Band Structure Analysis, Mechanical and Thermoelectric Properties of CdSe - First Principles DFT Study

Manjula Muthurathinam[1], Chandra Kumar Dixit[2], Shasi Kant Gupta[3] and Muthumari Murugananthan[4]

[1] Post Doctoral Researcher, Lincoln University College, Malaysia

[2] Director, Institute of Engineering & Technology, Dr Shakuntala Misra National Rehabilitation University, Lucknow, India 226017

[3] Adjunct Professor, Lincoln University College, Malaysia

[4] Assistant Professor, Jerusalem College of Engineering, Chennai-600100, India

Email ID: pdf.manjula@lincoln.edu.my

Abstract: The detailed band structure analysis along with elastic, mechanical and thermoelectric properties calculations of CdSe have been made by using Density Functional Theory (DFT) in conjunction with Wien2k code, where the exchange-correlation effects were treated using the Generalized Gradient Approximation (GGA). The band structure and density of states of CdSe is analysed in terms of contribution from various s, p and d-states of the constituent Cd and Se elements. This detailed analysis reveals the semiconductor nature of CdSe with the band gap value of 0.468 eV and major contribution around the fermi energy level is due to Cd - s and Se -p states. The calculated elastic constants and mechanical properties confirms the mechanical stability and ductility of the studied material. From the thermoefficiency calculation, the CdSe is identified as a suitable material for thermoelectric applications.

Keywords: DFT, Electronic properties, Ductile/Brittle analysis, Thermoelectric properties

Introduction

Now-a-days, the research rapidly increased on design and development of thermoelectric materials (TEM) and its devices, because TEM and their devices fulfill the demands of sustainable and environmental free power sources by converting heat into electricity directly from human body. The efficiency of thermoelectric materials is determined by the dimensionless figure of merit ZT [1,2]. Cadmium selenide (CdSe), a II–VI semiconductor with a direct band gap [3] and excellent optoelectronic properties [4,5], has recently attracted increasing attention as a promising thermoelectric material due to its favorable electronic transport characteristics and tunable thermal conductivity. Due to its moderate band gap, relatively high carrier mobility, and the possibility of tailoring its electronic and phonon transport through doping, alloying, strain engineering, and nanostructuring, CdSe offers significant potential for enhancing thermoelectric performance. Further, its mechanical flexibility in low-dimensional forms, such as thin films and nanostructures, makes CdSe an attractive candidate for next-generation flexible and wearable energy-harvesting devices [6]. Consequently, understanding and optimizing the structural, electronic, and thermoelectric properties of CdSe is of considerable interest for developing efficient, environmentally sustainable thermoelectric technologies.

Teshome Gerbaba Edossa [7] studied the mechanical, thermal and thermodynamic properties of zinc-blende CdS and CdSe. Lei Guo et al., [8] explores the structural, elastic, electronic, optical, lattice dynamical and thermodynamic properties of CdX (X= S,Se and Te) using DFT. Mohammed Ameri et al.,

[9] investigated structural, electronic and thermodynamic properties of $CdS_{1-x}Se_x$ ternary alloys. E. Deligoz et al., [10] discussed the elastic, electronic and lattice dynamical properties of CdS, CdSe and CdTe. Perin et al., [11] ZnX and CdX (X = S, Se, Te) bilayers show visible band gaps, tunable electronic properties, and exciton binding energies, with ZnTe/CdS transitioning from type-I to type-II under strain. D.N. Alhilfia and A.S. Al-Kabbibb [12] reported characterization and application of electrochemical deposition CdSe thin films. S. Lany et al., [13] investigated the assessment of correction methods for the band-gap problem and for p-d repulsion in Zn and Cd chalcogenides. Y. Benkrima et al., [14] studied the structural and optical properties of CdSe using first principles calculations. T.G. Eddossa et al., [15] reported the properties of zinc blende and wurtzite cadmium selenide using density functional and hubbard correction. In the present study, we have reported the complete analysis of CdSe includes structural, electronic properties- band structure and density of states, elastic properties, mechanical stability with ductile/brittle analysis and thermo-efficiency for thermoelectric applications.

