

THERMOELECTRIC PROPERTIES OF PDSE₂ MONOLAYER: A FIRST-PRINCIPLES CALCULATION

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Abstract

All forms of heat engines waste a sizeable part of heat due to their low efficiency. Thermoelectric (TE) materials can make use of this waste heat to generate electricity. The figure of merit ZT of a material is crucial in determining the energy conversion efficiency. However, to-date there is no large-scale application of TE power generator (TEG) due to unavailability of environmental friendly and high ZT materials. In recent studies it was noted that reduction in the dimensionality of TE materials can decrease thermal conductivity and hence increase ZT. In this regard, 2D monolayer materials are considered promising candidates for TEG. Palladium diselenide (PdSe₂) is historically known as high Seebeck coefficient materials but there is still insufficient knowledge on their monolayer phase. In this work, the full-potential linearised augmented plane wave method based on density functional theory implemented in WIEN2k code is used to predict the structural and electronic properties of palladium diselenide. Different exchange correlations (xc) functional are used to take account of xc energy and potential. From the data of band energies obtained from WIEN2k calculations, BoltzTraP is used to calculate the TE properties. Our first-principles calculations show that Wu-Cohen GGA (WC-GGA) reproduces experimental cell parameters of PdSe₂ material. The obtained results of the band gap energy with PBE+GGA potential was found closer to the experimental data. TE properties calculations show that the better performance can be obtained by reducing the dimension of a materials. Interestingly, monolayer of PdSe₂ offer the highest ZT of 1.0074 at crystal direction y at temperature of 60 K with chemical potential of -0.1233 Ry. Hence this work showed successful enhancement of the TE properties for PdSe₂ by reducing their dimension.

Keywords: Density Functional Theory, LAPW, palladium diselenide, TB-mBJ, Thermoelectric.

1. Introduction

The typical cars driven by internal combustion engine lose about 75 % of the energy contributed by burning of petrol [1]. In many cases, large amount of heat is dissipated, indicating the low efficiency of the energy conversion. In order to increase the efficiency of internal combustion of engine, a lot of further research work is needed in the materials selection and the device designing. One of the possible choices are the thermoelectric (TE) materials which can provide a solution to these problems by recovering the useful electrical energy from the waste heat. TE devices have a range of advantages such as they can convert thermal energy directly into electrical energy, no extra parts that reduce efficiency [2]. Moreover, because they are solid state devices, no wear out due to mechanical movement, no extra maintenance and noiseless. Also, they have a long-life span, particularly used in constant heat source and scalable in which low to high voltage can be generated by changing the size. There are many review articles published from 2010 onward which indicates the popular trend of TE related studies [3-6]. Even though there are lots of studies on TE materials and devices, the large-scale production and applications of TE generators (TEG) is still not available. Zheng et al. [7] reported that the reasons behind this is not only the low efficiency

