypical example, we find additional strong coupling between the Pb–Pb layers, as evidenced by detailed analysis of the differential charge density plot. The coupling is covalent-like and can be fine-tuned to obviously reduce the phonon thermal conductivity but slightly change the electronic transport of PbSe layer. As a consequence, a maximum $ZT$ value of 2.5 can be realized at 900 K for the $p$-type system. Our work also offers an effective and feasible design strategy to enhance the thermoelectric performance of similar layered structures.

Keywords: thermoelectric materials, first-principles, Boltzmann transport theory, interlayer coupling, group-IV chalcogenides, van der Waals interactions

1. Introduction
Thermoelectric (TE) materials can directly convert heat into electrical energy without generating other by-products, which have attracted much attention from science community for their environmentally friendly advantages [1]. Usually, the performance of a TE material can be described by the dimensionless figure-of-merit $ZT = S^2\sigma T/(\kappa_e + \kappa_l)$ [2–4], where $S$ is the Seebeck coefficient, $\sigma$ is the electrical conductivity, $T$ is the absolute temperature, $\kappa_e$ is the electronic thermal conductivity, and $\kappa_l$ is the lattice thermal conductivity [5, 6]. An ideal TE material must possess high power factor ($PF = S^2\sigma$) and low thermal conductivity ($\kappa = \kappa_e + \kappa_l$) or at least one of them [7, 8]. However, it is usually difficult to greatly enhance the $ZT$ value because these transport coefficients are coupled with each other [9–12]. For example, the Seebeck coefficient decreases with increasing carrier concentration while the electrical conductivity is reversed. It is therefore urgently desirable to find new effective approaches to improve power factor and/or reduce thermal conductivity. For example, it was suggested that using low-dimensional systems or nanostructures could be an appropriate way to enhance the TE performance due to the quantum confinement effect and phonon-boundary scattering [13, 14].

Since the discovery of graphene in 2004 [15], many other two-dimensional (2D) materials and their derivatives have been intensively studied owing to their unique physical properties and promising application potentials. In particular, some of them are found to exhibit good TE performance such as bismuth-based layered materials [16, 17], 2D transition metal dichalcogenides (TMDs) [18–20], indium telluride monolayer [21] and phosphorene [22]. Recently, a special phosphorene-like GeTe monolayer was identified in the GeTe/Sb$_2$Te$_3$ superlattice [23–25] and hexagonal crystal Ge$_4$Se$_3$Te [26]. It is thus reasonable to expect that a series of 2D layered group-IV chalcogenides $AX$ ($A$ = Si, Ge, Sn, Pb and $X$ = Se, Te) with a unique stacking order of $X$–$A$–$A$–$X$ could be exfoliated form their bulk counterparts. Indeed, Sa et al [27] and Liu et al [28] demonstrated the thermodynamic stability of such layered unit via first-principles calculations. As bulk PbTe is a traditional...
Moreover, such novel phosphorene-like monolayer phase of PbSe is 50-fold richer than that of Te in the Earth [29]. In this work, we focus on the PbSe since it is nature to ask if these layered structures also exhibit intrinsically lower thermal conductivity, as previously found for the β-SnSe layer [30]. In this work, we investigate the electronic, phonon and thermoelectric transport properties of PbSe layer by combining first-principles calculations with Boltzmann theory. It is found that the 2D PbSe exhibits a maximum $p$-type $ZT$ value of 2.2 at 900 K. Interestingly, we find certain strong coupling between the neighboring Pb layers in addition to the weak van der Waals (vdW) interactions, which could be used to fine tune the thermoelectric performance of such layered structure.

2. Computational method

Within the framework of density functional theory (DFT) [31, 32], the electronic properties of the PbSe layer are calculated using the projector augmented wave (PAW) [33] method, as implemented in the Vienna $ab$ initio simulation package (VASP) [34]. The exchange-correlation energy is described by the Perdew–Burke–Ernzerhof (PBE) [35] functional under the generalized gradient approximation (GGA) [36, 37]. The energy cutoff is set to 500 eV and the Brillouin zone is sampled with a $15 \times 15 \times 1$ Monkhorst-Pack $k$-mesh. For our 2D system, we adopt a vacuum distance of 18 Å to eliminate the interactions between the PbSe layer and its periodic images. To effectively account for the vdW interactions between the Pb–Pb layers, we use the Tkatchenko–Scheffler method with iterative Hirshfeld partitioning (DFT-TS/HI) [38]. The energy convergence criteria is $10^{-4}$ eV for the structure relaxations. Based on the calculated energy band structure, the semiclassical Boltzmann transport theory [39] is applied to evaluate the electronic transport properties including the Seebeck coefficient $S$, the electrical conductivity $\sigma$, and the electronic thermal conductivity $\kappa_e$. In addition, we adopt the deformation potential (DP) theory [40] to evaluate the relaxation time $\tau$, and the effect of spin–orbit coupling (SOC) is explicitly considered in all the calculations.