Methodology

Structural, electronic, mechanical and thermoelectric properties of CdSe have been studied by using first principles calculations based on density functional theory [16] were executed via the Wien2k package [17]. The crystal structure was optimized using the Perdew-Berke Ernzerhof - Generalized Gradient Approximation (PBE-GGA) [18,19] exchange-correlation functional. Muffin-tin sphere radii (RMT) were set to 2.42 a.u. for cadmium and 2.15 a.u for selenium, treating Cd - $4d^{10}$ $5s^2$ and Se - $4s^2 3d^{10}$ $4p^4$ are as valance state electrons. To ensure precise wave function expansion, the plane-wave cutoff parameter was fixed $R_{MT} \times K_{max} = 7.0$, $l_{max} = 10$ and the $G_{max} = 12$. Energy convergence was achieved using 10 x 10 x 10 Monkhorst -Pack point mesh yielding 1000 total k-points. The crystal structure visualizations were generated using XCrySDen code. Finally, semi-classical Boltzmann transport theory was applied through the BoltzTraP [20] code to evaluate the thermoelectric parameters.

Results and Discussions

Structural Properties

The structural properties of CdSe were investigated using density functional theory (DFT) through full geometry optimization. The equilibrium crystal structure was obtained by minimizing the total energy with respect to the unit-cell volume and atomic positions until the convergence criteria for energy and atomic forces were satisfied. The optimized lattice parameters were subsequently used for calculating the electronic, mechanical, optical, and thermoelectric properties. Figure 1a shows the cubic structure of CdSe with space group F-43m belonging to the space group number 216 and the structural information are given Table 1. The optimized lattice constant is obtained through total energy minimization and the calculated total energy for different lattice constants are used in Birch-Murnaghan equation of state to attained the ground state properties given in Table 2 and the volume optimization curve is shown in Figure 1b. The calculated lattice constant a_0 = 6.2042 (A^0) and bulk modulus = 45.109 (GPa) are good agreement with reported values. The binary CdSe is a direct band gap semiconductor having E_g = 0.468 eV, where valence band maximum (VBM) and conduction band minimum (CBM) are located at 'Γ' symmetry point.

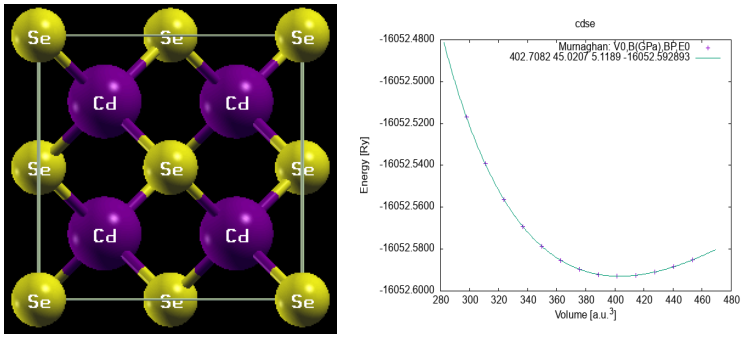


Figure 1. (a) Structure and (b) volume optimization curve of CdSe

Table 1. Structural properties of CdSe

Parameter/ Alloy	Atomic Position	Structure	Space group	No. of atoms in unit cell	E_g (eV)	NOE	E_F(Ry)
CdSe	Cd (0.25,0.25,0.25) Se (0,0,0)	Cubic	216 - F-43m	2	0.468 (GGA) 0.417 [9]	34	0.16517(GGA)

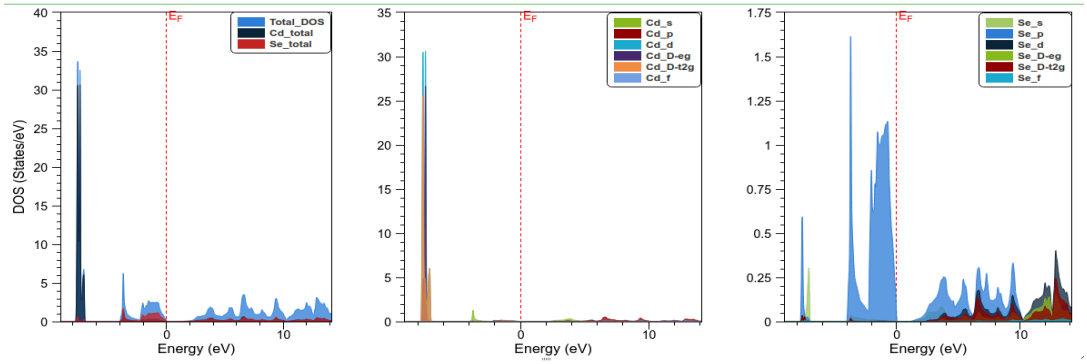
Table 2. Calculated lattice parameter a_0 (A^0), Volume (a.u.)^3, bulk modulus B(GPa), pressure derivative bulk modulus B' and total energy E_0 (Ry) for CdSe