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of TE materials, but because of the low reproducibility of some proclaimed high figure of merit, ZT materials. The figure of merit of a material is defined by many properties. The properties that give direct impact are Seebeck coefficient S , electrical conductivity σ , and thermal conductivity κ . These three properties are interrelated and in general, interfere each other negatively. In order to overcome the negative correlation between electrical conductivity and thermal conductivity, various methods have been proposed. One of the methods is reducing the dimension of the materials. Many studies have shown that by reducing the dimension, the figure of merit of a material can be increased due to a decrease in lattice thermal conductivity [8-10]. There are also studies which show that transition metal dichalcogenide is a possible way to increase figure of merit by making monolayer into few layers compared to the bulk structure [11, 12]. Palladium disulphide and palladium diselenide have shown reasonable Seebeck coefficient [13] values, recent study showed higher Seebeck coefficient values for monolayer phase which attracts the interest of authors to initiate this study [14]. Despite of the possibility to develop a good TE material, there are nosatisfied outcomes from the ab initio study [14, 15] on the electronic properties for bulk and monolayer phases of palladium dichalcogenide when compared with experimental results. The situation becomes more interesting as only one experimental study related to monolayer palladium dichalcogenide was found to date [16] and few computational studies [14, 17-19]. The figure of merit of a material is defined by many properties. The properties that give direct impact are Seebeck coefficient S , electrical conductivity σ , and thermal conductivity κ . There are other properties that also govern the performance of TE materials as mentioned by Hamid Elsheikh et al. [5] but is out of the scope of this study. These three properties are interrelated and in general, interfere each other negatively. In addition, the study of Sun et al. [14] on TE properties of palladium diselenide is also yet incomplete. There is no study on TE properties of palladium diselenide as far as the authors knowledge. This study intends to determine the electronic properties and thermoelectric properties of PdSe₂ monolayer within density functional theory, (DFT) based approaches and Boltzmann transport equation. PdSe₂ crystal was first successfully produced by Grønvold and Røst [20] with orthorhombic structure and lattice constants of $a = 5.741 \text{ \AA}$, $b = 5.886 \text{ \AA}$, $c = 7.691 \text{ \AA}$. Compared to PdS₂, palladium diselenide PdSe₂ has drained more attention from the researchers. At the year 1957 [20], the PdSe₂ crystal was produced and showed the same type of structure as PdS₂. The lattice constants obtained are $a = 5.741 \text{ \AA}$, $b = 5.866 \text{ \AA}$, and $c = 7.691 \text{ \AA}$. Toward 1967, the band gap energy of PdSe₂ was found to be 0.4 eV [21]. In 2004, Soulard et al. [22] have done an investigation to find out the stable structure of PdSe₂ under pressure. Under ambient pressure, PdSe₂ appears as a PdS₂ structure which is consistent with the previous study, but the lattice constants are refined to $a = 5.7457 \text{ \AA}$, $b = 5.8679 \text{ \AA}$, and $c = 7.6946 \text{ \AA}$. There are two studies using DFT to obtain electronic properties, where first study [15] obtained band gap energy of 0.03 eV. Sun et al. [14] also found that monolayer phase has a band gap energy of 1.43 eV which is quite close to 1.3 eV. The study of Sun et al. has also shown that PdSe₂ monolayer has high Seebeck coefficient of more than $200 \mu\text{V K}^{-1}$. In condensed matter physics/material science, there are two possible ways to analyze the material properties [23, 24]. One of the ways is to characterize the material experimentally for its physical properties but in some cases, it is impossible to furnish experiments with required conditions for characterization or synthesis [25]. The other option is to solve many-body problems by solving quantum mechanical equation within the density functional theory (DFT) approach [26]. The reliability of the second approach has already been established in chemistry and physics for predicting various properties of materials which were difficult to explore experimentally for their device applications.

It has been established that first-principles many-body calculations would be suitable with fully self-consistent GW, because it provides true quasi particle energies [27]. However, both self-consistent and nonself-consistent GW approaches are computationally prohibited for surfaces calculations [28]. On the other hand, it is generally accepted that first-principles calculations based on local density approximation (LDA) and generalised gradient approximation of PBE [29] are practical for surface states calculations [28, 30-33]. Therefore, this work describes the implementation of first-principles approach to study the electronic band structure and thermoelectric properties of PdSe₂ monolayer.

2. Computational Details

In this work, the geometry optimizations of PdSe₂ in the orthorhombic crystal structure were performed based on full potential linearized augmented plane wave (FP-LAPW) [34] method using different exchange-correlation functional as implemented in well-known computer code called WIEN2k [35]. For full first-principles philosophy, our calculations were started with the optimized structure. In this approach of computations, the unit cell is partitioned into two parts and in each part of the simulated unit cell, wave function, potential as well as the charge density are treated within different basis sets as can be seen in the details of this methodology in reference [27] and many other ones. However, for exchange-correlation potentials, we use local density approximation (LDA), Wu-Cohen parameterized GGA (WC-GGA), Perdew-Burke-Ernzerh of parameterized generalized gradient approximation (PBE-GGA) [36] and Perdew-Burke-Ernzerh of parameterized generalized gradient approximation for solids and surfaces (PBEsol-GGA) for structural optimization. In addition to the above-mentioned exchange-correlation functionals, we also used TB-mBJ approximation for the calculations of various properties to overcome the severe underestimation of the band gaps within GGA and LDA. In the calculations, the plane-wave cutoff, defined by the product of the minimum radius of the muffin-tin spheres R_{MT} and the magnitude of the largest k -