The phonon dispersion relations of the PbSe layer are obtained by using the harmonic approximation via finite displacement method [41], which is coded in the so-called PHONOPY package [42]. We employ a $7 \times 7 \times 1$ and a $4 \times 4 \times 1$ supercell in the calculations of the second- and third-order interatomic force constants (IFCs), respectively. The ShengBTE package [43], in which the Peierls–Boltzmann transport equation is implemented, is used for the calculations of phonon transport properties. Furthermore, we adopt a fine $q$-grid mesh of $90 \times 90 \times 1$ to guarantee the convergence of lattice thermal conductivity.

3. Results and discussion

The top- and side-views of the geometrical structure of the PbSe layer are shown in figure 1. It forms stacks in the sequence of Se–Pb–Pb–Se with the space group of $P\bar{3}m1$ which is quite different from that of cubic PbSe. Similar to graphene, the 2D PbSe exhibits a hexagonal honeycomb lattice. However, there are two buckled sub-layers which may cause intrinsically lower lattice thermal conductivity compared with that of planar 2D materials [44, 45]. In addition, we find threefold and sixfold rotational symmetries along the $z$-direction for the Pb and Se sites, respectively. Such a structural characteristic could result in a special band shape and thus affect the electronic transport properties [46]. Table 1 lists the optimized lattice parameters of the PbSe layer, where the results with and without vdW functional are both given for comparison. We see that the lattice constants and the Pb–Se bond length change less by the consideration of vdW interactions. However, there are obvious reductions of the interlayer distance and the Pb–Pb bond length, which confirms the existence of weak vdW forces between neighboring layers in the 2D group-IV chalcogenides. It should be noted that the cleavage energy of the PbSe layer, defined as the minimum energy required to exfoliate the monolayer from the bulk counterpart, was previously calculated to be 0.30–0.38 J m$^{-2}$ [28], which is comparable to that of graphite (0.37 J m$^{-2}$ [47]). Moreover, we have calculated the formation energy of our PbSe layer which is defined by $E_f = E_{PbSe} - (E_{Pb} + E_{Se})$. Here the $E_{PbSe}$, $E_{Pb}$, and $E_{Se}$ are the total energy of the PbSe layer, the bulk Pb, and the bulk Se, respectively. The formation energy $E_f$ is found to be $-0.18$ eV/atom, which confirms the stability.
Figure 3. (a) The band structure of PbSe layer at two different interlayer distances. (b) The energy distribution of top valence band in the whole Brillouin zone. (c) The room temperature electrical conductivity and Seebeck coefficient as a function of carrier concentration along the \(x\)-direction. (d) The room temperature power factor as a function of carrier concentration along the \(x\)-direction.

of our PbSe monolayer. On the other hand, we want to mention that the interlayer binding energy of the system is found to be 93 meV/atom, which is significantly larger than that of typical vdW materials such as graphite (31 meV/atom) [48]. Moreover, the Pb–Pb bond was previously reported to be the strongest in all the 2D group-IV chalcogenides [27]. It is thus reasonable to expect that, in addition to the weak vdW interactions, there should be also certain strong coupling between two sub-layers of the 2D PbSe, as previously found for the SnSe with larger interlayer binding energy (146 meV/atom) [49]. In this regard, our PbSe monolayer may not be considered as a ‘real’ or ‘pure’ vdW material.

To have a better understanding of such kind of coupling, we plot in figure 2(a) the differential charge density of the PbSe layer, which is defined as:

\[
\Delta \rho_1 = \rho_{\text{total}} - \sum \rho_{\text{atoms}}
\]  

where \(\rho_{\text{total}}\) is the total charge density of the PbSe layer, and the 2nd term means superposition of atomic charge densities. In combination with the Bader charge analysis, we find that \(\sim0.55\) charge is transferred from Pb to Se atoms which suggests that the Pb–Se bond is ionic-like. Besides, there are smaller amount of charges gathered around the Pb atoms, as if they are attracted by neighboring Pb atoms of the other sub-layer. To further investigate the charge distribution between the sub-layers, we plot in figure 2(b) the interlayer differential charge density given by:

\[
\Delta \rho_2 = \rho_{\text{total}} - \sum \rho_{\text{sub-layer}}
\]  

where \(\rho_{\text{sub-layer}}\) is the charge density of each sub-layer. We see obvious charge accumulation between the Pb–Pb layers, which is reminiscent of covalent-like bond. Such an observation further confirms the existence of strong interlayer coupling in the 2D PbSe system, which is very similar to the layered SnSe exhibiting rather giant anharmonicity [50].