Parameter/ Alloy	a_0 (A^0)	V (a.u.)^3	B(GPa)	B'	E_0 (Ry)
CdSe	6.204 6.05(exp) 6.16[8] 6.258[9]	402.899	45.109 52.4 [8] 43.06 [9]	4.8831 5.1 [8] 4.26 [9]	-16052.592908

Electronic Properties

Density of States

To understand the contributions of individual atomic orbitals to the electronic structure, the total and partial density of states histogram of CdSe plotted and presented in Figure 2 . In Figure 2, it is clearly shown that below the fermi level is mainly due to Cd - s, d states and Se- s, p- states; above the fermi level is mainly due to Cd - s states; less contribution from p states and Se-s, p states. Around the fermi is mainly due to Cd -s and Se-p states. The absence of electronic states at the Fermi level confirms the semiconducting nature of the material. The finite band gap observed in the DOS spectrum is consistent with the electronic band structure calculations, indicating that electron excitation from the valence band to the conduction band requires external energy. The significant overlap between Cd and Se orbitals demonstrates strong orbital hybridization, which influences the electronic transport and optical response of CdSe. The dominant Se-4p character near the valence band maximum (VBM) and Cd-5s character near the conduction band minimum (CBM) suggest that electronic transitions mainly occur between these orbitals. Such electronic characteristics are favorable for optoelectronic and thermoelectric applications because they facilitate carrier excitation and transport under thermal or optical stimulation.



(a)

Figure 2. Total and partial density of states of CdSe

Band Structure

Figure 3 shows the calculated energy band structure of CdSe. The detailed analysis has been made by using fat band structure of Cd and Se all states shown in Figure 4 and 5 respectively. To explain in detail, it is divided into three regions:

Region 1: The bottom region below the fermi energy level -

(i) around -4 eV in valence band is due to Cd- s and Se-p states shown in Figure 4a, 5b

(ii) around -7 eV is orifinated by Cd- d, d-eg and d-t2g states shown in Figure 4c, 4d ,4e

(iii) around -12 eV is purely due to Se - s states shown in Figure 5a

Region 2: centre region around the fermi energy level

(i) around the fermi energy level is mainly due to Cd - s, p states and Se -s, p state shown in Figures 4a, 4b and 5a, 5b respectively

Region 3: The top region above the fermi energy level -

(i) around 4.8 eV is mainly due to Cd -s, Se- p states and very less contribution from Se -s state

(ii) around 5.2 eV is mainly by Cd-p states

(iii) around 6.4 eV mainly because of Cd - s, Se - p states shown in Figure 4a, 5b and there is less contribution from Cd- p and Se - s states shown in Figure 4b and 5a respectively.