vector in the plane wave expansion $K_{\max}(R_{MT}K_{\max})$ [37] was set to 9. The Fourier expansion of the charge density (G_{\max}) [37] was set at 12. 300 k -points were used to perform calculations of the first Brillouin zone integration in the reciprocal space by employing Monkhorst–Pack scheme[38]. The self-consistency was found to be stabilized and converged at 10^{-4} Ry. For the electronic density of states calculations, a denser mesh of 1200 special k -points was used. The transport properties (electrical conductivity, thermal conductivity, Seebeck coefficient) were then calculated using BoltzTraP with denser k mesh with the best perform xc functional for band gap energy estimation. Boltzmann Transport Properties, or BoltzTraP[39], is a program to obtain electronic transport properties of a material by solving Boltzmann transport equation (BTE). This program is written using Fortran 90 and can be interfaced with WIEN2k. BoltzTraP supports the change of doping concentration which is useful to modify the semiconductor material into n-type or p-type. It uses the energy eigenvalues for all k -points generated from lapw1 module to compute density of states at chemical potential $n(u)$, Seebeck coefficient S , electrical conductivity per relaxation time σ/τ , Hall coefficient RH , electronic thermal conductivity per relaxation time (κ/τ), electronic specific heat (c), and Pauli magnetic susceptibility in terms of chemical potential μ , and temperature T . BoltzTraP also calculates the electrical conductivity tensor, electronic thermal conductivity tensor, Seebeck coefficient tensor, and Hall tensor. The version used is version 1.2.5. The electrical conductivity ($\sigma_{\alpha\beta}$) is calculated using the equation below.

$$\sigma_{\alpha\beta}(T; \mu) = \frac{1}{\Omega} \int \partial_{\alpha\beta}(\varepsilon) \left[\partial f_{\mu} \frac{(T; \varepsilon)}{\partial \varepsilon} \right] d\varepsilon \tag{1}$$

where:

- $\sigma_{\alpha\beta}$ is the electrical conductivity,
- Ω is the volume of the unit cell,
- f_{μ} is the Fermi-Dirac distribution function,
- μ is the chemical potential.

Thermoelectric effect consists of a few different physical phenomena such as the Seebeck effect, Peltier effect, and Thomson effect. The focus of this work is on the Seebeck effect only, so the TE effect discussed in this paper is referred to the Seebeck effect. The Seebeck effect is the phenomena that by giving a temperature difference to a material, an electrical potential difference will be generated. The Seebeck coefficient is given by

$$S = \frac{\Delta V}{\Delta T} \tag{2}$$

The figure of merit (ZT) is a measure of the efficiency of a TE material or device which is described by the following equation:

$$ZT = \frac{S^2 \sigma T}{\kappa} \tag{3}$$

where:

- S is the Seebeck coefficient,
- σ is the electrical conductivity,
- T is the absolute temperature,
- κ is the thermal conductivity

3. Results and Discussion

3.1 Structural optimization

From Figure 1, the simulated layered complex structure of the PdSe₂ crystallized in an orthorhombic crystal unit cell structure can be seen. The simulated unit cell was then optimized over a range $\pm 10\%$ around the equilibrium position at the level of different exchange-correlation functionals. Our obtained PdSe₂ results for the structural properties in the orthorhombic crystal structure are presented in Table 1. In Table 1, the calculated results at the level of different exchange-correlation energy/potential functional along with available experimental results are shown. From our calculations of the lattice parameters, it is noted that the results of the lattice constants calculated within WC-GGA are in good agreement with the experimental measurements [20] compared to other exchange-correlation functionals, with a minute average error of less than 1%, due to its high efficiency for predicting structural parameters. As expected, PBE-GGA has shown somehow overestimation whereas LDA based results are found underestimated in comparison with experiment. However, the results of the lattice parameters computed via PBEsol-GGA are just slightly larger than the experimental one.

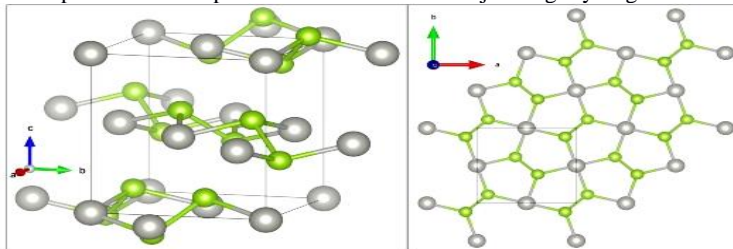


Figure 1: The unit cell of PdSe₂ and a -b plane view of PdSe₂ monolayer where the black lines indicate one-unit cell. Grey sphere represents Pd and green sphere represent Se.