Figure 3(a) plots the energy band structures of the 2D PbSe layer at equilibrium interlayer distances of 2.876 Å. For comparison, the result at a larger distance of 2.930 Å is also shown. We see that both cases exhibit almost the same band structure with a moderate band gap of 0.55 eV (PBE value). It should be mentioned that standard DFT calculations usually underestimate the band gap, which can be efficiently addressed by adopting the GW approximation of the many-body effects or using hybrids functionals such as Heyd–Scuseria–Ernzerhof functional (HSE). As the actual gap value does not affect obviously the thermoelectric performance [51, 52], and both the HSE and GW approaches are very time-consuming for the calculations of transport coefficients, here we adopt the standard DFT calculations with PBE functional. Note that the conduction band minimum (CBM) of our PbSe layer is located at the \(\Gamma\) point while the valence band maximum (VBM) appears between the \(\Gamma\) and \(K\) points. Besides, there is a valence band extremum (VBE) along the \(\Gamma M\) direction and its energy is very close to that of VBM. Furthermore, we see from figure 3(b)
that both the VBM and VBE show a band degeneracy of three $(N_c = 3)$ in the whole Brillouin zone, which is originated from the threefold rotational symmetry discussed above. As a consequence, the PbSe layer can exhibit larger total density of state (DOS) effective mass ($m_{\text{total}}$) around the VBM, which is calculated by:

\[ m_{\text{total}} = N_e m_{\text{VBM}} + N_h m_{\text{VBE}} \]  

Here $m_{\text{VBM}}$ and $m_{\text{VBE}}$ are the DOS effective mass for the VBM and VBE, respectively. Such kind of multi-valley structure could simultaneously enhance the Seebeck coefficient and the electrical conductivity, as found in previous works [53].

In figure 3(c), we plot the room temperature Seebeck coefficient (absolutely value) and electrical conductivity as a function of carrier concentration for our 2D PbSe. We first focus on the intrinsic system with interlayer distance of 2.876 Å. In the whole concentration range of $1 \times 10^{18}$–$10^{21}$ cm$^{-3}$, we see that the $p$-type Seebeck coefficient is obviously larger than that of $n$-type, which is consistent with the multi-valley band structure. Note that at much smaller concentration of $4.45 \times 10^{16}$ cm$^{-3}$, a maximum $p$-type Seebeck coefficient of 1010 μV/K can be achieved, which is in good agreement with previous theoretical result [54]. On the contrary, we find that the $n$-type system exhibits larger electrical conductivity than that of $p$-type, which is caused by the stronger band dispersion and smaller DOS effective mass of the CBM (i.e., light band). Collectively, such findings lead to a higher $p$-type PF of $6.12 \times 10^{-3}$ W mK$^{-1}$ [2] at optimized concentration of $8.21 \times 10^{19}$ cm$^{-3}$ (figure 3(d)), where the corresponding Seebeck coefficient can reach 388 μV/K which is larger than those found in many good TE materials such as Bi$_2$Te$_3$ (320 μV/K) [55] and Cu$_2$Se (160 μV/K) [56]. Meanwhile, the corresponding electrical conductivity is found to be $4.1 \times 10^3$ S m$^{-1}$, which is also comparable with that of Bi$_2$Te$_3$ (5.0 $\times 10^3$ S m$^{-1}$) [57]. On the other hand, we see from figures 3(c) and (d) that increasing the interlayer distance only leads to small changes of the electronic transport coefficients. For example, the maximum PF is slightly decreased to $5.75 \times 10^{-3}$ W mK$^{-1}$ [2] at carrier concentration of $8.21 \times 10^{19}$ cm$^{-3}$, where the corresponding Seebeck coefficient and electrical conductivity are 345 μV/K and $4.8 \times 10^3$ S m$^{-1}$, respectively. Such a difference can be attributed to the fact that the system with larger interlayer distance exhibits relatively lower relaxation time ($\tau$), which can be simply obtained by using the DP theory assuming the single parabolic band (SPB) model [58]. For 2D system,

\[ \tau = \frac{2\hbar^3C}{3k_BTm_{\text{dos}}^*E} \]  

Here $C$, $m_{\text{dos}}^*$, $T$ and $E$ are the elastic modulus, the averaged DOS effective mass, the absolute temperature, and the deformation potential constant, respectively. Considering the degeneracy of the VBE and the VBM, the averaged DOS effective mass of a single valley is given by $m_{\text{dos}}^* = m_{\text{total}}/N_c$.