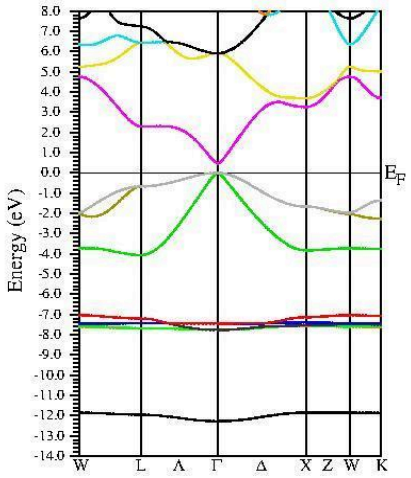


Figure 3. Energy band structure of CdSe

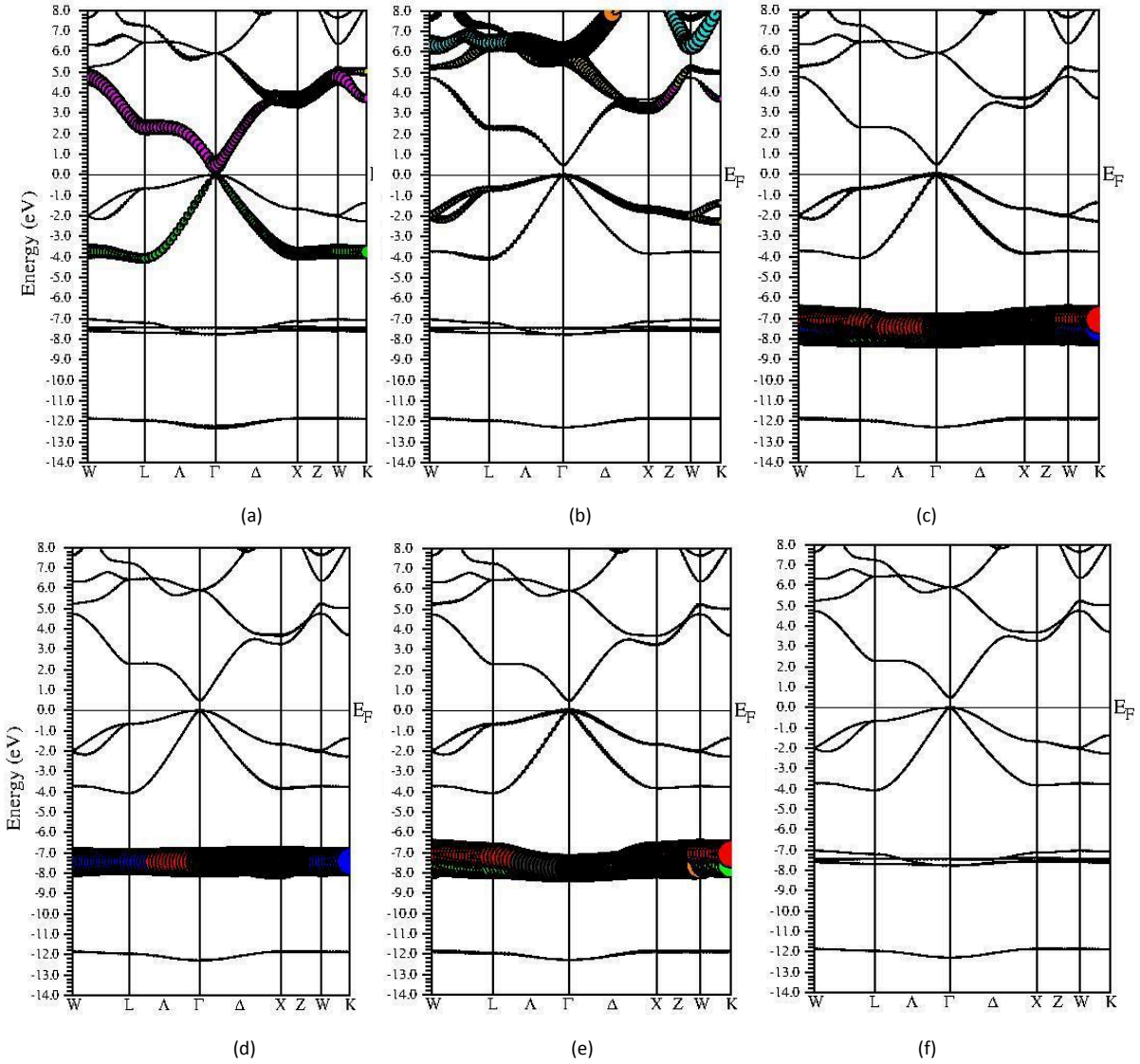
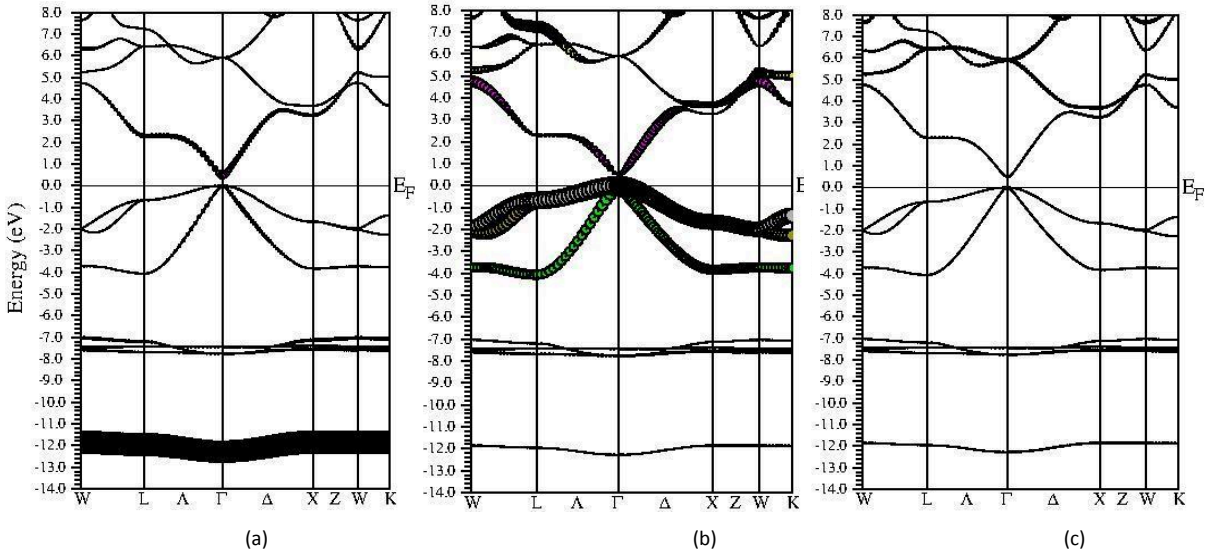
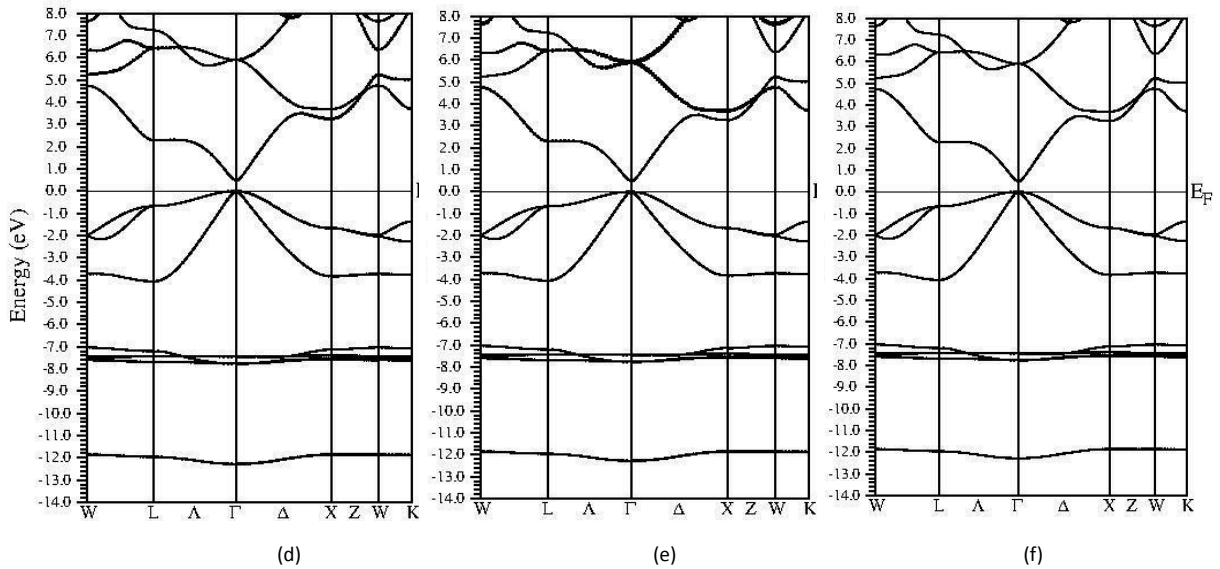