Table 1: Calculated and experimental lattice constants of PdSe₂

Ref.	XC	a (Å)	b (Å)	c (Å)
Present work	LDA	5.8304	5.8874	6.8498
	PBE-GGA	5.7867	5.9635	8.6076
	WC-GGA	5.7578	5.8512	7.6822
	PBEsol	5.8720	5.9386	7.9436
Experiment [20]		5.741	5.866	7.691

3.2 Electronic structure calculations

Elaborating electronic properties of the PdSe₂ mono-layer semiconducting material is very important for understanding its thermoelectric behaviors for device applications. Here, the electronic band structure calculations using optimized structure are performed using the FP-LAPW method with different exchange-correlation functionals such as LDA, LDA+TB-mBJ, PBE-GGA, and TB-mBJ +PBE-GGA functionals. The band structures of PdSe₂ with different exchange-correlation were calculated and analyzed along special symmetry directions of the irreducible Brillouin zone (BZ) Y(0, 0, 1/2), Γ(0, 0, 0), Z(0, 1/2, 0), X(1/2, 0, 0), S(1/2, 0, 1/2), setting Fermi energy level scale at 0 eV represented by a black dash as can be seen in Figure 3. Results from different approximations are compared in order to assess their performance in electronic band structure calculation of PdSe₂ mono-layer in the orthorhombic crystal structure. The calculated band structures for PdSe₂ mono-layer within LDA, LDA+TB-mBJ, PBE-GGA and TB-mBJ+PBE-GGA are displayed in Figure 3.

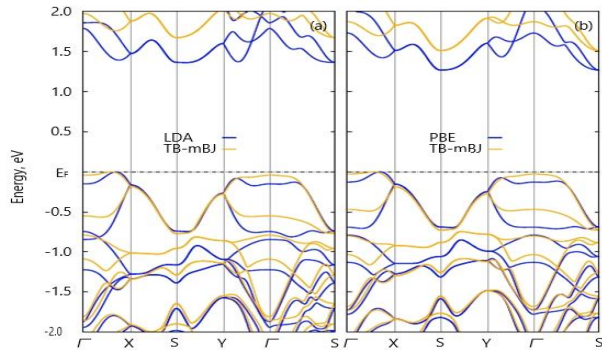


Figure 2: Band structures of monolayer phase PdSe₂ using (a) LDA xc functional (b) PBE GGA xc functional

As can be seen from Figure 3, the qualitative natures of the band structures plots with different exchange-correlation functionals are similar, indicating the reliability of our first-principles calculations. Our band structure calculations for PdSe₂ mono-layer with all exchange-correlation functionals show that the bottom of the conduction band is located at S point and the top of the valence band located at Γ toward X direction, showing that PdSe₂ semiconducting material possess indirect band gap, in agreement with experimental measurements [16]. However, the calculated band gap value of 1.27 eV within PBE-GGA is in good agreement with the experimental result of 1.3 eV [16]. The calculated fundamental band gap value using different exchange-correlation potentials for comparison with experimental are listed in Table 2. On the other hand, our band structure calculations show that TB-mBJ on top of PBE-GGA and LDA overestimate the band gap of PdSe₂ mono-layer whereas bare LDA underestimate the energy gap.

Table 2. Calculated and experimental energy gaps of PdSe₂.

	Methods	Band gap (eV)
Present work	LDA	1.18
	LDA+TB-mBJ	1.47
	PBE-GGA	1.27
	PBE-GGA+TB-mBJ	1.51
Previous work	PBE-GGA+SOC+TB-mBJ	1.43
	Experimental[16]	1.30

3.3 Thermoelectric Properties of Bulk Phase Palladium Dichalcogenides

Experimental studies have demonstrated that the thermoelectric properties of different 2D materials, namely, Bi₂Te₃ and Bi₂Se₃, were improved with the reducing of their thick-ness [40, 41], several previous experiments on MoS₂ thin films and disordered layered WSe₂ have also demonstrated very low thermal conductivities [42, 43]. Therefore, it would be

interesting to study the thermoelectric properties in monolayer of PdSe₂. The chemical potential μ range being investigated is -0.31177 Ry to 0.08123 Ry while the temperature T range is 15 K to 1500 K. The grid size for μ is 0.00050 Ry and for T is 15 Ry. The maximal Seebeck coefficient S, electrical conductivity per relaxation time σ/τ , and figure of merit ZT of PdSe₂ monolayer identified were tabulated in Table 3. Our calculated Seebeck coefficient, electrical conductivity per relaxation time and figure of merit ZT are shown in Figure.3. Our calculations show that PdSe₂ monolayer offer highest ZT of 1.0074 at crystal direction y at temperature of 60K with chemical potential of -0.1233Ry. In a nutshell, this work successfully exploited the enhancement of the figure of merit with the 2D dimensionality of PdSe₂ material.