The calculated room temperature relaxation time and related parameters of PbSe layer are summarized in table 2. Indeed, we see that the intrinsic system with $d = 2.876$ Å exhibits an $n$-type ($p$-type) relaxation time of 68.7 fs (34.5 fs), as compared with 80.9 fs (40.6 fs) of the system with $d = 2.930$ Å. Since the band structures for these two different interlayer distances are almost the same, the averaged DOS effective mass and the deformation potential constant of them are basically the same. However, the elastic modulus of the system at $d = 2.930$ Å is relatively larger compared with that at $d = 2.876$ Å, which leads to larger relaxation time and thus increased electrical conductivity shown in figure 3(c).

Figure 4(a) plots the phonon dispersion relations of the PbSe layer at two different interlayer distances, where the phonon DOS is also given for the intrinsic system. (b) The temperature dependent lattice thermal conductivity. (c) The atomic displacement parameters of Pb atoms as a function of temperature. (d) The energy variation as a function of interlayer distance.

| Interlayer distance (Å) | Carrier type | $C$ (eV/Å$^2$) | $m_{\text{dos}}^*/m_e$ | $E$ (eV) | $\tau$ (fs) |
|-------------------------|--------------|----------------|-------------------|---------|------------|
| 2.876                   | Electron     | 3.592          | 0.153             | −6.79   | 68.7       |
|                         | Hole         | 3.592          | 0.664             | −6.48   | 34.5       |
| 2.930                   | Electron     | 4.276          | 0.150             | −6.76   | 80.9       |
|                         | Hole         | 4.276          | 0.664             | −4.79   | 40.6       |

Table 2. The room temperature relaxation time and related parameters of PbSe layer at two different interlayer distances.
The phonon group velocity and the average relaxation time of three acoustic branches for the PbSe monolayer at two different interlayer distances.

| Interlayer distance (Å) | Branch  | Group velocity (km s\(^{-1}\)) | Relaxation time (ps) |
|-------------------------|---------|-------------------------------|----------------------|
| 2.876                   | ZA      | 8.19                          | 8.32                 |
|                         | TA      | 15.92                         | 15.97                |
|                         | LA      | 24.25                         | 15.22                |
| 2.930                   | ZA      | 7.55                          | 8.27                 |
|                         | TA      | 14.51                         | 14.87                |
|                         | LA      | 22.28                         | 13.29                |

Figure 5. (a) The temperature dependence of the ZT values for the PbSe layer at two different interlayer distances. (b) The carrier concentration dependence of the corresponding maximum ZT values.
300 K to 1000 K. We see that at equilibrium interlayer distance of 2.876 Å, the PbSe layer exhibits better p-type TE performance than that of n-type one, where we find a room temperature $ZT$ value of 0.8 and 0.3, respectively. The maximum $ZT$ of 2.2 is achieved at temperature of 900 K, with a p-type carrier concentration of $7.66 \times 10^{20}$ cm$^{-3}$. Such a $ZT$ value is obviously higher than those of traditional good TE materials such as PbTe [63, 64] and Bi$_2$Te$_3$ [65]. If the interlayer distance is increased to 2.930 Å, the $ZT$ value can be further increased to 2.5 at carrier concentration of $1.08 \times 10^{20}$ cm$^{-3}$, which is comparable to that of SnSe [66, 67]. The carrier concentration dependence of the maximum $ZT$ values are summarized in figure 5(b) at these two interlayer distances, where the optimal temperature is 800 K and 900 K for the n- and p-type systems, respectively. As discussed above, the enhanced TE performance of the PbSe layer can be attributed to the fact that reduced interlayer coupling obviously decreases the lattice thermal conductivity (figure 4(b)) without much change to the electronic transport properties (figure 3(d)).

4. Summary

In summary, we demonstrate by first-principles calculations and Boltzmann transport theory that the 2D PbSe could exhibit rather higher $ZT$ value, which is caused by the multi-valley band structure around the VBM and unique atomic stacking with buckled sub-layers. Furthermore, we find that weak vdW interactions and strong interlayer coupling coexist between neighboring Pb layers, which could be fine-tuned to further enhance the TE performance of the system. In principle, our work provides a new perspective for the application of 2D group-IV chalcogenides as high performance TE materials, and could be generalized to other similar layered systems and 2D heterostructures.

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