Figure 4. fat band structure of Cd (a) s- (b) p- (c) d- (d) d-eg (e) d-t2g (f) f -states





(d) (e) (f)

Figure 5. fat band structure of Se (a) s- (b) p- (c) d- (d) d-eg (e) d-t2g and (f) f-states

Elastic, Mechanical and Thermal Properties

The mechanical properties of CdSe were investigated through its elastic constants, which provide fundamental insight into the material's response to external mechanical stress. For a cubic crystal structure, only three independent elastic constants, namely C_{11}, C_{12}, and C_{44} are required to evaluate its mechanical behavior [21]. These elastic constants were calculated using the IR-Elast package [22], and the obtained values are presented in Table 4. The calculated elastic constants are used to assess various mechanical characteristics of CdSe, including its stiffness, hardness, ductility, brittleness, and overall mechanical stability. The mechanical stability of cubic material verified using the Born's stability criteria which require that $C_{11} > 0$, $C_{44} > 0$, $C_{11} + 2C_{12} > 0$. In addition, the calculated elastic moduli satisfy the cubic stability condition $C_{11} > B > C_{12}$, confirming the structural stability of CdSe. Based on the calculated elastic constants, several important mechanical properties including Young's modulus (E), Shear modulus (G), Bulk modulus (B), Vicker's micro hardness (H_v), Cauchy's pressure (C_{12}-C_{44}), G/B ratio and Poisson's ratio (v) were determined and summarized in Table 3.