Table 3: The minimal of Seebeck coefficient S, the maximal of Seebeck coefficient S, electrical conductivity per relaxation time σ/τ , and figure of merit ZT for monolayer phase PdSe₂

	Minimal	Temperature T, k	Chemical Potential μ, Ry
S_{xx}	-0.0034 VK ⁻¹	105	-0.0963
S_{yy}	-0.0034 VK ⁻¹	30	-0.1173
S_{zz}	-0.0034 VK ⁻¹	105	-0.0958
Minimal			
	Temperature T, k	Chemical Potential μ, Ry	
S_{xx}	0.0034 VK ⁻¹	75	-0.1138
S_{yy}	0.0034 VK ⁻¹	30	-0.1223
S_{zz}	0.0034 VK ⁻¹	75	-0.1043
σ_{xx}/τ	$4.1 \times 10^{21} Sm^{-1}s^{-1}$	15	-0.2118
σ_{yy}/τ	$4.9 \times 10^{21} Sm^{-1}s^{-1}$	15	-0.2348
σ_{zz}/τ	$4.2 \times 10^{20} Sm^{-1}s^{-1}$	15	-0.2558
ZT_{xx}	1.0000	120	-0.1018
ZT_{yy}	1.0074	60	-0.1233
ZT_{zz}	1.0010	180	-0.1093

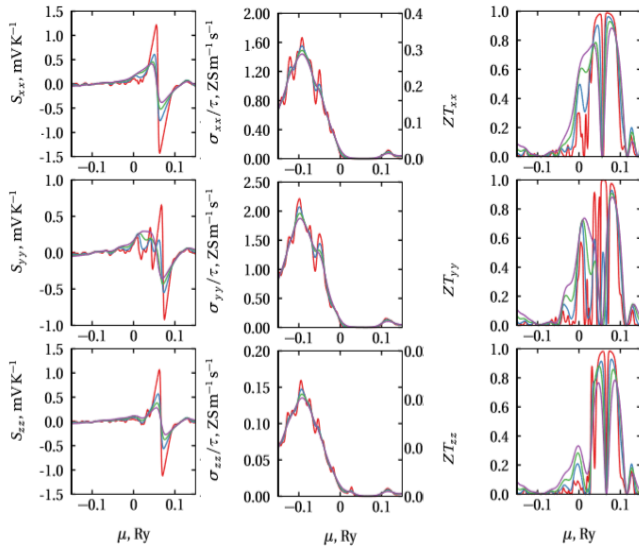


Figure 3: Seebeck coefficient S, electrical conductivity per relaxation time σ/τ , and figure of merit ZT for monolayer phase PdSe₂.

Conclusion

In summary, structural, electronic and thermoelectric properties of PdSe₂ monolayer were studied by highly accurate full-potential linearized augmented plane wave (FP-LAPW) approach based on DFT within local density approximation (LDA), Wu-Cohen parameterized GGA(WC-GGA), Perdew-Burke-Ernzerhof of generalized gradient approximation for solids and surfaces (PBEsol-GGA), Perdew-Burke-Ernzerhof parameterized generalized gradient approximation (PBE-GGA), and modified Becke-Johnson exchange potential (TB-mBJ) with PBE-GGA functionals. The results showed that WC-GGA and PBEsol-GGA functional are more appropriate for predicting structural properties of PdS₂. Additionally, the predicted energy gap of 1.27 eV within PBE-GGA functionals is in nice agreement with available experimental results. TE properties calculations indicated that the better performance can be obtained by reducing the dimension of the materials. Monolayer of

PdSe₂ offer the highest ZT of 1.0074 at crystal direction y at temperature of 60 K with chemical potential of -0.1233 Ry. In a nutshell, this work successfully exploited the enhancement of the figure of merit with the 2-D dimensionality of PdSe₂ material.

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