Based on the calculated results, CdSe is identified as a ductile material having positive Cauchy's pressure (5.33), G/B ratio of 0.38 (< 0.57) and Poisson's ratio 0.33 (> 0.25). The calculated Vickers microhardness suggests that CdSe possesses moderate hardness. The Kleinman parameter explains the relative preference for bond bending to bond stretching under external deformation. Its value generally ranges from 0 to 1; where 0 - corresponds to a material that predominantly undergoes bond bending and 1 - indicates a preference for bond stretching. The calculated Kleinman parameter for CdSe is 1.391, indicates that bond bending is preferred in this material. The calculated elastic constants were further used to estimate the thermal properties of the material. Debye temperature (θ_D) was determined from average sound velocity $\mathbf{v}_m$ which is used to investigate the behaviour of the heat capacity of solids. From Table 4, we have noted lower Debye temperature, large Grüneisen parameter and maximum melting temperature, it indicates weak covalent nature of CdSe material.

Table 3. Elastic and Mechanical properties of CdSe

	C_{12}-C_{44} (GPa)	C_{11}(GPa)	C_{12}(GPa)	C_{44}(GPa)	B (GPa)	G (GPa)	E (GPa)	G/B	v	H_v (GPa)
CdSe	5.33	50.79 57.61 [7] 58.8 [8]	41.16 39.78 [7] 48.9[8]	35.83 21.97 [7] 25.2[8]	44.37 45.72[7] 52.2 [8]	16.72 15.30[7] 13.3 [8]	44.56 41.26[7] 36.8 [8]	0.38	0.33 0.34[7] 0.38[8]	2.228

Table 4. Thermal properties of CdSe

Parameter/ Alloy	V_L (m/s)	V_S (m/s)	V_m(m/s)	θ_D (K)	Tm(K)	γ
CdSe	3538 3422[7]	1772 1646[7]	1988 1829[7]	191 175[7]	553	1.99

Thermoelectric properties

Using semi-classical Boltzmann equation implemented in Boltztrap code, the thermoelectric properties of CdSe material are studied at room temperature and the calculated values are presented in Table 6. The high Seebeck coefficient, high electrical conductivity and low thermal conductivity are the required parameters for good efficient thermoelectric material [20]. The figure of merit increases spontaneously according to the formula,

$$ZT = \frac{S^2 \frac{\sigma}{\tau} T}{k_e + k_l} \qquad [1]$$

Where S is the Seebeck coefficient, σ is the electrical conductivity, τ is the relaxation time, T is the temperature, k_e is the electronic thermal conductivity and k_l is the lattice thermal conductivity.

Table 6. Thermoelectric properties of CdSe at 300 K for Fermi energy

Parameters	CdSe
Seebeck Coefficient (S) (μV/K)	274
σ/τ x 10^{18} [1/(Ω m s)]	1.41
S^2 σ/τ x 10^{16} [μW m^{-1} K^{-2} s^{-1}]	10.586
Thermal Conductivity (κ^0) x 10^{12} [W/(m K s)]	41.244
Electronic Specific Heat (c) [J/(mol K)]	0.122
Hall Coefficient (R_H) x 10^{-7} [m^3/C]	1.424
Pauli Magnetic (χ) x 10^{-11} [m^3/mol]	3.63

Metal chalcogenide-based materials have attracted significant attention owing to their promising thermoelectric properties, which arise from their favorable electronic structure and unique atomic arrangement. From the Table 6, the positive Seebeck value indicates that CdSe is a p-type semi conducting material. From the results, CdSe has reached the maximum power factor due to the thermal excitation of positive electrons (holes) and is very suitable for thermoelectric applications. Also, we noted electronic specific heat, Hall Coefficient and Pauli magnetic susceptibility at 300 K.

The thermoelectric properties such as seebeck coefficient, electrical conductivity and power factor for various temperature are plotted and shown in Figure 7 (a,b &c) respectively. In Figure 7a, the seebeck coefficient first increases from 100 K to 400K and reaches the maximum at 400K and then decreases to 800K. Electrical conductivity is a measure of a material's capability to move electric charge carriers throughout the material. In general, electrical conductivity is a measure of a material's ability to conduct electric current. As the temperature increases from 100 K to 800 K, the electrical conductivity of CdSe increases continuously, indicating enhanced charge carrier transport at elevated temperatures.

The dimensionless figure of merit ((zT)) is the key parameter used to evaluate the thermoelectric efficiency of a material and it depends on the S, σ, κ_e and T. For a good thermoelectric material, the material should have a high S and σ and low κ_e values.

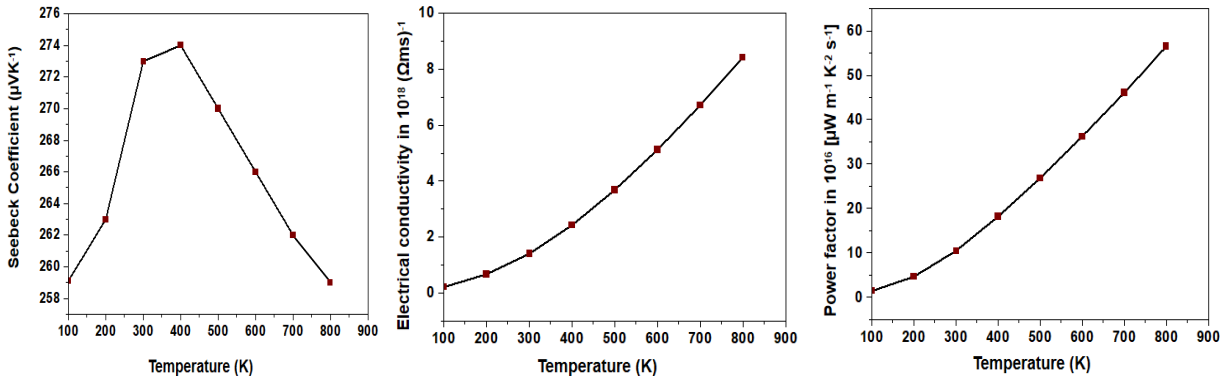


Figure. 7 Seebeck coefficient, Electrical conductivity, Power Factor of CdSe

Conclusions

In the present work, the density function theory is used to calculate structural, electronic, elastic, mechanical and thermoelectric properties of cadmium selined using Wien2k software. From the detailed band structure analysis and density of states calculations, the semiconducting nature of the CdSe is confirmed with direct band gap value E_g = 0.468 eV for PBE-GGA. The above results have been assessed by DOS histograms and the major influences around the fermi level are from Cd- s and Se -p states. The stability of the material is confirmed by Born stability conditions which are calculated using the elastic parametersl. From the ductile/brittle analysis, the chalcogenide CdSe identified as ductile material with less hardness. Thermoelectric properties have been calculated using BoltzTraP code implemented with Wien2k software. The calculated positive seebeck coefficient S = 274 (μV/K) indicates the CdSe is a p-type semiconducting material. The calculated power factor for CdSe is 10.586 x 10^{16} (μW m^{-1} K^{-2} s^{-1}). From the study, it is concluded that the CdSe is a ductile p-type thermoelectric material suitable for flexible wearable thermoelectric applications.

References

1. M. Manjula, Pandiyarasan Veluswamy, Denis Kuznetsov, S. Krishnaveni and M. Muthumari, “Influence of ternary and quaternary inclusion on bandgap tuning of CaTe – Prediction of Potential Thermoelectric Materials. Journal of Electronic Materials, vol. 50, pp. 1759 – 1771, 2021. https://doi.org/10.1007/s11664-020-08485-0
2. M. Muthumari, M.Manjula, Pandiyarasan Veluswamy and Denis Kuznetsov, “First principles calculations to investigate structural, electronic, mechanical, thermoelectric and optical properties of Bi-and Se-doped SnTe”, Journal of Physics and Chemistry of Solids, vol.176, pp. 111232, 2023. https://doi.org/10.1016/j.jpcs.2023.111232
3. S.H. Wei and S.B. Zhang, “Structure stability and carrier localization in CdX (*X* = S, Se, Te) semiconductors,"Phys. Rev B, vol. 62, pp. 6944, 2000. https://doi.org/10.1103/PhysRevB.62.6944
4. Hussein Hakim Abed, Mohsin K Al-Khaykanee, Hayder M Abduljalil, Mudar Ahmed Abdulsattar, “Investigation of thermoelectric properties of cadmium selenide CdnSen (n= 7, 11, 13) molecular junctions: a DFT study”, J Mol Model, vol. 30, pp. 12, 2023. https://doi.org/10.1007/s00894-023-05805-z
5. C. E. Hurwitz, “Electron-beam pumped lasers of CdSe and CdS”, Phys. Lett., vol. 8, pp.121-124, 1966. https://doi.org/10.1063/1.1754516
6. N. Benkhettou, D. Rached, B. Soudini, and M. Driz, “High-pressure stability and structural properties of CdS and CdSe,” Phys. Status. Solidi B, vol.241, pp. 101, 2004. https://doi.org/10.1002/pssb.200301907
7. Teshome Gerbaba Edossa, “Desntiy functional theory study of mechanical, thermal, and thermodynamic properties of zinc-blende CdS and CdSe”, Scientific reports, vol.15, pp. 39135, 2025. https://doi.org/10.1038/s41598-025-26168-w
8. Lei Guoa, Shengtao Zhanga, Wenjiang Fengb, GeHua, Wenpo Lia, “A first-principles study on the structural, elastic, electronic, optical, lattice dynamical, and thermodynamic properties of zinc-blende CdX (X = S, Se, and Te),” Journal of Alloys and Compunds, vol. 579, pp. 583-593, 2013. http://dx.doi.org/10.1016/j.jallcom.2013.07.096
9. Mohammed Ameri, Fouzia Mired, Ibrahim Ameri and Y. Al-Douri, “First-principle investigations of structural, electronic and thermodynamic properties of CdS1−*x*Se*x* *t*ernary alloys: (0.0 ≤ *x* ≤ 1.0),” Mater. Express, vol. 4, pp. 521-532, 2014. https://doi.org/10.1166/mex.2014.1199
10. E. Deligoz, K. Colakoglu, and Y. Ciftci, “Elastic, electronic, and lattice dynamical properties of CdS, CdSe, and CdTe,” Phys. B, vol.373, pp.124, 2006. https://doi.org/https://doi.org/10.1016/j.physb.2005.11.099
11. G. Perin, D. Kuritza, R. Barbosa, G. Tresco, R.B. Pontes, R.H. Miwa, and J.E. Padilha, "First-principles study of bilayers ZnX and CdX (X = S, Se, Te) direct band-gap semiconductors and their van der Waals heterostructures," *Physical Review Materials*, vol. 7, no. 10, p. 104003, 2023. https://doi.org/10.1103/PhysRevMaterials.7.104003
12. D.N. Alhilfia and A.S. Al-Kabbibb, “Characterization and application of electrochemical deposition Cdse thin films,” Chalcogenide Letters, vol.21, pp. 641-649, 2024. https://doi.org/10.15251/CL.2024.218.641

13. S.Lany & A. Zunger, “Assessment of correction methods for the band-gap problem and for p-d repulsion in Zn and Cd chalcogenides”, Phys. Rev. B, vol.81, pp. 113201, 2010. https://doi.org/10.1103/PhysRevB.81.113201
14. Y. Benkrimaa, D. Belfennacheb, R. Yekhlefb and A. M. Ghalebd, “First-principle investigations of structural and optical properties of CdSe,” Chalcogenide Letters, vol. 20, pp. 609 -618, 2023. https://doi.org/10.15251/CL.2023.208.609
15. T.G. Edossa & M.M. Woldemariam, “Electronic, structural, and optical properties of zinc blende and wurtzite cadmium selenide (CdSe) using density functional theory and Hubbard correction,” Phys. Chem. Solid State, vol. 22, pp. 16–23, 2021. https://doi.org/10.15330/pcss.22.1.16-23
16. Hohenberg and W. Kohn, “Inhomogeneous Electron Gas” Phys. Rev. B, Vol. 136, 864, 1964. https://doi.org/10.1103/PhysRev.136.B864
17. P. Blaha, K. Schwarz, G. K. H. Madsen, D. Kvasnicka, and J. Luitz, WIEN2k An Augmented Plane Wave Plus Local Orbitals Program for Calculating Crystal Properties (Vienna University of Technology, Vienna), 2008.
18. J. P. Perdew, S. Burke, and M. Ernzerhof, “ Generalized Gradient Approximation Made Simple”, Phys. Rev. Lett., vol. 77, pp. 3865, 1996. https://doi.org/10.1103/PhysRevLett.77.3865
19. F. Tran and P. Blaha, “Accurate Band Gaps of Semiconductors and Insulators with a Semilocal Exchange-Correlation Potential” Phys. Rev. Lett., vol.102, pp.226401, 2009. https://doi.org/10.1103/PhysRevLett.102.226401
20. M.Manjula, M.Muthumari and E.Viswanathan, "Thermoelectrics in alkaline earth metal tellurides of ATe2 type - A first-principles study", Physica Scripta, vol. 100, pp. 025925, 2025. https://doi.org/10.1088/1402-4896/ada591
21. M.Sundareswari, M.Manjula, D.Sivaprahasam and M. Muthumari, “Structure, electronic and thermoelectric properties of novel cubic Ir3V(1-x)Tix (x= 0.125, 0.25, 0.75, 0.875) refractory materials”, Computational Condensed Matter, vol. 39, pp. e00892, 2024. https://doi.org/10.1016/j.cocom.2024.e00892
22. M. Sundareswari, M. Manjula, D. Prabhu and D. Sivaprahasam, “Mechanical Properties of Ir3V1-xTix intermetallic Compounds”, Materials Letters, vol.358, pp. 135867, 2024. https://dx.doi.org/10.2139/ssrn.4656431